Aromatic Step Growth Polymers Bearing Pendant Clickable Groups: Synthesis, Characterization and Chemical Modifications

Thesis Submitted to AcSIR For the Award of
the Degree of

DOCTOR OF PHILOSOPHY
In
Chemical Sciences

By
Samadhan S. Nagane
(AcSIR Reg. No.: 10CC13A26018)

Under the guidance of
Dr. Prakash P. Wadgaonkar

CSIR-National Chemical Laboratory,
Pune-411008, INDIA
2018

To My Mentor

Dr. Prakash P. Wadgaonkar

सीएसआईआर - राष्ट्रीय रासायनिक प्रयोगशाला
(वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद)
डॉ. होमी भाभा मार्ग, पुणे - 411 008, भारत
CSIR - NATIONAL CHEMICAL LABORATORY
(Council of Scientific & Industrial Research)
Dr. Homi Bhabha Road, Pune - 411 008, India

Certificate

This is to certify that the work incorporated in this Ph.D. thesis entitled **"Aromatic Step Growth Polymers Bearing Pendant Clickable Groups: Synthesis, Characterization and Chemical Modifications"** submitted by **Mr. Samadhan S. Nagane** to Academy of Scientific and Innovative Research (AcSIR) in fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy in Chemical Sciences**, embodies original research work carried out under my supervision. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have been duly cited and acknowledged.

Nganes
Samadhan S. Nagane
(Student)

PPWadgaonkar
Prakash P. Wadgaonkar
(Supervisor)

Communication Channels

☎
NCL Level DID : 2590
NCL Board No. : +91-20-25902000
EPABX : +91-20-25893300
: +91-20-25893400

FAX
Director's Office : +91-20-25902601
COA's Office : +91-20-25902660
SPO's Office : +91-20-25902664

WEBSITE
www.ncl-india.org

Declaration by the Candidate

I hereby declare that the original research work embodied in this thesis entitled, **"Aromatic Step Growth Polymers Bearing Pendant Clickable Groups: Synthesis, Characterization and Chemical Modifications"** submitted to the Academy of Scientific and Innovative Research (AcSIR) for the award of the Degree of the Doctor of Philosophy (Ph.D.) is the outcome of experimental investigations carried out by me under the supervision of Dr. Prakash P. Wadgaonkar, Chief Scientist, CSIR-National Chemical Laboratory, Pune. I affirm that the work incorporated is original, and has not been submitted to any other Academy, University or Institute for the award of any Degree or Diploma.

Nganes

Samadhan S. Nagane
(Research Student)

July 2018
CSIR-National Chemical Laboratory
Pune-411008

Acknowledgements

The work embodied in a Ph.D. dissertation is not solely a mark of personal efforts and I am grateful to several individuals for their support and love.

Firstly, I am extremely fortunate to have had **Dr. Prakash P. Wadgaonkar** *as a research advisor, a great human being and a great scientist. He taught me fundamentals of polymer science and encouraged me to grow from a humble student to a better professional. He was open to share and discuss his scientific knowledge and experiences at all the times. It was a privilege for me to work for such an iconic figure in the field of polymer science, and I will always remember his kindness and generosity towards his students. He was and will be my mentor and role model forever. The research embodied in this dissertation can all be traced back towards his brilliant mind, and I hope he would be proud to see it brought to fruition.*

I express my thanks to Council of Scientific and Industrial Research (CSIR) for the research fellowship and financial support. I would also like to express my gratitude to Prof. Ashwinikumar Nangia (Director, CSIR-NCL), Dr. Vijayamohanan Pillai and, Dr. Sourav Pal (former Directors of CSIR-NCL) for giving me the opportunity to work at CSIR-NCL. It is my pleasure to thank Dr. U. K. Kharul (Chair, PSE Division), Dr. Ashish Lele (former Chair, PSE Division) and Dr. A. J. Varma (former Chair, PSE Division) for allowing me to work in Polymer Science and Engineering Division and providing instrumental facilities and infrastructure to perform the research work.

I am thankful to my Doctoral Advisory Committee (DAC) members, Dr. M. V. Badiger, Dr. A. V. Ambade, and Dr. C.V. Rode for the regular assessment of my research work, suggestions, valuable advices and fruitful discussions during the DAC meetings which helped me to build and to improve upon my research skills.

I owe my gratitude to Mr. Shamal K. Menon, Dr. P. R. Rajamohanan, Dr. Bimlesh Lochab (Shiv Nadar University, Noida), Mr. Anandrao S. Patil, Dr. Nilakshi Sadavarte Dr. C. V. Avadhani, Dr. K. Guruswamy, Dr. Ajith Kumar, Dr. Satish Ogale, Dr. Samir Chikkali, Dr. S. P. Chavan, Dr. J. Nithyanandhan, Dr. Sayam Sen Gupta, Dr. C. Ramesh, Dr. B. B. Idage, Dr (Mrs.). S. B. Idage, Dr. D. S. Reddy, Dr. A. T Biju, Dr. Kadhiravan Shanmuganathan, and Dr. K. Krishnamoorthy for their kind support and help throughout the PhD. tenure.

I appreciate Student Academic Office (SAO) Chairman Dr. M. S. Shashidhar and Dr. C. G. Suresh and staff members including Mrs. Kolhe Madam and Shri. S. Iyer Sir for their kind help and co-operation throughout the PhD tenure.

I would like to express my sincere thanks to Dr. Pandurang Honkhambe, Dr. Ankush Mane, Dr. Sushilkumar Jadhav, Dr. Rahul Shingte, Dr.Arvind More, Dr. Arun Kulkarni, Dr. Anjana Sarkar, Dr. Snehalata Bapat, Dr. Dnyaneshwar Palaskar, Dr. Prakash Sane, Dr. Sharad Pasale, Dr. Savita Kumari, Dr. Bhausaheb Tawade, Dr. Dilip Raut, Dr. Shyambo, Dr. Murugesan, Dr. Aarti Shedge, Dr. Prakash Babu and Dr. Ravindra Patil for valuable suggestions during my PhD. tenure.

The life of a Ph.D. student can only be truly understood by others who are in the same realm. Therefore, I take this opportunity to express my deep sense of gratitude to labmates and friends Dr. Sachin Kuhire, Durgaprasad, Dr. Bharat Shrimant, Amol, Ketan, Dr. Nagendra, Dr. Naganath, Dr. Sachin Patil, Dr. Indravadan Parmar, Uday, Nitin Basutkar, Deepak, Geethika, Deepshikha, Vikas, Sachin Basutkar, Kavita, Ashwini, Sagar, Dr. Shraddha, Dr. Sayali, Rupali, Nitin Valsange, Jagdish, Dr. Satyawan, Abhijeet, Dr. Ikhlas Gadwal, Yogesh, and Clement Ravet who made my life in the lab easier and more enjoyable. You guys are really fabulous. Thank you all !!!

I wish to thank my friends Dr. Tushar Khopade, Dr. Pradeep Lansonkar, Balasaheb Jawale, Dr. Chinmay, Dr. Amol Kotamale, Dr. Pravin Bhale, Dnyaneshwar Sirsat, Dr. Pradeep Pachfule, Dr. Aslam Tamboli, Vijay, Shrikant, Shahaji, Nilesh, Rahul, Satej, Ram, Nagesh Gattuvar, Vivek Kulkarni and Sachin Jadhav for their help.

My special thanks to the family members. Words cannot express how grateful I am to my mother, and father, for all of the sacrifices that they made for me. I am indebted to my grandparents, uncles, aunts, brothers and sisters for their immense love, support and patience beyond limits. I would like to express appreciation to my beloved wife, Pragati, for her tremendous support, and thank my lovely daughter, Sanskruti, for all the joy and laughter that she brought into my life.

Finally, I am grateful to the "God-Almighty" for giving me the strength and determination to put my chin up when faced with hardships in life.

… Samadhan S. Nagane

Table of Contents

Chapter 3: (Co)polycarbonates Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modifications

Chapter 4: Thermally Reversible Cross-linked (Co)poly(arylene ether)s *via* Furan-Maleimide Diels-Alder Reaction

Chapter 4a: (Co)poly(ether sulfone)s Containing Pendant Furyl Groups: Synthesis, Characterization and Chemical Modification

Chapter 4b: (Co)poly(ether ether ketone)s Containing Pendant Furyl Groups: Synthesis, Characterization and Chemical Modification

Chapter 5: **Chemical Modification of Aromatic Polyesters and Polycarbonates *via* Maleimide-Thiol Click Reaction**

Chapter 5a: **(Co)polyesters Containing Pendant Maleimide Groups: Synthesis, Characterization and Chemical Modifications**

Chapter 5b: **(Co)polycarbonates Containing Pendant Maleimide Groups: Synthesis, Characterization and Chemical Modifications**

Chapter 6: Post-Modification of Aromatic (Co)polyesters *via* Azide-Maleimide Cycloaddition Reaction

Chapter 6a: (Co)polyesters Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modifications

---

Chapter 6b: (Co)polyesters Containing Pendant Maleimide Groups Based on Bisphenol Derived from Levulinic Acid: Synthesis, Characterization and Chemical Modifications

---

Chapter 7: Summary and Conclusions

Introduction

The field of post-modification of polymers by click chemistry approach has witnessed a rapid growth in the past two decades and has found utility for synthesis of functional polymers and to tune the properties of polymers to be used in a variety of applications. In 2001, Sharpless and coworkers[1] defined click reactions as a group of reactions that "…must be modular, wide in scope, give very high yields, generate only inoffensive by-products that can be removed by non-chromatographic methods, and be stereospecific (but not necessarily enantioselective)". There are several examples of click reactions such as Cu-catalyzed azide-alkyne cycloaddition (CuAAC), the metal-free furan-maleimide Diels-Alder reaction, thiol-maleimide reaction and so on which fulfill the criteria of click reactions. These click reactions have been widely applied in the field of polymers affording access to the next generations of polymeric materials.

Statement of the Problem

Bisphenols are versatile and valuable difunctional monomer building blocks which are useful for synthesis of different classes of aromatic step growth polymers such as polyesters, polycarbonates, poly(arylene ether)s, epoxy resins, cyanate esters, etc. These aromatic step growth polymers cover a wide range of properties and find applications in various industries such as aviation, electronics, gas separation, adhesives, coatings, etc. For more specific applications and to further broaden the application areas of these polymers, the chemical modification of polymer backbone is often required in order to acquire desired properties. The purpose of post-polymerization modification is to introduce various functional groups into these polymeric materials and/or impart the physico-chemical properties of interest without significantly impairing their characteristic properties. The incorporation of pendant functional groups such as azido, furyl, and maleimide is of particular interest as these groups provide a useful platform for efficient post-modification by click chemistry approach. The post-modification by click chemistry approach has so far been predominantly applied to aliphatic polymers such as polyesters, polyamides, polycarbonates, polyurethanes, etc. On the other hand, the click chemistry modifications of aromatic step growth polymers such as polycarbonates, polyesters, polyamides, poly(arylene ether)s, etc obtained *via* functional monomer approach is an emerging field of research and its scope and limitations have not been fully defined.

Aims and Objectives

The present work was primarily focused on the synthesis of aromatic step-growth polymers containing pendant clickable groups *via* functional monomer approach and the chemical modification of synthesized polymers using appropriate click reactions to produce functional polymers. The following specific objectives were chosen for the work.

1. Design and synthesis of bisphenol monomers containing pendant clickable groups such as azido, furyl or maleimide.
2. Synthesis and characterization of aromatic step-growth polymers such as polycarbonates, polyesters, and poly(arylene ether)s based on synthesized bisphenols bearing clickable functional group under appropriate reaction conditions.
3. Chemical modifications of aromatic step growth polymers bearing pendant clickable groups using azide-alkyne, maleimide-thiol and azide-maleimide click reactions.
4. Thermal and photochemical cross-linking of aromatic polyesters and polycarbonates bearing pendant azido groups.
5. Thermally reversible cross-linking of poly(arylene ether)s bearing pendant furyl groups with bismaleimides.

Methodology Used

A) Synthesized bisphenols containing pendant azido group and polycarbonates therefrom; chemical modification was carried out quantitatively by CuAAC reaction.

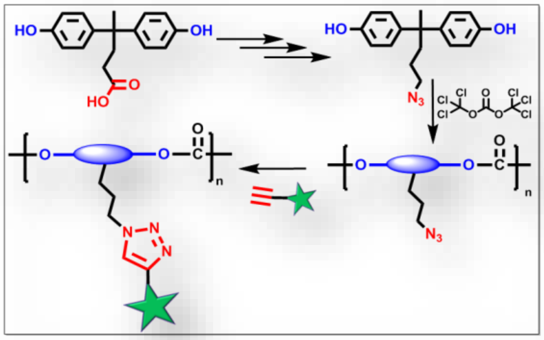
B) The cross-linking studies on polyesters and polycarbonates bearing pendant azido groups were carried out under thermal and photochemical conditions, respectively and the thermal and mechanical properties of cross-linked polymers were investigated.

C) Synthesized poly(ether sulfone)s and poly(ether ether ketone)s starting from bisphenol containing pendant furyl group; and investigated thermo-reversible cross-linking using furan-maleimide Diels-Alder reaction.

D) Demonstrated maleimide-thiol and azide-maleimide click reactions on synthesized aromatic polymers containing respective pendant clickable groups.

Sample Results

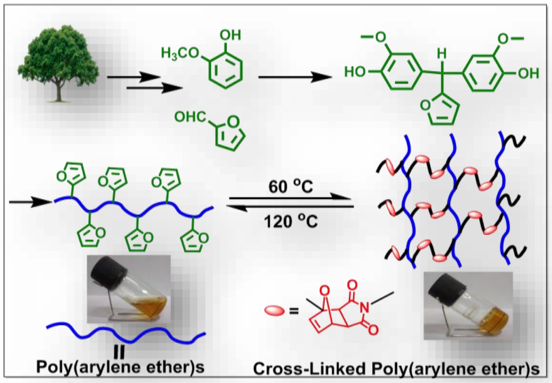
Scheme 1: (Co)polycarbonates Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modification



i. A bisphenol containing pendant azido group *viz*; 4, 4’ – (5-azidopentane-2, 2-diyl) diphenol was synthesized and utilized for the preparation of (co)polycarbonates containing pendant azido groups *via* phosgene route. (Co)polycarbonates exhibited reasonably high molecular weights and film forming nature. The chemical modification of aromatic polycarbonate containing pendant azido groups was carried out using CuAAC reaction with fluorescence active alkyne. The post-functionalized polycarbonate was characterized by FT-IR and ^{1}H-NMR spectroscopy, GPC and UV-Vis spectra.

ii. The cross-linking studies of aromatic polycarbonates bearing pendant azido groups were carried out under photochemical conditions. The cross-linked polymers were characterized by solubility tests, FT-IR, TGA and tensile testing.

Scheme 2: Thermally Reversible Cross-linked (Co)poly(arylene ether)s via Furan-Maleimide Diels-Alder Reaction

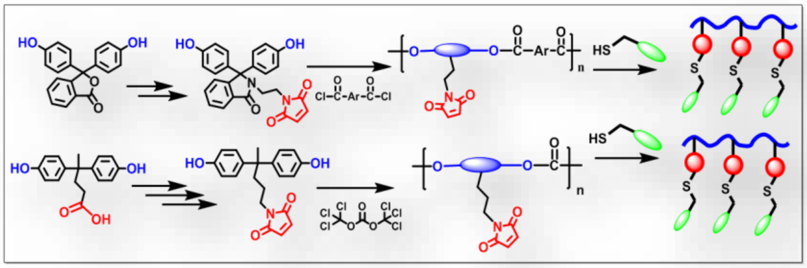


i. A fully bio-based bisphenol containing pendant furyl group, namely, 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) was synthesized by base-catalyzed condensation of furfural with guaiacol-both of which are derived from lignocellulose. New (co)poly(ether sulfone)s were prepared by polycondensation of BPF or mixtures of BPF and bisphenol-A with 4,4′-difluorodiphenyl sulfone in N N-dimethylacetamide as a solvent in the presence of K_2CO_3.

ii. A series of new (co)poly(ether ether ketone)s containing pendant furyl groups was synthesized by polycondensation of BPF or mixtures of BPF and bisphenol-A with 4,4′-difluorobenzophenone in N N-dimethylacetamide as a solvent in the presence of K_2CO_3.

(Co)poly(arylene ether)s were characterized by inherent viscosity measurements, GPC, FT-IR, ^{1}H and ^{13}C NMR spectroscopy, X-ray diffraction studies, TGA and DSC. Most interestingly, the pendant furyl groups in (co)poly(arylene ether)s provide reactive sites for click modification and cross-linking *via* Diels-Alder reaction with maleimides and bismaleimides, respectively. Cross-linked (co)poly(arylene ether)s were prepared by Diels-Alder reaction of (co)poly(arylene ether)s containing pendant furyl groups with bismaleimides at 60 °C. The crosslinked polymers underwent retro Diels-Alder reaction at 120 °C. These (co)poly(arylene ether)s containing pendant furyl groups are potentially useful as thermo-recyclable materials.

Scheme 3: Post-Modification of Aromatic Polyesters and Polycarbonates via Maleimide-Thiol Click Reaction

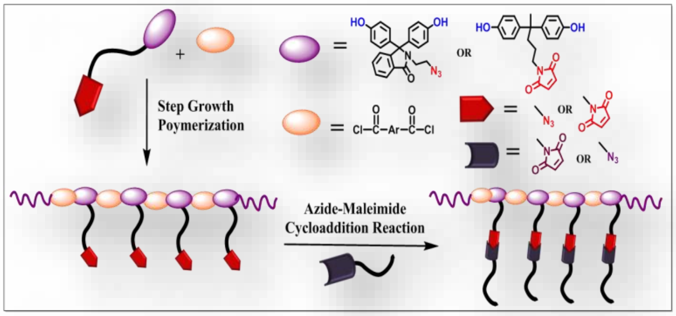


i. A new bisphenol containing pendant maleimide group, namely, N-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-MA) was synthesized. New aromatic polyesters containing pendant maleimide groups were synthesized by solution polycondensation of PPH-MA with aromatic diacid chlorides namely, isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) while copolyesters were synthesized by polycondensation of various molar ratios of PPH-MA and bisphenol-A with IPC.

ii. A new bisphenol containing pendant maleimide group *viz.* 4, 4' – (5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) was synthesized starting from 4, 4'-bis (4-hydroxyphenyl) pentanoic acid. New aromatic (co)polycarbonates containing pendant maleimide groups were synthesized by polycondensation of BPA-MA or varying compositions of BPA-MA and bisphenol-A with triphosgene.

(Co)polyesters and (co)polycarbonates were characterized by inherent viscosity measurements, GPC, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, TGA and DSC. The chemical modification of polymers containing pendant maleimide groups by maleimide-thiol click reaction using different thiols was carried out and the modified polymers were characterized by GPC, FT-IR and ^{1}H-NMR spectroscopy.

Scheme 4: Post-Modification of Aromatic Polyesters via Azide-Maleimide Cycloaddition Reaction



i. A new bisphenol containing pendant azido group *viz.* 2-(2-azidoethyl)-3,3-bis(4-hydroxyphenyl) isoindolin-1-on (PPH-N_3) was synthesized starting from commercially available phenolphthalein. New aromatic (co)polyesters containing pendant azido groups were synthesized by solution polycondensation of PPH-N_3 or different molar ratios of PPH-N_3 and bisphenol-A with aromatic diacid chlorides.

ii. New aromatic (co)polyesters bearing pendant maleimide groups were synthesized by polycondensation of 4, 4' – (5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) or various mixtures of BPA-MA and bisphenol-A with aromatic diacid chlorides.

(Co)polyesters were characterized by inherent viscosity measurements, GPC, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, TGA and DSC. The chemical modification of aromatic polyesters bearing pendant azido or maleimide groups was carried out *via* azide-maleimide cycloaddition reaction using different maleimides/azides. The quantitative post-functionalization reactions were demonstrated by FT-IR and ^{1}H-NMR spectroscopy.

List of Abbreviations

T_g	Glass transition temperature
T_{10}	10% Decomposition temperature
T_m	Melting transition
TLC	Thin layer chromatography
TPC	Terephthalic acid chloride
IPC	Isophthalic acid chloride
PPH	Phenolphthalein
BPA	2,2-Bis(4-hydroxyphenyl)propane or bisphenol-A
BPF	4,4'-(Furan-2-ylmethylene)bis(2-methoxyphenol)
PC	Polycarbonate
PES	Polyester
PSU	Poly(ether sulfone)s
PEEK	Poly(ether ether ketone)s
BMI	1,1’-(Methylenedi-1,4-phenylene)bismaleimide
TEG	1,8-Bis(maleimido)-triethylene glycol
NMP	*N*-Methyl-2-pyrrolidone
DMAc	*N*,*N*-Dimethylacetamide
DMF	*N*,*N*-Dimethylformamide
THF	Tetrahydrofuran
η_{inh}	Inherent viscosity
GPC	Gel permeation chromatography
$\overline{M_n}$	Number average molecular weight
$\overline{M_w}$	Weight average molecular weight
WAXD	Wide angle X-ray diffraction
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry

List of Tables

List of Schemes

List of Figures

Chapter-1

Introduction and Literature Survey

1.1 Introduction

The field of synthetic polymer chemistry is relatively new as compared to other chemical sub-disciplines such as natural products or analytical chemistry. In 1830's Charles Goodyear, reported 'original' reaction in the field of polymer science wherein he added sulfur to the natural rubber in order to produce a durable elastic material in a process that came to be known as 'vulcanization'.[1] At that time, the chemical structure of natural polymers was largely unidentified. However, still chemists were able to alter the properties of these natural materials by suitable chemical modifications. Completely synthetic polymers have historically been useful substitutes for natural materials with desirable properties, such as nylon substituting for the more laboriously produced silk, or polyurethane coatings substituting for lacquer made from insect resin. The recent progress in the field of polymer science over the last 60 years has vividly demonstrated that the area of chemical modification of polymers is still having widespread potential to influence different practical and commercial applications from materials to biology and medicine.

Polymers of natural origin are wide spread in biological systems. Proteins, DNA and carbohydrates are macromolecules composed of the monomers such as amino acids, nucleotides and saccharides, respectively. Nature has developed complex systems depending on coded sequences that determine the chemical and material properties of biopolymers. Just as Nature has developed methods to synthesize polymers from biological components, developments in the construction of synthetic polymers have led to an increasing number of polymerization methods, especially in the last three decades. The efforts to develop newer methods have been aimed at producing materials possessing higher and higher degrees of control over the particular arrangement and order of monomer units within a polymer chain. This increased control has led to a wide range of potential material architectures, which in turn has led to a wide range of properties for continuously growing number of newer applications.

It is not surprising that Biology and Nature have served as constant source of inspiration for current trends in synthetic polymer chemistry leading to increasing degree of control, order, and functionality. Nature has developed mechanisms to generate polymers with virtually the same length, sequence, and stereochemistry, and currently the best that chemists can achieve depends largely upon manipulating statistical processes and rates. As a result, chemists must look for ways to reliably alter the properties of polymers that go beyond the tools that Nature has been able to develop. By approaching the synthesis and modification of polymeric materials from a different point of view, one can take the best of what Nature has to offer while concurrently going beyond its boundaries. Many of the imminent practical challenges in polymer chemistry will necessarily be material in scope, and solutions will depend upon developing new ways to modify, tune, and alter the polymer properties in addition to developing new techniques to synthesize those polymeric materials.[2]

1.2 Click chemistries

Since 2001, click chemistry has had a profound impact upon materials chemistry and engineering, polymer science, biomedical engineering and so on. Although click chemistry has made many of the recent advances in polymer design possible, Sharpless and coworkers initially espoused it as an approach to the design of pharmaceutical drug libraries.[3]

Click chemistry is not one particular reaction, but is instead a set of reactions that share common characteristics. The term click chemistry was coined by Sharpless et al.[3] and is defined as "click reactions are intended to be modular, high in yield, wide in scope and should generate inoffensive byproducts that are easily removed by non-chromatographic methods, is stereospecific but not necessarily enantioselective, uses simple reaction conditions, is not sensitive to oxygen or water, uses easily accessible reagents, requires no solvent or solvent that is easily removed, enables simple product isolation, has a high thermodynamic driving force and goes rapidly to completion". Finally, click reactions are intended to be chemoselective between reactive groups on the constituent reagents, i. e. there should be no undesirable side reactions with functional groups other than where the reaction is intended.

Click chemistry is a philosophy of linking components together, so it is ideal for the synthesis, modification, and functionalization of natural and synthetic polymeric materials.[4–6] To date, however, the term 'click chemistry' has been expanded to a number of reactions and its precise definition continues to be a source of debate for polymer chemists.[7] Several types of reactions have been reported which may satisfy the criteria of "click" reactions. Majority of the click reactions involve carbon-heteroatom bond formation, for example (i) cycloadditions of unsaturated molecules (most commonly Huisgen 1,3-dipolar cycloaddition,[3,8–10] but also Diels–Alder reaction), (ii) nucleophilic ring-opening reactions of strained heterocyclic electrophiles (epoxides, aziridines and aziridinium ions),[11] (iii) carbonyl chemistry, except for the "aldol" type reactions (ureas, oximes and hydrazones),[12,13] (iv) additions to carbon–carbon multiple bonds (especially thiol–ene chemistry but also Michael additions).[14–17] Different types of click reactions and their criteria are schematically represented in **Figure 1.1**.

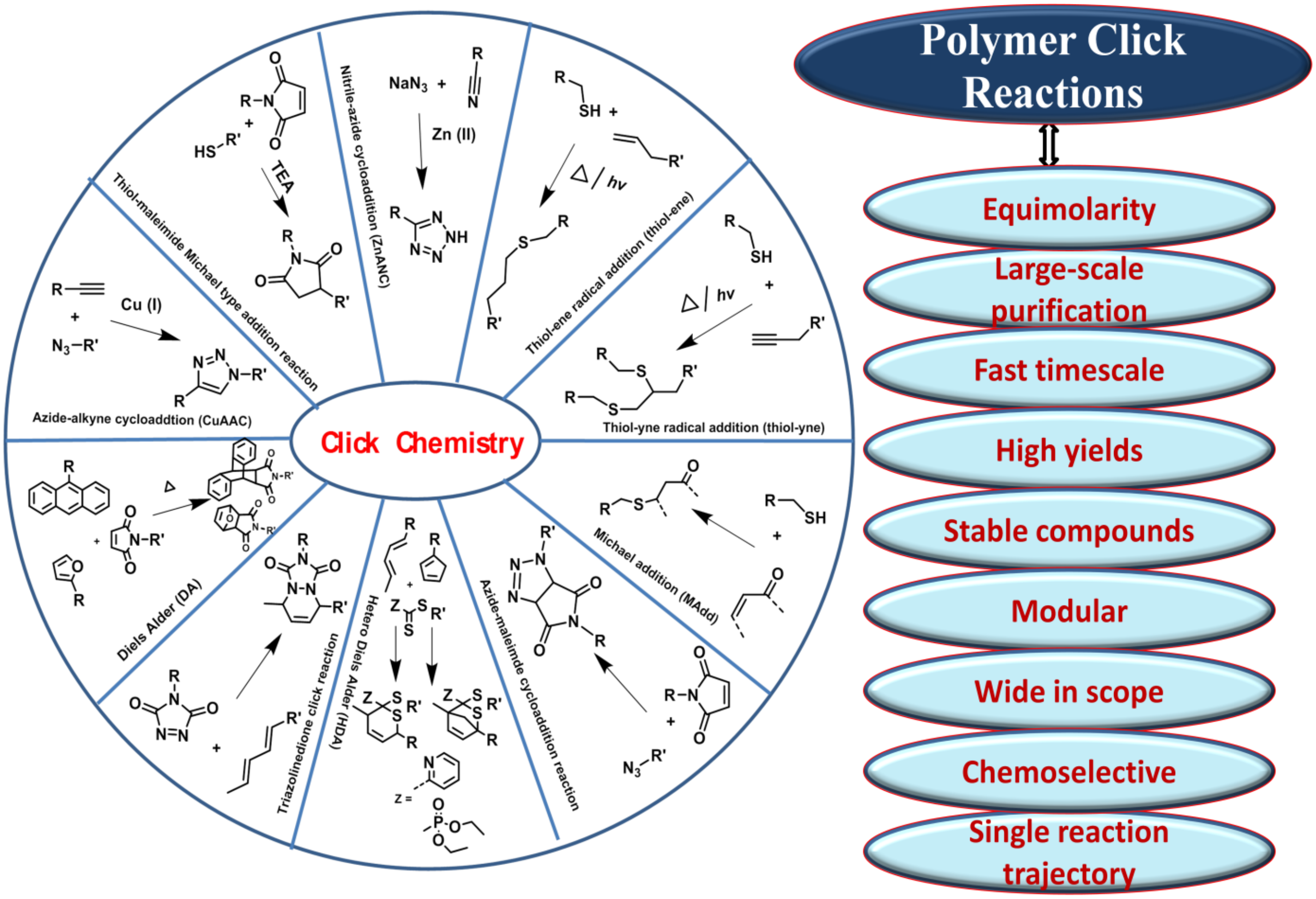


Figure 1.1. Types of click reactions and criteria for click reactions.[7,18]

Of these click reactions, Cu-catalyzed azide-alkyne cycloaddition (CuAAC), the metal-free furan-maleimide Diels-Alder reaction and thiol-ene reactions, have been most widely utilized in the field of polymers affording vast array of advanced polymers. Click chemistry has found extensive applications to facilitate synthesis of complex macromolecular architectures having various topologies such as linear polymers, block copolymers, stars, graft copolymers, cross-linked polymers, cyclic polymers, dendrimers, etc (**Figure 1.2**).[10,19–25]

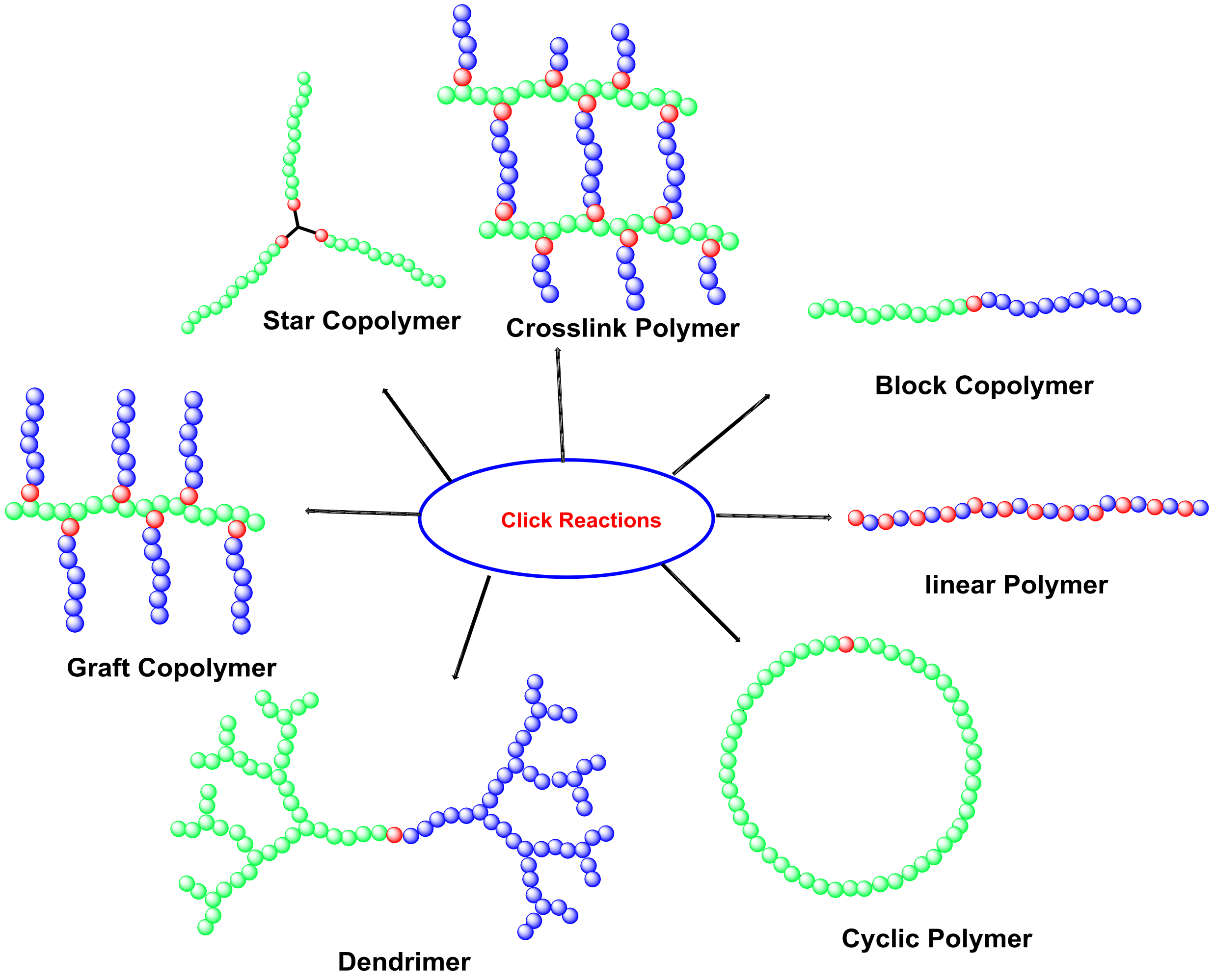


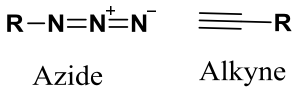
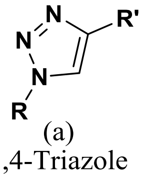
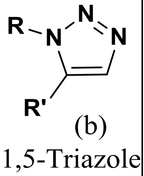
Figure 1.2. Illustrative examples of discrete macromolecular architectures obtained *via* click reactions.

A large number of articles and reviews are available dealing with the different types of click reactions such as azide-alkyne cycloaddition (CuAAC), thiol-ene, thiol-yne, Michael addition, Diels-Alder cycloaddition, thiol-isocyanate addition reaction, nitrile oxide-alkyne cycloaddition, triazolinedione click reaction, etc.[5,7,10,26–51] However, detailed discussion of each of these types of click reactions is beyond the scope of this thesis. The present thesis is mainly focused on exploitation of CuAAC, Diels-Alder click reactions and thiol-maleimide Michael type addition reaction and these reactions are briefly discussed in the following sections.

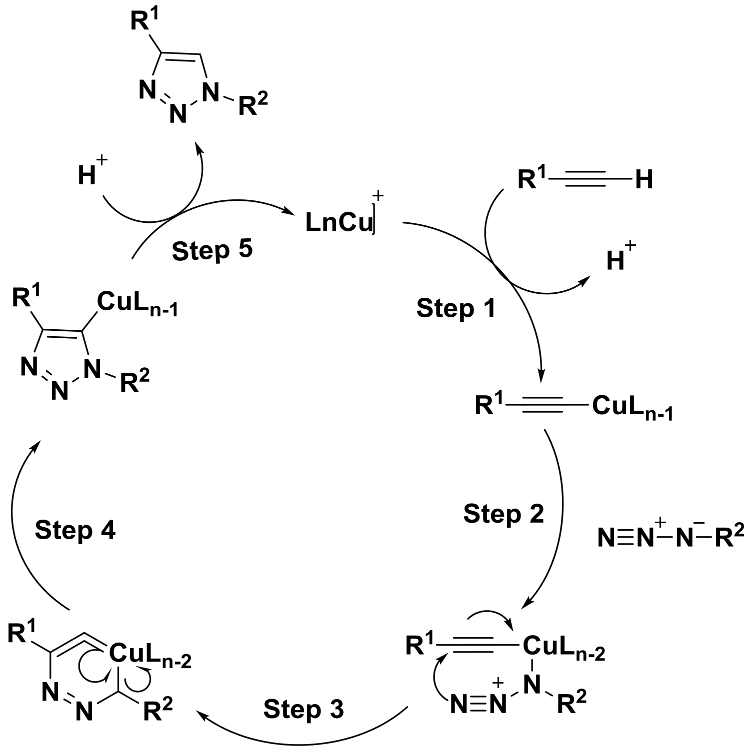
1.2.1 Azide-alkyne cycloaddition

The premier click reaction is the Huisgen 1, 3-dipolar cycloaddition reaction between an azide and an alkyne. Since its re-introduction as an effective coupling reaction by Sharpless, variations of the thermal Huisgen reaction have been introduced using catalysts and ring-strain to promote the cycloaddition. Taken together, azide-alkyne click chemistry has been implemented in numerous areas of chemistry, from synthesis, surface functionalization to drug discovery. Although azide-alkyne cycloaddition chemistry has become the gold-standard of click chemistries, the development, expansion, and application of click chemistry philosophy to other chemical reactions has opened new synthetic and material possibilities.

Table 1.1. Examples of click chemistry using azide-alkyne cycloadditions to form substituted 1,2,3-triazoles

Components	Adduct	Variations	References
 Azide Alkyne	 (a) 1,4-Triazole  (b) 1,5-Triazole	1. Cu(I) Catalyzed (a only)	52–59
		2. Ru(II) catalyzed (b only)	60
		3. Thermal activation (a and b)	61

Of the variations on azide-alkyne cycloaddition chemistry (**Table 1.1**), the most widely adopted synthetic strategy is to use a catalytic amount of copper(I) to preferentially generate the *E*-regioisomer of a 1,2,3-triazole from an azide and a terminal alkyne.[52] This reaction, known as copper catalyzed azide-alkyne cycloaddition (CuAAC), has been used widely in large part because it places the substituents of triazole in the least sterically hindered orientation at 1 and 4 positions. The reported mechanism of CuAAC reaction is illustrated in **Scheme 1.1.** Although the mechanism is still being debated,[53] CuAAC generally proceeds with minimal Cu^+ that can be provided directly in aqueous or organic solution by the reduction of a soluble Cu^{2+} salt, a ligated Cu^+ complex,[54–56] or even by a small amount of salt in conjunction with the equilibrium amount of dissolved Cu^+ from a solid copper wire.[57] In synthetic chemistry, general CuAAC techniques have been developed to form triazoles in a one pot reaction from the product of a substrate with trimethylsilylacetylene followed by deprotection and CuAAC with a second azido-functional substrate.[58,59] Since the azide and alkyne do not readily react with most biological functionalities, CuAAC has also been widely used to synthesize nucleotide and nucleoside derivatives.[62]



Scheme 1.1. Schematic representation of mechanism of CuAAC reaction.

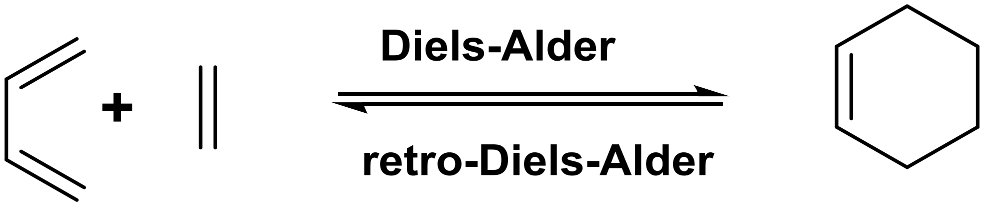
Variations of CuAAC have been developed where it is desirable to have an iodo or sulfonyl-functionalized triazole.[63–65] Additionally, if ruthenium(II) is used in place of copper(I), the *Z*-regioisomer of 1,2,3-triazole is preferentially formed with substituents in more sterically hindered 1 and 5 positions of triazole (**Table 1.1**).[60] The reaction between the azide and the alkyne can also be induced thermally at around 70 °C to generate a mixture of *E* and *Z* regioisomers of the triazole.[61]

Additionally, the inherent reactivity of azido functional group is high and can be activated by either thermal condition or UV irradiation. This reaction is based on decomposition of azide functional group upon thermal activation or UV irradiation resulting into the formation of highly reactive nitrene intermediate which can subsequently react with neighboring polymer backbone and results into cross-linking.[66–74]

The major shortcoming of CuAAC click reaction is difficulty of copper removal which is imperative in some delicate applications such as drug-delivery. Therefore, it is highly desirable to develop catalyst free azide-alkyne cycloaddition reaction. Furthermore, due to explosive nature of azides it is difficult to handle them on large scale, making this click reaction less attractive to scale up on industrial level.[31,39]

1.2.2 Diels-Alder reaction

Diels–Alder reaction is one among the foremost reactions employed in the field of chemistry and was introduced by Otto Diels and Kurt Alder who were awarded the Nobel Prize in 1950 for their pioneering research.[75] Diels-Alder click reaction involves a straightforward [4 + 2] cycloaddition reaction between an electron-rich diene and an electron poor dienophile to form a stable cyclohexene adduct as illustrated in **Scheme 1.2**.[76,77]



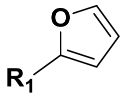
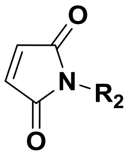
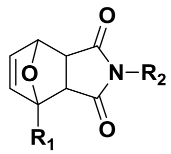
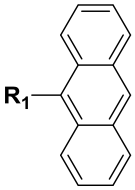
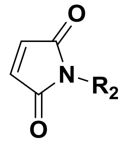
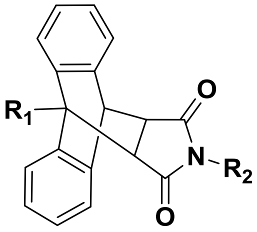
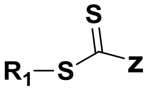
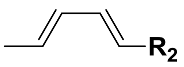
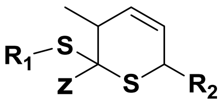
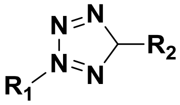
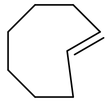
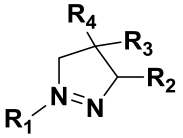
Scheme 1.2. General mechanism of Diels-Alder/retro Diels-Alder reactions of dienophile and diene.

The beauty of this reaction is that very low energy is required to form a six membered Diels-Alder adduct and the formation and functionalization of numerous compounds is feasible by this method. Diels-Alder reaction gives not only carbon–carbon bonds but also heteroatom–heteroatom bonds (hetero-Diels–Alder, HDA). Some attractive features of Diels-Alder/retro-Diels–Alder reactions are thermal reversibility controlled by temperature.[78]

Apparently, some Diels–Alder reactions easily satisfy the several criteria of ‘‘click’’ chemistry.[79] Additionally, an advantage of these reactions is that they can proceed in the absence of a metal catalyst. The chemical structures of well-known dienes, dienophiles and their reaction products are depicted in **Table 1.2**.

A group of polymer chemists has proposed modified definition of click chemistry in the context of polymers, in order to assess whether a Diels-Alder reaction employed for polymers can be classified as a “click” reaction.[7] Because of the major differences between macromolecular synthesis and organic synthesis, few more requirements have been added to original definition of Sharpless’ in order to adapt a new one: (i) a simple large-scale purification process, (ii) to use equimolar quantities of the building blocks and (iii) a reasonable timescale and no requirement of tedious fine-tuning of reaction conditions. Therefore, it is more appropriate to call some Diels–Alder reactions as ‘‘click-type’’ or simply ‘‘efficient conjugation’’ methods.

Table 1.2. Selected well-known Diels–Alder reactions in polymer chemistry

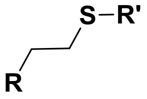
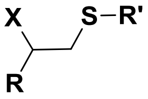
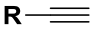
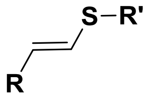
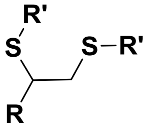
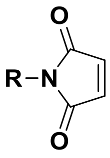
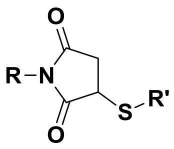
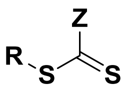
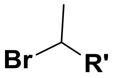
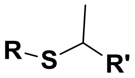
Components	Adduct	References
 **Furan**  **Maleimide**		80–83
 **Anthracene**  **Maleimide**		24,84–86
 **Dithioester**  **Diene**		87
 **Tetrazine**  **Cyclooctene**		88–90

Diels-Alder click reaction has been employed extensively in polymer chemistry for synthesis of macromolecular architectures such as block copolymers, telechelic polymers, graft polymers, star-branched polymers, dendrimers, bioconjugates and so on. Diels-Alder reaction can also be used in the formation of highly cross-linked networks and in the preparation of self-healing materials.[39,48,91]

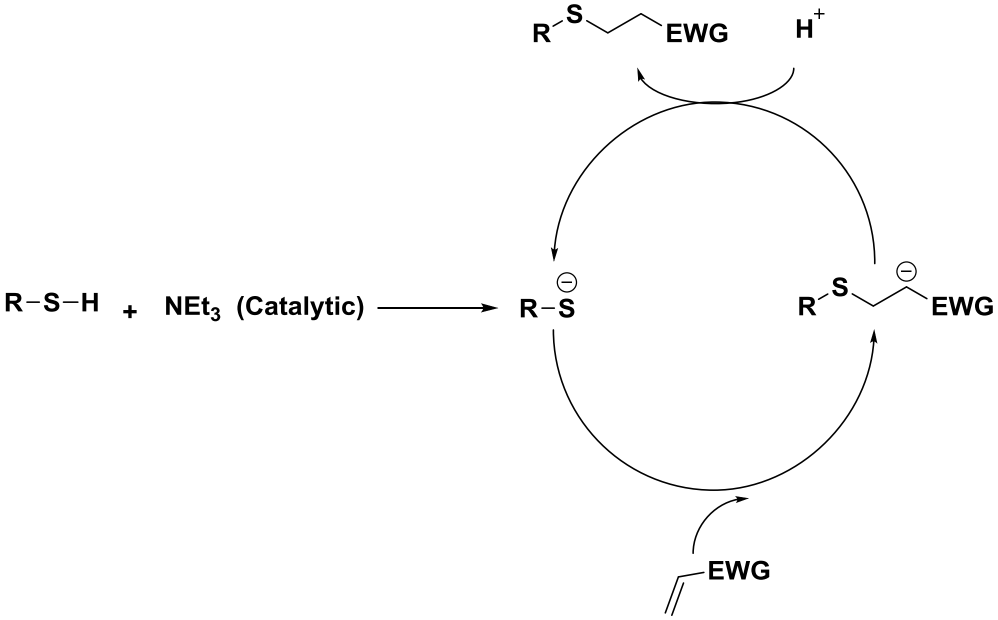
1.2.3 Thiol-ene, thiol-yne and thiol-maleimide addition reaction

Three of the most widely utilized reactions to be identified with the click chemistry philosophy are the reaction of thiols with alkenes (thiol-ene), alkynes (thiol-yne) and maleimides (Michael addition reaction) (**Table 1.3**).[14,92–94] Reaction of a thiol with a terminal alkene generates an anti-Markovnikov thioether where sulfur is bound to the less substituted carbon of alkene. Reaction with a terminal alkyne first generates the monoaddition product of an alkenyl sulfide, but in the presence of excess thiol, a second addition across the alkene generates a dithioacetal. These thioetherification reactions are most often induced photochemically in the presence of a radical initiator, although they can also be effected thermally.[14] A special case of thiol-ene reaction is Michael addition of a thiol to activated alkene in the presence of catalytic amount of a base or an acid.[94] For the efficient Michael addition, C=C must be activated (electron deficient) and therefore such reactions are less versatile than radical-mediated thiol-ene reactions. However, given the large number of commercially available activated enes, including multifunctional species, there is clearly considerable scope for synthesis of novel and interesting materials.

Table 1.3. Various thiol-ene click chemistries

Components	**Adduct**	**References**
 **Alkene** $H-S-R'$ **Thiol**	 **Thioether**	14,92,93,95
 **Alkene** $X-S-R'$ **Sulfenyl halide**	 **Halothioether**	95
 **Alkyne** $H-S-R'$ **Thiol**	 **Alkenyl sulfide, or**  **Dithioacetal**	95
 **Maleimide** $H-S-R'$ **Thiol**	 **Michael addition product**	94
 **Dithioester**  **Bromide**	 **Thioether**	96

As mentioned above, a thia-Michael or conjugate addition reaction involves the base/nucleophile-mediated addition of a thiol to an activated vinylene group and these types of reactions proceed under conditions of Michael addition reaction. For the efficient reaction to proceed, different activated ene substrates are used such as fumarate esters, (meth)acrylates and maleimide derivatives. There are many examples in the literature of base-catalyzed thiol-ene reactions.[94] In comparison to traditional Michael addition reaction, here in case of conjugate Michael addition, use of a weak base catalyst such as triethylamine is sufficient to catalyze the process (**Scheme 1.3).**



Scheme 1.3. The proposed base-catalyzed mechanism for the hydrothiolation of an activated C=C bond.

The deprotonation of thiol using triethylamine results in the formation of corresponding thiolate anion and triethylammonium cation. Thiolate anion, which is a powerful nucleophile, undergoes 1,4-conjugate addition along the activated C=C bond resulting in to the formation of an enolate, which is a very strong base. This anion abstracts a proton either from a thiol or from the ammonium cation resulting in to the thiol-ene product, again with regioselective formation of anti-Markovnikov product. The process involves the generation of much stronger base (the carbanion) from relatively weak base (triethylamine).

In polymer chemistry, thiol-ene, thiol-yne and thiol-maleimide chemistries have become very heavily adopted in recent years because of their chemical compatibility to bridge functional groups present in both material and biological applications.[95,97–99] It is also applicable in the field of polymer modification, surface and particle pattering, fabrication of optical components, bioorganic synthesis, curing of hard protective coatings, imprint nanolithography and many other applications.[7,15,39,95]

1.3 Functionalization of polymers

In case of industrial applications of step-growth polymers, the monomer composition and molecular weight have profound influence on their properties which eventually dictate their end applications.[100] The chemical modification helps to tune properties of polymeric materials. For the first time in the year 1840, Hancock and Ludersdorf reported independently the modification of natural polymers that involved transformation of soft sticky natural rubber into an elastic and tough material through treatment with sulfur.[101] In the year 1847, nitrocellulose was reported by Schonbein while in 1865 cellulose acetate was prepared by Schutzenberger, which had found wide range of applications in different fields such as artificial silk, membrane materials and photographic films.[102] Sernuik et al. in 1948, reported for the first time, the functionalization of synthetic polymers which included use of aliphatic thiols to perform functionalization of butadiene polymers by thiol-ene reaction.[103]

As most of the commercially available step-growth polymers do not contain any functionality on their backbone, so further altering and modification of polymers become difficult, making them unsuitable for various applications such as biomedical, smart materials and nanomaterials.[103] In order to carry out the modification of polymers two techniques are majorly followed such as (i) chain-end functionalization and (ii) side-chain functionalization. The first type of functionalization results into reduced molecular weight of polymers and less number of functionalities are present on each polymer chain. While in case of second type of functionalization large number of functional groups can be introduced on the polymer backbone, making this technique to be the most promising for polymer modification.

During polymerization process, the functional groups can be introduced on polymer backbone to a large extent by incorporating functional monomer. However, as the functional groups may be required to be protected and deprotected during the polymerization process, this becomes little bit tedious. These additional protection and deprotection steps are a major hurdle during industrial scale up. Also as the reactivity of functional groups gets severely affected by the polymer structure, organic transformations required for chemical modification may become less efficient when applied to a polymer chain. Due to these shortcomings, the scientific community has shifted its focus of research in polymer modification towards field of “click chemistry”, which avoids extra protection-deprotection steps and involves efficient chemical transformations.[104,105]

Different click reactions can be effectively utilized for carrying out side chain functionalization in case of step-growth polymers. Side functionalities can be introduced either by direct reaction onto the polymer chain itself (Post-functionalization approach) or by the introduction of functionality at the monomer stage (Functional monomer approach). Both of these side chain functionalization approaches are elaborated in the following sections.

1.3.1 Post-functionalization approach

In order to modify the properties of polymers such as poly(ether sulfone)s and poly(ether ether ketone)s, the post-modification approach has been widely used to broaden their applicability. The schematic illustration of post-functionalization approach is presented in **Figure 1.3**.

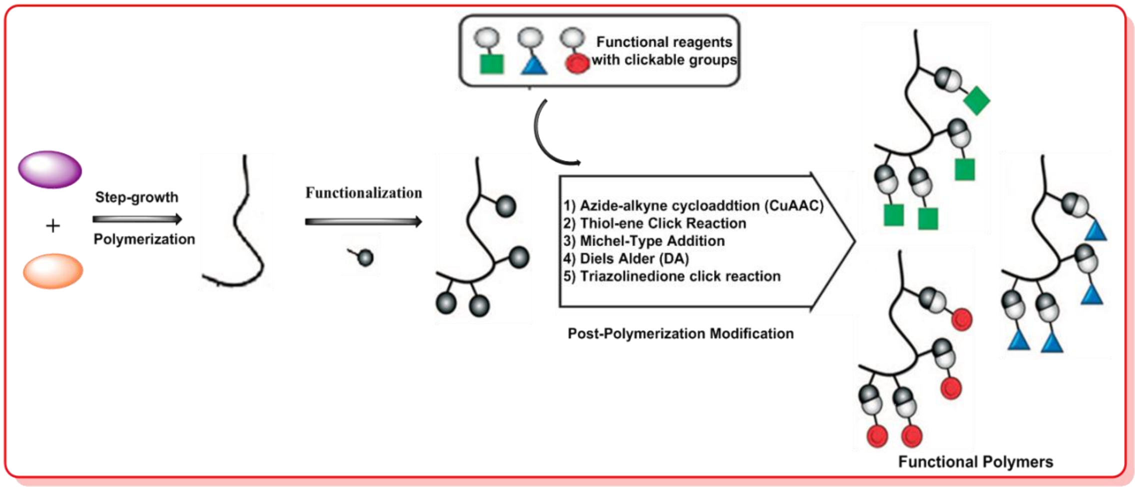
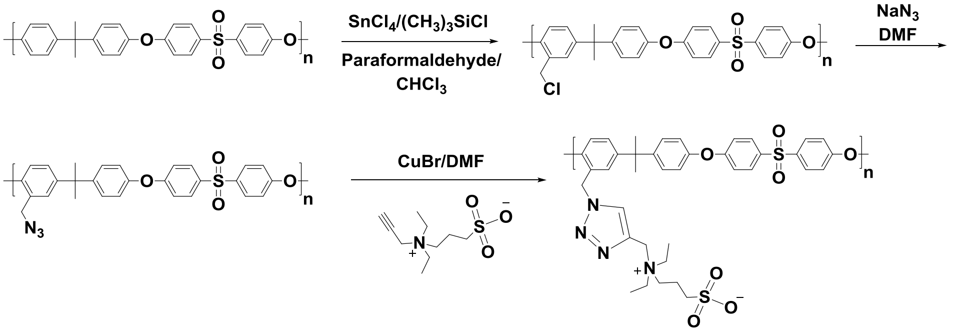
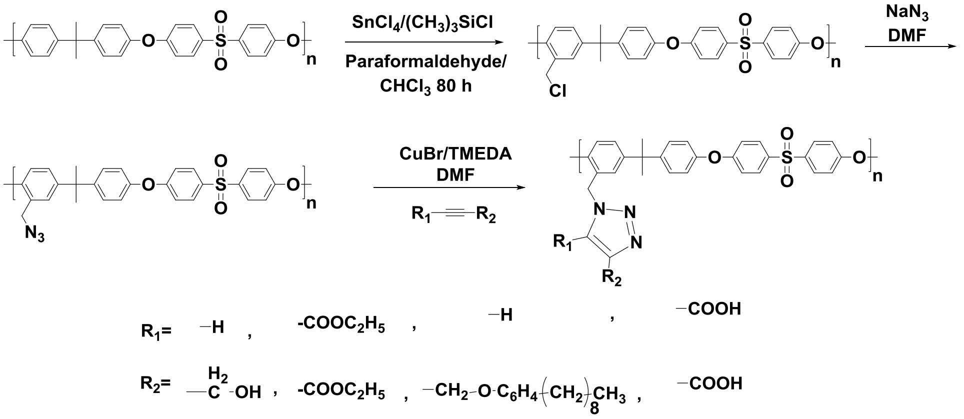
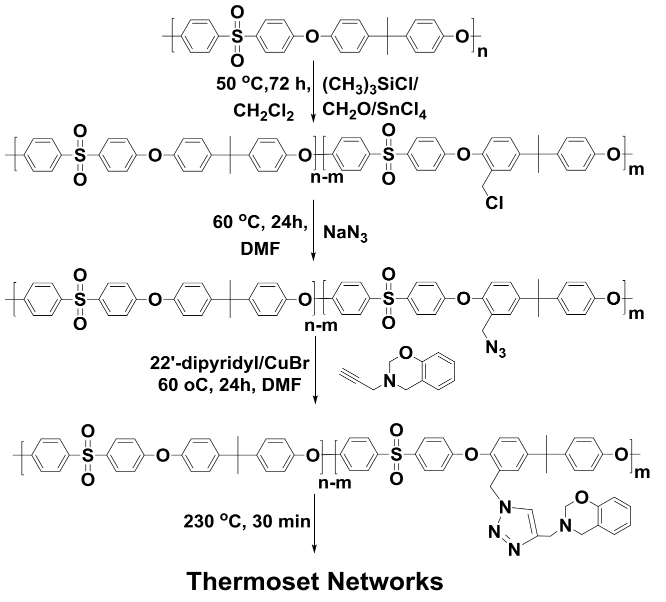
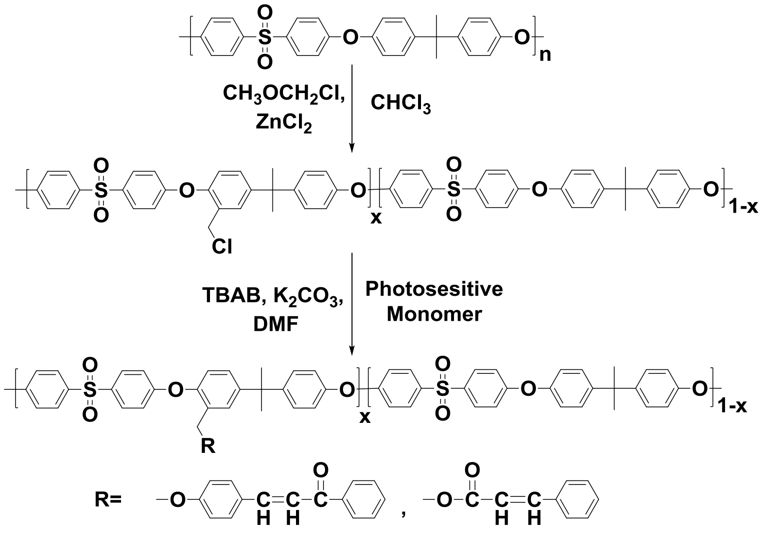


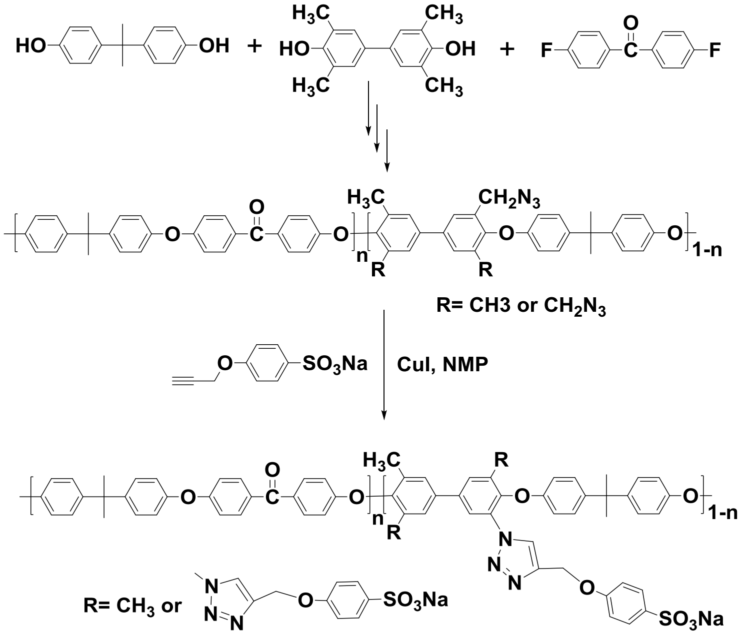
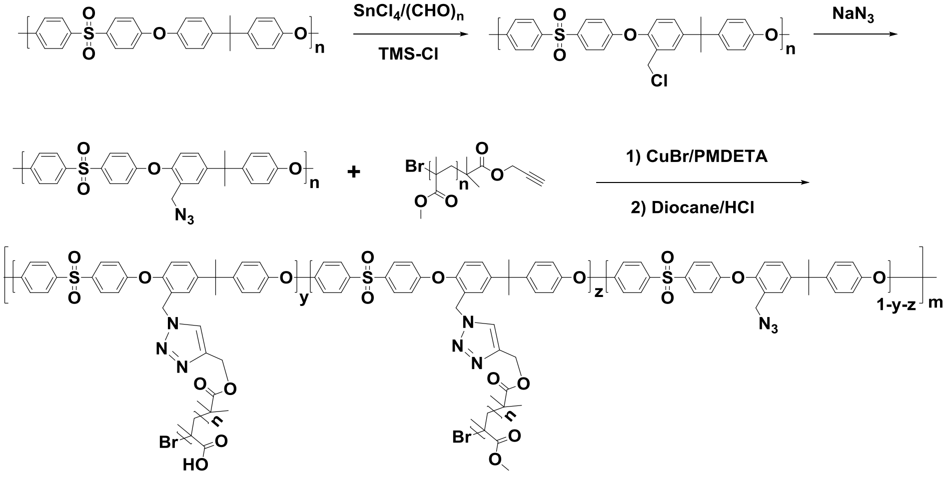
Figure 1.3. Synthesis of functional step-growth polymers by post-functionalization approach.

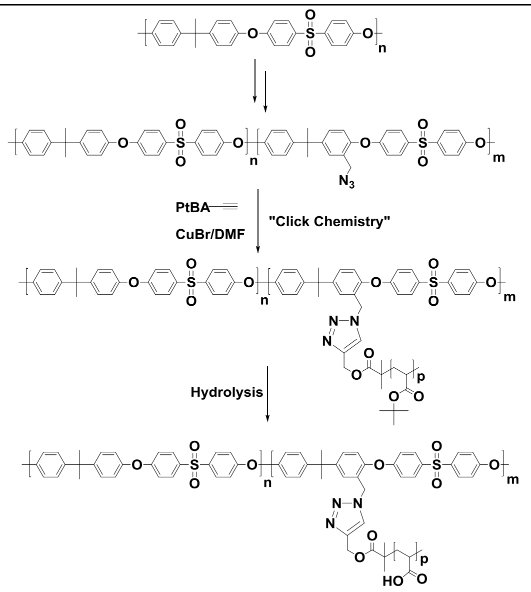
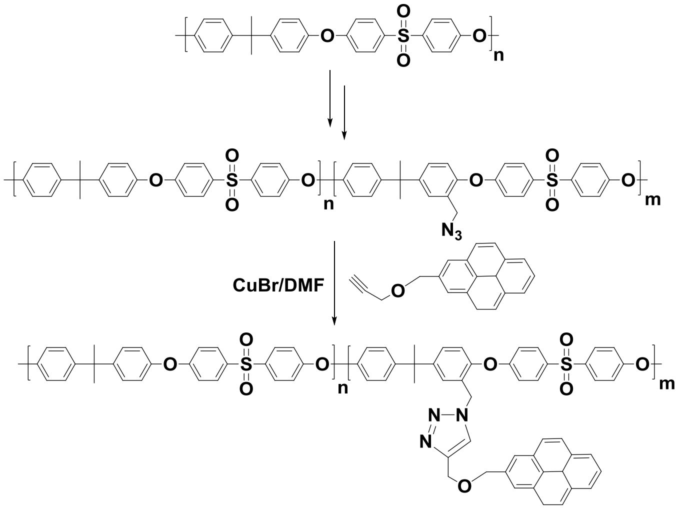
The desired chemical components can be efficiently linked up on polymer backbone at various points (known as clickable groups) with the help of click reactions. These groups can be introduced by post-modification of polymers through different type of reactions such as lithiation, halomethylation and/or sulfonation, as shown in **Table 1.4**. Polymers may be subsequently modified by the appropriate click reactions. However, this modification approach is associated with shortcomings such as non-quantitative reactions, and difficulties to control degree of modification. **Table 1.4** enumerates representative examples of step-growth polymers modified with the help of click chemistry using post-functionalization approach.

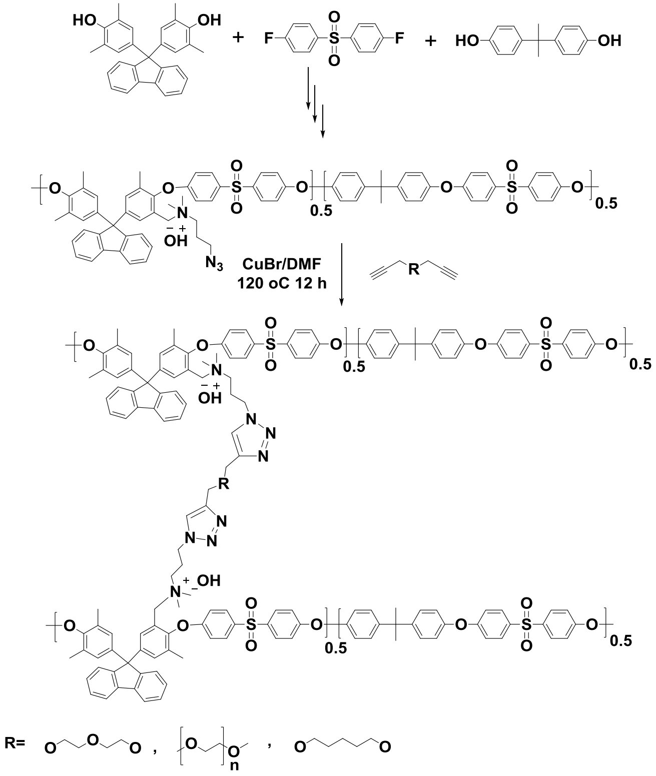
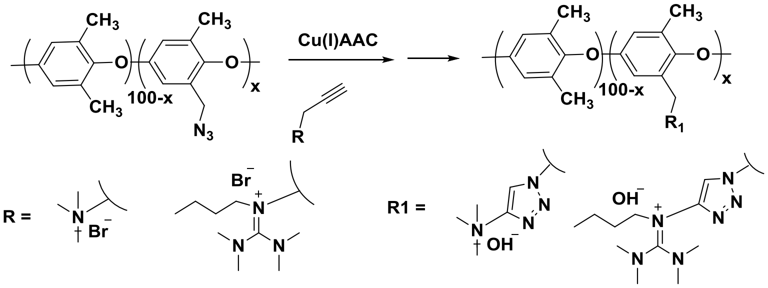
Table 1.4. Chemical modification of aromatic step-growth polymers *via* post-modification approach

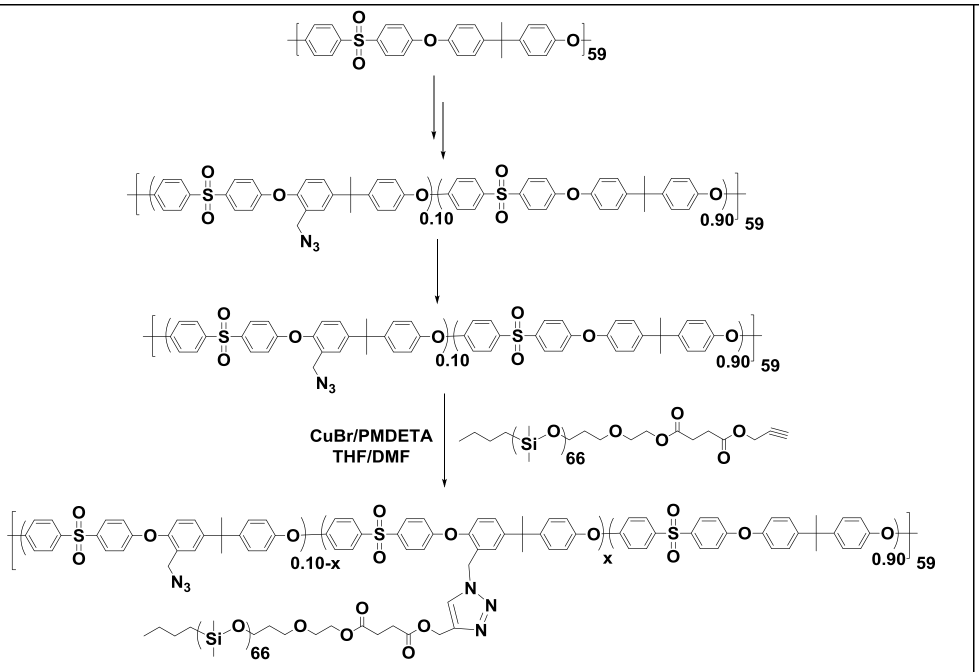
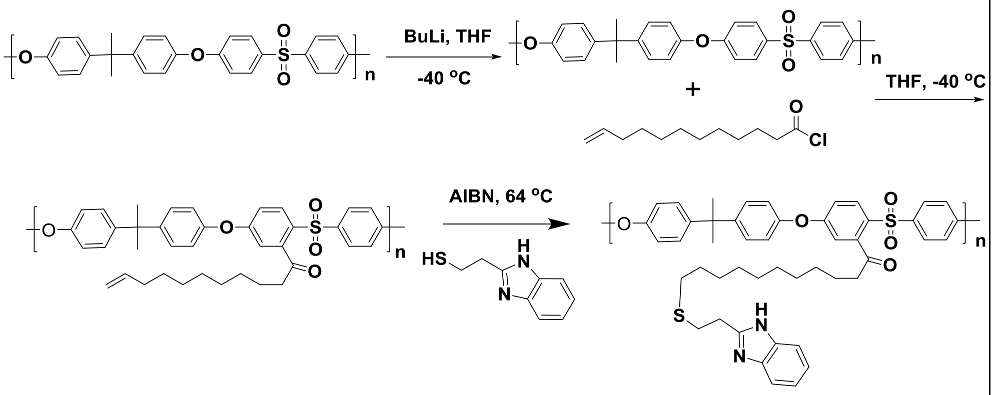
Sr. No.	Polymer	Reference
1	 A zwitterionic functional poly(ether sulfone) was synthesized by grafting zwitterionic sulfobetaine complex containing propargyl group onto poly(ether sulfone) possessing pendant azido groups. The modified poly(ether sulfone) displayed increased hydrophilic properties and excellent antifouling characteristics.	106
2	 Poly(ether sulfone)s bearing pendant azido groups were prepared using chloromethylation followed by azidation reaction, and the azido groups were subsequently modified *via* CuAAC click reactions to obtain poly(ether sulfone)s with the range of functional groups.	107

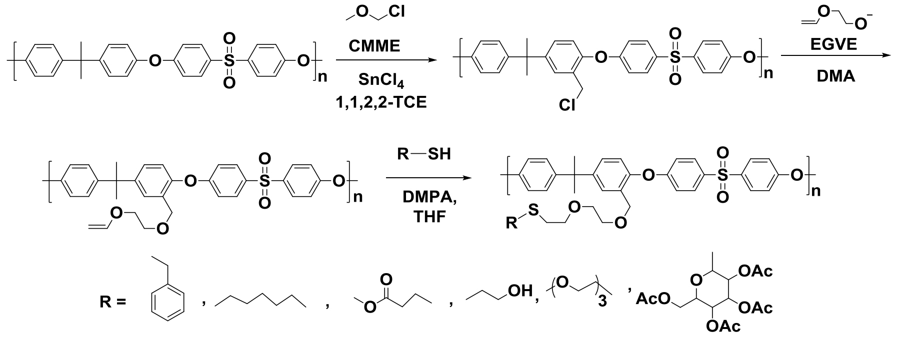
3	 The overall procedure involved preparation of self-curable polysulfone containing pendant benzoxazine moieties using different chemical transformations such as chloromethylation, azidation and CuAAC reactions. The polymer containing pendant benzoxazine groups was allowed to form cross-linked polysulfone under thermal condition.	108
4	 The photosensitive poly(ether sulfone)s containing pendant chalcone or cinnamoyl moieties were prepared from chloromethylated polysulfones. The photo-crosslinking of polymers bearing pendant chalcone or cinnamoyl units resulted into cross-linked polysulfones, which exhibited enhanced thermal, mechanical and chemical resistance.	109

5	 A series of sulfonated poly(arylene ether ketone)s containing clusters of sulfophenyl groups were prepared using sequence of reactions namely, polycondensation, bromination, azido-functionaliztion and sulfophenylation. The prepared membranes exhibited high proton conductivity.	110
6	 A combination of ATRP and CuAAC click reaction was made use of for synthesis of amphiphilic binary graft copolymer polysufone-*graft*-[poly(methyl mehtacrylate)-*random*-poly(acrylic acid)]. The hydrophilized membranes exhibited increased water flux while maintaining their mechanical properties.	111

7	 The CuAAC reaction was demonstrated for the preparation of amphiphilic poly(ether sulfone)-g-polyacrylic acid copolymers. The approach of combining controlled living polymerization and click chemistry methods provided fair control on hydrophilic characteristics of poly(ether sulfone)s. Poly(ether sulfone)-g-polyacrylic acid copolymers exhibited reduced protein fouling and cell adhesion properties compared to parent poly(ether sulfone).	112
8	 The fluorescence active poly(ether sulfone)s were prepared by CuAAC click reaction of poly(ether sulfone) containing pendant azido groups with 1-[(2-propynyloxy)methyl]pyrene.	113

9	 Poly(ether sulfone)s possessing pendant azido groups connected to the backbone *via* quaternary ammonium moieties were prepared and were subsequently reacted with three different dialkyne cross-linking agents *via* CuAAC click reaction to obtain cross-linked anion exchange membranes useful as components of fuel cells.	114
10	 The introduction of clicked 1,2,3-triazole moieties into poly(2,6-dimethylphenylene oxide) (PPOs) backbone by CuAAC click reaction was demonstrated to effectively enhance ionic conduction in anion exchange membranes. The obtained membranes exhibited a considerably higher conductivity (up to 10 times) compared to that of anion exchange membranes without triazole groups.	115

11	 About 10% of repeating units of commercial poly(ether sulfone)s were first chloromethylated. The introduced chloride groups were then substituted by azide moieties using sodium azide as the nucleophile. Furthermore, alkyne-terminated poly(dimethylsiloxane) was grafted onto poly(ether sulfone)s by CuAAC click reaction to obtain graft copolymer which exhibited anti-smudge properties.	116
12	 Poly(ether sulfone) containing pendant benzimidazole units which are potentially useful as membrane material in fuel cells was prepared by reaction of lithiated poly(ether sulfone) with 10-undecenoyl chloride, followed by thiol-ene click reaction with 2-(2-benzimidazolyl)ethanethiol.	117

13	 The vinyl ether groups were incorporated as pendant groups to poly(ether sulfone) backbone and were subsequently transformed into different functional groups by thiol-ene click reaction.	118

1.3.2 Functional monomer approach

With the help of different suitable functional monomers, various clickable groups, *viz.*, azido, maleimide, furyl, alkene, alkyne, etc. can be introduced into the polymer backbone. The schematic illustration of this approach is shown in **Figure 1.3**.

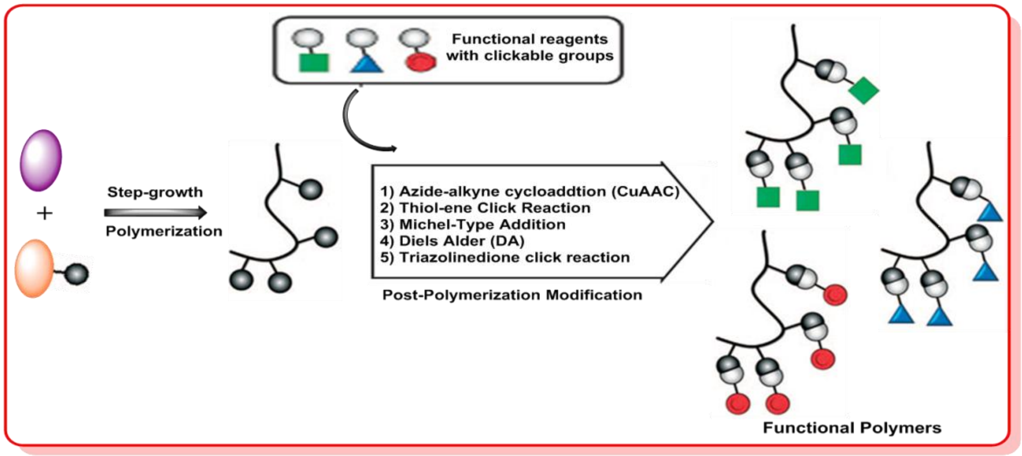
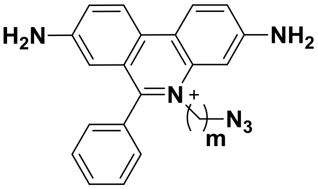
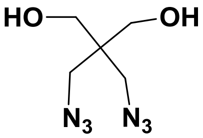
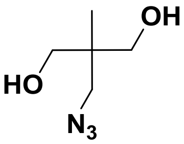
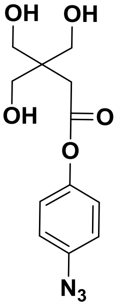
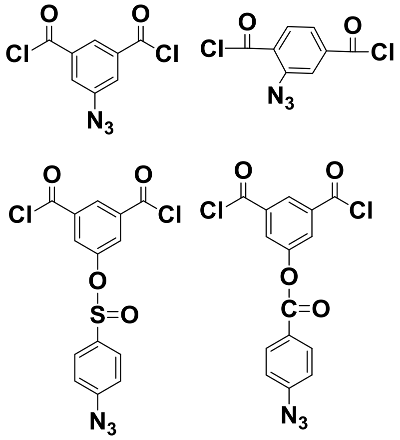
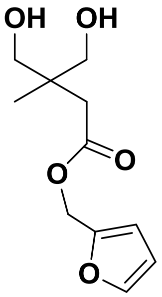
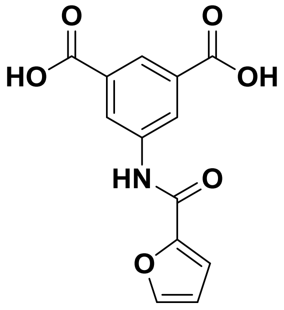
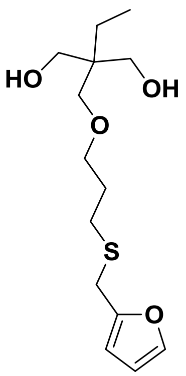


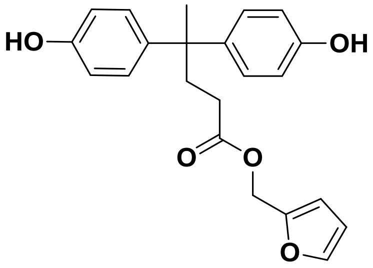
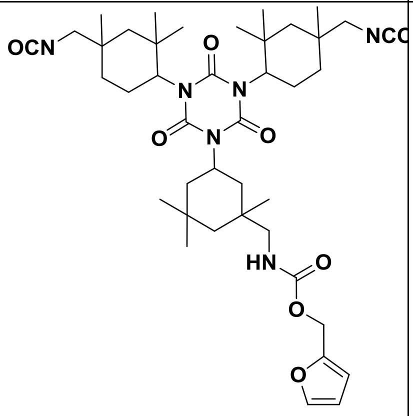
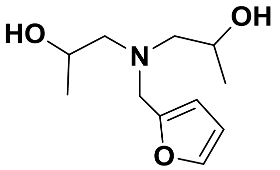
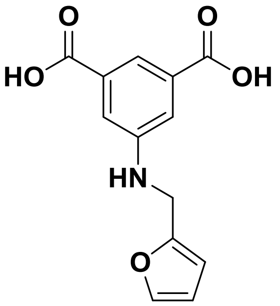
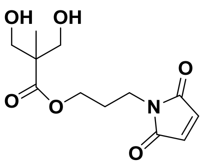
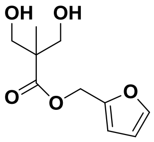
Figure 1.4. Synthesis of functional step-growth polymers by functional monomer approach.

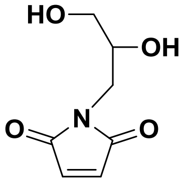
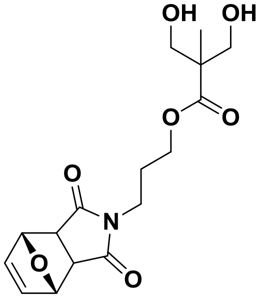
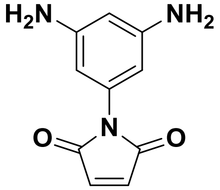
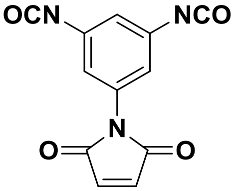
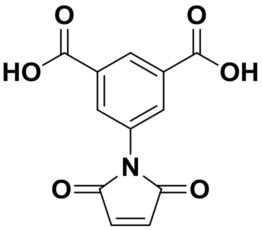
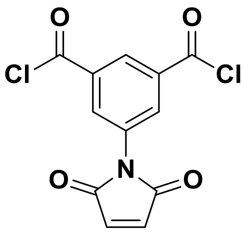
Several published reports deal with synthesis of clickable monomers which can be employed for the synthesis of different classes of step-growth polymers having clickable groups attached to the polymer backbone. With the use of monomers having functional group(s) which are inert towards polymerization conditions, reactive functional polymers can be synthesized directly. The clickable groups present on the polymer backbone can further be modified using appropriate click reaction to incorporate additional functionality and/or alter the physicochemical properties of interest without significantly impairing their characteristic properties. Clickable difunctional monomers need to be designed and synthesized specially due to their lack of availability from commercial sources. In comparison to their utilization in aliphatic polymers, different type of click reactions such as, CuAAC, thiol-ene, Diels-Alder, and so on have been relatively less explored in the field of aromatic step-growth polymers. Copolymerization of clickable difunctional monomers gives an opportunity to perform orthogonal click reactions. Moreover, one type of difunctional clickable monomer can be utilized to synthesize different types of step-growth polymers by appropriate choice of comonomers. **Table 1.5** lists representative polymers reported from clickable difunctional monomers.

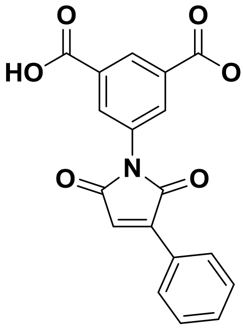
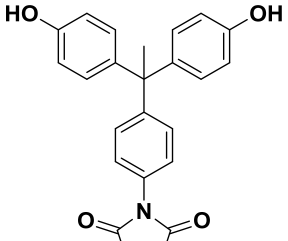
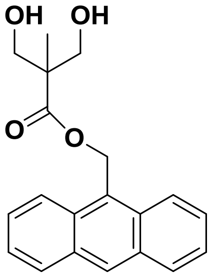
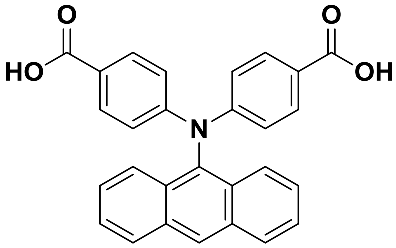
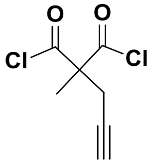
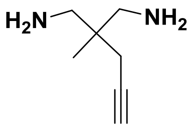
Table 1.5. List of difunctional monomers bearing pendant azido, furyl, maleimide, anthracene, alkyne or allyl group

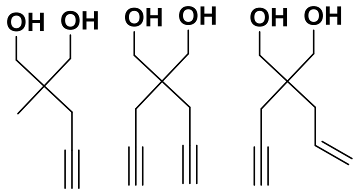
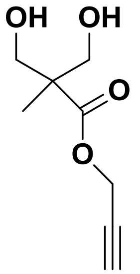
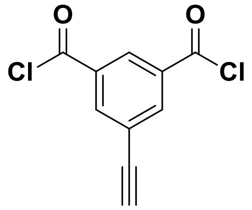
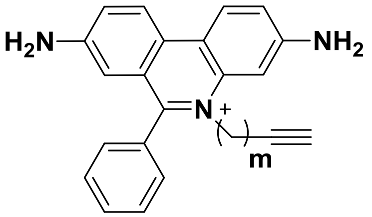
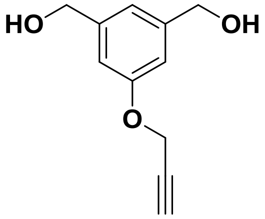
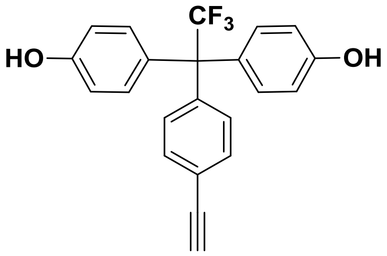
Sr. No.	Difunctional monomers bearing clickable group	Polymer	References
(A) Difunctional monomers containing pendant azido group			
1		The compound was used as potent acetylcholinesterase (AChE) inhibitor using *in-situ* CuAAC click reaction.	119
2		Polytriazoles potentially useful as adhesives and coatings were prepared by CuAAC click reaction.	120
3		Aliphatic polyesters containing pendant azido groups were synthesized using enzymatic polycondensation and post-modified *via* CuAAC click reaction.	121
4		The azido compound was coupled with carbon nano-tubes *via* CuAAC click reaction. The multi-walled carbon nano-tubes were incorporated into polyurethanes *via* reaction with diisocyanates.	122

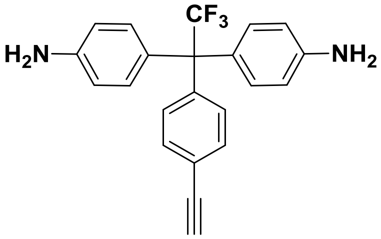
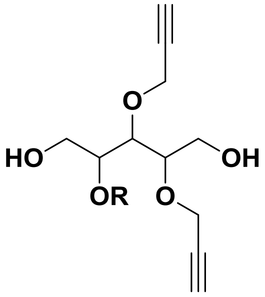
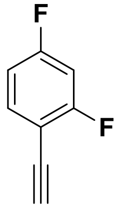
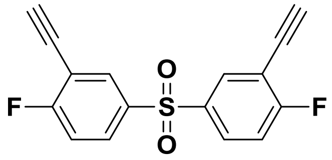
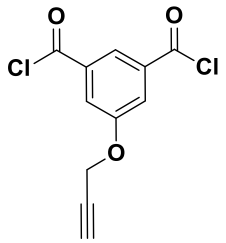
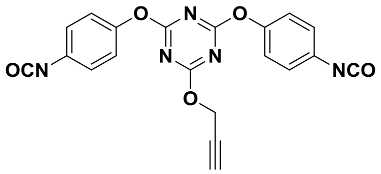
5		Aromatic polyesters and polyamides containing pendant azido groups were synthesized and subsequently cross-linked under thermal and photochemical conditions. Additionally, polyamides bearing pendant azido groups were post-modified by CuAAC click reaction.	72,123,124
	(B) Difunctional monomers containing pendant furyl group		
6		Aliphatic polyesters bearing pendant furyl groups were synthesized and thermo-reversibility of cross-linked polyesters was evaluated.	125
7		Thermally corss-linkable aromatic polyamides were synthesized by direct polycondensation of 5-(furamido)isophthalic acid with different aromatic diamines.	126
8		The diol monomer containing pendant furyl group was used as a component in the preparation of thermo-remendable shape memory polyurethanes.	127

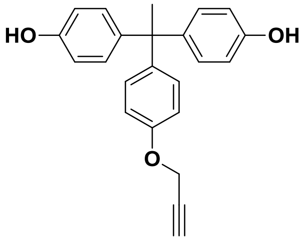
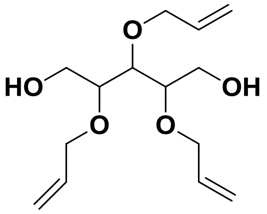
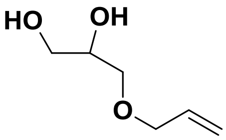
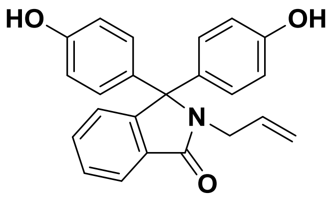
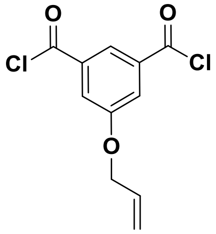
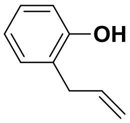
9		Bio-based phenolic resin was synthesized by polymerizing furfuryl diphenolate, furfuryl gallate and furfural.	128
10		Furfuryl alcohol was used to modify one of the isocyanate groups of IPDI trimer with the aim of preparing reversible cross-linked polypropylene glycol-based polyurethanes *via* Diels-Alder reaction.	129
11		Thermally reversible poly(ether-urethane) networks were prepared by Diels-Alder cross-linking reaction of furyl-containing poly(ether-urethane) with bismaleimides.	130
12		Aromatic polyamides containing pendant furyl groups were synthesized and were subsequently converted into recyclable themosets by Diels-Alder click reaction.	131
(C) Difunctional monomers containing pendant maleimide group			
13	 	Single component self-healing polyurethanes were synthesized based on thermo-reversible furan/maleimide Diels-Alder click reaction.	132

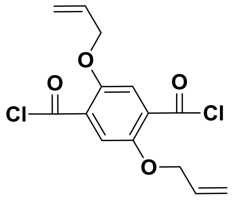
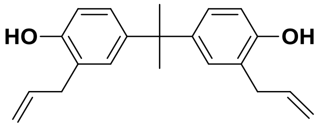
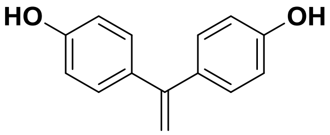
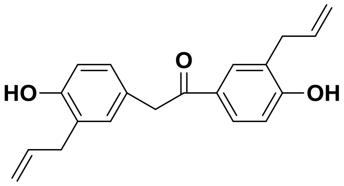
14		Aliphatic polyurethanes containing pendant maleimide groups were synthesized and thermo-reversibly cross-linked polymers were prepared by Diels-Alder reaction.	133
15		Aliphatic polyurethanes and polycarbonates containing pendant maleimide groups were synthesized and were subsequently post-modified by metal-free thiol-maleimide Michel type addition click reaction.	98,99
16		Aromatic polyimides bearing pendant maleimide groups were synthesized and were thermally cured.	134
17		Polyurethanes containing pendant maleimide groups were synthesized and were cross-linked by thermal treatment as well as by furan/maleimide Diels-Alder reaction.	135,136
18		Aromatic polyesters and polyamides bearing pendant maleimide groups were prepared and were subsequently cross-linked by thermal treatment as well as by furan/maleimide Diels-Alder reaction.	137–141
19		A series of cross-linkable aromatic polyketones and polyamides containing pendant maleimide groups were synthesized and were cross-linked under thermal conditions.	142–144

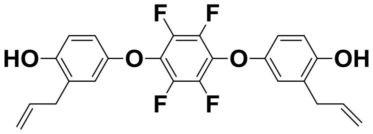
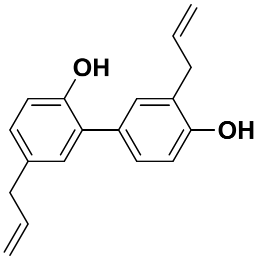
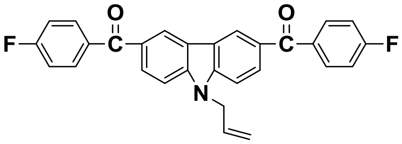
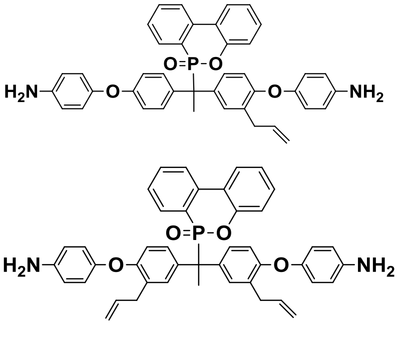
20		Aromatic diacid containing pendant phenylmaleimide groups was incorporated into PET. The modified PET exhibited self-extinguishing and anti-dripping properties.	145
21		Bisphenol containing pendant maleimide group was synthesized and its potential applications were claimed.	146
(D) Difunctional monomers containing pendant anthracene group			
22		Aliphatic polyurethanes and polycarbonates containing pendant anthracene moieties were synthesized and were post-modified by Diels-Alder click reaction.	84,85,147
23		A series of polyamides bearing pendant anthryl groups were syntheiszed from dicarboxylic acid and aromatic diamines by direct phosphorylation polycondensation.	148
(E) Difunctional monomers containing pendant alkyne group			
24	 	Aliphatic polyamides containing pendant alkyne groups were prepared and were functionalized with two types of functionlization reactions namely CuAAC and thiol-yne radical addition reaction.	149

25		Alkyne functionalized aliphatic polyesters and polyurethanes were synthesized and were post-modified by CuAAC click reactions.	36,150–152
26		The diol monomer was used to synthesize clickable polyurethanes.	147
27		The diacid monomer was employed for preparation of clickable thin film composite polyamide membranes which allowed a very simple and easy surface modification of the membrane by CuAAC click chemistry.	153
28		The diamine containing pendant porpargyl group was used as potent acetylcholinesterase (AChE) inhibitors through in-*situ* CuAAC click chemistry.	119
29		Polyurethanes bearing pendant alkyne groups were synthesized and were post-functionalized by CuAAC click reaction.	36,154
30		Poly(arylene ether)s were synthesized and were cured under thermal conditions.	155,156

31		Aromatic polyimides and copolyimides containing pendant alkyne groups were prepared and were subsequently cross-linked *via* thermal treatment.	157
32		Biodegradable graft or comb-like aliphatic polyurethanes were synthesized and were post-modified *via* CuAAC click reaction.	158
33		Copoly(arylene ether)s containing pendant alkyne groups were synthesized and cross-linked polymers were prepared by thermal curing.	159
34		Poly(ether sulfone)s containing pendant alkyne groups ware prepared and were subsequently post-modified by CuAAC click reaction.	160
35		Aromatic polyesters were prepared and were post-modified by CuAAC click reaction.	104
36		A series of linear aromatic polyurethanes possessing pendant alkyne groups was prepared. Polyurethanes were post-functionalized by CuAAC click reaction.	161

37		Aromatic polyesters were prepared and were post-modified by CuAAC click reaction.	104
(F) Difunctional monomers containing pendant alkene group			
38		Polyurethanes containing multiple pendant allyloxy groups were synthesized and were post-functionalized by thiol-ene click reaction with different thiols.	162,163
39		Aliphatic polyurethanes containing pendant allyl groups were prepared and were post-modified *via* thiol-ene click reaction.	152
40		Aromatic polyesters bearing pendant allyl groups were prepared from allyl group containing bisphenol and different aromatic diacid chlorides by interfacial polycondensation method and their properties were studied.	164
41		Aromatic polyamides and polyesters were prepared and post-functionalized by thiol-ene click reaction.	104
42		Synthesis and characterization of poly(arylene ether) containing allyl groups was carried out by oxidative coupling copolymerization of 2-allyl-6-methylphenol with 2,6-dimethylphenol, followed by thermal curing.	165

43		A series of aromatic copolyamides bearing pendant allyloxy groups were synthesized. Thermal treatment of polyamides led to the formation of polymers containing pendant hydroxyl groups *via* Claisn rearrangement. Polyamides bearing reactive allyloxy and hydroxy groups are potentially useful as sizing agent of Kevlar fibers to improve interfacial adhesion of rubber- or epoxy-based composites.	166,167
44		The diallyl bisphenol was utilized for the preparation of different classes of polymers such as aromatic polycarbonates and poly(arylene ether)s. Subsequently, polymers containing pendant allyl groups were post-modified by different reactions such as thiol-ene, hydrosilylation, olefin metathesis, photo/thermal curing etc, to alter polymer properties.	168–175
45		Poly(ether sulfone)s containing pendant allyl groups were synthesized and were chemically modified using thiol-ene reaction to produce corresponding sulfonated derivatives for applications in fuel cells.	176
46		Aromatic polyesters containing pendant allyl groups exhibiting impressive thermal properties characteristics of nonflammable materials were	177

		synthesized. Furthermore, these polyesters were cross-linked *via* UV-mediated thiol-ene click reaction using multifunctional thiol cross-linker.	
47		Thermally curable aromatic poly(arylene ether)s were prepared by polycondensation of allyl functionalized bisphenol with decafluorobiphenyl.	178
48		Partially bio-based aromatic polycarbonates containing pendant allyl groups were synthesized by phosgene route.	179
49		Carbazole based poly(aryl ether ketone)s containing pendant allyl groups were synthesized and their thermal curing behavior was studied.	180
50		Polyimides containing pendant allyl groups were synthesized and were cross-linked by thermal treatment to enhance their thermal and mechanical properties.	181,182

The incorporation of functional groups into polymer backbone followed by their functionalization offered an efficient pathway to modify their physico-chemical properties such as bioactivity, hydrophilicity, elasticity, etc. These properties are highly useful for different applications such as self-healing, membranes with antifouling properties, anion transport exchange membranes, etc.

1.4 Summary

The fascinating approach of post-polymerization modification for synthesis of functional polymers helps to overcome the problems of limited functional group tolerance in case of different polymerization methods. The quantitative and selective functional group tolerant transformations are mandatory for the success of this approach. As click chemistry fulfills most of the criteria, it is ideally suited for the synthesis of various functional step-growth polymers. In this chapter, two different strategies, namely, post-functionalization approach and functional monomer approach to obtain side chain functionalized polymers using various click reactions, e.g. 1, 3-dipolar cycloaddition, Diels-Alder reaction and thiol-based ligations were highlighted. These reactions are generally fast, regiospecific, and offer high yields under mild reaction conditions. It is envisioned that the combination of step-growth polymerization and click chemistry approach will continue to flourish in the near future leading to new functional step-growth polymers and broaden their physico-chemical properties meeting the demands of newer applications.

1.5 Scope and objectives of the Thesis

Bisphenol-A (BPA) is one of the highest-volume difunctional step-growth monomers currently produced on an industrial scale. In 2008, about 4 million tons of BPA was produced globally and it was anticipated to increase to about 8 million tons per annum in 2018. BPA is a versatile and valuable difunctional monomer building block which is useful for synthesis of different classes of aromatic step growth polymers such as polyesters, polycarbonates, polyphosphonates, poly(arylene ether)s, epoxy resins, cyanate esters, etc. These polymers find broad range of applications in various industries such as construction, packaging, coatings, electronics, aerospace and so on. For more targeted applications and to further broaden the application range of these polymers, post-polymerization modification of polymer backbone is highly essential in order to acquire desired properties. The aim of post-polymerization modification is to introduce different functional groups into these polymeric materials and/or impart the physico-chemical properties of interest without significantly impairing their characteristic properties. The incorporation of pendant functional groups such as azido, furyl, and maleimide is of particular interest as these groups provide a useful platform for efficient post-modification by click chemistry approach. The post- modification by click chemistry approach has so far been predominantly applied to aliphatic polymers such as polyesters, polyamides, polycarbonates, polyurethanes, etc. On the other hand, the click chemistry modifications of aromatic step growth polymers such as polycarbonates, polyesters, polyamides, poly(arylene ether)s, etc obtained *via* functional monomer approach is an emerging field of research and its scope and limitations have not been fully defined.

The overall objective of the present thesis was to develop strategies for synthesis of aromatic step-growth polymers bearing pendant clickable groups *via* functional monomer approach and to study the chemical modification of synthesized polymers using appropriate click reactions so as to obtain functional polymers. The following specific objectives were chosen for the work.

1. Design and synthesis of bisphenol monomers containing pendant ‘clickable’ groups such as azido, furyl or maleimide.
2. Synthesis and characterization of aromatic step growth polymers such as polycarbonates, polyesters, and poly(arylene ether)s based on synthesized bisphenols bearing clickable functional group under appropriate reaction conditions.
3. Chemical modifications of aromatic step growth polymers containing pendant clickable groups using azide-alkyne, maleimide-thiol and azide-maleimide click reactions.
4. Photochemical cross-linking of polyesters and polycarbonates containing pendant azido groups.
5. Thermally reversible cross-linking of poly(arylene ether)s containing pendant furyl groups with bismaleimides.

1.6 References

1. Raue, M., Wambach, M., Glöggler, S., Grefen, D., Kaufmann, R., Abetz, C., Georgopanos, P., Handge, U. A., Mang, T., Blümich, B., Abetz, V. *Macromol. Chem. Phys.*, 2014, **215**, 245–254.
2. Ober, C. K., Cheng, S. Z. D., Hammond, P. T., Muthukumar, M., Reichmanis, E., Wooley, K. L., Lodge, T. P. *Macromolecules*, 2009, **42**, 465–471.
3. Kolb, H. C., Finn, M. G., Sharpless, K. B. *Angew. Chem. Int. Ed.*, 2001, **40**, 2004–2021.
4. Qin, A., Lam, J. W. Y., Tang, B. Z. *Macromolecules*, 2010, **43**, 8693–8702.
5. Golas, P. L., Matyjaszewski, K. *Chem. Soc. Rev.*, 2010, **39**, 1338–1354.
6. Nandivada, H., Jiang, X., Lahann, J. *Adv. Mater.*, 2007, **19**, 2197–2208.
7. Barner-Kowollik, C., Du Prez, F. E., Espeel, P., Hawker, C. J., Junkers, T., Schlaad, H.,

Van Camp, W. *Angew. Chem. Int. Ed.*, 2011, **50**, 60–62.

8. Rostovtsev, V. V., Green, L. G., Fokin, V. V., Sharpless, K. B. *Angew. Chem. Int. Ed.*, 2002, **41**, 2596–2599.
9. Tornøe, C. W., Christensen, C., Meldal, M. *J. Org. Chem.*, 2002, **67**, 3057–3064.
10. Sumerlin, B. S., Vogt, A. P. *Macromolecules*, 2010, **43**, 1–13.
11. Kumaraswamy, G., Ankamma, K., Pitchaiah, A. *J. Org. Chem.*, 2007, **72**, 9822–9825.
12. Heredia, K. L., Tolstyka, Z. P., Maynard, H. D. *Macromolecules*, 2007, **40**, 4772–4779.
13. Dirksen, A., Dawson, P. E. *Bioconjug. Chem.*, 2008, **19**, 2543–2548.
14. Campos, L. M., Killops, K. L., Sakai, R., Paulusse, J. M. J., Damiron, D., Drockenmuller, E., Messmore, B. W., Hawker, C. J. *Macromolecules*, 2008, **41**, 7063–7070.
15. Killops, K. L., Campos, L. M., Hawker, C. J. *J. Am. Chem. Soc.*, 2008, **130**, 5062–5064.
16. Koo, S. P. S., Stamenović, M. M., Prasath, R. A., Inglis, A. J., Du Prez, F. E., Barner-Kowollik, C., Van Camp, W., Junkers, T. *J. Polym. Sci. Part A Polym. Chem.*, 2010, **48**, 1699–1713.
17. Prasath, R. A., Gokmen, M. T., Espeel, P., Du Prez, F. E. *Polym. Chem.*, 2010, **1**, 685–692.
18. Mansfeld, U., Pietsch, C., Hoogenboom, R., Becer, C. R., Schubert, U. S. *Polym. Chem.*, 2010, **1**, 1560–1598.
19. Döhler, D., Michael, P., Binder, W. H. *Macromolecules*, 2012, **45**, 3335–3345.
20. An, S. Y., Noh, S. M., Nam, J. H., Oh, J. K. *Macromol. Rapid Commun.*, 2015, **36**, 1255–1260.
21. Chen, Y., Guan, Z. *J. Am. Chem. Soc.*, 2010, **132**, 4577–4579.
22. Yu, T.-B., Bai, J. Z., Guan, Z. *Angew. Chem. Int. Ed.*, 2009, **48**, 1097–1101.
23. Morgenroth, F., Reuther, E., Müllen, K. *Angew. Chem. Int. Ed.*, 1997, **36**, 631–634.
24. Gacal, B., Durmaz, H., Tasdelen, M. a, Hizal, G., Tunca, U., Yagci, Y., Demirel, A. L. *Macromolecules*, 2006, **39**, 5330–5336.
25. Urbani, C. N., Bell, C. A., Lonsdale, D. E., Whittaker, M. R., Monteiro, M. J. *Macromolecules*, 2007, **40**, 7056–7059.
26. Gauthier, M. A., Gibson, M. I., Klok, H. A. *Angew. Chem. Int. Ed.*, 2009, **48**, 48–58.
27. Döhler, D., Michael, P., Binder, W. H. *Acc. Chem. Res.*, 2017, **50**, 2610–2620.
28. Xi, W., Scott, T. F., Kloxin, C. J., Bowman, C. N. *Adv. Funct. Mater.*, 2014, **24**, 2566–

2566.

29. An, S. Y., Arunbabu, D., Noh, S. M., Song, Y. K., Oh, J. K. *Chem. Commun.*, 2015, **51**, 13058–13070.
30. Iha, R. K., Wooley, K. L., Nyström, A. M., Burke, D. J., Kade, M. J., Hawker, C. J. *Chem. Rev.*, 2009, **109**, 5620–5686.
31. Fournier, D., Hoogenboom, R., Schubert, U. S. *Chem. Soc. Rev.*, 2007, **36**, 1369.
32. Michinobu, T. *Chem. Soc. Rev.*, 2011, **40**, 2306.
33. Kempe, K., Krieg, A., Becer, C. R., Schubert, U. S. *Chem. Soc. Rev.*, 2012, **41**, 176–191.
34. Roy, N., Bruchmann, B., Lehn, J.-M. *Chem. Soc. Rev.*, 2015, **44**, 3786–3807.
35. Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2014, **52**, 3147–3165.
36. Fournier, D., Du Prez, F. *Macromolecules*, 2008, **41**, 4622–4630.
37. Rivero, G., Nguyen, L.-T. T., Hillewaere, X. K. D., Du Prez, F. E. *Macromolecules*, 2014, **47**, 2010–2018.
38. Espeel, P., Du Prez, F. E. *Macromolecules*, 2015, **48**, 2–14.
39. Blasco, E., Sims, M. B., Goldmann, A. S., Sumerlin, B. S., Barner-Kowollik, C. *Macromolecules*, 2017, **50**, 5215–5252.
40. Lecomte, P., Riva, R., Jérôme, C., Jérôme, R. *Macromol. Rapid Commun.*, 2008, **29**, 982–997.
41. Le Droumaguet, B., Velonia, K. *Macromol. Rapid Commun.*, 2008, **29**, 1073–1089.
42. Belbekhouche, S., Guerrouache, M., Carbonnier, B. *Macromol. Chem. Phys.*, 2016, **217**, 997–1006.
43. Binder, W. H. *Macromol. Rapid Commun.*, 2008, **29**, 951–951.
44. Meldal, M. *Macromol. Rapid Commun.*, 2008, **29**, 1016–1051.
45. Goldmann, A. S., Glassner, M., Inglis, A. J., Barner-Kowollik, C. *Macromol. Rapid Commun.*, 2013, **34**, 810–849.
46. Dai, Y., Zhang, X., Xia, F. *Macromol. Rapid Commun.*, 2017, **38**, 1700357.
47. Tasdelen, M. A. *Polym. Chem.*, 2011, **2**, 2133–2145.
48. Liu, Y.-L., Chuo, T.-W. *Polym. Chem.*, 2013, **4**, 2194–2205.
49. Lowe, A. B. *Polym. Chem.*, 2014, **5**, 4820–4870.
50. Hall, D. J., Van Den Berghe, H. M., Dove, A. P. *Polym. Int.*, 2011, **60**, 1149–1157.
51. Lowe, A. B. *Polymer*, 2014, **55**, 5517–5549.

52. Meldal, M., Tornøe, C. W. *Chem. Rev.*, 2008, **108**, 2952–3015.

53. Buckley, B. R., Dann, S. E., Heaney, H. *Chem. - A Eur. J.*, 2010, **16**, 6278–6284.

54. Rodionov, V. O., Presolski, S. I., Gardinier, S., Lim, Y. H., Finn, M. G. *J. Am. Chem. Soc.*, 2007, **129**, 12696–12704.

55. Rodionov, V. O., Presolski, S. I., Díaz Díaz, D., Fokin, V. V., Finn, M. G. *J. Am. Chem. Soc.*, 2007, **129**, 12705–12712.

56. Presolski, S. I., Hong, V., Cho, S.-H., Finn, M. G. *J. Am. Chem. Soc.*, 2010, **132**, 14570–14576.

57. Wang, Q., Chan, T. R., Hilgraf, R., Fokin, V. V., Sharpless, K. B., Finn, M. G. *J. Am. Chem. Soc.*, 2003, **125**, 3192–3193.

58. Ackermann, L., Potukuchi, H. K., Landsberg, D., Vicente, R. *Org. Lett.*, 2008, **10**, 3081–3084.

59. Friscourt, F., Boons, G.-J. *Org. Lett.*, 2010, **12**, 4936–4939.

60. Zhang, L., Chen, X., Xue, P., Sun, H. H. Y., Williams, I. D., Sharpless, K. B., Fokin, V. V., Jia, G. *J. Am. Chem. Soc.*, 2005, **127**, 15998–15999.

61. Kappe, C. O., Van der Eycken, E. *Chem. Soc. Rev.*, 2010, **39**, 1280–1290.

62. Amblard, F., Cho, J. H., Schinazi, R. F. *Chem. Rev.*, 2009, **109**, 4207–4220.

63. Spiteri, C., Moses, J. E. *Angew. Chem. Int. Ed.*, 2010, **49**, 31–33.

64. Hein, J. E., Tripp, J. C., Krasnova, L. B., Sharpless, K. B., Fokin, V. V. *Angew. Chem. Int. Ed.*, 2009, **48**, 8018–8021.

65. Raushel, J., Fokin, V. V. *Org. Lett.*, 2010, **12**, 4952–4955.

66. Park, J., Lee, C., Jung, J., Kang, H., Kim, K.-H., Ma, B., Kim, B. J. *Adv. Funct. Mater.*, 2014, **24**, 7588–7596.

67. Bang, J., Bae, J., Löwenhielm, P., Spiessberger, C., Given-Beck, S. A., Russell, T. P., Hawker, C. J. *Adv. Mater.*, 2007, **19**, 4552–4557.

68. Lee, S., Lee, B., Kim, B. J., Park, J., Yoo, M., Bae, W. K., Char, K., Hawker, C. J., Bang, J., Cho, J. *J. Am. Chem. Soc.*, 2009, **131**, 2579–2587.

69. Al Akhrass, S., Ostaci, R.-V., Grohens, Y., Drockenmuller, E., Reiter, G. *Langmuir*, 2008, **24**, 1884–1890.

70. Schuh, K., Prucker, O., Rühe, J. *Macromolecules*, 2008, **41**, 9284–9289.

71. Lê, D., Liénafa, L., Phan, T. N. T., Deleruyelle, D., Bouchet, R., Maria, S., Bertin, D.,

Gigmes, D. *Macromolecules*, 2014, **47**, 2420–2429.

72. Trigo-López, M., Barrio-Manso, J. L., Serna, F., García, F. C., García, J. M. *Macromol. Chem. Phys.*, 2013, **214**, 2223–2231.
73. Albuszis, M., Roth, P. J., Pauer, W., Moritz, H.-U. *Polym. Chem.*, 2016, **7**, 5414–5425.
74. Shibata, Y., Tanaka, H., Takasu, A., Hayashi, Y. *Polym. J.*, 2011, **43**, 272–278.
75. Diels, O., Alder, K. *Justus Liebig's Ann. der Chemie*, 1928, **460**, 98–122.
76. Sauer, J., Sustmann, R. *Angew. Chem. Int. Ed.*, 1980, **19**, 779–807.
77. Nicolaou, K. C., Snyder, S. A., Montagnon, T., Vassilikogiannakis, G. *Angew. Chem. Int. Ed.*, 2002, **41**, 1668–1698.
78. Ripoll, J. L., Rouessac, A., Rouessac, F. *Tetrahedron*, 1978, **34**, 19–40.
79. Inglis, A. J., Barner-Kowollik, C. *Macromol. Rapid Commun.*, 2010, **31**, 1247–1266.
80. Szalai, M. L., McGrath, D. V., Wheeler, D. R., Zifer, T., McElhanon, J. R. *Macromolecules*, 2007, **40**, 818–823.
81. Polgar, L. M., Kingma, A., Roelfs, M., van Essen, M., van Duin, M., Picchioni, F. *Eur. Polym. J.*, 2017, **90**, 150–161.
82. Wang, A., Niu, H., He, Z., Li, Y. *Polym. Chem.*, 2017, **8**, 4494–4502.
83. Zhang, Y., Dai, Z., Han, J., Li, T., Xu, J., Guo, B. *Polym. Chem.*, 2017, **8**, 4280–4289.
84. Agar, S., Durmaz, H., Gunay, U. S., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 521–527.
85. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.
86. Durmaz, H., Colakoglu, B., Tunca, U., Hizal, G. *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 1667–1675.
87. Inglis, A. J., Sinnwell, S., Stenzel, M. H., Barner-Kowollik, C. *Angew. Chem. Int. Ed.*, 2009, **48**, 2411–2414.
88. Blackman, M. L., Royzen, M., Fox, J. M. *J. Am. Chem. Soc.*, 2008, **130**, 13518–13519.
89. Devaraj, N. K., Upadhyay, R., Haun, J. B., Hilderbrand, S. A., Weissleder, R. *Angew. Chem. Int. Ed.*, 2009, **48**, 7013–7016.
90. Li, Z., Cai, H., Hassink, M., Blackman, M. L., Brown, R. C. D., Conti, P. S., Fox, J. M. *Chem. Commun.*, 2010, **46**, 8043–8045.
91. Tasdelen, M. A. *Polym. Chem.*, 2011, **2**, 2133.

92. Hoyle, C. E., Bowman, C. N. *Angew. Chem. Int. Ed.*, 2010, **49**, 1540–1573.

93. Hoyle, C. E., Lee, T. Y., Roper, T. *J. Polym. Sci. Part A Polym. Chem.*, 2004, **42**, 5301–5338.

94. Mather, B. D., Viswanathan, K., Miller, K. M., Long, T. E. *Prog. Polym. Sci.*, 2006, **31**, 487–531.

95. Hoyle, C. E., Lowe, A. B., Bowman, C. N. *Chem. Soc. Rev.*, 2010, **39**, 1355–1387.

96. Xu, J., Tao, L., Boyer, C., Lowe, A. B., Davis, T. P. *Macromolecules*, 2010, **43**, 20–24.

97. Dondoni, A. *Angew. Chem. Int. Ed.*, 2008, **47**, 8995–8997.

98. Onbulak, S., Tempelaar, S., Pounder, R. J., Gok, O., Sanyal, R., Dove, A. P., Sanyal, A. *Macromolecules*, 2012, **45**, 1715–1722.

99. Billiet, L., Gok, O., Dove, A. P., Sanyal, A., Nguyen, L.-T. T., Du Prez, F. E. *Macromolecules*, 2011, **44**, 7874–7878.

100. Rogers, M. E., Long, T. E., Turner, S. R. In *Introduction to Synthetic Methods in Step-Growth Polymers* John Wiley & Sons, Inc., Hoboken, NJ, USA 2003; pp. 1–16.

101. Cunningham, W. A. *J. Chem. Educ.*, 1935, **12**, 120.

102. Oesper, R. E. *J. Chem. Educ.*, 1929, **6**, 677.

103. Serniuk, G. E., Banes, F. W., Swaney, M. W. *J. Am. Chem. Soc.*, 1948, **70**, 1804–1808.

104. Kumari, S. Ph.D. Thesis, Savitribai Phule Pune University, India, 2013.

105. Billiet, L., Fournier, D., Du Prez, F. *Polymer*, 2009, **50**, 3877–3886.

106. Xu, C., Gu, S., Huang, J., Xu, W., Xia, H., Du, J., Liu, H., Yang, H., Zhou, Y., Bai, Z. *J. Appl. Polym. Sci.*, 2015, **132**, 41327–41332.

107. Gaina, C., Gaina, V., Ionita, D. *Polym. Int.*, 2011, **60**, 296–303.

108. Dizman, C., Altinkok, C., Tasdelen, M. A. *Des. Monomers Polym.*, 2017, **20**, 293–299.

109. Tie, W., Zhong, Z., Li, L., Zhang, A., Shen, F., Lee, M.-H., Li, X.-D. *Eur. Polym. J.*, 2012, **48**, 2070–2075.

110. Qi, Z., Gong, C., Liang, Y., Li, H., Wu, Z., Feng, W., Wang, Y., Zhang, S., Li, Y. *Int. J. Hydrogen Energy*, 2015, **40**, 9267–9277.

111. Yang, Y., Miao, L., Hu, J., Liu, G., Tu, Y., Lin, S., Liu, F., Li, F., Wu, Y., Zhang, G., Zou, H. *J. Mater. Chem. A*, 2014, **2**, 10410–10423.

112. Yilmaz, G., Toiserkani, H., Demirkol, D. O., Sakarya, S., Timur, S., Yagci, Y., Torun, L. *J. Polym. Sci. Part A Polym. Chem.*, 2011, **49**, 110–117.

113. Toiserkani, H., Yilmaz, G., Yagci, Y., Torun, L. *Macromol. Chem. Phys.*, 2010, **211**, 2389–2395.
114. Hu, B., Miao, L., Bai, Y., Lü, C. *Polym. Chem.*, 2017, **8**, 4403–4413.
115. Li, N., Guiver, M. D., Binder, W. H. *ChemSusChem*, 2013, **6**, 1376–1383.
116. Shen, K., Hu, H., Wang, J., Liu, G. *Polymer*, 2017, **132**, 198–205.
117. Persson, J. C., Josefsson, K., Jannasch, P. *Polymer*, 2006, **47**, 991–998.
118. Park, E. J., Lee, W.-H., Bae, C. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 3237–3243.
119. Manetsch, R., Krasiński, A., Radić, Z., Raushel, J., Taylor, P., Sharpless, K. B., Kolb, H. C. *J. Am. Chem. Soc.*, 2004, **126**, 12809–12818.
120. Díaz, D. D., Punna, S., Holzer, P., McPherson, A. K., Sharpless, K. B., Fokin, V. V., Finn, M. G. *J. Polym. Sci. Part A Polym. Chem.*, 2004, **42**, 4392–4403.
121. Naolou, T., Busse, K., Kressler, J. *Biomacromolecules*, 2010, **11**, 3660–3667.
122. Huang, K., Pisharath, S., Ng, S.-C. *Tetrahedron Lett.*, 2015, **56**, 577–580.
123. Laridon, U. L., Antwerp, W., Delzenne, G. A., Lo, K. *US Patent 3345171A*, 1967.
124. Trigo-López, M., Pablos, J. L., García, F. C., Serna, F., García, J. M. *J. Polym. Sci. Part A Polym. Chem.*, 2014, **52**, 1469–1477.
125. Summers, Christopher J Makal, Umit Day, Roger W. Haddleton, D. M. *Polym. Priprint*, 2011, **52**, 393.
126. Diakoumakos, C. D., Mikroyannidis, J. A. *Eur. Polym. J.*, 1995, **31**, 761–767.
127. Rivero, G., Nguyen, L.-T. T., Hillewaere, X. K. D., Du Prez, F. E. *Macromolecules*, 2014, **47**, 2010–2018.
128. Wei, Z. E. *CN Patent 103319670A*, 2013.
129. Irusta, L., Fernández-Berridi, M. J., Aizpurua, J. *J. Appl. Polym. Sci.*, 2017, **134**, 1–9.
130. Gaina, C., Ursache, O., Gaina, V., Varganici, C. D. *Express Polym. Lett.*, 2013, **7**, 636–650.
131. Luo, K., Li, J., Duan, G., Wang, Y., Yu, J., Zhu, J., Hu, Z. *Polymer*, 2018, **142**, 33–42.
132. Willocq, B., Khelifa, F., Brancart, J., Van Assche, G., Dubois, P., Raquez, J.-M. *RSC Adv.*, 2017, **7**, 48047–48053.
133. Yu, S., Zhang, R., Wu, Q., Chen, T., Sun, P. *Adv. Mater.*, 2013, **25**, 4912–4917.
134. Lee, J., Lee, W., Kim, H., Soo, J. *KR Patent 101208437B1*, 2012.
135. Varganici, C.-D., Ursache, O., Gaina, C., Gaina, V., Rosu, D., Simionescu, B. C. *Ind. Eng.*

Chem. Res., 2013, **52**, 5287–5295.

136. Gaina, C., Gaina, V., Ciobanu, C. *J. Appl. Polym. Sci.*, 2009, **113**, 3245–3254.
137. Serna, F. J., de Abajo, J., de la Campa, J. G. *Br. Polym. J.*, 1987, **19**, 453–458.
138. Bandyopadhyay, P., Banerjee, S. *Ind. Eng. Chem. Res.*, 2014, **53**, 18273–18282.
139. Liu, Y.-L., Lee, H.-C. *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 4632–4643.
140. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
141. Liu, Y.-L., Li, S.-H., Lee, H.-C., Hsu, K.-Y. *React. Funct. Polym.*, 2006, **66**, 924–930.
142. Mikroyannidis, J. A. *J. Polym. Sci. Part A Polym. Chem.*, 1990, **28**, 669–677.
143. De Abajo, J., De Santos, E. *Angew. Makromol. Chemie*, 1983, **111**, 17–27.
144. Serna, F. J., De Abajo, J., De La Campa, J. G. *J. Appl. Polym. Sci.*, 1985, **30**, 61–69.
145. Dong, X., Chen, L., Duan, R.-T., Wang, Y.-Z. *Polym. Chem.*, 2016, **7**, 2698–2708.
146. Zhen, C., Yat, S., Ling, Q., Hui, thin S., Peng, S., Yan, H., Cheng, P. *CN Patent 103373950B*, 2013.
147. Demirel, E., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 480–486.
148. Yen, H., Liou, G.-S. *J. Polym. Sci. Part A Polym. Chem.*, 2008, **46**, 7354–7368.
149. Billiet, L., Hillewaere, X. K. D., Du Prez, F. E. *Eur. Polym. J.*, 2012, **48**, 2085–2096.
150. Mandal, J., Krishna Prasad, S., Rao, D. S. S., Ramakrishnan, S. *J. Am. Chem. Soc.*, 2014, **136**, 2538–2545.
151. Billiet, L., Fournier, D., Du Prez, F. *J. Polym. Sci. Part A Polym. Chem.*, 2008, **46**, 6552–6564.
152. Ott, C., Easton, C. D., Gengenbach, T. R., McArthur, S. L., Gunatillake, P. A. *Polym. Chem.*, 2011, **2**, 2782–2784.
153. Dieck, R. L. *EP Patent 2191887 A1*, 2010.
154. Xue, Y., Ma, D., Zhang, T., Lin, S., Shao, S., Gu, N. *J. Macromol. Sci. Part A Pure Appl. Chem.*, 2014, **51**, 456–464.
155. Ansong, O., Antoine, M. D., Nwokogu, G. C., Hergenrother, P. M. *J. Org. Chem.*, 1994, **59**, 2506–2510.
156. Jensen, B. J., Hergenrother, P. M., Nwokogu, G. *J. Macromol. Sci. Part A*, 1993, **30**, 449–458.
157. Jensen, B. J., Hergenrother, P. M., Nwokogu, G. *Polymer*, 1993, **34**, 630–635.

158. Begines, B., De-Paz, M.-V., Alcudia, A., Galbis, J. A. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 3888–3900.

159. Jeong, M.-H., Lee, K.-S., Lee, J.-S. *Macromolecules*, 2009, **42**, 1652–1658.

160. Zhang, X., Yue, B., Yan, L., Zeng, G., Tao, S. *Int. J. Hydrogen Energy*, 2016, **41**, 4740–4750.

161. Garg, K., Chatterjee, D., Wadgaonkar, P. P. *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 1008–1020.

162. Ferris, C., de Paz, M. V., Galbis, J. A. *J. Polym. Sci. Part A Polym. Chem.*, 2011, **49**, 1147–1154.

163. Ferris, C., de Paz, M. V., Galbis, J. A. *Macromol. Chem. Phys.*, 2012, **213**, 480–488.

164. Korshak, V. V., Vinogradova, S. V., Salazkin, S. N., Komarova, L. I. *Eur. Polym. J.*, 1974, **10**, 967–973.

165. Fukuhara, T., Shibasaki, Y., Ando, S., Ueda, M. *Polymer*, 2004, **45**, 843–847.

166. Du, S., Wang, W., Yan, Y., Zhang, J., Tian, M., Zhang, L., Wan, X. *Chem. Commun.*, 2014, **50**, 9929–9931.

167. Wang, W., Qi, X., Guan, Y., Zhang, F., Zhang, J., Yan, C., Zhu, Y., Wan, X. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 2050–2059.

168. Li, Y., Wang, X., Xie, M., Liang, Y., Liu, X., Wang, C. *High Perform. Polym.*, 2014, **26**, 1015–1024.

169. Li, Y., Wang, X., Xie, M., Liu, X., Wang, C. *Int. J. Hydrogen Energy*, 2013, **38**, 16276–16285.

170. Maji, S., Asrey, R., Kumar, S., Saxena, C., Kumar, N., Vyas, K. D., Banerjee, S. *J. Appl. Polym. Sci.*, 2010, **116**, 3708–3717.

171. Mollah†, M. S. I., Seo†, D. W., Islam, M. M., Lim, Y. D., Cho, S. H., Shin, K. M., Kim, J. H., Kim, W. G. *J. Macromol. Sci. Part A Pure Appl. Chem.*, 2011, **48**, 400–408.

172. Yin, M., Li, F., Yan, Y., Liu, X., Wang, C., Chao, D. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 2321–2330.

173. Papadimitriou, K. D., Paloukis, F., Neophytides, S. G., Kallitsis, J. K. *Macromolecules*, 2011, **44**, 4942–4951.

174. Xin, Y., Sakamoto, J., van der Vlies, A. J., Hasegawa, U., Uyama, H. *Polymer*, 2015, **66**, 52–57.

175. Gao, S., Zhao, C., Na, H. *J. Power Sources*, 2012, **214**, 285–291.

176. Summers, G. J., Kasiama, M. G., Summers, C. A. *Polym. Int.*, 2016, **65**, 798–810.

177. Choudhary, U., Mir, A. A., Emrick, T. *Macromolecules*, 2017, **50**, 3772–3778.

178. Tkachenko, I. M., Shekera, O. V., Shevchenko, V. V. *Polym. Sci. Ser. B,* 2013, **55**, 336–343.

179. Wacker, K. T., Kristufek, S. L., Lim, S.-M., Kahn, S., Wooley, K. L. *RSC Adv.*, 2016, **6**, 81672–81679.

180. Wang, F., Wang, Z., Wang, H., Zhou, G. *Polym. Int.*, 2015, **64**, 858–866.

181. Lin, C. H., Chang, S. L., Wang, Y. R., Hsu, C. K., Juang, T. Y. *J. Polym. Sci. Part A Polym. Chem.*, 2013, **51**, 1734–1741.

182. Lin, C. H., Wong, T. I., Wang, M. W., Chang, H. C., Juang, T. Y. *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 513–520.

Chapter-2

Materials, Characterization and Techniques

2.1 Materials

2.1.1 Chemicals

4, 4’-Bis (4-hydroxyphenyl) pentanoic acid, guaiacol, furfural, lithium aluminium hydride (LAH), calcium hydride, carbon tetrabromide, triphenyl phosphine, 10% Pd/C, maleic anhydride, phenolphthalein, 2-aminoethanol, 1, 2- diaminoethane, triphosgene, bis(4-fluorophenyl) sulfone, 4, 4′-difluorobenzophenone, 1, 1’-(methylenedi-1,4-phenylene)bismaleimide (BMI), *N*-methylmaleimide (NMI), 2, 2’-(ethylenedioxy)bis(ethylamine), 1-aminohexane, 4-chlorothiophenol and 1-adamantanethiol were purchased from commercial sources and were used as received. Bisphenol-A (BPA) (Aldrich Chemicals) was sublimed under reduced pressure prior to use. Terephthaloyl chloride (TPC) (Aldrich Chemicals) and isophthaloyl chloride (IPC) (Aldrich Chemicals), were purified by distillation under reduced pressure.[1] 1-(Azidomethyl)pyrene, 1-pyrenecarboxaldehyde, propargyl bromide, copper(I) bromide and sodium hydride were purchased from TCI Chemicals (India) Pvt. Ltd. and were used as received. Sodium sulfate, potassium carbonate, glacial acetic acid, sodium azide, triethylamine (TEA), sodium hydroxide, sulphuric acid and hydrochloric acid were procured from Thomas Baker Ltd., Mumbai, India and were used as received. 1,8-Bis(maleimido)-triethylene glycol (TEG),[2] *N*-hexylmaleimide[3] and 1-[(2-propynyloxy)methyl]pyrene[4] were synthesized according to literature procedures.

2.1.2 Solvents

N,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were purchased from Aldrich Chemicals and were distilled prior to use. Toluene, chloroform, dichloromethane, methanol, ethyl acetate, pet ether, and ethanol were procured from Alfa Aesar. All the solvents were of reagent grade and were purified according to standard procedures.[5]

2.2 Characterization and Techniques

Different techniques were used for characterization of monomers and polymers and are listed below.

2.2.1 Melting point

Melting points were recorded on Electrothermal MEL-TEMP apparatus and are uncorrected.

2.2.2 IR Spectroscopy

IR spectroscopy was used to analyze functional groups present in the monomers and polymers. IR spectra were recorded on Perkin Elmerspectrum GX spectrophotometer in the range 4000-400 cm^{-1} using either chloroform solvent or KBR pellets.

2.2.3 NMR Spectroscopy

NMR spectra were recorded on a Bruker 200, 400 or 500 MHz spectrometer at resonance frequencies of 200, 400 or 500 MHz for ^{1}H NMR and 50, 100 or 125 MHz for ^{13}C NMR measurements using $CDCl_{3,}$ Acetone-d_6, DMSO-d_6 or Methanol-d_4 as a solvent.

2.2.4 HR-MS analysis

HR-MS analysis of monomers was carried out on Thermo Scientific Q-exacative with Accela 1250 Pump.

2.2.5 Solubility tests

The solubility of polymers was tested at 3 wt % concentration in various organic solvents at room temperature.

2.2.6 Inherent viscosity

Inherent viscosity of polymers was determined with 0.5 % (w/v) solution of polymer in chloroform at 30±0.1 ^{o}C using Ubbelhode suspended level viscometer. Inherent viscosity was calculated using the equation

$$n_{inh}= \frac{2.303}{c} xlog\ t/t_0$$

where, *t* and t_0 are flow times of polymer solution and solvent, respectively and *c* is concentration of polymer solution

2.2.7 Gel Permeation Chromatography (GPC)

Molecular weights and dispersity values of polymers were determined on Thermo-Finnigan make gel-permeation chromatography (GPC) using chloroform as an eluent at a flow rate of 1 mL min^{-1} at 25 ^{o}C. Sample concentration was 2 mg mL^{-1} and narrow dispersity polystyrenes were used as calibration standards.

2.2.8 X-Ray Diffraction (XRD)

X-Ray diffractograms of polymer films were obtained on Rigaku Dmax 2500 with a scanning rate of 2°/min.

2.2.9 Thermogravemetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on Perkin Elmer: STA 6000, at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere.

2.2.10 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was performed with DSC Q10 at a heating rate of 10 °C/ min under nitrogen atmosphere.

2.2.11 Mechanical properties

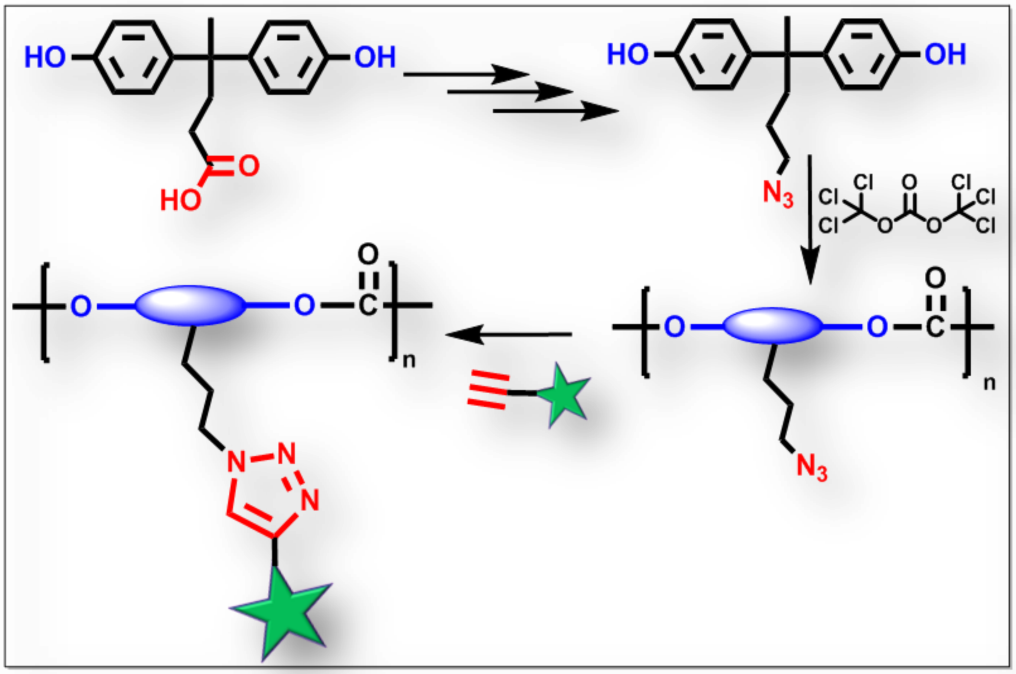
Mechanical properties such as tensile strength, elongation at break and Young's modulus were measured on polymer films using Rheometrics Scientifics (Model Mark IV) (UK) instrument at room temperature with strain rate of 1.5 mm/min. The measurements were carried out on 4-6 samples for each polymer and the data was averaged.

2.3 References

1. Fox, M. A., J. K. W. Organic Chemistry.
2. Kim, Y. H., Stites, W. E. *Biochemistry*, 2008, **47**, 8804–8814.
3. Khayum, M. A., Kandambeth, S., Mitra, S., Nair, S. B., Das, A., Nagane, S. S., Mukherjee, R., Banerjee, R. *Angew. Chem. Int. Ed.*, 2016, **55**, 15604–15608.
4. Kantheti, S., Narayan, R., Raju, K. V. *Polym. Int.*, 2015, **64**, 267–274.
5. Armarego, K. N., Perrin, D. D. Purification of Laboratory Chemicals" Butterworth-Heinemann, Oxford, 4th Edition, Butterworth Heinemann, 1996.

Chapter-3

(Co)polycarbonates Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modifications



3.1 Introduction

Aromatic polycarbonates contain repeating carbonate linkages (-OCO-O-) in the polymer chain. In 1953, aromatic polycarbonate based on bisphenol A was independently reported by Herman Schnell at Bayer, AG and Daniel Fox at erstwhile General Electric (now SABIC).[1] Polycarbonates exhibit desirable combination of properties such as high thermal stability, excellent optical properties, high dimensional stability, outstanding toughness, easy processability, low water uptake, etc.[2,3] By virtue of these properties, polycarbonates qualify as suitable alternatives to glass, wood and other polymeric materials. Aromatic polycarbonates find applications in different fields such as optical, consumer articles, electrical, packaging, construction, medical devices and so on.[2–5] To further widen their application areas, it is desirable to synthesize polycarbonates containing pendant functional groups which allow chemical modifications to be performed in order to tune the properties.

For the synthesis of aliphatic polycarbonates, a range of difunctional monomers and ROP monomers containing functional groups have been reported in the literature.[6–8] The pendant clickable functional groups which have been incorporated in to aliphatic polycarbonates include: azido,[6,9,10] allyl,[11–17] alkyne,[7,18–21] furyl,[22] norbornene,[23,24] maleimide,[25–27] active ester [28,29] and anthryl.[30] These functional groups have been further modified by appropriate click reactions to obtain aliphatic polycarbonates with a desired set of properties. However, very little attention has been paid to the synthesis of aromatic polycarbonates containing pendant clickable functional groups except for aromatic polycarbonates containing pendant allyl groups.[31–33]

Polymers containing pendant azido groups are of particular interest as azido group provides an excellent handle for quantitative chemical modifications *via* copper catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Additionally, inherent reactivity of azido functional group is high and it can be activated by either thermal conditions or UV irradiation. The decomposition of azido functional group upon thermal treatment or UV irradiation results into the formation of reactive nitrene intermediate with the liberation of nitrogen. The reactive nitrene intermediate can subsequently react with neighbouring polymer backbone and results into the formation of cross-linked structure.[34–44]

The purpose of the present work is two-fold. Firstly, the synthesis of bisphenol *viz.*, 4, 4’-(5-azidopentane-2, 2-diyl) diphenol (AZBPA), containing pendant azido group starting from 4, 4’-bis (4-hydroxyphenyl) pentanoic acid. Furthermore, the synthesis of polycarbonates bearing pendant azido groups was accomplished by polycondensation of AZBPA with triphosgene. Copolycarbonates were also synthesized by polycondensation of varying molar ratios of AZBPA and bisphenol-A with triphosgene. (Co)polycarbonates were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Subsequently, the post-modification of polycarbonate containing pendant azido groups was carried out using CuAAC reaction with 1-[(2-propynyloxy)methyl]pyrene. Additionally, (co)polycarbonates containing pendant azido groups were cross-linked under UV irradiation and, thus improving the thermal stability and mechanical properties of cross-linked aromatic (co)polycarbonates. This work has demonstrated how the azide functionality, as a reactive functional group, can be installed into aromatic polycarbonates and can be exploited for both photo-crosslinking and chemical modification by CuAAC reaction.

3.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR, HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC, XRD and tensile testing are given in **Chapter 2**.

3.2.1 Synthesis of bisphenol bearing pendant azido group

3.2.1.1 Synthesis of methyl 4, 4’-bis (4-hydroxyphenyl) pentanoate

Into a 250 mL two necked round-bottom flask equipped with a reflux condenser were charged, 4, 4’-bis (4-hydroxyphenyl) pentanoic acid (5.0 g, 17.47 mmol), and methanol (150 mL). The reaction mixture was stirred for 15 minutes, followed by the addition of concentrated sulphuric acid (0.3 mL). The reaction mixture was refluxed for 8 h. Methanol was removed under reduced pressure and ethyl acetate (300 mL) was added to the reaction mixture. The ethyl acetate solution was washed with saturated brine solution (3 x 50 mL) and dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether: ethyl acetate (50:50, v/v) as an eluent to afford methyl 4, 4’-bis (4-hydroxyphenyl) pentanoate.

Yield: 4.76 (91 %); Melting point- 90 ^{o}C; IR (KBr): 3320, 1730 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d$_6$, δ/ppm): 9.24 (s, 2H,), 6.97 (d, 4H), 6.69 (d, 4H), 3.53 (s, 3H), 2.28 (t, 2H), 2.01-2.08

(m, 2H), 1.47 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d$_6$, δ/ppm):174.5, 156.2, 141.0, 129.0, 115.7, 51.6, 45.1, 37.6, 29.3, 28.1; HRMS ESI$^+$: (M+Na)$^+$m/z calculated for $C_{18}H_{20}O_4Na$: 323.1254, found: 323.1243.

3.2.1.2 Synthesis of 4, 4'-(5-hydroxypentane-2, 2-diyl) diphenol

Into a 250 mL two necked round-bottom flask equipped with a dropping funnel were charged, lithium aluminum hydride (1.89 g, 49.98 mmol) and dry THF (80 mL). The solution of methyl 4, 4'-bis(4-hydroxyphenyl) pentanoate (5.0 g, 16.66 mmol) in dry THF (30 mL) was added over a period of 30 minutes. Effervescences were observed during the addition. The reaction mixture was stirred for 8 h, cooled and then moist sodium sulfate was added to deactivate lithium aluminum hydride. Dilute HCl (10 mL) was added to dissolve the formed salt and ethyl acetate (150 mL) was added. The ethyl acetate solution was washed with saturated brine solution (3 x 30 mL), sodium bicarbonate solution (3 x 30 mL), and water (2 x 50 mL). The ethyl acetate layer was separated, dried over sodium sulfate, filtered and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether: ethyl acetate (60:40, v/v) as an eluent to afford 4, 4'-(5-hydroxypentane-2, 2-diyl) diphenol as a white powder.

Yield: 3.40 g (75 %); Melting point- 136 °C; IR (KBr): 3150 cm^{-1}; ^{1}H NMR (200 MHz, Acetone-d$_6$, δ/ppm): 8.28 (s, 2H), 7.05 (d, 4H), 6.75 (d, 4H), 3.53 (t, 2H), 2.06-2.10 (m, 2H), 1.56 (s, 3H), 1.31-1.39 (m, 2H); ^{13}C NMR (50 MHz, Acetone-d$_6$, δ/ppm): 155.9, 142.0, 129.1, 115.5, 63.2, 45.2, 39.2, 29.4, 28.5; HRMS ESI$^+$: (M+Na)$^+$m/z calculated for $C_{17}H_{19}O_3Na$: 295.1305, found: 295.1302.

3.2.1.3 Synthesis of 4, 4'-(5-bromopentane-2, 2-diyl) diphenol

Into a 250 mL two necked round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet were placed 4, 4'-(5-hydroxypentane-2, 2-diyl) diphenol (5.0 g, 18.38 mmol), carbon tetrabromide (7.31 g, 22.05 mmol) and dry THF (60 mL) and the solution was cooled to 0 °C. The solution of triphenyl phosphine (5.78 g, 22.05 mmol) in dry THF (20 mL) was added dropwise and the reaction mixture was stirred at room temperature for 4 h. THF was evaporated under reduced pressure and the reaction mixture was washed with water (2 x 50 mL) and extracted into dichloromethane. The dichloromethane solution was washed with saturated brine solution (3 x 50 mL) and dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether: ethyl acetate (85:15, v/v) as an eluent to afford 4, 4'-(5-bromopentane-2, 2-diyl) diphenol as a pale yellow oily liquid.

Yield: 5.40 g (88 %); ^{1}H NMR (200 MHz, $CDCl_3$, δ/ppm): 7.05 (d, 4H), 6.75 (d, 4H), 6.03 (s, 2H), 3.36 (t, 2H), 2.17 (t, 2H), 1.62-1.69 (m, 2H), 1.58 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, δ/ppm):153.3, 141.6, 128.3, 114.8, 44.6, 40.6, 34.6, 28.3, 28.0; HRMS ESI$^+$: $(M+Na)^+$m/z calculated for $C_{17}H_{19}BrO_2Na$: 359.0443, found: 359.0439.

3.2.1.4 Synthesis of 4, 4'-(5-azidopentane-2, 2-diyl) diphenol

Into a 250 mL single necked round-bottom flask equipped with a nitrogen inlet were added 4, 4'-(5-bromopentane-2, 2-diyl) diphenol (5.0 g, 14.92 mmol) and *N*, *N*-dimethylformamide (60 ml). Sodium azide (4.85 g, 74.63 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was washed with water (3 x 50 mL) and was extracted into ethyl acetate (100 mL). The ethyl acetate solution was washed with saturated brine solution (3 x 50 mL) and dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether: ethyl acetate (70:30, v/v) as an eluent to afford 4, 4'-(5-azidopentane-2, 2-diyl) diphenol as a pale yellow oily liquid.

Yield: 4.20 g (95 %); IR (Chloroform): 3354, 2098 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.06 (d, 4H), 6.78 (d, 4H), 6.39 (s, 2H), 3.26 (t, 2H), 2.12 (t, 2H), 1.60 (s, 3H), 1.39-1.46 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, δ/ppm):153.2, 141.5, 128.3, 114.8, 51.9, 44.6, 38.8, 27.8, 24.4; HRMS ESI$^+$: $(M+Na)^+$m/z calculated for $C_{17}H_{19}N_3O_2Na$: 320.1369, found: 320.1367.

3.2.2 Synthesis of (co)polycarbonates bearing pendant azido groups

Into a 50 mL three necked round bottom flask equipped with a nitrogen balloon, an addition funnel, and a magnetic stirrer were charged AZBPA (1.50 g, 5.05 mmol) and dry dichloromethane (6 mL). The reaction mixture was cooled to 0 ^{o}C and the solution of triethylamine (2.11 mL, 15.14 mmol) in dry dichloromethane (3 mL) was added dropwise over a period of 10 min. To the reaction mixture, the solution of triphosgene (0.63 g, 2.12 mmol) in dichloromethane (3 mL) was added dropwise and stirred at 0 ^{o}C for 15 min. The reaction mixture was allowed to warm to 25 ^{o}C and stirring was continued at that temperature for 4 h. The reaction mixture was neutralized with aqueous hydrochloric acid (2 M) and was extracted with dichloromethane (2 × 100 mL). The dichloromethane solution was washed with water (2 × 100 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure at 30 °C. The concentrated polymer solution was poured into methanol (1000 mL) and the precipitated polymer was filtered and washed with methanol. The polymer was dissolved in dichloromethane (10 mL) and reprecipitated into methanol (1000 mL), filtered and dried under reduced pressure at room temperature for 12 h.

A similar procedure was followed for the synthesis of other (co)polycarbonates.

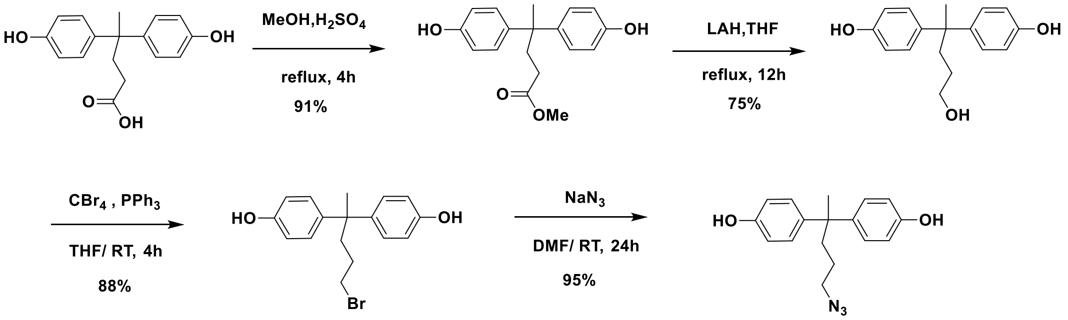
3.2.3 Post-modification of azido functionalized polycarbonate with 1-[(2-propynyloxy)methyl]pyrene

To a Schlenk tube equipped with a magnetic stirring bar were added AZPC-2 (0.20 g, 0.69 mmol), 1-[(2-propynyloxy)methyl]pyrene (0.25 g, 0.83 mmol) and THF (10 mL). Copper bromide (2.5 mg, 0.017 mmol) and triethylamine (1.75 mg, 0.017 mmol) were added and the reaction mixture was stirred under nitrogen atmosphere at room temperature. The reaction mixture was concentrated and precipitated into methanol to remove the catalyst residue and excess of 1-[(2-propynyloxy)methyl]pyrene. The modified polycarbonate was filtered and dried in vacuum at room temperature for 8 h.

3.3 Results and discussion

3.3.1 Monomer synthesis

The synthesis of desired bisphenol containing pendant azido group *viz.*, 4, 4’-(5-azidopentane-2, 2-diyl) diphenol (AZBPA) was achieved in four steps starting from commercially available 4, 4’-bis (4-hydroxyphenyl) pentanoic acid which in turn is derived from levulinic acid- a platform chemical obtained from biomass **(Scheme 3.1)**.[45]



Scheme 3.1. Synthesis of 4, 4’-(5-azidopentane-2, 2-diyl) diphenol (AZBPA).

In the first step, 4, 4’-bis (4-hydroxyphenyl) pentanoic acid was esterified using methanol in the presence of catalytic amount of concentrated sulphuric acid to yield 4, 4’-bis (4-hydroxyphenyl) pentanoate. 4, 4’-Bis (4-hydroxyphenyl) pentanoate was subsequently converted into 4, 4’-(5-hydroxypentane-2,2-diyl)-diphenol on reduction with lithium aluminium hydride in the second step. Further, bromination of 4, 4’-(5-hydroxypenentane-2, 2-diyl) diphenol using carbon tetrabromide as a brominating agent in the presence of triphenyl phosphine under Apple reaction conditions afforded 4, 4’-(5-bromopentane-2, 2-diyl) diphenol. Finally, the conversion of 4, 4’-(5-bromopentane-2, 2-diyl) diphenol into AZBPA was accomplished by nucleophilic substitution reaction of bromide group using sodium azide in the presence of DMF as a solvent. The molecular structure of bisphenol monomer AZBPA was analyzed by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy. Low molecular weight azides are generally explosive-especially under acidic conditions.[46] However, AZBPA was safe to handle at room temperature. No decomposition or explosion was observed when it was vacuum dried at room temperature for one day. Nonetheless, AZBPA should always be handled with precaution like other azido compounds.[6]

In IR spectrum of AZBPA (**Figure 3.1**), the characteristic band of azido group appeared at 2098 cm^{-1}.

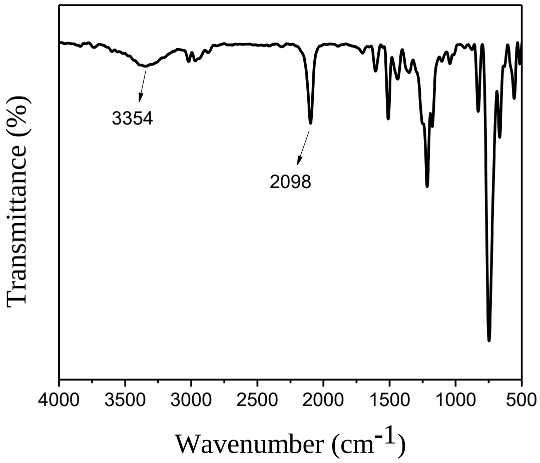


Figure 3.1. IR spectrum of 4, 4’-(5-azidopentane-2, 2-diyl) diphenol.

Figure 3.2 represents ^{1}H NMR spectrum of AZBPA along with the assignments. The two phenolic -OH groups appeared as a broad peak at 6.39 δ ppm and four aromatic protons *meta* to phenolic -OH groups appeared as a doublet at 7.06 δ ppm. The four aromatic protons *ortho* to phenolic -OH groups appeared as a doublet at 6.78 δ ppm. Methylene protons “d” and “e” appeared as separate triplets at 3.26 δ ppm and 2.12 δ ppm, respectively. Methyl protons “f” appeared as a singlet at 1.60 δ ppm. Methylene protons “g” showed a multiplet over the range 1.39-146 δ ppm.

^{13}C NMR spectrum of AZBPA along with assignments is presented in **Figure 3.3.**

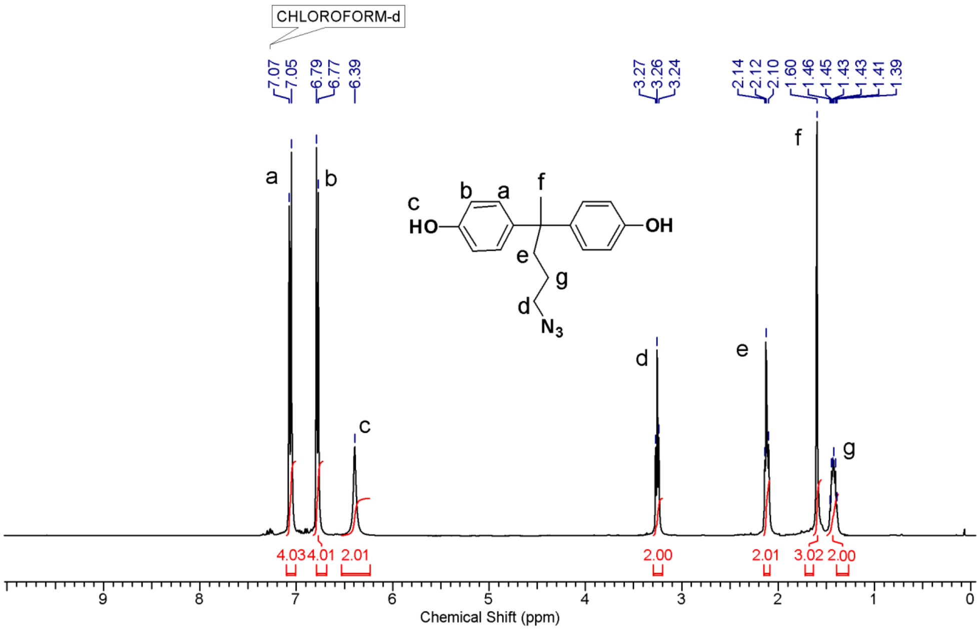


Figure 3.2. ^{1}H NMR spectrum (in $CDCl_3$) of 4, 4’-(5-azidopentane-2, 2-diyl) diphenol.

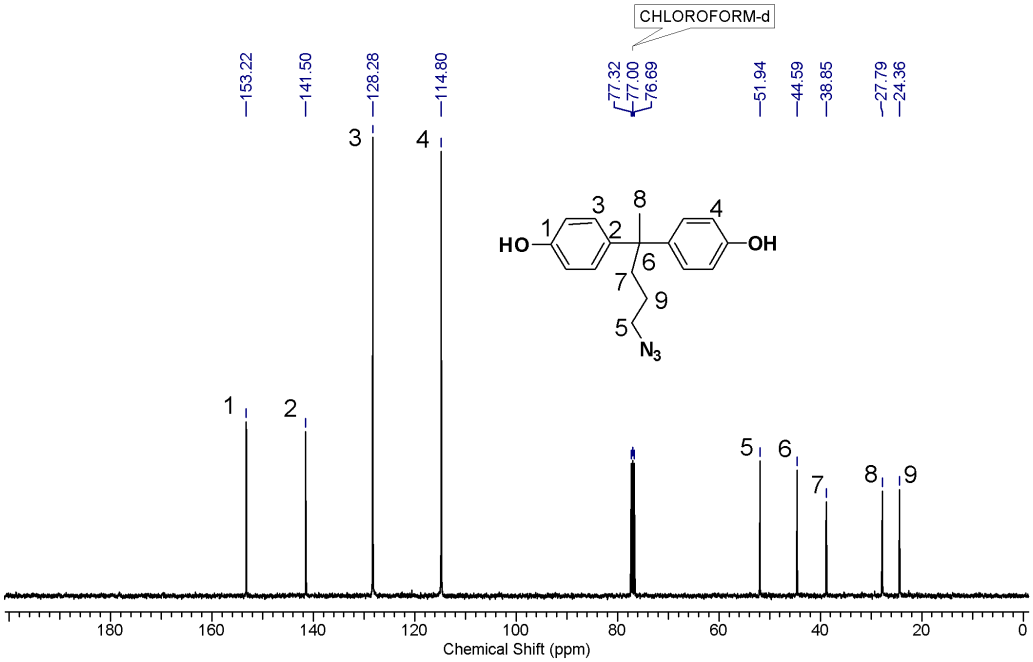


Figure 3.3. ^{13}C NMR spectrum (in $CDCl_3$) of 4, 4’-(5-azidopentane-2, 2-diyl) diphenol.

HRMS of AZBPA is shown in **Figure 3.4**. HRMS showed peak at 320.1367 corresponding to ([M+Na$^+$]) of AZBPA (Calcd. ([M+Na]$^+$) for $C_{17}H_{19}N_3O_2Na$ =320.1369).

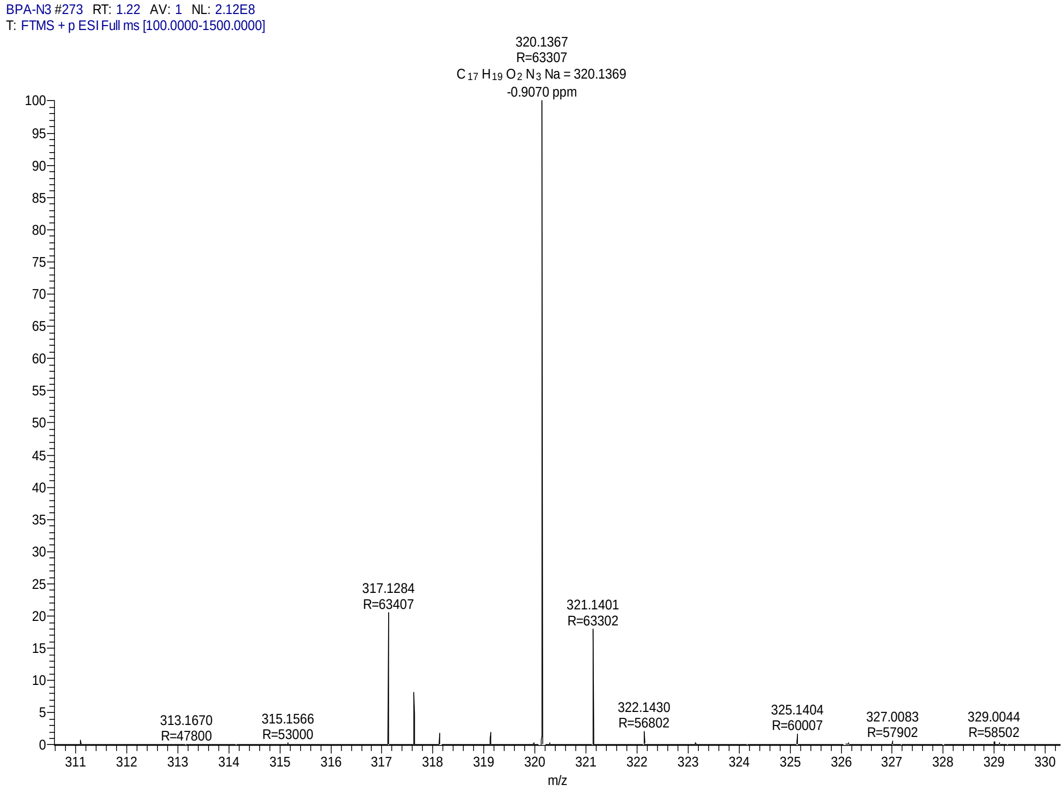
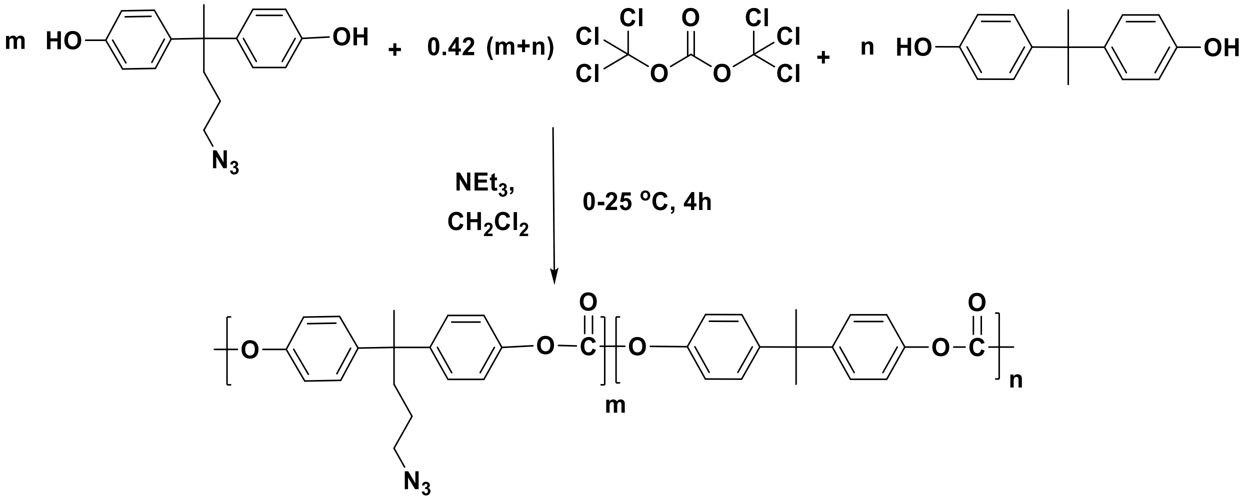


Figure 3.4. HRMS of 4, 4’-(5-azidopentane-2, 2-diyl) diphenol.

3.3.2 Synthesis of (co)polycarbonates bearing pendant azido groups

Several methods for the preparation of aromatic polycarbonates have been reported which include: the Schotten-Baumann reaction of bisphenol and phosgene in an amine-catalyzed interfacial polycondensation reaction,[47] direct reaction of phosgene with a bisphenol solution containing a tertiary amine[48] and base-catalyzed transesterification of a bisphenol with a monomeric carbonate such as diphenyl carbonate.[49] The solution polycondensation method was employed for the synthesis of (co)polycarbonates as outlined in **Scheme 3.2**. While BPA-based polycarbonate is commercially prepared using phosgene gas, the literature indicated that relatively high molecular weight polycarbonates can also be obtained using more convenient triphosgene on a laboratory scale.[50–53] Phosgene is difficult to handle on the laboratory scale due to its high toxicity and gaseous nature. Triphosgene is a less hazardous substitute for phosgene with relatively equivalent reactivity and solid crystalline nature. Triphosgene is, therefore, preferred as a source of carbonate for the laboratory scale synthesis of polycarbonates.

In this study, aromatic (co)polycarbonates bearing pendant azido groups were synthesized by polycondensation of AZBPA or a mixture of AZBPA and BPA with triphosgene **(Scheme 3.2)**.



Scheme 3.2. Synthesis of (co)polycarbonates bearing pendant azido groups.

The solution polymerization reactions were carried out at room temperature (0 ^{o}C/15 min, 25 ^{o}C/4 h) in dichloromethane as a solvent (7-11 wt. % solid content) in the presence of triethyl amine as described in the experimental section. At these lower temperatures, the azido group is stable and there is no risk of decomposition of the azido group. No end capping agent was used in polycarbonate synthesis. The molar stoichiometry of bisphenol:triphosgene employed was 1:0.42 which was based on the work of Boyles et al. who demonstrated the formation of high molecular weight polycarbonates under such stoichiometric conditions.[54] At the end of polymerization reactions, polycarbonates were isolated by precipitation in methanol and were purified by re-precipitation into excess methanol from chloroform solution. As a reference material, BPA-based polycarbonate *viz.,* PC-BPA was prepared using same reaction conditions. Results of synthesis of (co)polycarbonates are summarized in **Table 3.1**.

Inherent viscosity and number average molecular weight ($\overline{M_n}$) of (co)polycarbonates were in the range 0.63-0.77 dL/g and 35,400-42,200 g/mol, respectively. The dispersity values for (co)polycarbonates were in the range 2.0-2.3 as can be expected for step growth polymerizations. Thus, $\overline{M_n}$ as well as dispersity values of polycarbonates from azido functional bisphenol were comparable to that of bisphenol-A based polycarbonate ($\overline{M_n}$= 36,700 g/mol, dispersity = 2.2) demonstrating that AZBPA monomer is equally reactive in polycarbonate synthesis.

Table 3.1. Molar composition, inherent viscosity and molecular weight of (co)polycarbonates

(Co)polycarbonate	AZBPA mol %	BPA mol %	η_{inh} [a] dL/g [a]	Molecular weight [b]		Dispersity
				$\overline{M_n}$	$\overline{M_w}$	
AZPC-1	100	00	0.63	35,400	71,900	2.0
AZPC-2	50	50	0.73	41,900	87,100	2.1
AZPC-3	30	70	0.77	42,200	91,400	2.2
AZPC-4	10	90	0.69	37,600	85,300	2.3
PC-BPA	00	100	0.66	36,700	79,800	2.2

a: η_{inh} was measured with 0.5% (w/v) solution of (co)polycarbonate in chloroform at 30 ± 0.1 °C, b: Measured by GPC in chloroform using polystyrene calibration standard.

All the (co)polycarbonates were readily soluble in organic solvents such as dichloromethane, chloroform, THF, DMSO, and DMAc and could be cast into transparent, tough and flexible films from their chloroform solutions. A representative film of AZPC-1 is shown in **Figure 3.5**.

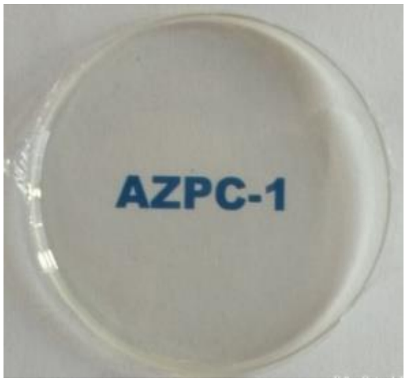


Figure 3.5. Film of polycarbonate AZPC-1.

3.3.3 Structural characterization

The formation of polycarbonates was confirmed by IR spectroscopy. As shown in **Figure 3.6**, IR spectrum of AZPC-1 exhibited strong absorption band corresponding to pendant azido group at 2093 cm^{-1} and the typical absorption band of carbonate linkage appeared at 1770 cm^{-1}.

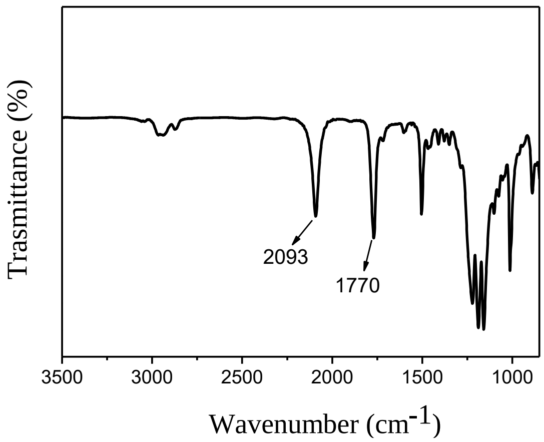


Figure 3.6. IR spectrum of polycarbonate AZPC-1.

The chemical structures of aromatic (co)polycarbonates containing pendant azide groups were further characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. In ^{1}H NMR spectrum (**Figure 3.7)** of polycarbonate AZPC-1, aromatic protons of AZBPA appeared in the range 7.19-7.24 δ ppm. The methyl protons were observed as a singlet, representing three protons, at 1.66 δ ppm. The signal of protons of methylene group attached to azido group was observed as a triplet at 3.25 δ ppm. The methylene protons of pendant alkane moiety labeled as “c” and “e” appeared as a triplet at 2.17 δ ppm and a multiplet in the range 1.36-142 δ ppm, respectively.

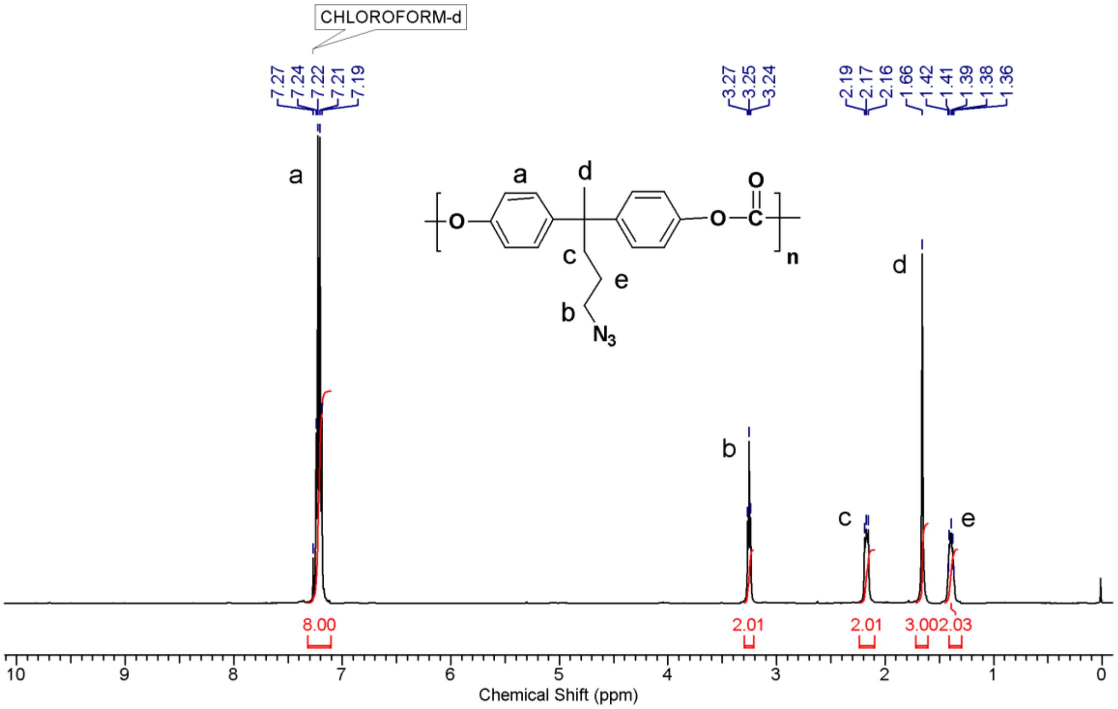


Figure 3.7. ^{1}H NMR spectrum (in $CDCl_3$) of polycarbonate AZPC-1.

^{13}C NMR spectrum of AZPC-1 along with assignments is shown in **Figure 3.8.** The carbonyl carbon of carbonate linkage appeared at 152.0 δ ppm.

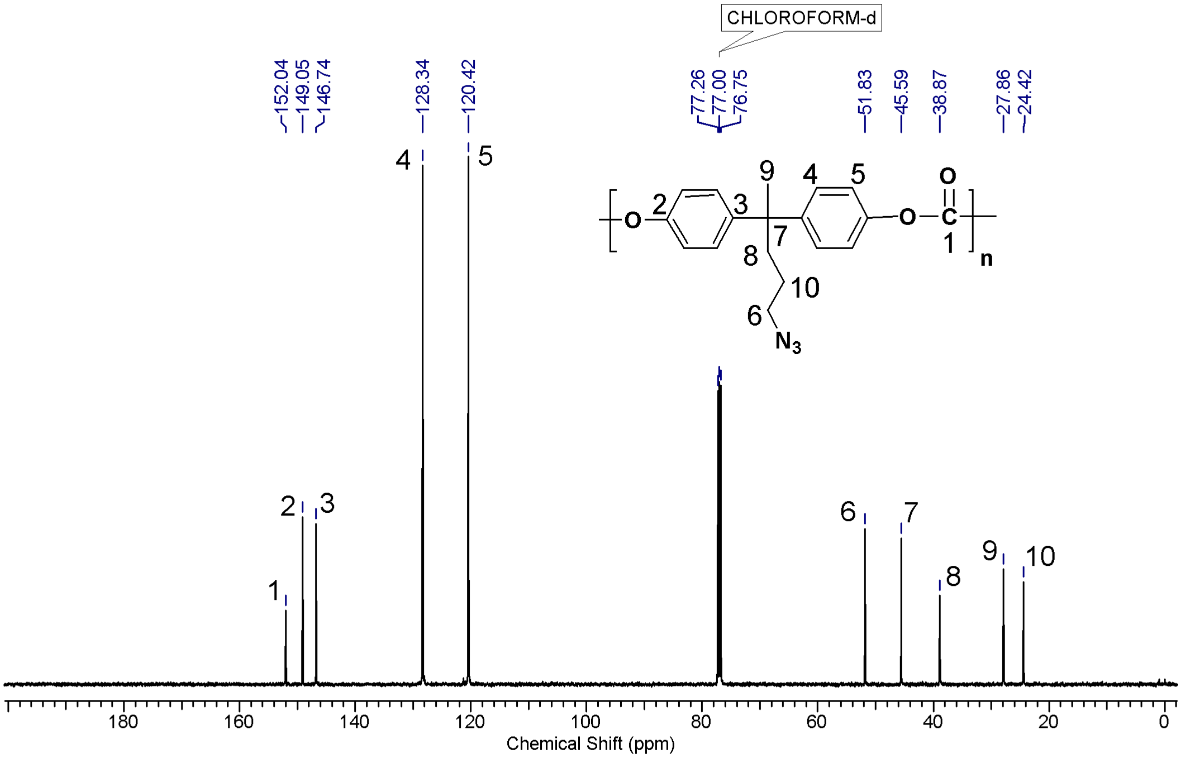


Figure 3.8. ^{13}C NMR spectrum (in $CDCl_3$) of polycarbonate AZPC-1.

^{1}H NMR spectra **(Figure 3.9)** confirmed the incorporation of bisphenol containing pendant azido group AZBPA and BPA, which was easily detectable by peaks due to methylene protons "b" of AZBPA as a triplet at 3.25 δ ppm and methyl protons "d" of BPA as a singlet at 1.69 δ ppm, respectively. The molar ratios of BPA and AZBPA in copolycarbonates were calculated by comparing the integrated intensity of methyl protons "d" of BPA with the methylene protons "b" adjacent to azido group of AZBPA. The data provided by this analysis is given in **Table 3.2**, wherein it can be seen that bisphenol containing pendant azido group AZBPA and BPA were successfully polymerized and the observed monomer ratios matched well with the feed composition. Overall, IR, ^{1}H NMR and ^{13}C NMR spectroscopy data revealed that (co)polycarbonates bearing pendant azido groups of desired composition were successfully obtained by solution polycondensation.

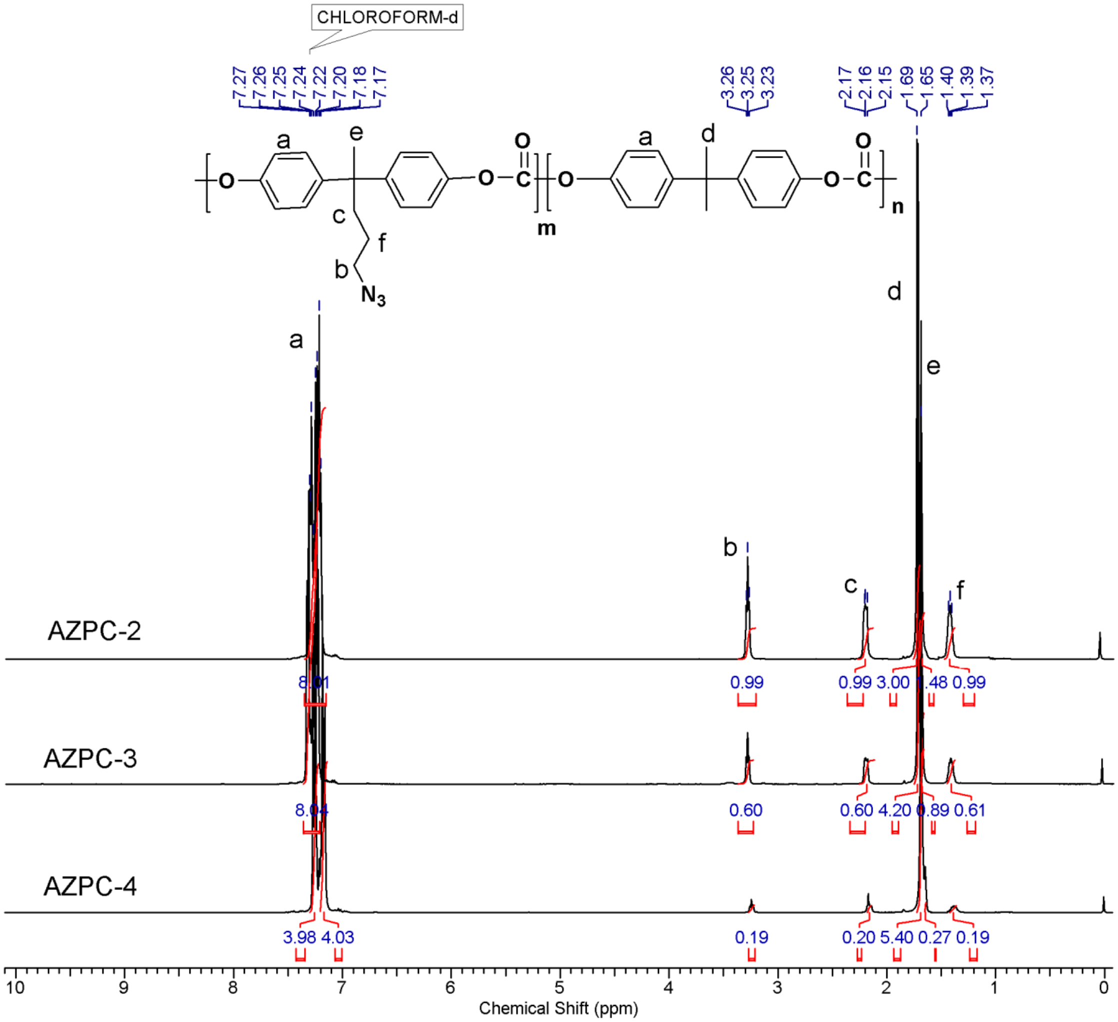
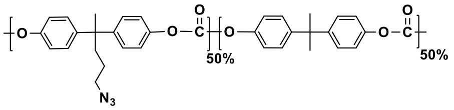
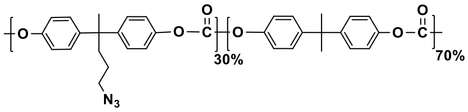
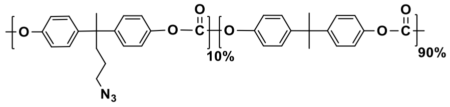


Figure 3.9. ^{1}H NMR specta (in CDCl$_3$) of copolycarbonates.

Table 3.2. Molar composition of copolycarbonates determined by ^{1}H NMR spectra

Copolycarbonate	**Structure of copolycarbonate**	**Feed AZBPA, mol %**	**Observed AZBPA, mol%**
AZPC-2		50	49.5
AZPC-3		30	30.0
AZPC-4		10	9.5

The microstructure of copolycarbonates derived from copolymerization of AZBPA and BPA with triphosgene was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, the copolymerization of BPA and AZBPA is expected to lead to formation of random copolymer with following possibilities of enchainment of two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 3.10**). ^{13}C NMR spectra of copolycarbonates showed clear evidence not only for the random copolycarbonate formation but also about the microstructural details as indicated by the multiplicity of the signals.

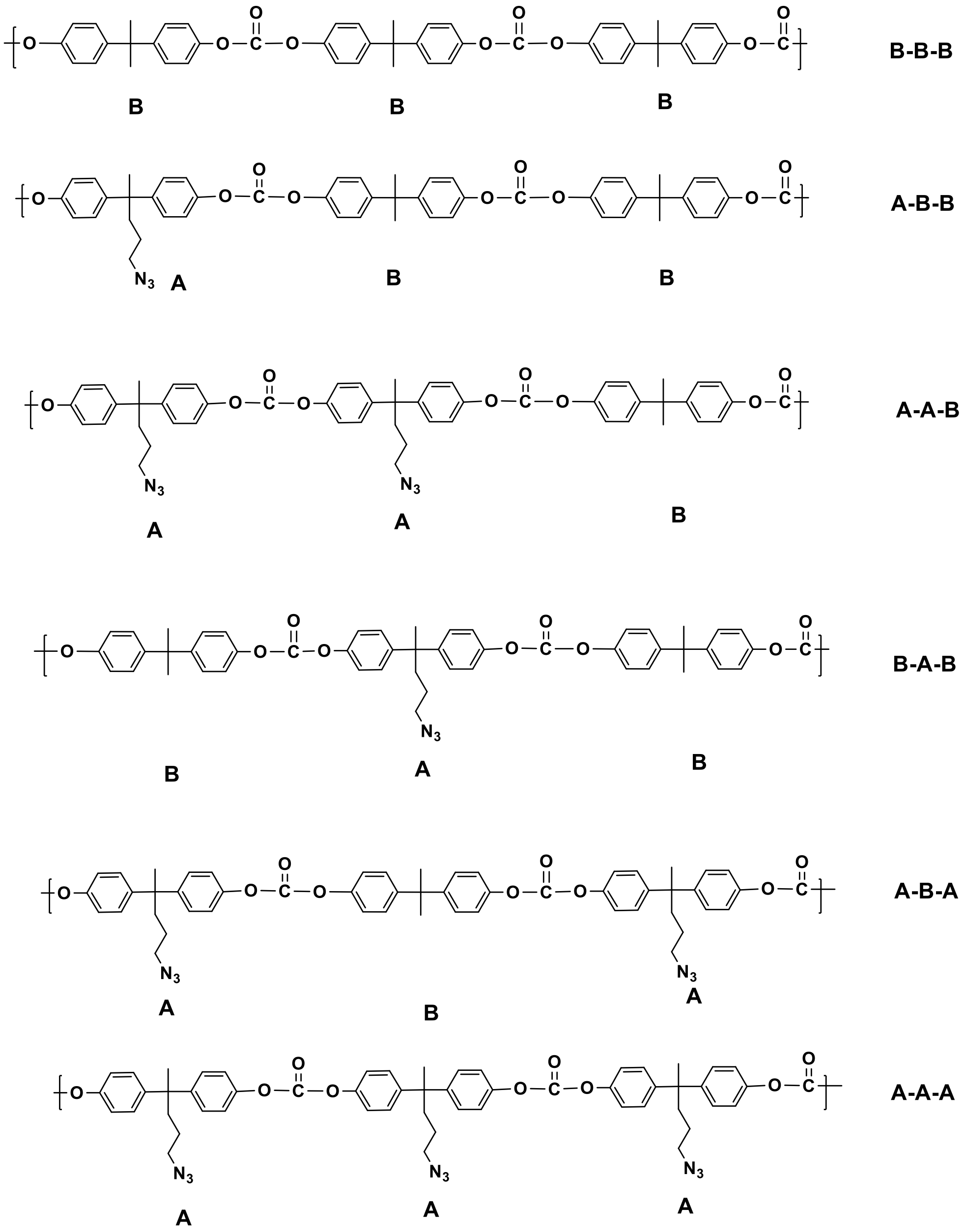


Figure 3.10. Possible arrangements of AZBPA and BPA units in copolycarbonates.

The assignments of carbon atoms in ^{13}C NMR spectrum of AZPC-2, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 3.11.**

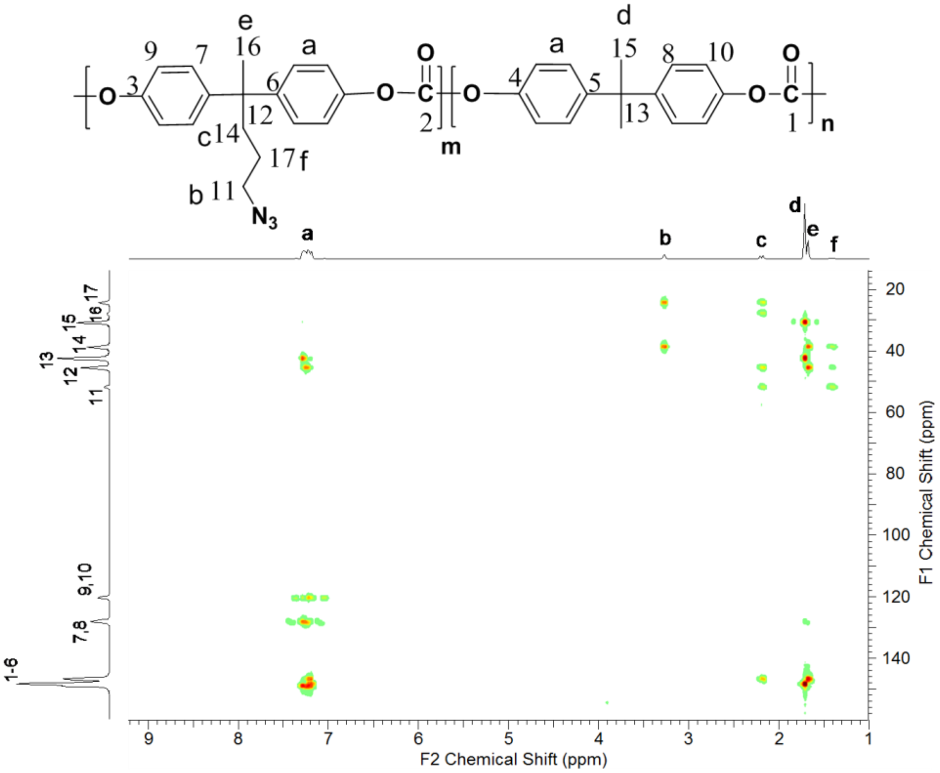


Figure 3.11. HMBC spectrum (in CDCl$_3$) of AZPC-2.

^{13}C NMR spectrum of AZPC-2 (50:50 mol % of AZBPA:BPA) along with assignments of carbon atoms is presented in **Figure 3.12.** For easy comparison, ^{13}C NMR spectra of homo-polycarbonate AZPC-1 and copolycarbonates AZPC-2 to AZPC-4 are also included in **Figure 3.12**. It is interesting to note that carbonyl carbon of carbonate linkage in copolycarbonate AZPC-2 exhibited three distinct peaks at 152.05 δ ppm, 152.09 δ ppm and 152.13 δ ppm for this particular copolymer. A comparison of the spectrum of AZPC-2 with that of AZPC-1 and AZPC-4 inferred that carbonyl peaks appeared at 152.05 δ ppm and 152.13 δ ppm originated from AAA and BBB arrangement of co-monomer units, respectively in copolycarbonate sample while a peak at 152.09 δ ppm corresponds to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peak corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of AZPC-3 and AZPC-4.

Some of the other carbons in ^{13}C NMR spectrum of AZPC-2 also exhibited similar features as indicated in **Figure 3.12**. It is also interesting to note that some of the carbon atoms of aromatic ring (for instance carbon atoms labeled as 5B and 6A) also showed more signals in copolycarbonate which is likely to be due to the loss of symmetry upon formation of copolymer comprising of comonomer units enchained in the manner as shown in **Figure 3.10** (A-A-B and A-B-B).

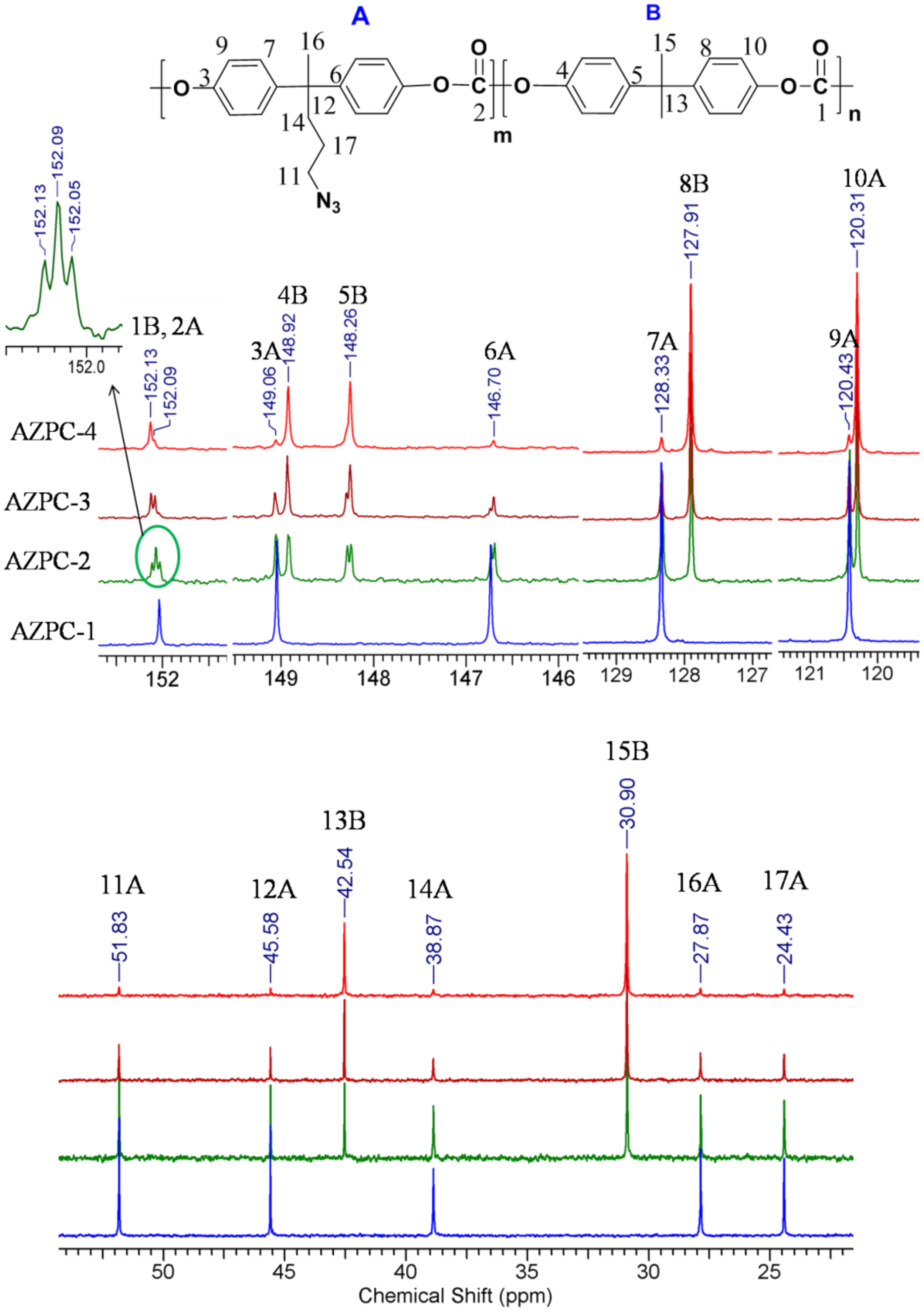


Figure 3.12. ^{13}C NMR spectra (in $CDCl_3$) of (co)polycarbonates.

3.3.4 X-Ray diffraction studies

X-Ray diffraction patterns of (co)polycarbonates containing pendant azido groups are shown in **Figure 3.13**. A broad halo at around 2θ = 10-30 ºC indicated that (co)polycarbonates are amorphous in nature.

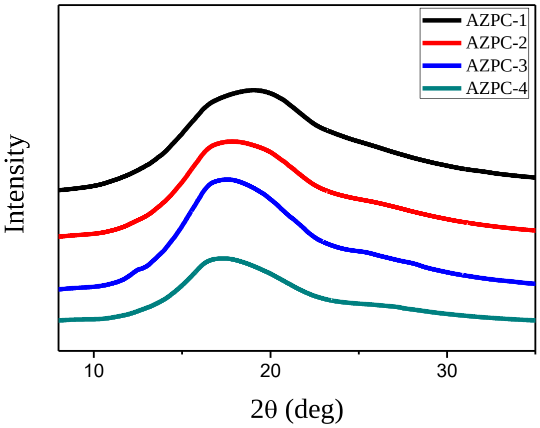


Figure 3.13. X-Ray diffractograms of (co)polycarbonates.

3.3.5 Thermal properties of (co)polycarbonates

The thermal behavior of (co)polycarbonates containing pendant azido groups was investigated by thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate 10 °C/min (**Figure 3.14A)**. Included in **Figure 3.14B** are thermogram (TG) and differential thermogram (DTG) curves of AZPC-2.

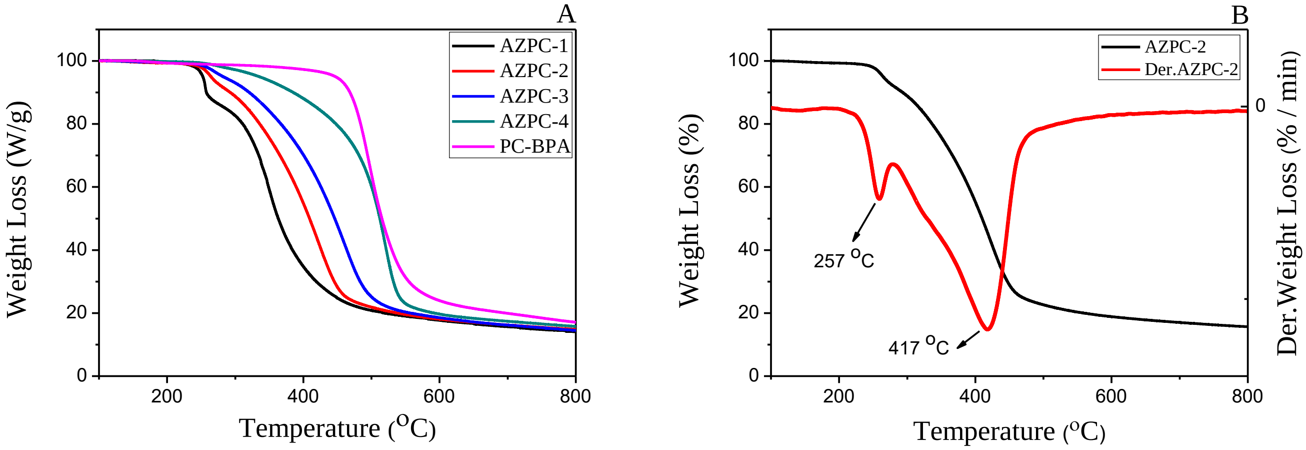


Figure 3.14. A) TG curves of (co)polycarbonates; B) Representative TG and DTG curves of copolycarbonate AZPC-2.

The thermal decomposition of polycarbonates containing pendant azido groups was found to take place essentially in two steps. The first step of the decomposition occurred in the temperature range 205-280 °C with a mass loss of around 8.2 %, which corresponds to theoretical mass loss due to release of nitrogen by decomposition of azido groups. Similar observations have been reported in the literature for thermal decomposition of polymers containing pendant azido groups.[43,55]

For the determination of T_g of (co)polycarbonates, the polymer samples were subjected to DSC measurements upto a temperature of 180 °C with a heating rate of 10 °C/min. As shown in **Figure 3.15** and from data in **Table 3.4**, polycarbonate based on AZBPA showed T_g at 106 °C which is lower by 41 °C than T_g value (147 °C) of reference polycarbonate based on BPA. This clearly results from the presence of pendant alkyl side chain with azido group which is responsible for decrease in the intermolecular interactions which in turn results in decrease in T_g. Copolycarbonates containing varying mole percent of AZBPA showed T_g values in the range 124 °C-143 °C and the values tend to decrease with increase in mol % incorporation of AZBPA.

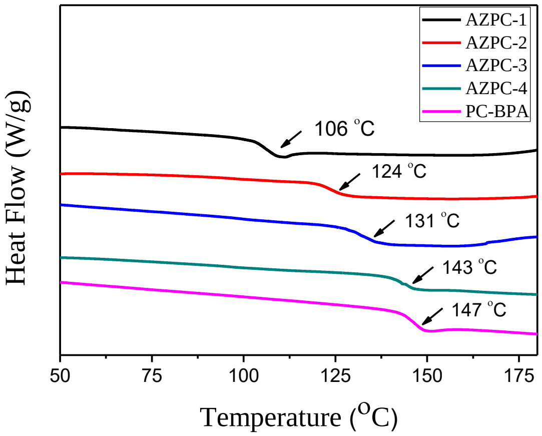


Figure 3.15. DSC curves of (co)polycarbonates.

(Co)polycarbonates bearing pendent azido groups were subjected to DSC analysis upto a temperature of 300 °C with a view to monitor the decomposition of azido groups accompanied by curing reactions. The first heating scan of DSC analysis of polycarbonates (**Figure 3.16A)** showed an exothermic peak maximum temperature at around 255 °C which could be attributed to energy released (ΔH_{exo}) due to thermal decomposition of azido groups and occurrence of cross-linking reactions involving nitrene intermediates. No exothermic peak was observed in the second heating scan of DSC (**Figure 3.16B**) indicating completion of decomposition and cross-linking reactions during the first heating scan.

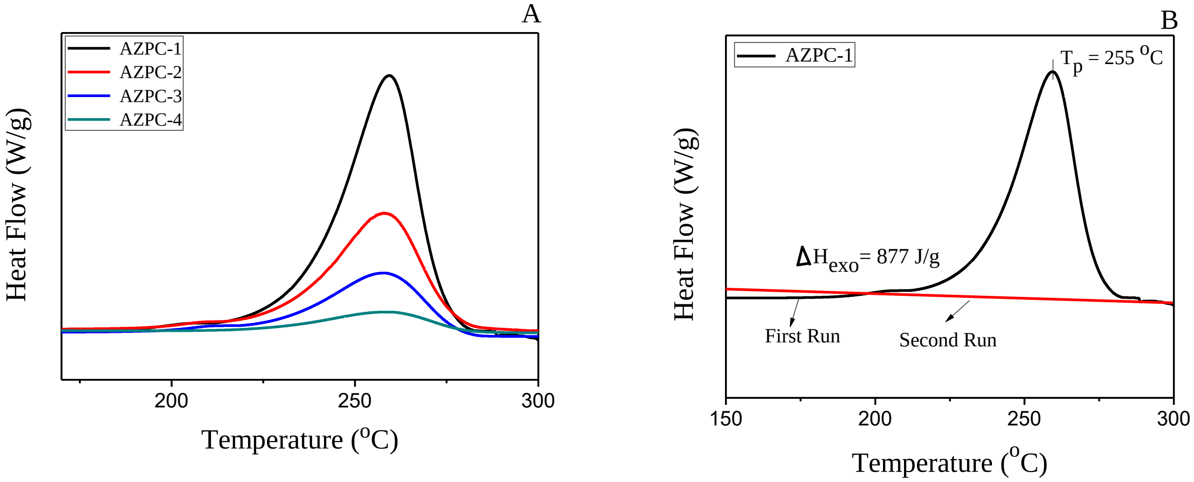


Figure 3.16. Exothermic heat flow during azide decomposition: A) The first heating cycle of (co)polycarbonates; B) Representative first and second heating cycles of polycarbonate AZPC-1.

As shown in **Figure 3.17** and from the results summarized in **Table 6a.3**, it was observed that the value of ΔH_{exo} was found to increase with the increase in content of AZBPA in (co)polycarbonates. A plot of energy released *vs.* mol % AZBPA content in (co)polycarbonates showed a linear relationship.

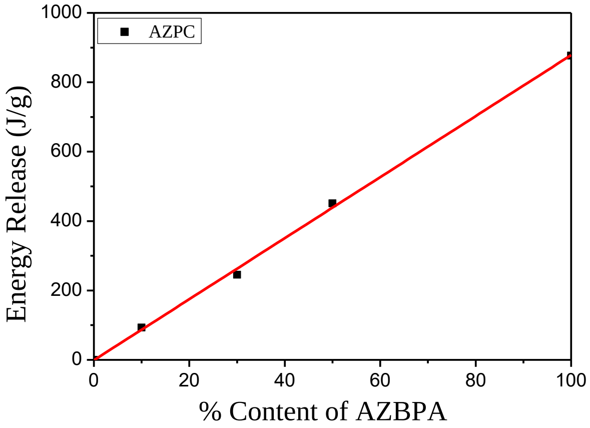
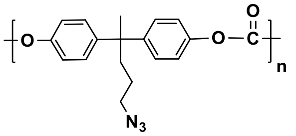
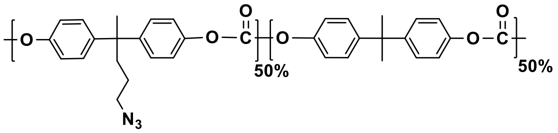
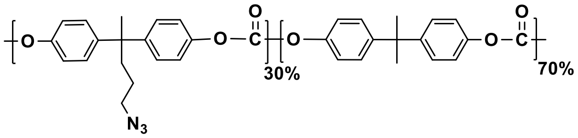
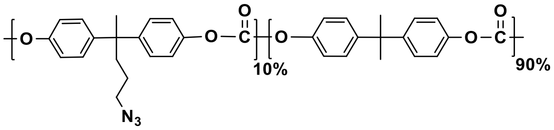
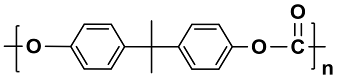


Figure 3.17. A plot of energy released *vs.* mol % AZBPA content in (co)polycarbonates.

Table 3.3. Thermal properties of (co)polycarbonates

(Co)polycarbonate	Structure of (co)polycarbonate	T_g(°C)^c	ΔH_{exo} (J/g)
AZPC-1		106	877
AZPC-2		124 (120.8)^c	451
AZPC-3		131 (129.4)^c	245
AZPC-4		143 (140.3)^c	93
PC-BPA		147	--

a: Measured by DSC on second heating scan with heating rate of 10 °C/min under nitrogen atmosphere, b: Exothermic heat flow measured by differential scanning calorimetry during azide decomposition accompanied by cross-linking, c: T_g values calculated by Fox equation.

The experimental T_g values of copolycarbonates were compared to the theoretical T_g values calculated by Fox equation.[56,57]

$$\frac{1}{T_{gc}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Where, T_{gc} is T_g of copolycarbonates and T_{g1} and T_{g2} are T_g of homo-polycarbonates derived from AZBPA and BPA, respectively (i.e. T_{g1}=106 °C, T_{g2}=147 °C). W_1 and W_2 represent weight fractions of AZBPA and BPA in copolycarbonates. The values of 1/T_g (co)polycarbonates were plotted against % weight fraction of AZBPA (**Figure 3.18).** The T_g values obtained from DSC exhibited a linear relationship with the weight % AZBPA. The calculated T_g values are included in **Table 3.3.**

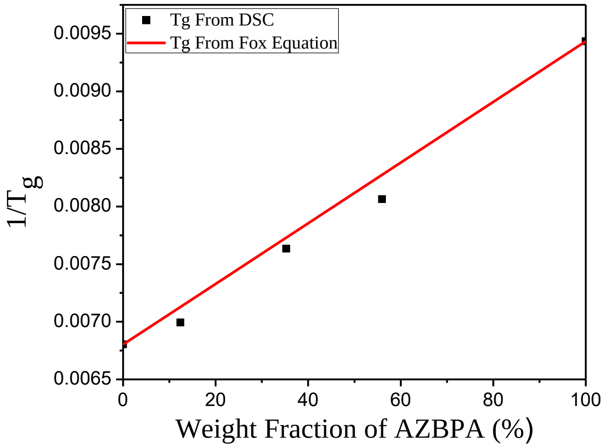
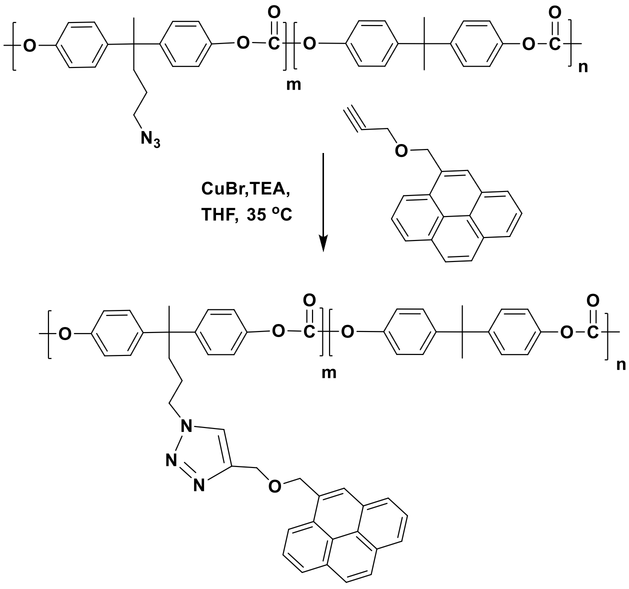


Figure 3.18. 1/T_g as a function of weight % of AZBPA in copolycarbonates.

3.3.6 Post-modification of copolycarbonate using click reaction

Click chemistry, and in particular CuAAC reaction, has been utilized for post-polymerization modification of aliphatic polycarbonates.[20,58,59] CuAAC click reaction appears to be a promising approach to perform post-modification reactions on aromatic polycarbonates bearing pendant azido groups due to its atom economy and high yielding nature under mild reaction conditions. Using CuBr/Et_3N as a catalyst, the reaction of 1-[(2-propynyloxy)methyl]pyrene with azido containing polycarbonate AZPC-2 (**Table 3.1, entry 2**) in dry THF yielded pyrene grafted polycarbonate AZPC-2-Py, as shown in **Scheme 3.3**.



Scheme 3.3. Click reaction of copolycarbonate AZPC-2 with 1-[(2-propynyloxy)methyl]pyrene.

The completion of click reaction of polycarbonate containing pendant azido groups (AZPC-2) with 1-[(2-propynyloxy)methyl]pyrene was followed by IR spectroscopy (**Figure 3.19**). The disappearance of absorption band at 2098 cm^{-1} associated with azido group evidenced the quantitative chemical transformation.

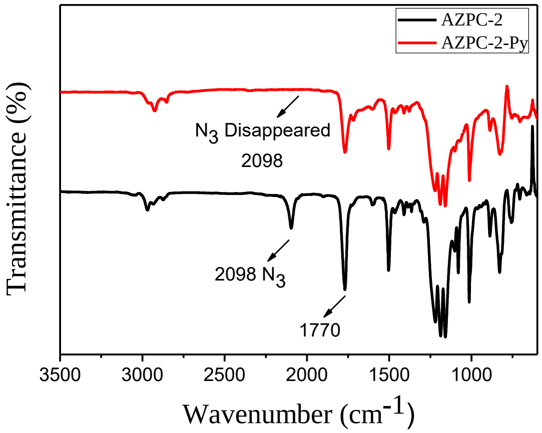


Figure 3.19. IR spectra of copolycarbonate AZPC-2 before (bottom) and after (top) CuAAC click reaction.

^{1}H NMR spectrum of polycarbonate obtained after chemical modification by click reaction with 1-[(2-propynyloxy)methyl]pyrene is depicted in **Figure 3.20**. The CuAAC click reaction was also shown to proceed in a quantitative manner as the methylene protons adjacent to azido group completely disappeared and new peak corresponding to methylene protons “f” appeared at 4.18 δ ppm. The attachment of pyrene units was further supported by appearance of characteristic aromatic peaks in the range of 8.21–8.00 δ ppm and additional peaks labeled as “d” and “e” corresponding to methylene protons linked to pyrene unit at 5.29 and 4.79 δ ppm, respectively.

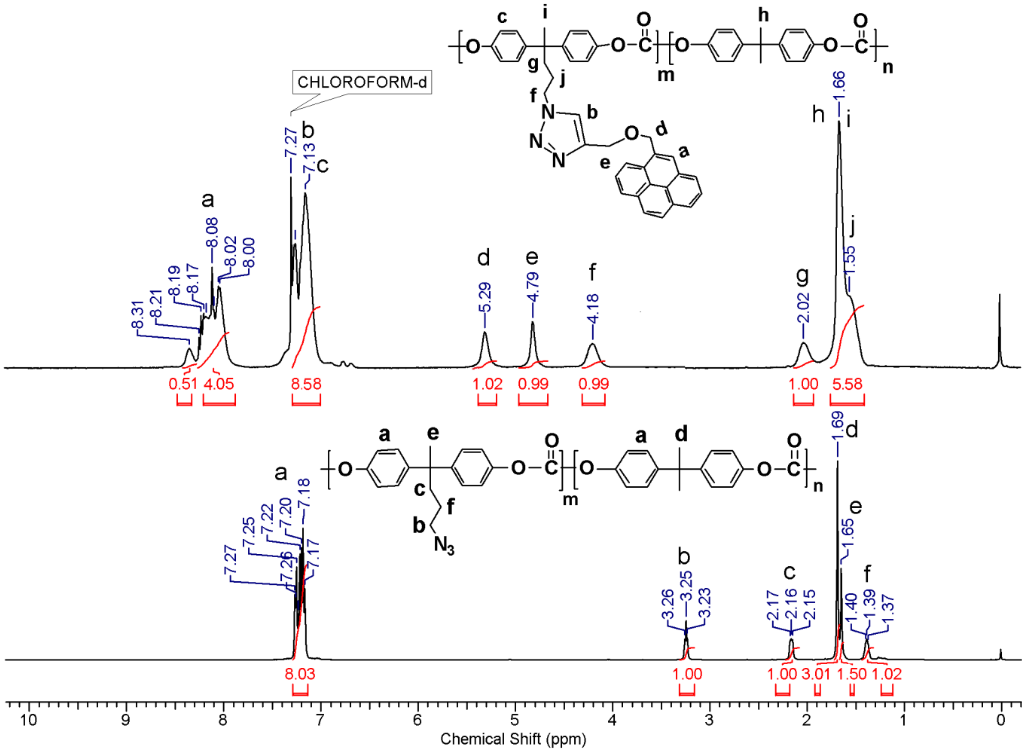


Figure 3.20. ^{1}H NMR spectra (in $CDCl_3$) of copolycarbonate AZPC-2 before (bottom) and after (top) CuAAC click reaction.

Figure 3.21 shows GPC traces of parent polycarbonate and post-functionalized polycarbonate (AZPC-2-Py) obtained by the click reaction. The post-polymerization functionalization of pendant azido groups in polymer backbone *via* CuAAC was shown to occur without observable polymer degradation.

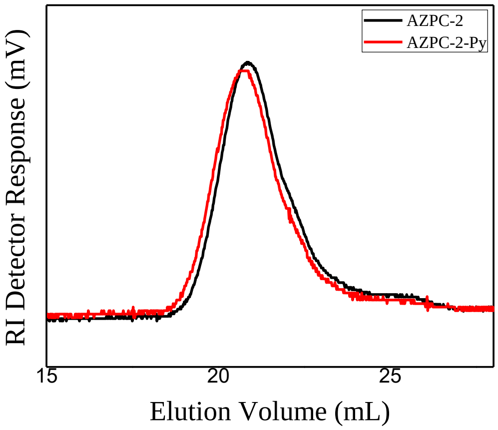


Figure 3.21. GPC traces of AZPC-2 and AZPC-2-Py.

The attachment of pyrene moiety was further supported by UV-Vis absorption spectroscopy (**Figure 3.22)**. UV-Vis spectrum of AZPC-2-Py displayed three bands at 315 nm, 329 nm and 344 nm which correspond to typical pyrene vibronic bands (314 nm, 328 nm and 345 nm).[60] As expected, AZPC-2 did not show any band corresponding to pyrene. The result indicated that pyrene moiety was incorporated in modified polycarbonate. Thus, a non fluorescent polycarbonate AZPC-2, was modified to obtain a fluorescence active aromatic polycarbonate.

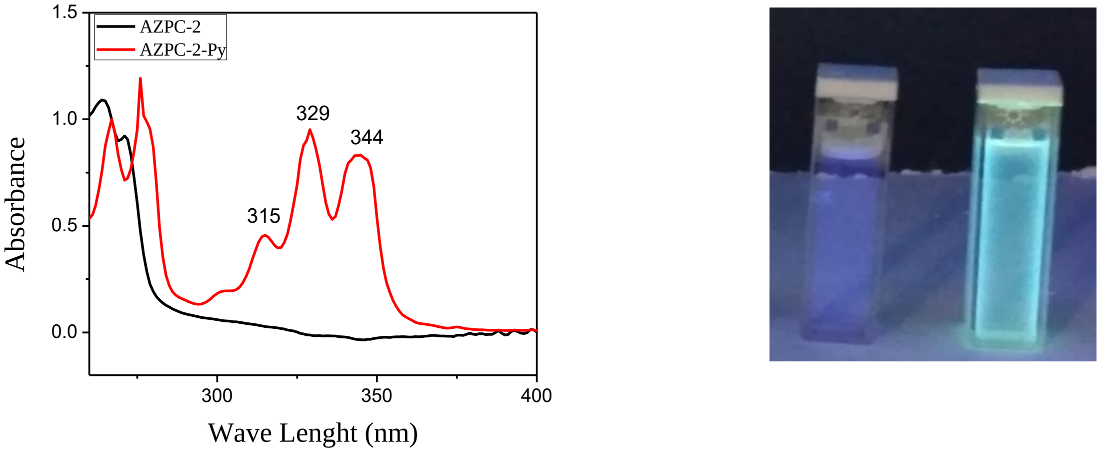
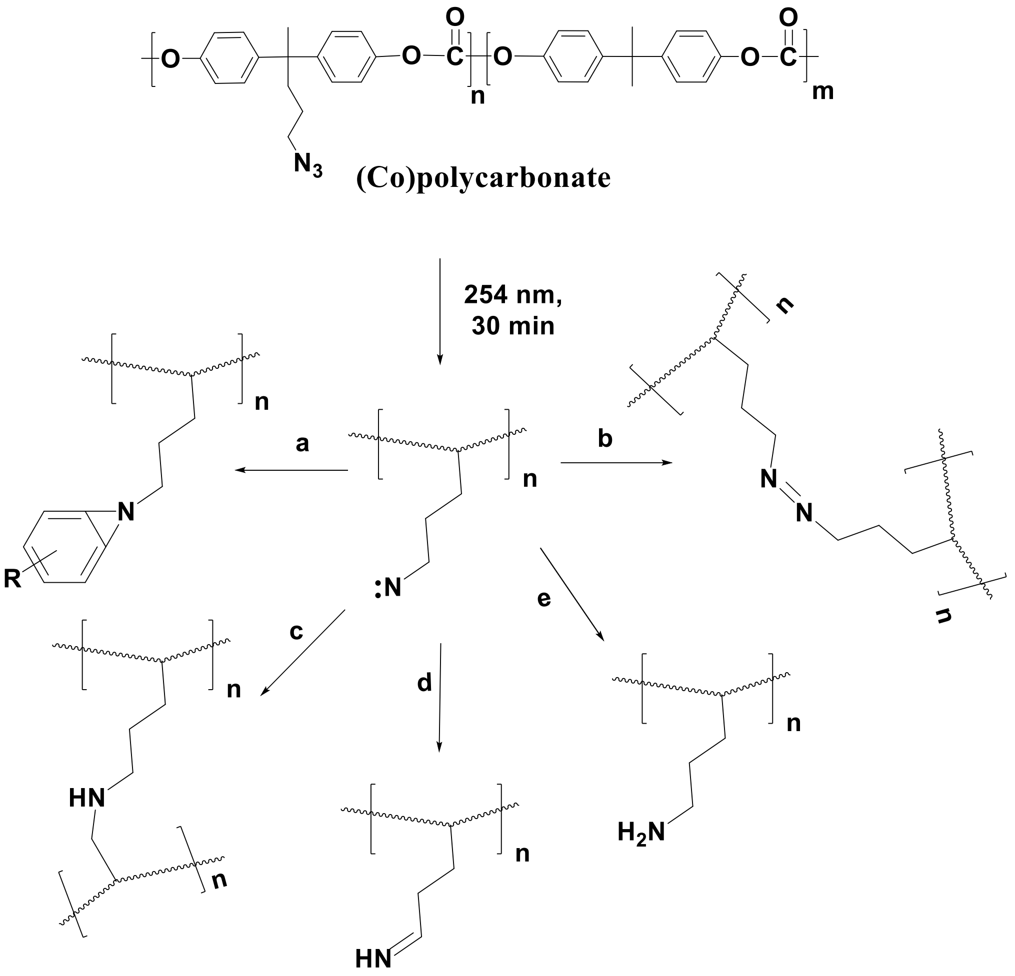


Figure 3.22. UV-Vis spectra of AZPC-2 and AZPC-2-Py.

3.3.7 UV cross-linking studies of aromatic (co)polycarbonates bearing pendant azido groups

Under ultraviolet (UV) irradiation, the azido functional group can be decomposed into highly reactive nitrene intermediate, which can subsequently form intra- and intermolecular bonds with neighboring polymer backbone to produce cross-linked structures.[36,61] The nitrenes are so reactive that they attack various chemical bonds including C-H, -NH, and O-H bonds as shown in **Scheme 3.4**.[37]



Scheme 3.4. Possible reactions on the azido group after UV treatment: (a) addition to double bond; (b) nitrene-nitrene coupling; (c) C-H bond insertion and (d), (e) H abstraction not leading to cross-linking.[37]

Polycarbonate films (thickness = 40-50 μm) were prepared by solution casting from chloroform solution and were exposed to UV irradiation at 254 nm for 30 min. Polycarbonate samples turned insoluble in chloroform due to cross-linking process that was ascribed to the transformation of azide moieties into highly reactive nitrene intermediates and their subsequent reactions with neighboring polymer chains. The cross-linking reaction was monitored using IR spectroscopy by following the intensity of azido group band appeared at 2094 cm^{-1} with respect to time. As a representative example, IR spectra of AZPC-1 before and after UV irradiation are depicted in **Figure 3.23**. The progressive decrease in absorption band of azido group was observed with the time of exposure and the band completely disappeared at exposure time of 30 min. An important question is whether any degradation occurs during UV irradiation of polycarbonate backbone.

Therefore, BPA-based polycarbonate which does not contain azido groups was used as a reference and was exposed to UV irradiation under identical conditions (254 nm/30 min). NMR spectrum and GPC trace of UV-treated BPA-based polycarbonate were identical with that of pristine sample indicating no evidence of backbone degradation. This result strongly supports that photo-degradation of polycarbonate backbone does not occur under the employed UV irradiation conditions.

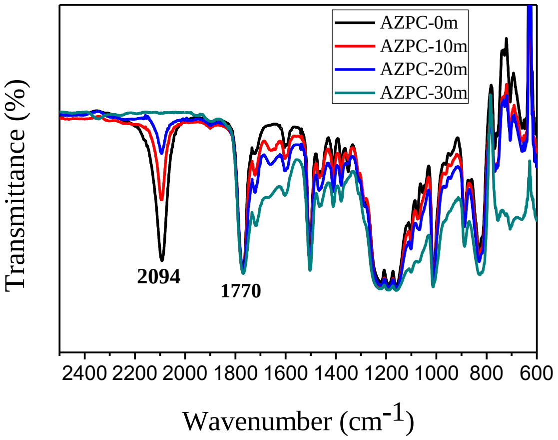


Figure 3.23. IR spectra of polycarbonate AZPC-1 after UV treatment at different time intervals.

UV cross-linked polycarbonates are denoted as UVTAZPC-1 to UVTAZPC-4. The thermal properties of cross-linked aromatic polycarbonates were investigated by TGA in nitrogen atmosphere at a heating rate 10 °C/min (**Figure 3.24A)**. A representative TG and differential thermogram (DTG) analysis curve of UVTAZPC-2 is depicted in **Figure 3.24B.**

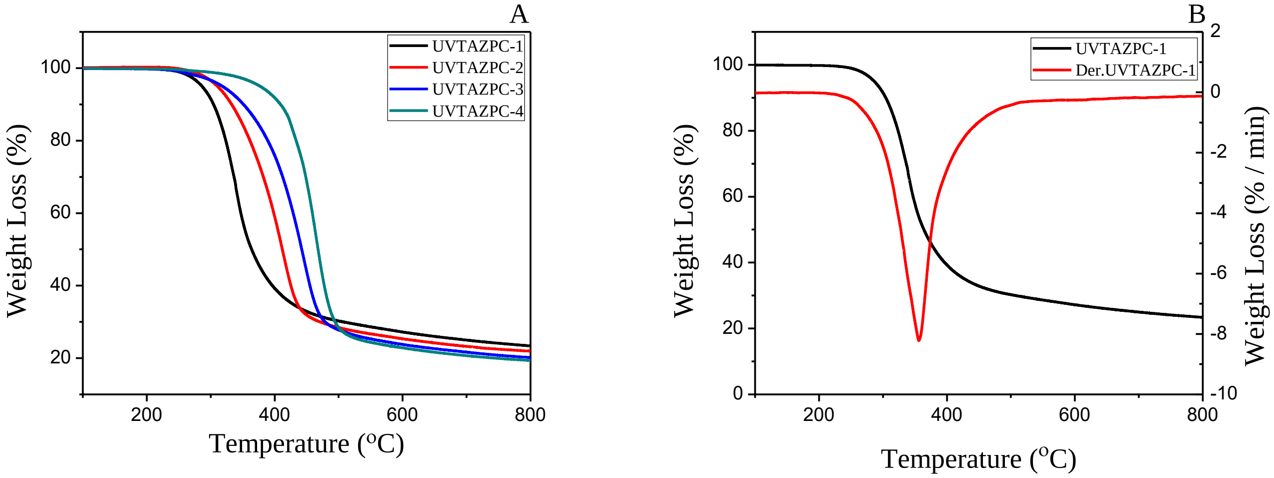


Figure 3.24. A) TG curves of copolycarbonates; B) TG and DTG curves of photo chemically cross-linked aromatic copolycarbonate UVTAZPC-2.

Table 3.4 gives % char yield values of cross-linked polycarbonates and that of corresponding pristine (co)polycarbonates containing pendant azido groups (AZPC-1 to AZPC-4). An increase in % char yield was observed in case of cross-linked polycarbonates compared to parent (co)polycarbonates containing pendant azido groups and % char yield values tend to increase with increase in the content of azido groups.

Table 3.4. % Char yield values of (co)polycarbonates before and after UV irradiation

(Co)polycarbonate	**Before UV irradiation**	**(Co)polycarbonate**	**After UV irradiation at 254 nm for 30 min**
	Char yield (%) [b]		**Char yield (%)** [b]
AZPC-1	14	UVTAZPC-1	23
AZPC-2	15	UVTAZPC -2	22
AZPC-3	15	UVTAZPC -3	20
AZPC-4	16	UVTAZPC -4	20

a: 10 % Weight loss (T_{10}), b: Weight residue at 800 °C.

3.3.8 Mechanical properties of (co)polycarbonates

The mechanical properties of aromatic (co)polycarbonates were evaluated on films (thickness = 40-50 μm). The transparent films of (co)polycarbonates containing pendant azido groups were prepared by casting from their chloroform solutions. In order to obtain transparent film of BPA-based polycarbonate, doctor blade technique was used and the solvent used was dichloromethane. The stress-strain curves of selected pristine polycarbonates and polycarbonates after UV irradiation are shown in **Figure 3.25A** and **Figure 3.25B**, respectively. The average values of six repeated measurements are summarized in **Table 3.5**. (Co)polycarbonates containing pendant azido groups exhibited excellent tensile strength and Young's modulus and the values were in the range 61.5-63.7 MPa and 1.49-1.55 GPa, respectively. These values are comparable to reference polycarbonate (PC-BPA) based on BPA. Interestingly, % elongation values of (co)polycarbonates containing pendant azido groups were higher than that of reference BPA-based polycarbonate. However, no systematic trend in % elongation values was observed in the series of (co)polycarbonates containing pendant azido groups with respect to mol % content of AZBPA. No explanation could be provided at this stage for these observations. As expected, increase in both Young’s modulus and tensile strength and decrease in % elongation values was observed in case of cross-linked polycarbonates compared to the corresponding pristine (co)polycarbonates.[41]

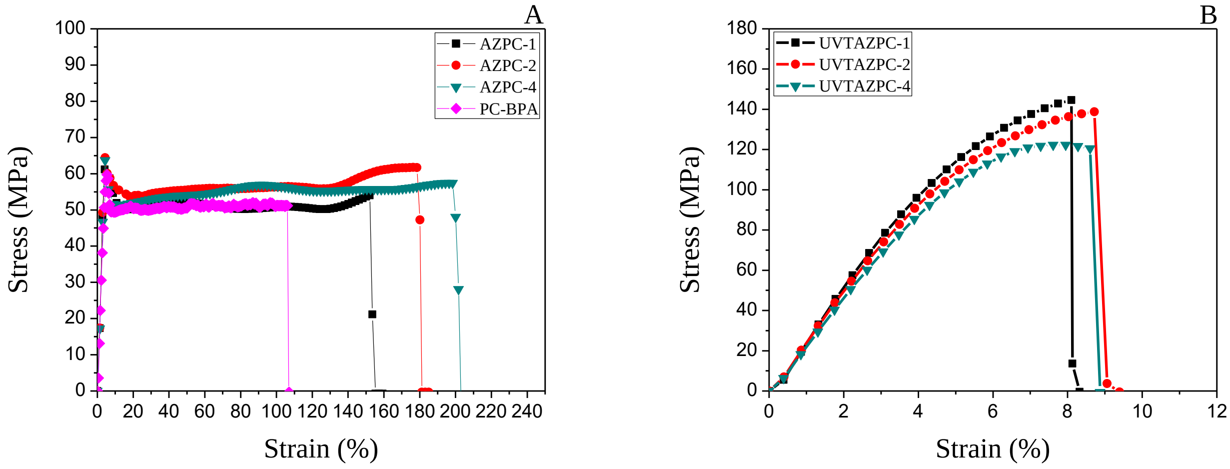


Figure 3.25. Stress-strain curves of (co)polycarbonates: A) Before UV irradiation; B) After UV irradiation.

Table 3.5. Mechanical properties of (co)polycarbonates before and after UV irradiation

	Before UV irradiation				After UV irradiation		
(Co)polycarbonate	**Young’s modulus (GPa)**	**Tensile strength (MPa)**	**Elongation (%)**	**(Co)polycarbonate**	**Young’s modulus (GPa)**	**Tensile strength (MPa)**	**Elongation (%)**
AZPC-1	1.55±0.09	61.5±0.6	152.1±17.4	UVTAZPC-1	2.67±0.11	144.5± 1.6	8.1±1.8
AZPC-2	1.54±0.05	64.4±0.8	178.9±25.1	UVTAZPC-2	2.51±0.21	138.8±2.4	9.3±1.3
AZPC-4	1.49±0.01	63.7±1.3	198.3±13.5	UVTAZPC-4	2.36±0.09	121.7±1.9	8.6±0.7
PC-BPA	1.50±0.3	59.8±0.4	106.2±7.8	--	--	--	--

3.4 Conclusions

A new azido functionalized bisphenol, namely, 4, 4’-(5-azidopentane-2, 2-diyl) diphenol (AZBPA) was successfully synthesized starting from commercially available 4, 4’-bis (4-hydroxyphenyl) pentanoic acid. Aromatic polycarbonate containing pendant azido groups was successfully synthesized from AZBPA and triphosgene by solution polycondensation technique. Copolycarbonates containing pendant azido groups were also synthesized by polycondensation of different molar proportions of AZBPA and BPA with triphosgene. Number-average molecular weights were in the range 35,400-42,200 g/mol indicating formation of high molecular weight polycarbonates. Glass transition temperature (T_g) values of polycarbonates were observed in the range 106-147 °C and T_g values decreased with increase in content of AZBPA in copolycarbonates. ΔH_{exo} of thermal curing reaction of polycarbonates studied by DSC in nonisothermal mode was observed in the range 93-877 J/g. The increase in ΔH_{exo} value was observed with increase in the content of azido functional groups in (co)polycarbonates. The feasibility of CuAAC reaction on pendant azido groups was demonstrated by reaction with 1-[(2-propynyloxy)methyl]pyrene. In the presence of CuBr/Et_3N as the catalyst system, click reaction proceeded quantitatively without affecting polycarbonate backbone. The complete conversion of pendant azido groups to triazoles was confirmed by IR and ^1H NMR spectral analysis. The photo-crosslinking of aromatic (co)polycarbonates containing pendant azido groups was carried out under UV irradiation to obtain cross-linked polycarbonates with enhanced thermal and mechanical properties.

3.5 References

1. Fox, D. W. High Performance Polymers: Their Origin and Development,Springer Netherlands, Dordrecht, 1986, 67-70.
2. Takeuchi, K. Polymer Science: A Comprehensive Reference, 2012, 363-376.
3. Thompson, T. P., Klemchuk, P. Polymer Durability; Clough, Roger L., Advances in Chemistry; American Chemical Society: Washington, DC, 1996, 303-317.
4. Brunelle, D., Korn, M. Advances in Polycarbonates ACS Symposium Series; American Chemical Society: Washington, DC, 2005, 1-5.
5. Pressman, E. J., Johnson, B. F., Shafer, S. J. Advances in Polycarbonates; ACS Symposium Series; American Chemical Society: Washington, DC, 2005, 22–38.
6. Zhang, X., Zhong, Z., Zhuo, R. *Macromolecules*, 2011, **44**, 1755–1759.
7. Hilf, J., Frey, H. *Macromol. Rapid Commun.*, 2013, **34**, 1395–1400.
8. Dai, Y., Zhang, X., Xia, F. *Macromol. Rapid Commun.*, 2017, **38**, 1700357.
9. Xu, J., Prifti, F., Song, J. *Macromolecules*, 2011, **44**, 2660–2667.
10. Ono, R. J., Liu, S. Q., Venkataraman, S., Chin, W., Yang, Y. Y., Hedrick, J. L. *Macromolecules*, 2014, **47**, 7725–7731.
11. Thomas, A. W., Dove, A. P. *Macromol. Biosci.*, 2016, **16**, 1762–1775.

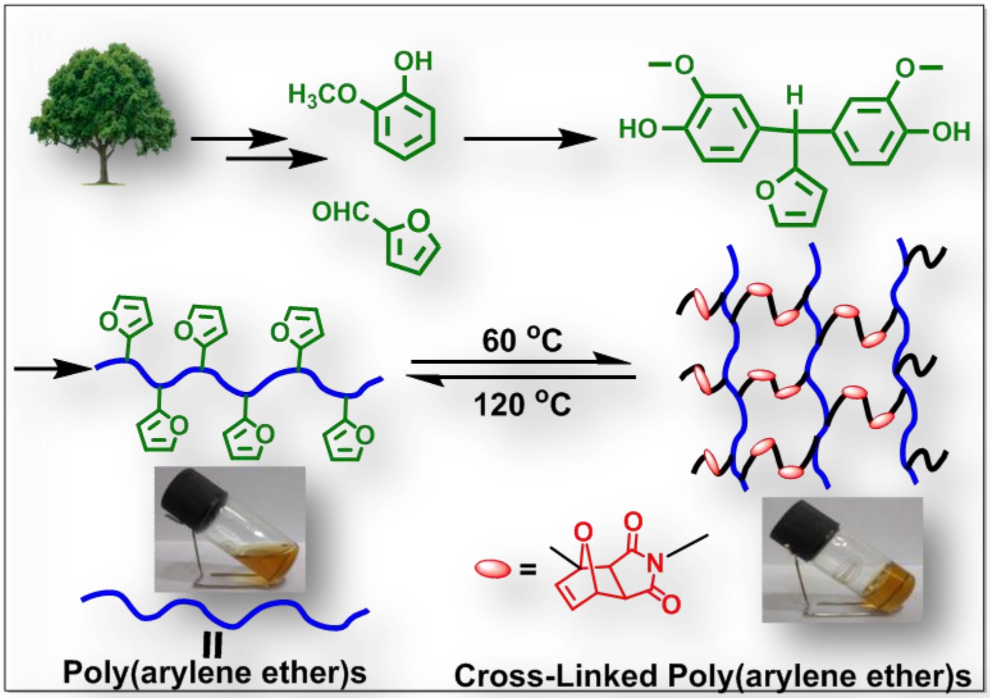
12. Tempelaar, S., Mespouille, L., Dubois, P., Dove, A. P. *Macromolecules*, 2011, **44**, 2084–2091.
13. Kühling, S., Keul, H., Höcker, H. *Makromol. Chemie*, 1990, **191**, 1611–1622.
14. Olsén, P., Odelius, K., Albertsson, A.-C. *Macromolecules*, 2014, **47**, 6189–6195.
15. Łukaszczyk, J., Jaszcz, K., Kuran, W., Listoś, T. *Macromol. Biosci.*, 2001, **1**, 282–289.
16. Olofsson, K., Malkoch, M., Hult, A. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 2370–2378.
17. He, F., Wang, Y.-P., Liu, G., Jia, H.-L., Feng, J., Zhuo, R.-X. *Polymer*, 2008, **49**, 1185–1190.
18. Li, T., Jing, X., Huang, Y. *Polym. Adv. Technol.*, 2011, **22**, 1266–1271.
19. Tempelaar, S., Barker, I. A., Truong, V. X., Hall, D. J., Mespouille, L., Dubois, P., Dove, A. P. *Polym. Chem.*, 2013, **4**, 174–183.
20. Han, Y., Shi, Q., Hu, J., Du, Q., Chen, X., Jing, X. *Macromol. Biosci.*, 2008, **8**, 638–644.
21. Hu, D., Peng, H., Niu, Y., Li, Y., Xia, Y., Li, L., He, J., Liu, X., Xia, X., Lu, Y., Xu, W. *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 750–760.
22. Hilf, J., Scharfenberg, M., Poon, J., Moers, C., Frey, H. *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
23. Williams, R. J., Barker, I. A., O'Reilly, R. K., Dove, A. P. *ACS Macro Lett.*, 2012, **1**, 1285–1290.
24. Murayama, M., Sanda, F., Endo, T. *Macromolecules*, 1998, **31**, 919–923.
25. Onbulak, S., Tempelaar, S., Pounder, R. J., Gok, O., Sanyal, R., Dove, A. P., Sanyal, A. *Macromolecules*, 2012, **45**, 1715–1722.
26. Voo, Z. X., Khan, M., Xu, Q., Narayanan, K., Ng, B. W. J., Bte Ahmad, R., Hedrick, J. L., Yang, Y. Y. *Polym. Chem.*, 2016, **7**, 656–668.
27. Xing, D., Ma, L., Gao, C. *Macromol. Biosci.*, 2014, **14**, 1429–1436.
28. Engler, A. C., Chan, J. M. W., Coady, D. J., O'Brien, J. M., Sardon, H., Nelson, A., Sanders, D. P., Yang, Y. Y., Hedrick, J. L. *Macromolecules*, 2013, **46**, 1283–1290.
29. Sanders, D. P., Fukushima, K., Coady, D. J., Nelson, A., Fujiwara, M., Yasumoto, M., Hedrick, J. L. *J. Am. Chem. Soc.*, 2010, **132**, 14724–14726.
30. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.

31. Mollah†, M. S. I., Seo†, D. W., Islam, M. M., Lim, Y. D., Cho, S. H., Shin, K. M., Kim, J. H., Kim, W. G. *J. Macromol. Sci. Part A Pure Appl. Chem.*, 2011, **48**, 400–408.
32. Xin, Y., Sakamoto, J., van der Vlies, A. J., Hasegawa, U., Uyama, H. *Polymer*, 2015, **66**, 52–57.
33. Wacker, K. T., Kristufek, S. L., Lim, S.-M., Kahn, S., Wooley, K. L. *RSC Adv.*, 2016, **6**, 81672–81679.
34. Park, J., Lee, C., Jung, J., Kang, H., Kim, K.-H., Ma, B., Kim, B. J. *Adv. Funct. Mater.*, 2014, **24**, 7588–7596.
35. Bang, J., Bae, J., Löwenhielm, P., Spiessberger, C., Given-Beck, S. A., Russell, T. P., Hawker, C. J. *Adv. Mater.*, 2007, **19**, 4552–4557.
36. Lee, S., Lee, B., Kim, B. J., Park, J., Yoo, M., Bae, W. K., Char, K., Hawker, C. J., Bang, J., Cho, J. *J. Am. Chem. Soc.*, 2009, **131**, 2579–2587.
37. Al Akhrass, S., Ostaci, R.-V., Grohens, Y., Drockenmuller, E., Reiter, G. *Langmuir*, 2008, **24**, 1884–1890.
38. Wu, G., Shi, F., Wang, Z., Liu, Z., Zhang, X. *Langmuir*, 2009, **25**, 2949–2955.
39. Schuh, K., Prucker, O., Rühe, J. *Macromolecules*, 2008, **41**, 9284–9289.
40. Lê, D., Liénafa, L., Phan, T. N. T., Deleruyelle, D., Bouchet, R., Maria, S., Bertin, D., Gigmes, D. *Macromolecules*, 2014, **47**, 2420–2429.
41. Trigo-López, M., Barrio-Manso, J. L., Serna, F., García, F. C., García, J. M. *Macromol. Chem. Phys.*, 2013, **214**, 2223–2231.
42. Albuszis, M., Roth, P. J., Pauer, W., Moritz, H.-U. *Polym. Chem.*, 2016, **7**, 5414–5425.
43. Gaina, C., Gaina, V., Ionita, D. *Polym. Int.*, 2011, **60**, 296–303.
44. Shibata, Y., Tanaka, H., Takasu, A., Hayashi, Y. *Polym. J.*, 2011, **43**, 272–278.
45. Nagane, S. S., Sane, P. S., Tavade, B. S., Wadgaonkar, P. P. *US Patent 9562004B2*, 2017.
46. Bräse, S., Gil, C., Knepper, K., Zimmermann, V. *Angew. Chem. Int. Ed.*, 2005, **44**, 5188–5240.
47. Morgan, P. W. *J. Polym. Sci. Part A*, 1964, **2**, 437–459.
48. Moore, J. A., Tannahill, T. *High Perform. Polym.*, 2001, **13**, 305–316.
49. Kim, W. B., Lee, J. S. *J. Appl. Polym. Sci.*, 2002, **86**, 937–947.
50. Sun, S.-J., Liao, Y.-C., Chang, T.-C. *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 1852–1860.

51. Marks, M. J., Munjal, S., Namhata, S., Scott, D. C., Bosscher, F., De Letter, J. A., Klumperman, B. *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 560–570.
52. Eiffler, J., Jueptner, G. A. *US Pat. 6,225,436*, 2001.
53. McCarthy, T. F., Schwind, D. B., Smith, G. C. *US Pat. 6,153,721*, 2000.
54. Boyles, D. A., Filipova, T. S., Bendler, J. T., Longbrake, G., Reams, J. *Macromolecules*, 2005, **38**, 3622–3629.
55. Varma, I. K., Choudhary, V., Gaur, B., Lochab, B., Oberoi, S., Chauhan, R. *J. Appl. Polym. Sci.*, 2006, **101**, 779–786.
56. T. G. Fox *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
57. Cheah, K., Cook, W. D. *Polym. Eng. Sci.*, 2003, **43**, 1727–1739.
58. Lu, C., Shi, Q., Chen, X., Lu, T., Xie, Z., Hu, X., Ma, J., Jing, X. *J. Polym. Sci. Part A Polym. Chem.*, 2007, **45**, 3204–3217.
59. Shi, Q., Chen, X., Lu, T., Jing, X. *Biomaterials*, 2008, **29**, 1118–1126.
60. Zhao, C., Wu, D., Lian, X., Zhang, Y., Song, X., Zhao, H. *J. Phys. Chem. B*, 2010, **114**, 6300–6308.
61. Park, J., Lee, C., Jung, J., Kang, H., Kim, K.-H., Ma, B., Kim, B. J. *Adv. Funct. Mater.*, 2014, **24**, 7588–7596.

Chapter-4

Thermally Reversible Cross-linked (Co)poly(arylene ether)s *via* Furan-Maleimide Diels-Alder Reaction



Chapter-4a

(Co)poly(ether sulfone)s Containing Pendant Furyl Groups: Synthesis, Characterization and Chemical Modifications

4a.1 Introduction

Poly(ether sulfone)s exhibit attractive chemical, thermal and mechanical properties and find a wide range of applications in the areas such as coatings,[1–3] microelectronic devices,[4,5] filtration membranes,[6–10] composites,[11–13] biomaterials[14] and fuel cells.[15–18] Although there have been significant developments in the synthesis and applications of poly(ether sulfone)s, they possess certain limitations such as poor tracking resistance, stress cracking with certain solvents and poor weathering properties. The strategy of functional group incorporation into poly(ether sulfone)s not only helps to overcome some of these limitations but also expands the range of potential applications of these high performance polymeric materials.[19–21]

The properties of poly(ether sulfone)s can be altered with the help of modification of chemical nature and composition of starting materials which are generally reactive aromatic dihalide monomers and bisphenols.[21–31] In recent years, two approaches are generally followed to introduce desired functionality into polymer chain: post-modification of synthesized polymers and functional monomer approach.[32] With the help of direct reaction of polymer backbone, one can incorporate different functional groups. However, this approach is fraught with certain shortcomings such as non-selective nature, incomplete reactions, etc.[32] In comparison to post-functionalization, the approach of using functional monomer is advantageous as it involves use of monomer bearing clickable group which is non-interfering with the polymerization reaction and acts as reactive handle that can be modified subsequently with the help of post-polymerization modification strategy.[22,33–35]

Recently, Diels-Alder reaction between furan and maleimide, which is an interesting [4+2] cycloaddition reaction, has gained remarkable popularity in material and polymer science.[36–42] Most of the fundamental criteria of click reactions are fulfilled by this cycloaddition reaction such as it is reagent-free, offers near quantitative yields and proceeds under milder conditions to yield thermo-reversible adducts.[38,43–45] This thermo-reversibility helps to fabricate innovative materials possessing self healing characteristics and reversible post-polymerization functionalization possibilities which are of great importance.[41,42,46–50] Diels-Alder reaction has been applied to polymers such as polyesters,[41,42] polyurethanes,[40,49,51–53] polyamides,[36–38] polyureas[49,54] and aliphatic polycarbonates.[39,55] To the best of our knowledge, furan-maleimide Diels-Alder click reaction has not been studied with aromatic poly(ether sulfone)s as a tool for reversible functionalization and cross-linking.

In the present work, a fully bio-based bisphenol containing pendant furyl group, namely, 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) was synthesized by base-catalyzed condensation of furfural with guaiacol-both of which are derived from lignocellulose. A new series of (co)poly(ether sulfone)s were prepared by polycondensation of BPF or varying compositions of BPF and bisphenol-A (BPA) with 4, 4'-(fluorodiphenyl sulfone) in N N-dimethylacetamide as a solvent. (Co)poly(ether sulfone)s were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA), differential scanning calorimetric studies (DSC) and tensile testing. Most interestingly, the pendant furyl groups in (co)poly(ether sulfone)s provide reactive sites for click modification and cross-linking *via* Diels-Alder reaction with maleimides and bismaleimides, respectively. Poly(ether sulfone) containing pendant furyl groups were cross-linked with bismaleimides namely, 1, 1'-(methylenedi-1, 4-phenylene)bismaleimide (BMI) and 1, 8-bis(maleimido)-triethylene glycol (TEG) and thermo-mechanical properties were examined. Furthermore, (co)poly(ether sulfone) based gels were prepared and their thermo-reversibility was demonstrated.

4a.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC, XRD and tensile testing are given in **Chapter 2**.

4a.2.1 Synthesis of bisphenol bearing pendant furyl group

4a.2.1.1 Synthesis of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol)

Into a 500 mL two necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were charged guaiacol (10.0 g, 80.64 mmol) and 20 % aqueous NaOH (5 % by weight based on guaiacol) at room temperature. Furfural (3.87 g, 40.32 mmol) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 4 h and then heated at 100 ^{o}C for 4 h. The reaction mixture was cooled to room temperature and was diluted with cold water (500 mL) with stirring. The solution was neutralized with dilute hydrochloric acid. The precipitated product was separated out by filtration and washed with cold water. The product was dissolved in dichloromethane (200 mL) and dichloromethane solution was washed with water (2 x 100 mL). The dichloromethane layer was separated, dried over anhydrous sodium sulfate, filtered and dichloromethane was removed under reduced pressure at room temperature. The product was recrystallized from ethanol: water (1:1, v/v) to afford white solid.

Yield: 15.17 g (58 %); Melting point- 145 ^{o}C; IR (KBr): 3445, 1510, 1072, 1012 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_{3,}$ δ/ppm): 7.39 (br.s, 1H), 6.87 (d, 2H), 6.70 (d, 2H), 6.66 (dd, 2H), 6.33 (s, 1H), 5.93(d, 1H), 5.59 (br. s, 2H), 5.34 (s, 1H), 3.82 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_{3,}$ δ/ppm): 157.2, 146.4, 144.3, 141.8, 133.9, 121.4, 114.1, 111.2, 110.0, 108.0, 55.8, 50.0; HRMS ESI^{+}: $(M+Na)^{+}$m/z calculated for $C_{19}H_{18}O_{5}Na$: 349.1046, found: 349.1043.

4a.2.2 Synthesis of (co)poly(ether sulfone)s bearing pendant furyl groups

A representative procedure for the synthesis of poly(ether sulfone)s is described below:

Into a 50 mL three necked round bottom flask equipped with a nitrogen inlet, a Dean-Stark trap fitted with a condenser and a magnetic stirring bar were charged BPF (1.0 g, 3.06 mmol), bis(4-fluorophenyl) sulfone (0.78 g, 3.06 mmol), anhydrous potassium carbonate (0.64 g, 4.60 mmol), N,N-dimethylacetamide (10 mL) and toluene (10 mL). The reaction mixture was refluxed at 140 ^{o}C with stirring for 2 h and water was removed by azeotropic distillation with toluene. Toluene was removed by distillation, and the reaction mixture was heated at 155 °C for 5 h to obtain viscous polymer solution. The reaction mixture was cooled to room temperature, the viscous reaction mixture was poured into methanol (100 mL); the precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and re-precipitated into methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature for 24 h.

A similar procedure was followed for the synthesis of other (co)poly(ether sulfone)s.

4a.2.3 Preparation of cross-linked copoly(ether sulfone) films

To the solution of copoly(ether sulfone) (PSU-2) containing pendant furyl groups (200 mg) in chloroform (10 mL), a stoichiometric amount of bismaleimide, namely, 1,1’-(methylenedi-1,4-phenylene)bismaleimide (BMI) or 1,8-bis(maleimido)-triethylene glycol (TEG) (furan/maleimide mol ratio = 1) was added. The mixture was stirred at 30 ^{o}C for 1 h and then the solution was poured into glass Petri-dish and the solvent was evaporated at room temperature to obtain a free-standing film. The film was kept at 60 ^{o}C in an oven for 36 h. The obtained cross-linked polymer film was used for further characterization.[36,41]

4a.2.4 Recyclability of cross-linked copoly(ether sulfone) films

The cross-linked polymer films were heated in chloroform at 120 °C for 10 min in a pressure tube. The solution of polymer was poured into glass Petri-dish and solvent was allowed to evaporate off. After complete evaporation of solvent, film was kept at 60 °C in an oven for 36 h. Mechanical properties of cross-linked polymers were characterized by tensile testing. The same procedure was repeated twice and tensile data were recorded.

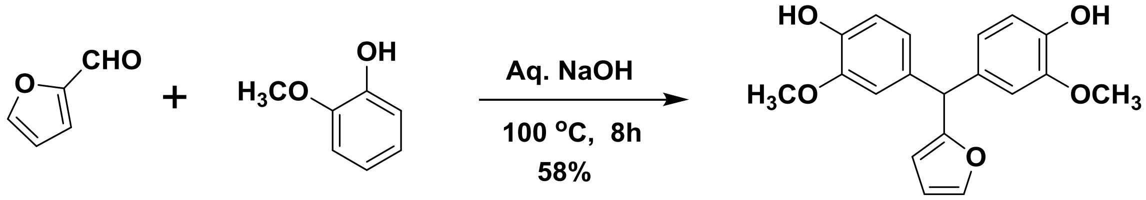
4a.2.5 Preparation of thermo-reversible cross-linked copoly(ether sulfone) gel

Into a sample vial were taken copoly(ether sulfone) (PSU-2) containing pendant furyl groups (100 mg) and DMAc (1 mL). To the solution was added, a stoichiometric quantity of bismaleimide (BMI or TEG) (furan/maleimide mol ratio = 1) in one lot. The sample vial was kept at 60 °C in an oven for 12 h. Cross-linking occurred and the system turned in to a gel. The polymer gel was thermally reversible and could be converted back to clear and fluid solution by heating at 120 °C for 10 min, during which the retro-DA reaction of furan-maleimide adduct occurred.

4a.3 Results and discussion

4a.3.1 Monomer synthesis

Scheme 4a.1 outlines the synthesis of 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) by reaction of furfural with guaiacol.



Scheme 4a.1. Synthesis of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol).

Bisphenol containing pendant furyl group was readily synthesized in one-step reaction by condensation of furfural with guaiacol in the presence of aqueous sodium hydroxide as a base at 100 °C.[56] After completion of reaction, dark red solid was obtained which was dissolved in excess water and acidified with 2 M HCl. The product was collected by filtration and was purified using column chromatography followed by recrystallization from water-ethanol system. BPF was characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

IR spectrum of BPF is reproduced in **Figure 4a.1**. The absorption band was observed at 3445 cm^{-1} corresponding to phenolic group. The furan ring (C=C) band was observed at 1510 cm^{-1} whereas furan breathing bands were observed at 1012 and 1072 cm^{-1}.

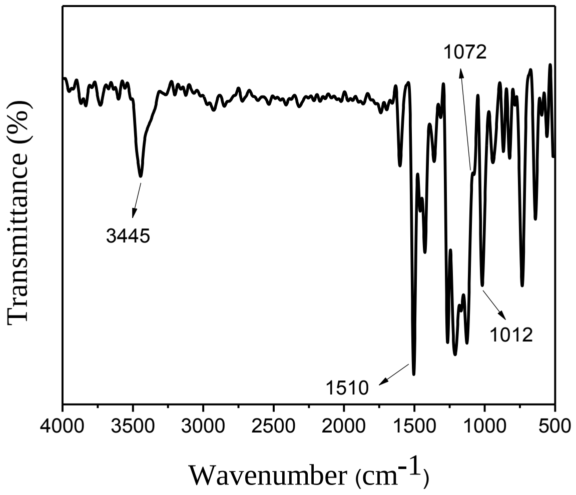


Figure 4a.1. IR spectrum of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol).

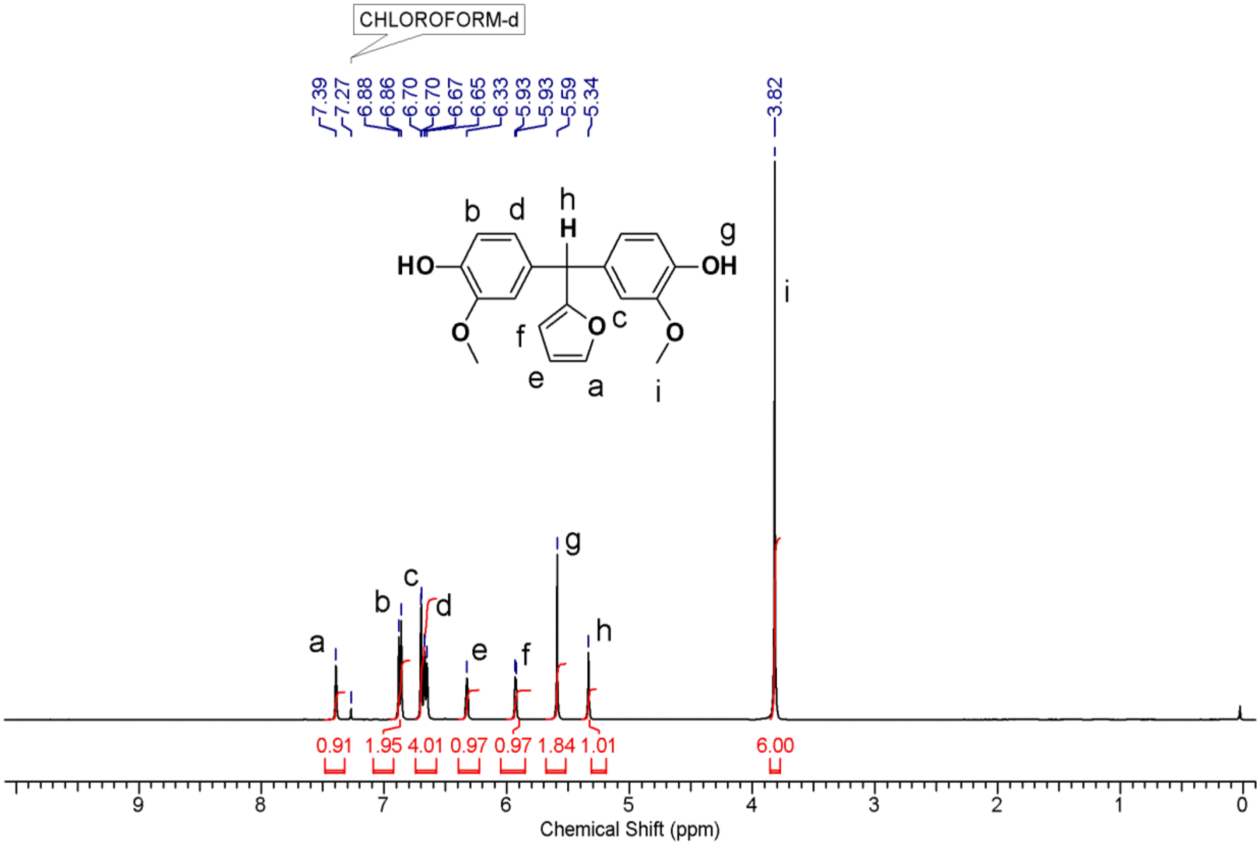


Figure 4a.2. ^{1}H NMR spectrum (in $CDCl_3$) of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol).

Figure 4a.2 depicts ^{1}H NMR spectrum of BPF. The proton adjacent to oxygen atom of furyl group appeared as a singlet at 7.39 δ ppm. A doublet was observed at 6.87 δ ppm corresponding to aromatic protons *ortho* to phenolic group on aromatic ring. Aromatic protons *ortho* to methoxy group exhibited a doublet at 6.70 δ ppm while aromatic protons *meta* to phenolic -OH group appeared as a doublet at 6.66 δ ppm. The furyl protons “e” and “f” appeared as a singlet at 6.33 δ ppm and a doublet at 5.93 δ ppm, respectively. The singlet peak at 5.34 δ ppm is attributed to the benzylic proton. Methoxy group attached to aromatic ring exhibited a singlet at 3.82 δ ppm.

^{13}C NMR spectrum of BPF (**Figure 4a.3**) was in accordance with the structure.

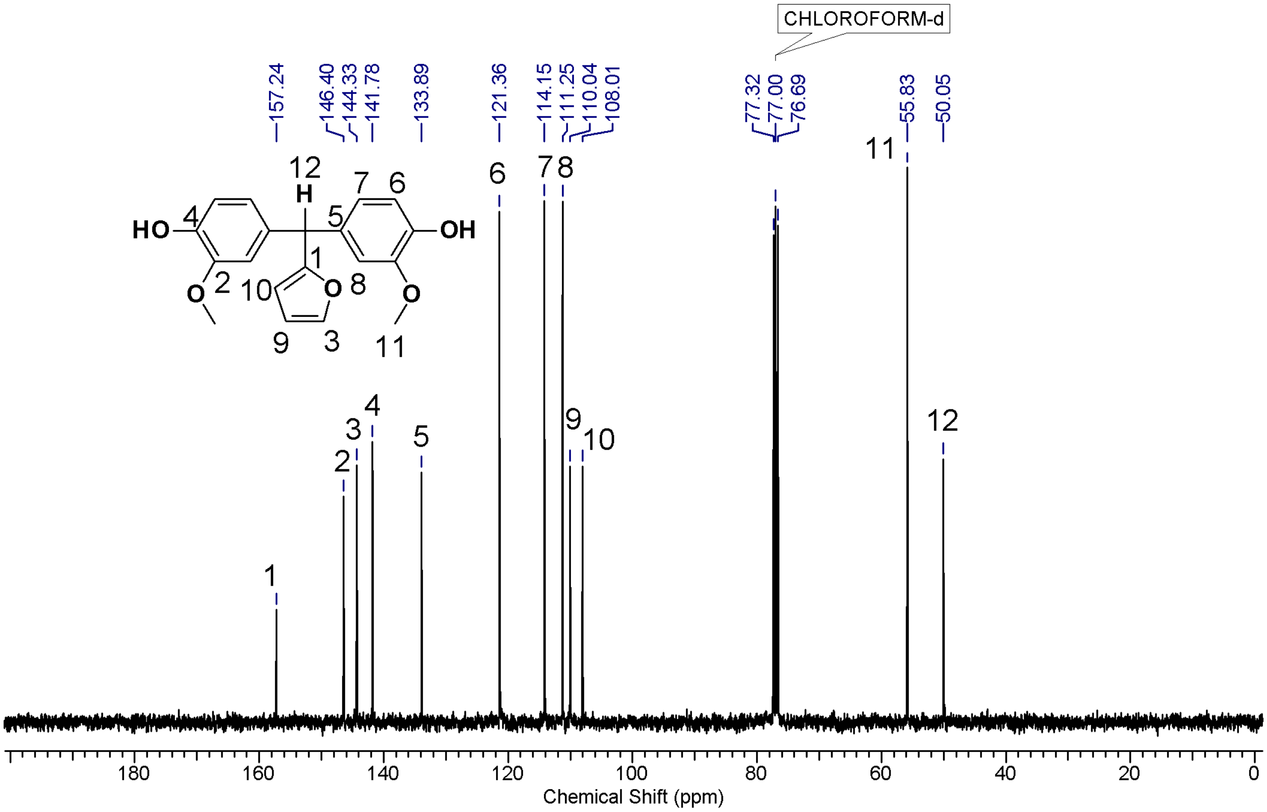


Figure 4a.3. ^{13}C NMR spectrum (in $CDCl_3$) of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol).

The chemical structure of BPF was further supported by HRMS analysis **(Figure 4a.4)**. HRMS showed signal at 349.1043 corresponding to $[M+Na]^+$ of BPF (calcd. $[M+Na]^+$ for $C_{19}H_{18}O_5Na$= 349.1046).

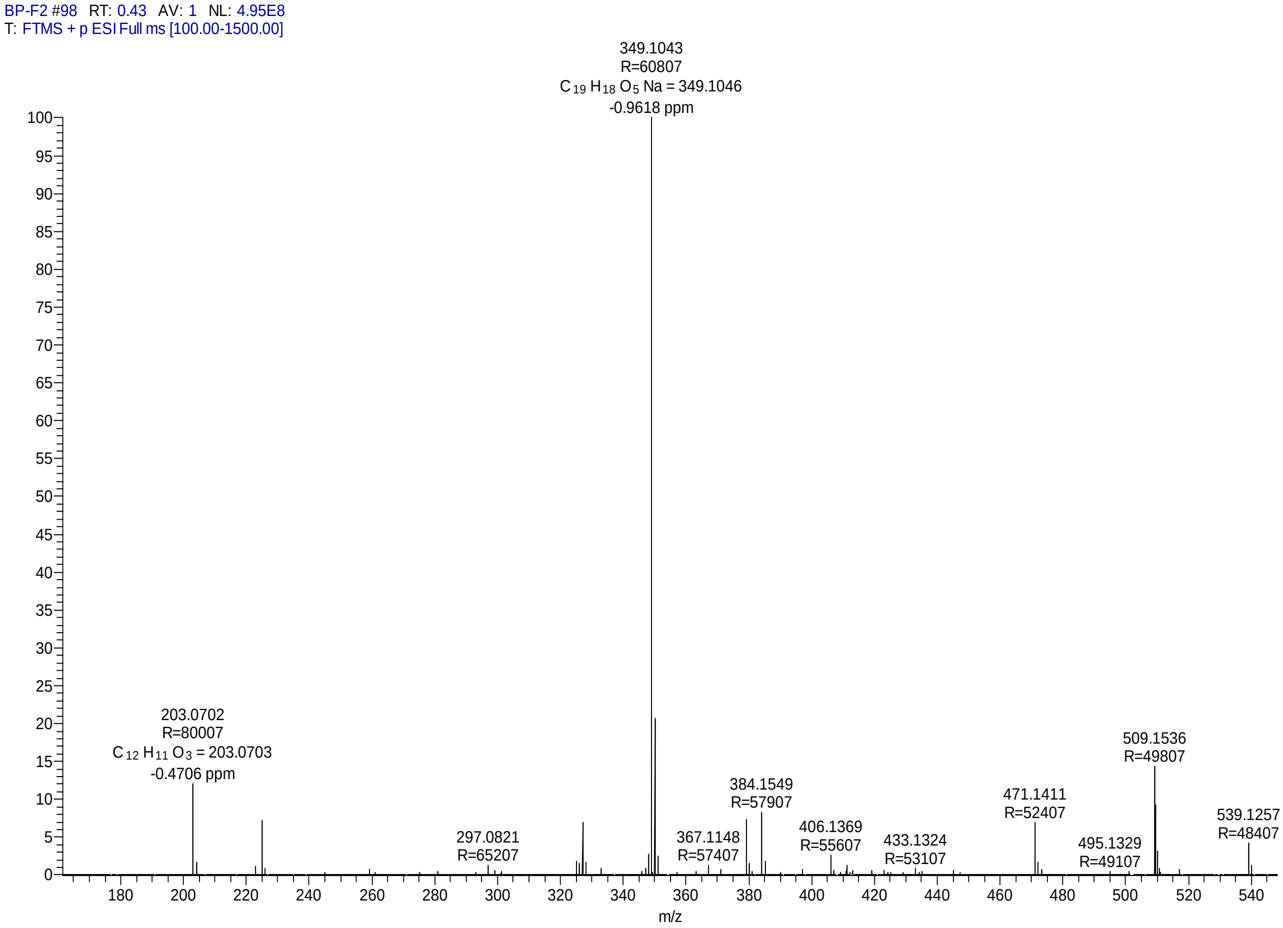
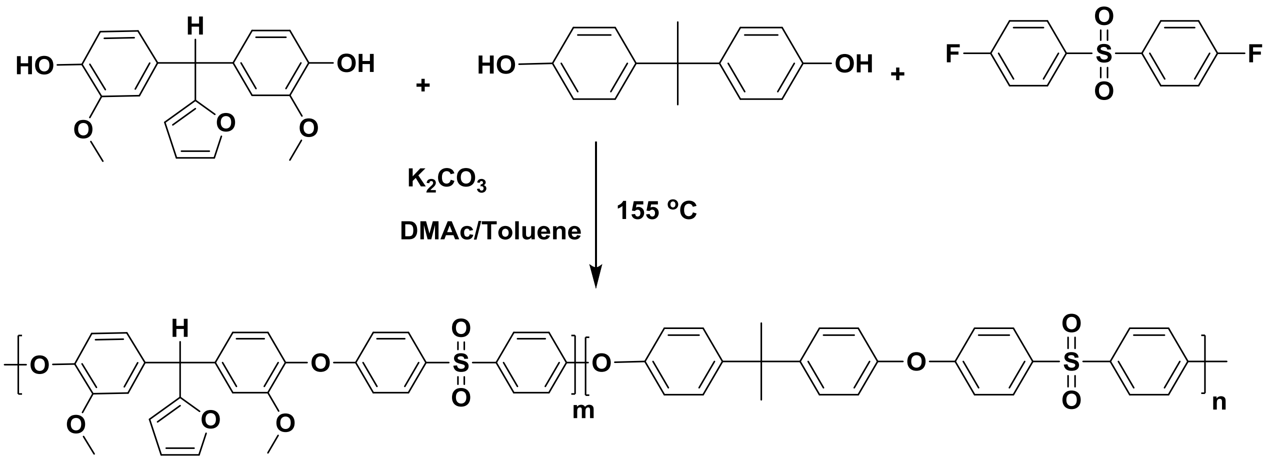


Figure 4a.4. HRMS of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol).

4a.3.2 Synthesis of (co)poly(ether sulfone)s bearing pendant furyl groups

(Co)poly(ether sulfone)s containing pendant furyl groups were synthesized by solution polycondensation of BPF or various feed ratios of BPF and BPA with bis(4-fluorophenyl) sulfone in the presence of anhydrous K_2CO_3 using DMAc as the solvent **(Scheme 4a.2)**. During the initial stage of the polymerization, reaction temperature was maintained at 140 ^oC, and the water generated was effectively removed with toluene through an azeotropic distillation. Polymerization reactions proceeded smoothly and no cross-linking was evident when the system was carefully purged with nitrogen and the reaction was performed at 155 ^oC for 5h. The resulting (co)poly(ether sulfone)s were precipitated into excess methanol. The results of synthesis of (co)poly(ether sulfone)s are presented in **Table 4a.1**.



Scheme 4a.2. Synthesis of (co)poly(ether sulfone)s bearing pendant furyl groups.

Inherent viscosity (η_{inh}) and number average molecular weights ($\overline{\mathbf{M_n}}$) of (co)poly(ether sulfone)s were in the range 0.92-1.47 dL/g and 91,300-1,31,000 g/mol, respectively. These data indicated the formation of high molecular weight polymers. However, molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards. The dispersity values were in the range 2.1-2.3, which is consistent with the results of a typical polycondensation reaction.

Table 4a.1. Molar composition, inherent viscosity and molecular weight of (co)poly(ether sulfone)s

(Co)poly(ether sulfone)	BPF (mol%)	BPA (mol%)	η_{inh} (dL/g)[a]	Molecular Weight[b]		Dispersity
				$\overline{M_n}$	$\overline{M_w}$	
PSU-1	100	00	0.92	91,300	2,07,000	2.2
PSU-2	50	50	1.06	98,100	2,28,000	2.3
PSU-3	30	70	1.15	1,02,000	2,35,000	2.3
PSU-4	10	90	1.47	1,31,000	2,76,000	2.1

a: η_{inh} was measured with 0.5 % (w/v) solution of (co)poly(ether sulfone) in chloroform at 30 °C±1 °C, b: Measured by GPC in chloroform using polystyrenes as calibration standard.

(Co)poly(ether sulfone)s could be cast into tough, transparent, and flexible films by casting from solution of polymers in chloroform and the photograph of a representative polymer film is shown in **Figure 4a.5.**

Figure 4a.5. Film of poly(ether sulfone) PSU-1.

4a.3.3 Structural characterization

The analysis data obtained from IR, ^{1}H NMR and ^{13}C NMR spectroscopy was used to support the formation of (co)poly(ether sulfone)s. IR spectrum of PSU-1 **(Figure 4a.6)** showed absorption bands at 1320 and 1148 cm^{-1} attributed to the presence of sulfone asymmetric and symmetric stretching, respectively whereas band of ether linkage appeared at 1223 cm^{-1}. The furan ring (C=C) stretching frequency was observed at 1500 cm^{-1} and furan breathing bands were observed at 1014 and 1072 cm^{-1}.

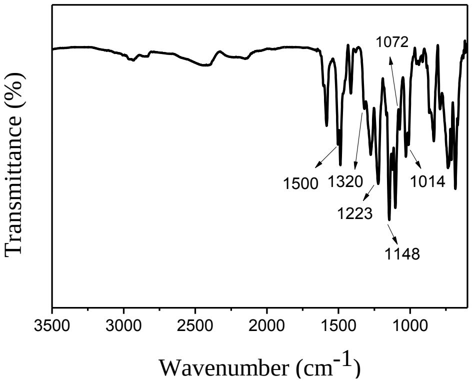


Figure 4a.6. IR spectrum of poly(ether sulfone) PSU-1.

^{1}H NMR spectrum, along with peak assignments, of poly(ether sulfone) containing pendant furyl groups (PSU-1) is shown in **Figure 4a.7**. The four *ortho* protons of aromatic ring attached sulfonyl group appeared as a doublet at 7.82 δ ppm and the remaining aromatic protons of polymer backbone appeared as a multiplet in the range 6.76-7.0 δ ppm. Benzylic proton and methoxy group protons appeared as separate singlets at 5.47 δ ppm and 3.70 δ ppm, respectively. The peaks at 7.43, 6.37 and 6.01 δ ppm were assigned to protons of furyl ring present in polymer backbone, which indicated that furyl ring was intact under the employed polymerization reaction conditions.

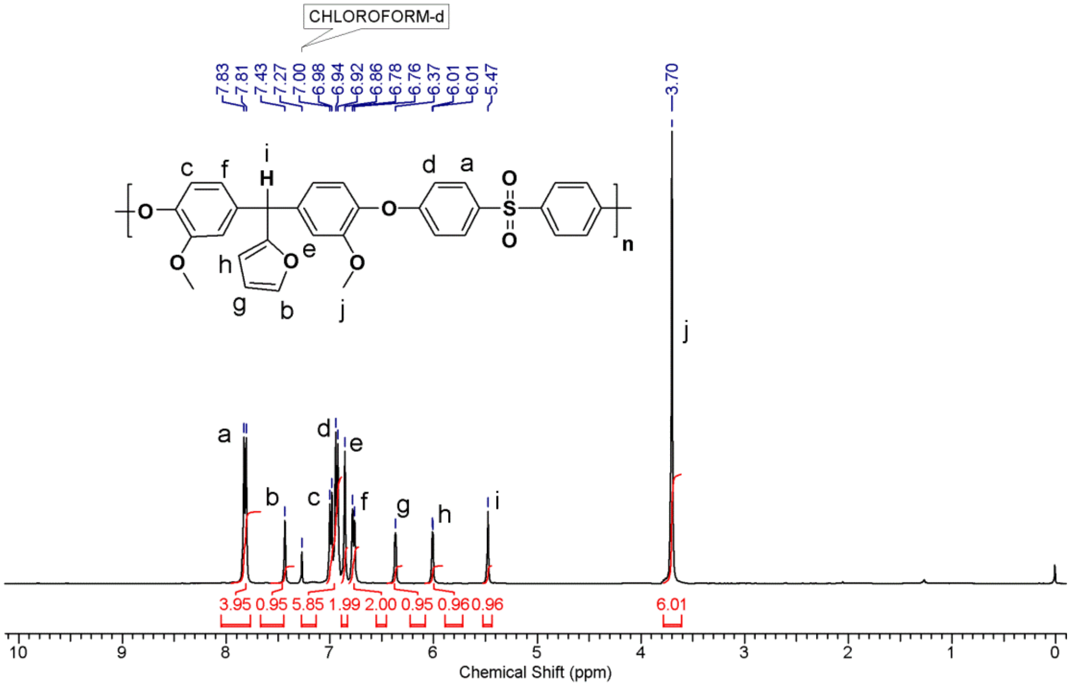


Figure 4a.7. ^{1}H NMR spectrum (in CDCl$_3$) of poly(ether sulfone) PSU-1.

^{13}C NMR spectrum of PSU-1 along with the assignments of carbon atoms is given in **Figure 4a.8**. The spectrum was in good agreement with the proposed molecular structure of poly(ether sulfone).

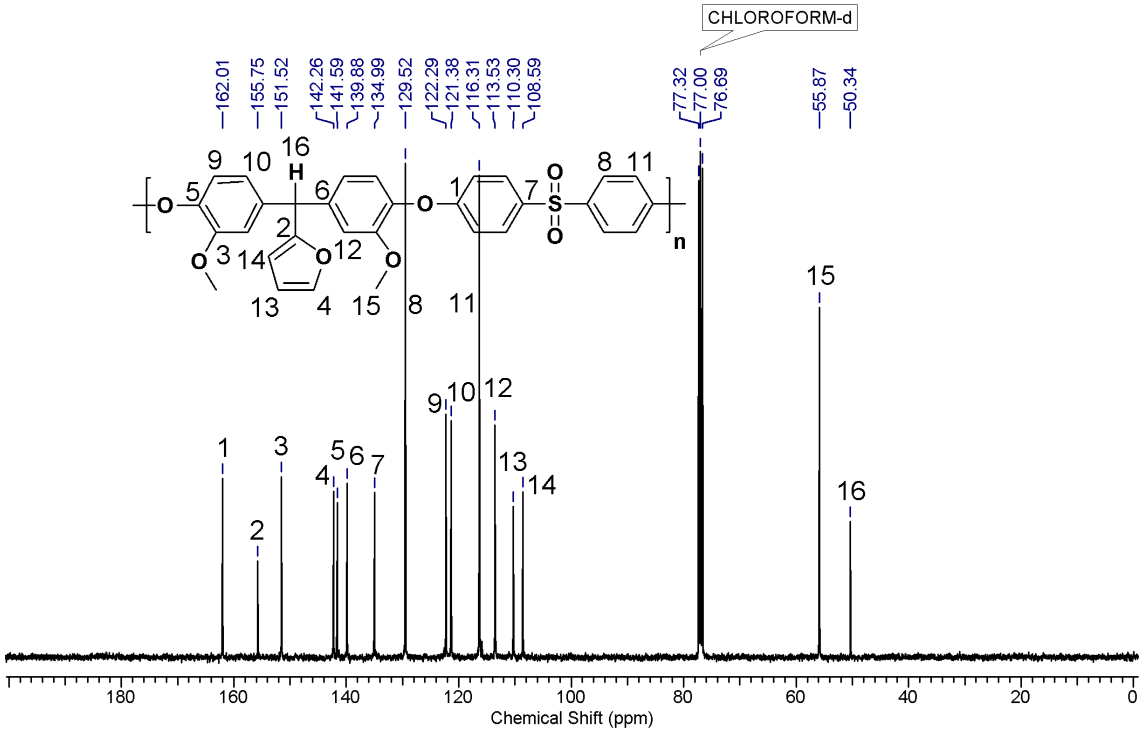


Figure 4a.8. ^{13}C NMR spectrum (in CDCl$_3$) of poly(ether sulfone) PSU-1.

According to present polymerization procedure for synthesis of copoly(ether sulfone), the content of bisphenol containing pendant furyl group incorporated in polymer backbone is controlled by amount of respective bisphenol taken in the polymerization reaction. In this way, a series of copoly(ether sulfone)s was prepared by varying the mole ratio of BPF/BPA **(Table 4a.1)**. The chemical structures of copoly(ether sulfone)s were confirmed by ^{1}H NMR spectroscopy reported in **Figure 4a.9**. ^{1}H NMR spectrum revealed that the furyl protons appeared at 7.83 δ ppm, 6.38 δ ppm and 6.02 δ ppm, indicating successful incorporation of furyl functionality in the polymer backbone. Thus, IR, ^{1}H NMR and ^{13}C NMR spectra confirmed the formation of (co)poly(ether sulfone)s bearing pendent furyl groups.

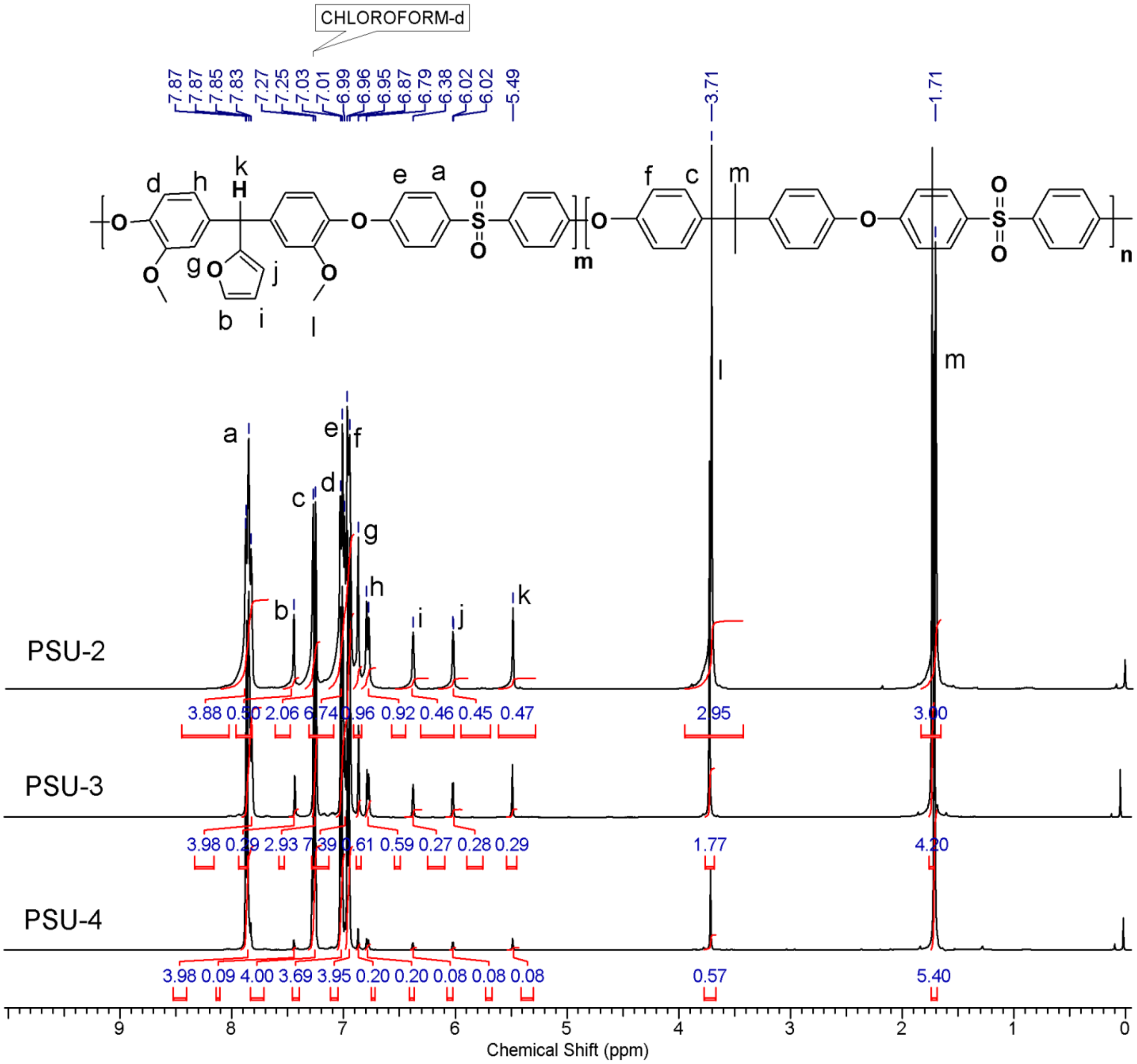
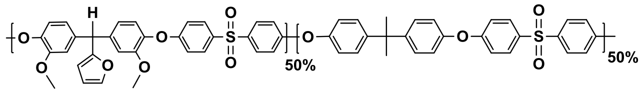
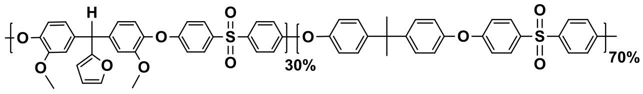
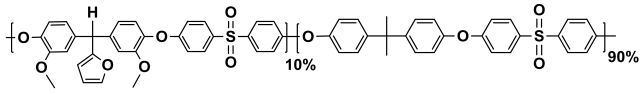


Figure 4a.9. ^{1}H NMR spectra (in $CDCl_3$) of copoly(ether sulfone)s.

The content of BPF incorporated in copoly(ether sulfone)s was determined from ^{1}H NMR spectra. For example, in the spectrum of copoly(ether sulfone)s PSU-2, the singlet at 1.71 δ ppm due to methyl group protons "m" from BPA units was integrated against the resonance at 3.71 δ ppm for methoxy protons "l" of BPF units. As reported in **Table 4a.2,** the experimental values determined from this relation are in good agreement with theoretical values based on the quantities of monomers used for polymerization reactions. Importantly, BPF was generally found to react in similar fashion as BPA itself, with no substitutive steric impedance to its reactivity resulting from the presence of methoxy groups.

Table 4a.2. Molar composition of copoly(ether sulfone)s determined by ^{1}H NMR spectra

Copoly(ether sulfone)	Structure of copoly(ether sulfone)	Feed BPF, mol %	Observed BPF, mol %
PSU-2		50	49.2
PSU-3		30	29.5
PSU-4		10	9.5

The microstructure of copoly(ether sulfone)s derived from copolymerization of BPA and BPF with bis(4-fluorophenyl) sulfone was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, copolymerization of BPA and BPF is expected to lead to formation of random copolymer with following possibilities of enchainment of the two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 4a.10**). ^{13}C NMR spectra of copoly(ether sulfone)s showed clear evidence not only for the random copoly(ether sulfone) formation but also about the microstructural details as indicated by multiplicity of the signals.

The assignments of carbon atoms in ^{13}C NMR spectrum of PSU-2, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 4a.11.**

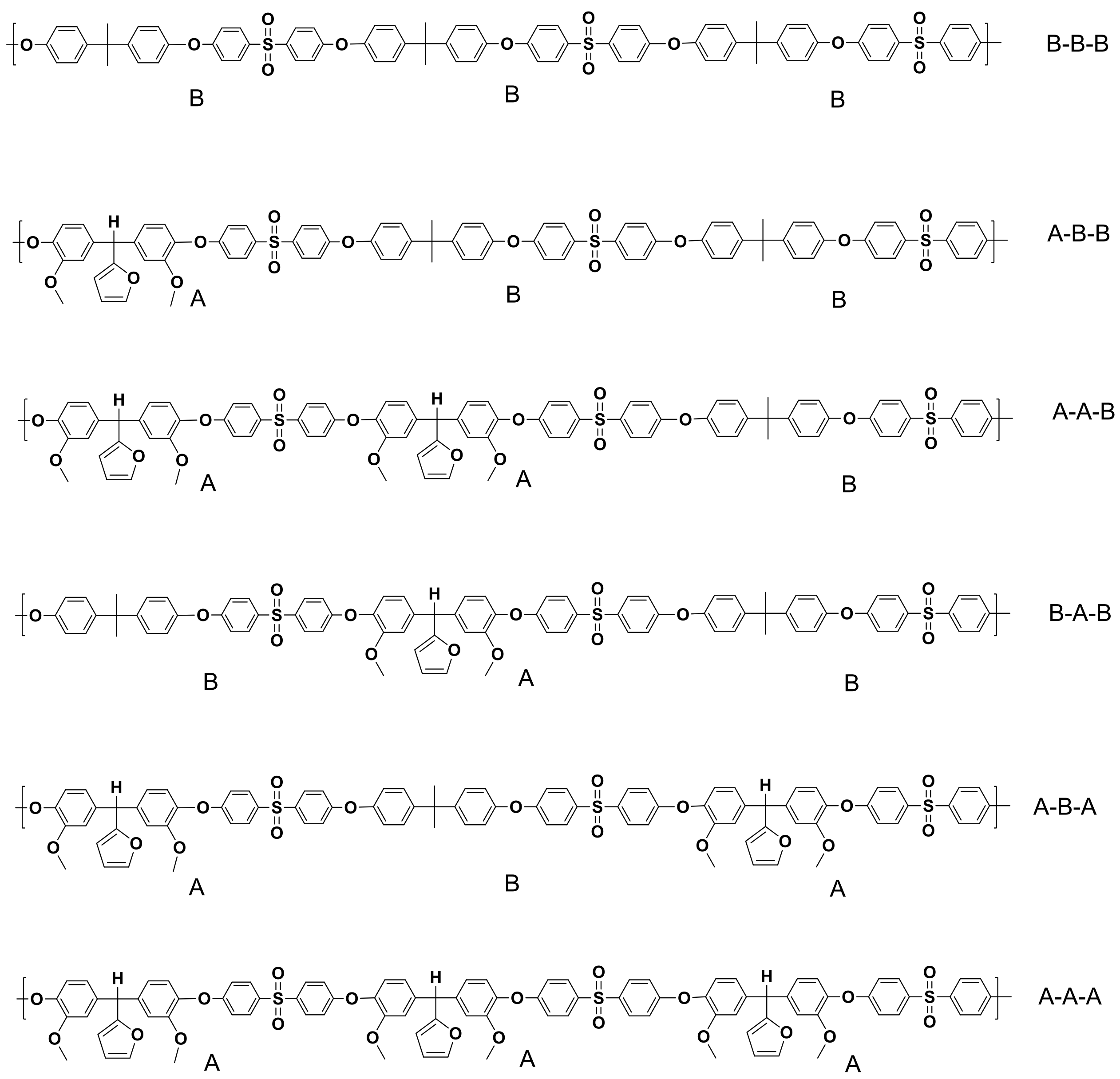


Figure 4a.10. Possible arrangements of BPF and BPA units in copoly(ether sulfone)s.

^{13}C NMR spectrum of PSU-2 (50:50 mol % of BPF:BPA) along with assignments of carbon atoms is presented in **Figure 4a.12.** For easy comparison, ^{13}C NMR spectra of homo-poly(ether sulfone) PSU-1 and copoly(ether sulfone)s PSU-2 to PSU-4 are also included in **Figure 4a.12**. It is interesting to note that the quaternary carbon labeled as “1A” and “2B” exhibited four distinct peaks at 161.88 δ ppm, 161.94 δ ppm, 162.01 δ ppm and 162.07 δ ppm for this particular copolymer. A comparison of spectrum of PSU-2 with that of PSU-1 and PSU-4 inferred that quaternary carbon peaks appeared at 162.01 δ ppm and 161.94 δ ppm originated from AAA and

BBB arrangement of co-monomer units, respectively in copoly(ether sulfone) while peaks at 161.88 δ ppm and 162.07 δ ppm correspond to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peak corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of PSU-3 and PSU-4.

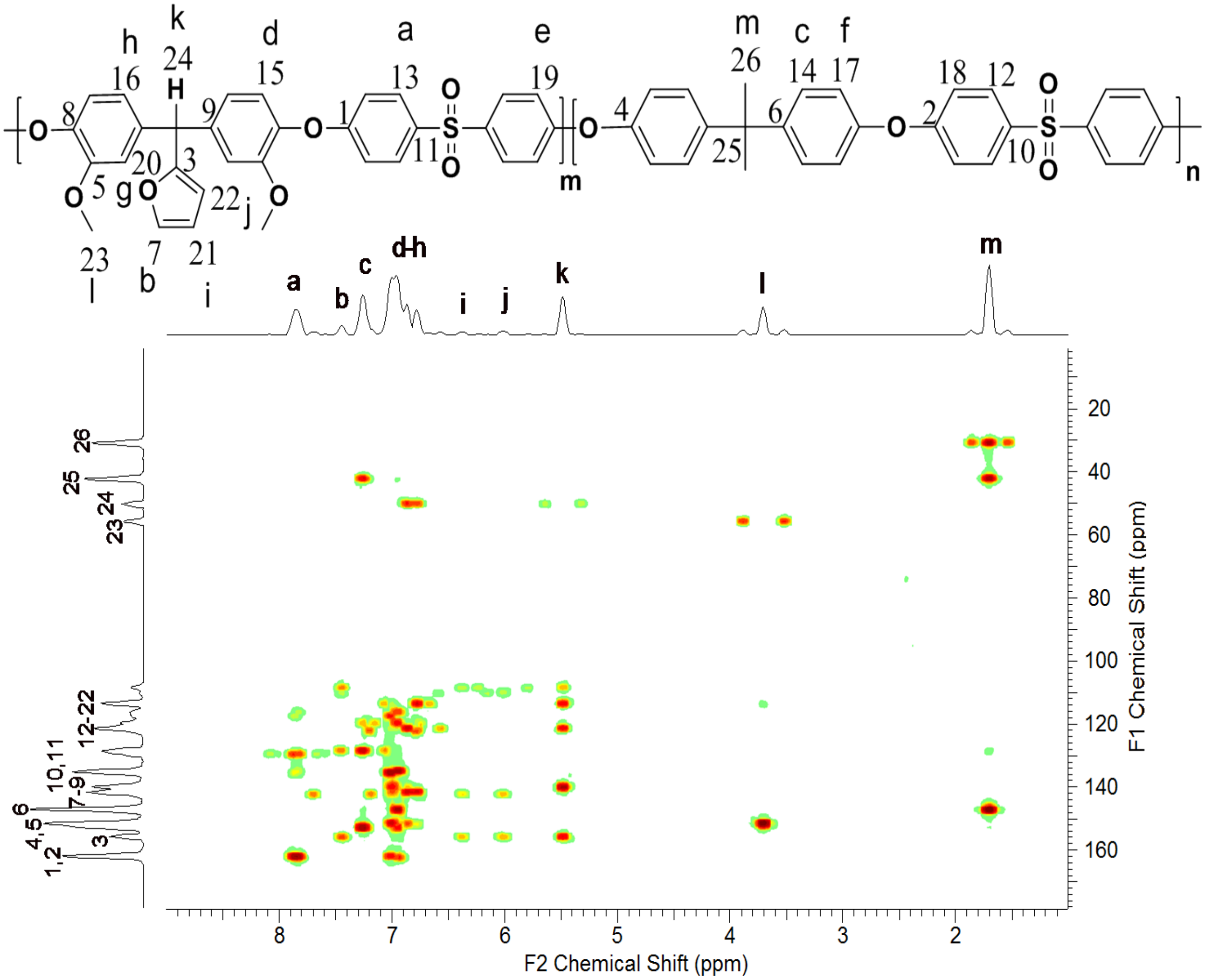


Figure 4a.11. HMBC spectrum (in $CDCl_3$) of PSU-2.

Some of the other carbons atoms in ^{13}C NMR spectrum of PSU-2 also exhibited similar features as indicated in **Figure 4a.12**. It is also interesting to note that some of the carbon atoms of aromatic ring (for instance carbon atom labeled as 4B, 6A, 10B and 11A) also showed more signals in copoly(ether sulfone) which is likely to be due to the loss of symmetry upon formation of copolymer comprising of co-monomer units enchained in the manner as shown in **Figure 4a.10** (A-A-B and A-B-B).

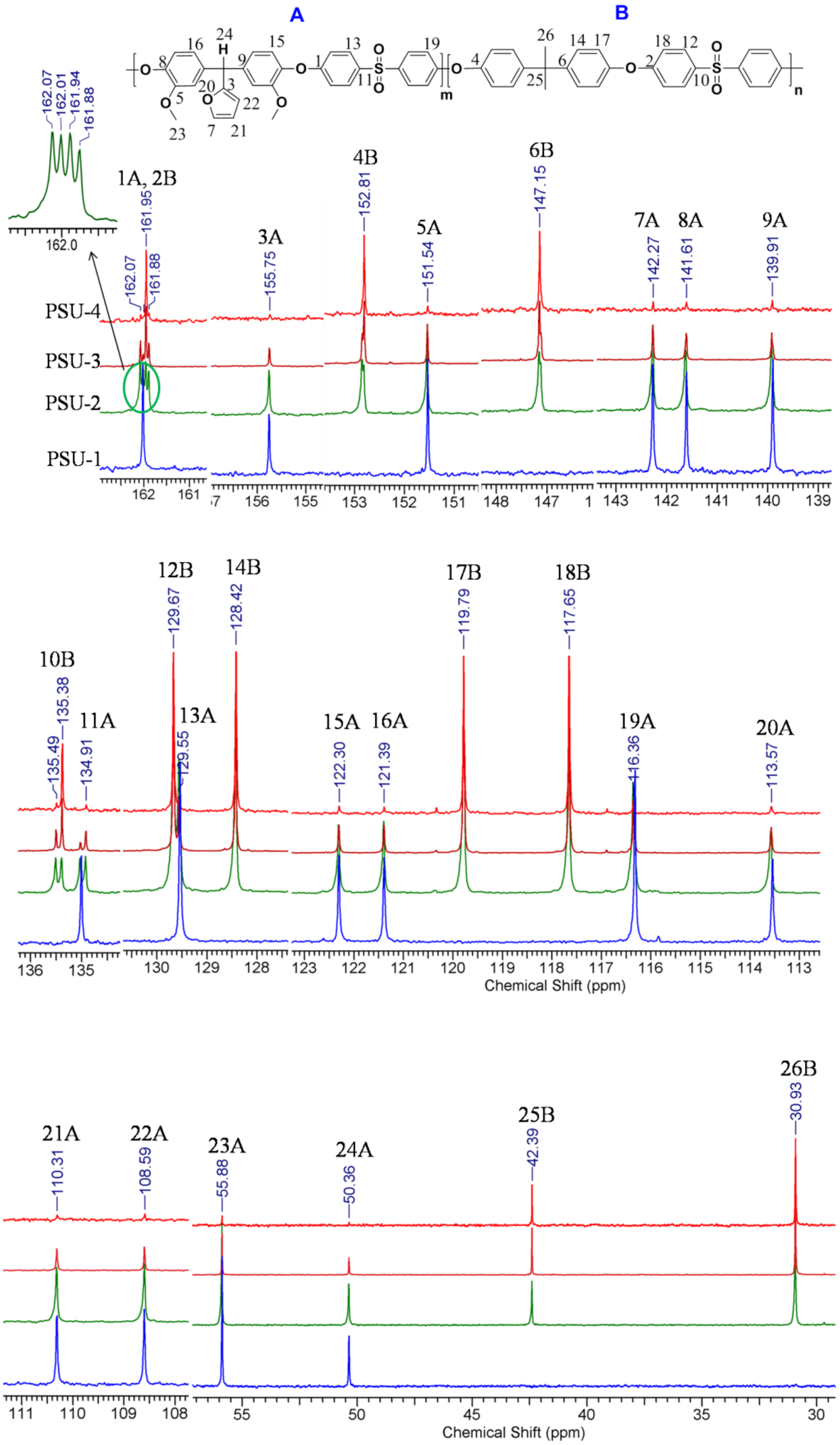


Figure 4a.12. ^{13}C NMR spectra (in $CDCl_3$) of (co)poly(ether sulfone)s.

4a.3.4 X-Ray diffraction studies

X-Ray diffractograms of (co)poly(ether sulfone)s are depicted in **Figure 4a.13**. The patterns of (co)poly(ether sulfone)s exhibited broad hallow at 2θ = ~10-30^o, which revealed their amorphous nature.

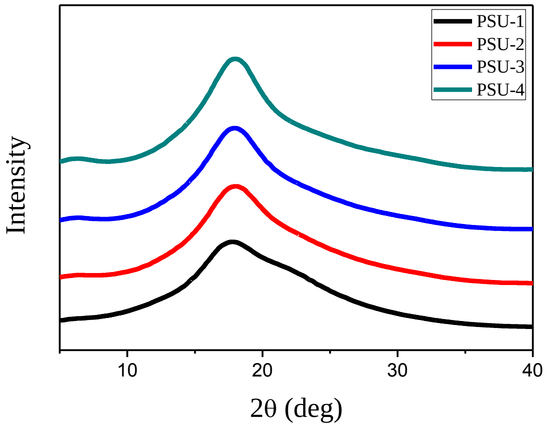


Figure 4a.13. X-Ray diffractograms of (co)poly(ether sulfone)s.

4a.3.5 Thermal properties of (co)poly(ether sulfone)s

The thermal stability of (co)poly(ether sulfone)s was evaluated by TGA at a heating rate at 10 ^{o}C/min under nitrogen. TG curves are shown in **Figure 4a.14A**. The 10 % weight loss temperature and weight residue at 800 ^{o}C are presented in **Table 4a.3**. Differential thermogravimetric analysis (DTG) of (co)poly(ether sulfone)s exhibited single stage degradation **(Figure 4a.14A)**.

The 10 % weight loss temperature of these (co)poly(ether sulfone)s is in the range 431-481 ^{o}C which indicated their good thermal stability. A comparison of T_{10} value of BPF-based poly(ether sulfone) (**Table 4a.3**, PSU-1) (431 ^{o}C) with that of T_{10} value of BPA-based poly(ether sulfone) (**Table 4a.3**, PSU-BPA) (489 ^{o}C) indicated that the former showed lower T_{10} value by 58 ^{o}C. The lower T_{10} value of furyl containing poly(ether sulfone) could be ascribed to the presence of thermally labile methoxy groups and tertiary hydrogen. In the series of copoly(ether sulfone)s, decrease in T_{10} value was observed with increase in the content of BPF.

The char yield of (co)poly(ether sulfone)s at 800 ^{o}C was found in the range 24-39 %. The relatively higher char yield observed in poly(ether sulfone) containing pendant furyl groups (PSU-1) compared to reference BPA-based poly(ether sulfone) (PSU-5) could be attributed to the presence of furyl groups which possess aromatic character and thus contribute to the formation of char residue.[57] The data clearly indicated that char yield in the series of copoly(ether sulfone)s increased with increase in BPF content.

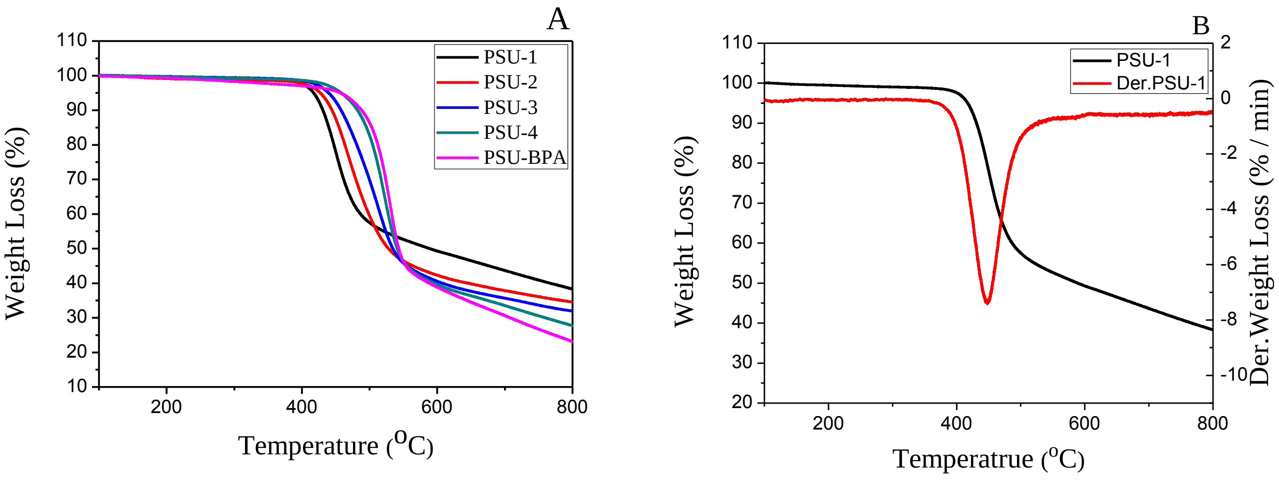


Figure 4a.14. A) TG curves of (co)poly(ether sulfone)s; B) Representative TG and DTG curves of poly(ether sulfone) PUS-1.

Glass transition temperature (T_g) of (co)poly(ether sulfone)s were evaluated by DSC under nitrogen **(Figure 4a.15)**. The data is summarized in **Table 4a.3**.

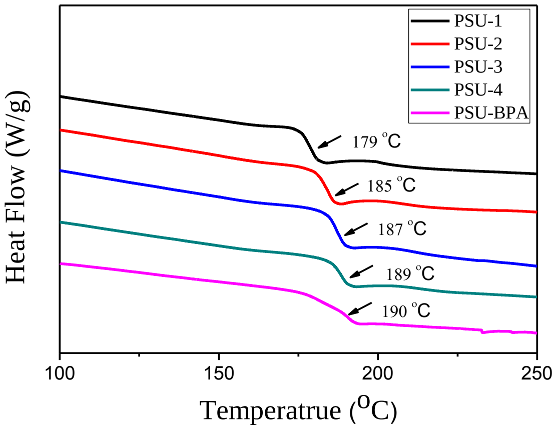
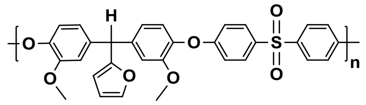
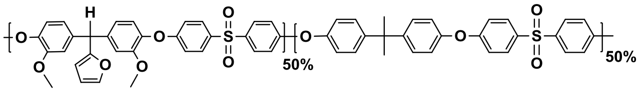
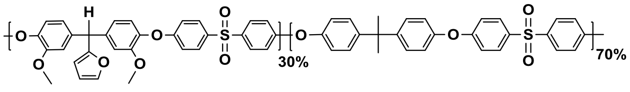
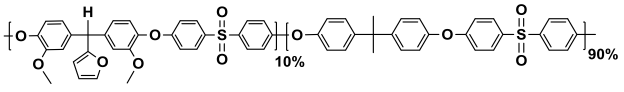
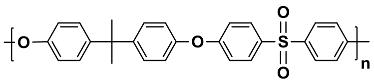


Figure 4a.15. DSC curves of (co)poly(ether sulfone)s.

T_g values of (co)poly(ether sulfone)s containing pendant furyl groups were in the range 179-190 °C. BPF-based poly(ether sulfone) (PSU-1) showed lower T_g value (179 °C) compared to BPA-based poly(ether sulfone) (PSU-BPA) (190 °C) by 11 °C. In the series of copoly(ether sulfone)s, T_g values decreased as BPF content was increased. It is difficult to pinpoint a single factor which influences T_g of polymer when comparing different chemical structures. Several factors such as the intrinsic conformational flexibilities of polymer chains, sizes, steric hindrance, flexibility of pendant groups and non-covalent interactions between polymer chains (i.e. steric, dipolar, hydrogen-bonding, van der Waals, etc) are responsible for affecting T_g.[58–60] The main probable reason for lower T_g values of poly(ether sulfone)s containing pendant furyl groups compared to BPA-based poly(ether sulfone) could be the presence of methoxy groups in the former. Methoxy substituent on BPF results into an asymmetric segment, which can result in less efficient packing. The pendant furyl groups also contribute to the disturbing of polymer chain packing.

Table 4a.3. Thermal properties of (co)poly(ether sulfone)s

(Co)poly(ether sulfone)	**Structure of (co)poly(ether sulfone)**	**T_{10} (^oC)^a**	**Char Yield (%)^b**	**T_g(^oC)^c**
PSU-1		431	39	179
PSU-2		444	35	185 (183.8)^d
PSU-3		458	32	187 (186.1)^d
PSU-4		481	28	189 (188.6)^d
PSU-BPA		489	24	190

a: 10 % Weight loss on TGA thermograms at a heating rate of 10 ^oC/min under nitrogen atmosphere, b: Char yield was measured at 800 ^oC, c: Measured by DSC on second heating scan with heating rate of 10 ^oC/min under nitrogen atmosphere, d: T_g values calculated by Fox equation.

The experimental T_g values of poly(ether sulfone)s were compared to the theoretical T_g values calculated by Fox equation[61].

$$\frac{1}{T_{gc}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Where, T_{gc} is the T_g of the copoly(ether sulfone)s and T_{g1} and T_{g2} are the T_g of homo-poly(ether sulfone)s derived from BPF and BPA, respectively (i.e. T_{g1}=179 ^{o}C, T_{g2}=190 ^{o}C). W_1 and W_2 represent weight fractions of BPF and BPA in copoly(ether sulfone)s. The 1/T_g values of (co)poly(ether sulfone)s were plotted against % weight fraction of BPF (**Figure 4a.16).** The T_g values obtained from DSC exhibited a near linear relationship with the weight % BPF. The calculated T_g values are given in **Table 4a.3.**

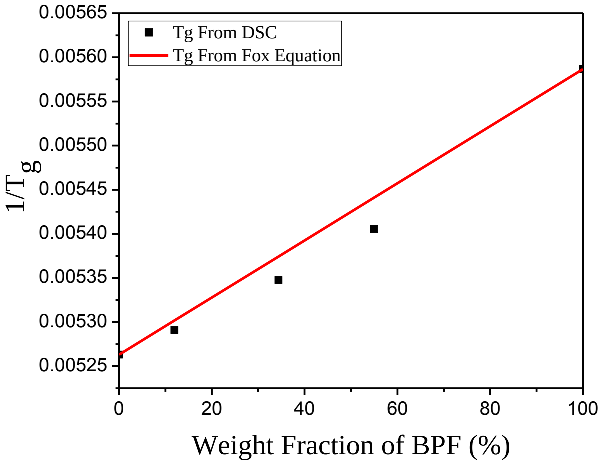


Figure 4a.16. 1/T_g as a function of weight % of BPF in copoly(ether sulfone)s.

4a.3.6 Mechanical properties of (co)poly(ether sulfone)s

The mechanical properties of aromatic (co) poly(ether sulfone)s were evaluated using polymer films (thickness = 50-60 μm) that were prepared by casting from their chloroform solutions. The stress-strain curves of (co) poly(ether sulfone)s are depicted in **Figure 4a.17**. The average values of tensile strength, Young's modulus and % elongation at break based on five repeated measurements are collected in **Table 4a.4**. (Co)poly(ether sulfone)s exhibited high Young's modulus (1.02 to 1.18 GPa) and tensile strength (76.7 to 83.8 MPa) and these values were more or less comparable to reference poly(ether sulfone) (PSU-BPA) based on BPA. The tensile strength and Young's modulus of (co)poly(ether sulfone)s revealed no significant variation across the compositional range studied. The elongation at break of poly(ether sulfone) based on BPF (PSU-1) was 21.4 % which was significantly lower than that of BPA-based poly(ether sulfone) which exhibited elongation at break of 89.7 %. A decrease in % elongation at break in copoly(ether sulfone)s was noticed with increase in the mol % of BPF. These data point out to the fact that ductility of (co)poly(ether sulfone)s suffered upon incorporation of bisphenol containing pendant furyl groups. The interpretation of mechanical property data requires further studies in order to probe the effect of incorporation of BPF into copoly(ether sulfone)s.

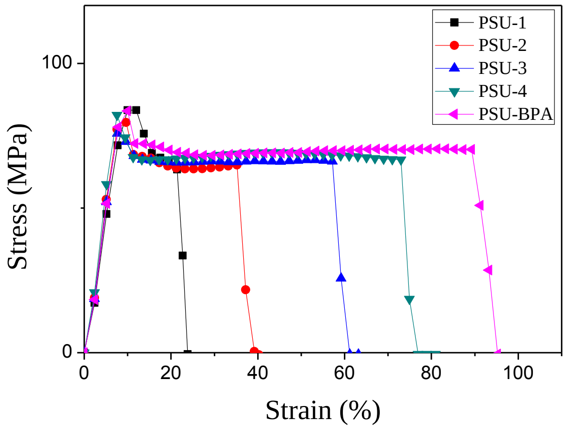
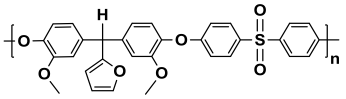
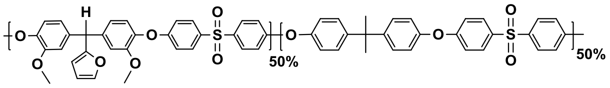
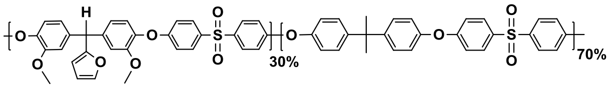
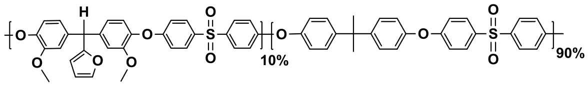
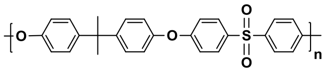


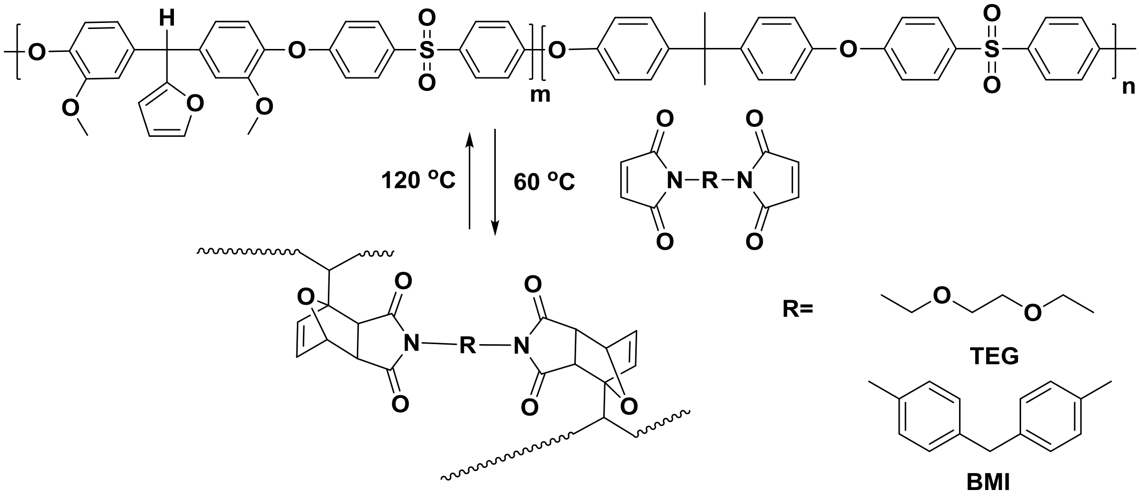
Figure 4a.17. Stress-strain curves of (co)poly(ether sulfone)s.

Table 4a.4. Mechanical properties of (co)poly(ether sulfone)s

(Co)poly(ether sulfone)	**Structure of (Co)poly(ether sulfone)**	**Young's Modulus (GPa)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**
PSU-1		1.02±0.07	83.8±0.7	21.4±3.8
PSU-2		1.11±0.03	79.5±0.3	35.2±4.2
PSU-3		1.08±0.09	76.7±0.4	57.2±6.2
PSU-4		1.18±0.11	82.1±0.8	73.0±13.4
PSU-BPA		1.10±0.04	83.5±0.3	89.7±9.7

4a.3.7 Thermally – reversible cross-linked copoly(ether sulfone) by Diels-Alder Chemistry

The pendant furyl groups present in copoly(ether sulfone)s provide entry into fabrication of thermally reversible cross-linked polymers *via* Diels-Alder reaction. In the recent years, the transformation of recyclable cross-linked polymers by Diels-Alder reaction has been studied intensively by several groups.[42,62–64] Copoly(ether sulfone) (PSU-2) derived from a mixture (50:50 mol %) of BPF and BPA was selected for cross-linking studies. PSU-2 was cross-linked with two bismaleimides *viz.*, BMI and TEG (furan/maleimide mol ratio =1) *via* Diels-Alder reaction (**Scheme 4a.3**).



Scheme 4a.3. Preparation of thermally reversible cross-linked copoly(ether sulfone) PSU-2.

Hereafter, cross-linked poly(ether sulfone) sample with BMI and TEG is referred as PSU-2-BMI and PSU-2-TEG, respectively. The film of cross-linked polymer was prepared by dissolution of polymer (PSU-2) and cross-linker (BMI or PEG) in chloroform. After complete evaporation of solvent, films were kept at 60 °C for 36 h. Thereafter, cross-linked polymer films were completely insoluble in chloroform which indicated that polymers were cross-linked successfully.

4a.3.8 Thermal studies of cross-linked copoly(ether sulfone)s

Diels-Alder and retro Diels-Alder reactions were studied using DSC analysis at a heating of 10 °C/min. DSC curves and data are presented in **Figure 4a.18** and **Table 4a.5**, respectively. PSU-2-BMI and PSU-2-TEG exhibited large endothermic transition with maxima at 100 °C and 105 °C, respectively in the first heating cycle. The second heating cycle also showed endothermic transition at 115 °C for PSU-2-BMI and at 117 °C for PSU-2-TEG. Due to the fast heating rate (10 °C/min), complete retro Diels-Alder reactions did not occur in the time scale of first heating cycle and hence endothermic transition was observed in the second heating cycle also. The cleavage of Diels-Alder adduct at slightly higher temperature in case of second heating cycle compared to the first cycle could presumably be attributed to retro Diels-Alder reaction of exo adducts. In general, exo adduct reverts at slightly higher temperature compared to endo adduct.[65] In the third heating cycle, endothermic transition was not detected indicating that complete cleavage of Diels-Alder adducts had occurred during the second heating cycle.

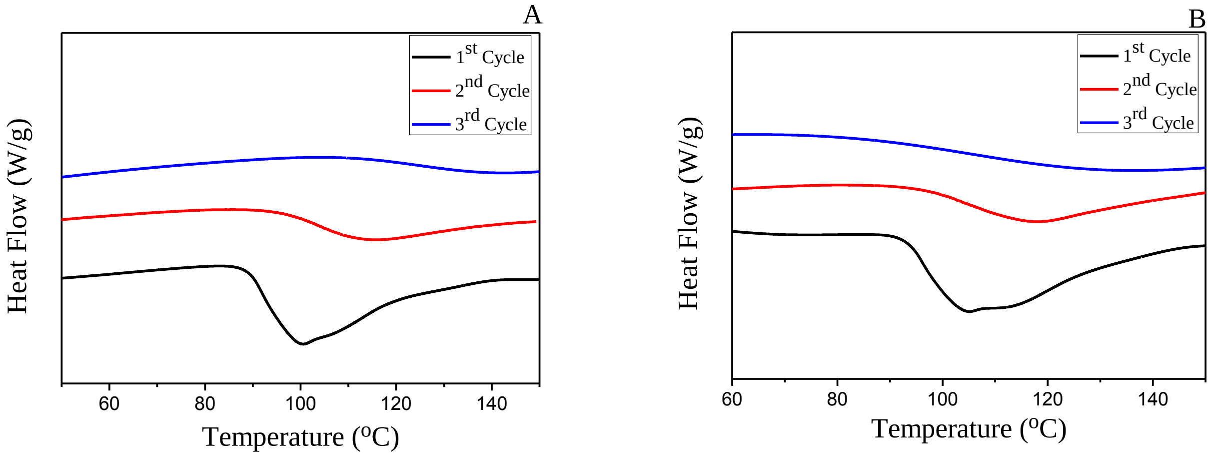


Figure 4a.18. DSC curves (first, second and third heating cycle) of cross-linked copoly(ether sulfone) PSU-2-BMI (A) and PSU-2-TEG (B).

Table 4a.5. Decross-linking temperature and absorbed energy for retro Diels-Alder reaction

Copoly(ether sulfone)	**1st Heating Cycle**		**2nd Heating Cycle**	
	T_{rDA} (°C)^a	**ΔH (J/g)^b**	**T_{rDA} (°C)^a**	**ΔH (J/g)^b**
PSU-2-BMI	100	15	115	6
PSU-2-TEG	105	22	117	7

a: Temperature corresponding to retro Diels-Alder reaction; b: Absorbed energy for retro Diels-Alder reaction.

4a.3.9 Thermo-reversible gels *via* Diels-Alder reaction

The solution of a mixture of PSU-2 and BMI (furan/maleimide mol ratio = 1) in DMAc was heated at 60 °C. A drastic increase in solution viscosity was observed by visual observation.

After 10 h, solution viscosity was so high that the gel did not flow even after inversion of vial (**Figure 4a.19**). The gel was heated at 120 ^{o}C for 10 min when the gel got converted into clear and low viscosity solution due to the decross-linking *via* retro Diels-Alder reaction. Upon cooling the solution to 60 ^{o}C, viscosity increased gradually and gel reformed completely without fluidity on standing for 12 h. This could be explained by the re-formation of Diels-Alder adduct. This process was repeated three times, indicating thermo-reversible character of PSU-2-BMI gel.

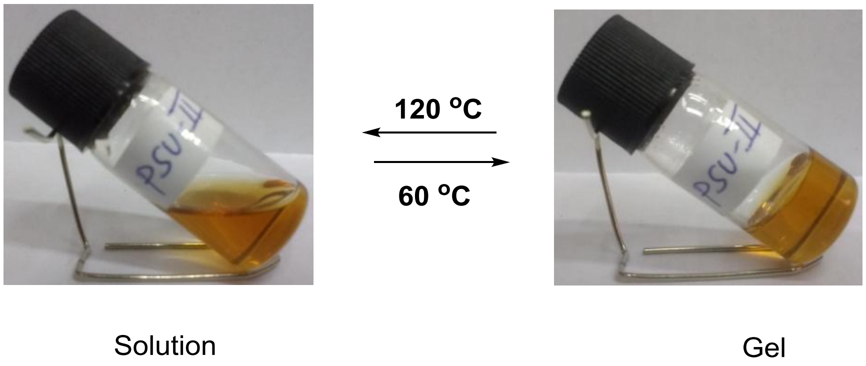


Figure 4a.19. Sol-gel transition of copoly(ether sulfone)-based organogel.

4a.3.10 Mechanical properties of cross-linked copoly(ether sulfone)s

Tensile tests were performed on linear copoly(ether sulfone) (PSU-2) and the corresponding cross-linked polymer. Tensile strength, Young's modulus and % elongation at break were analyzed from tensile measurements. Stress-strain curves are illustrated in **Figure 4a.20** and data on mechanical properties data is summarized in **Table 4a.6**.

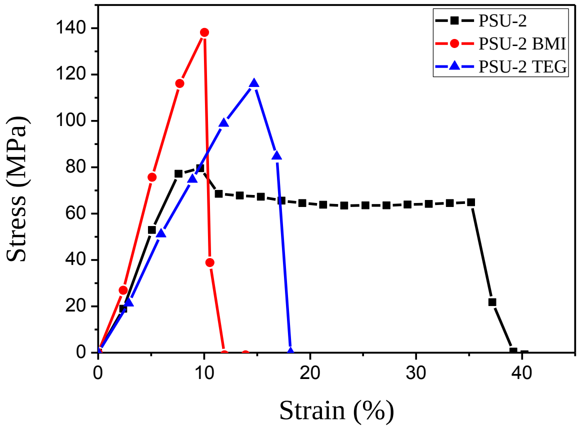


Figure 4a.20. Stress-strain curves of linear (PSU-2) and cross-linked copoly(ether sulfone)s (PSU-2-BMI and PSU-2-TEG).

In general, cross-linked polymeric materials exhibit higher tensile strength and lower % elongation at break compared to their parent linear polymers.[63] Tensile strength and Young's modulus of linear copoly(ether sulfone) (PSU-2) is 80 MPa and 1.11 GPa, respectively and it elongates up to 35.2 %. After cross-linking with BMI, tensile strength and Young's modulus increased to 138.2 MPa and 1.54 GPa whereas elongation at break decreased to the value of 10.0 %. So also, PSU-2-TEG showed increased tensile strength to 116.0 MPa and decreased elongation to the value of 14.7 %. Unlike in case of PSU-2-BMI, Young's modulus (0.89 GPa) of PSU-2-TEG decreased compared to linear copoly(ether sulfone) (1.11 GPa). The plausible explanation for decrease in Young's modulus of copoly(ether sulfone) cross-linked with TEG could be the presence of flexibilizing oxyalkylene segment in the cross-linker.[42]

Table 4a.6. Mechanical properties of copoly(ether sulfone)s and the corresponding cross-linked materials

Copoly(ether sulfone)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PSU-2	1.11±0.03	79.5±0.3	35.2±4.2
PSU-2-BMI	1.54±0.06	138.2±0.7	10.0±2.1
PSU-2-TEG	0.89±0.03	116.0±0.4	14.7±1.8

4a.3.11 Recycling of cross-linked copoly(ether sulfone)s

The thermally reversible cross-linking involving furan and maleimide groups not only helps to improve the mechanical properties under ambient condition, but also allows recyclability of the thermosets under appropriate thermal conditions. The fractured specimens of PSU-2-BMI, after tensile test measurements, were immersed in chloroform at room temperature and the samples did not dissolve due to their cross-linked nature. The specimens gradually dissolved in chloroform when the temperature was raised to 120 ^{o}C in a sealed tube. At 120 ^{o}C, the retro Diels-Alder reaction occurred resulting in the regeneration of poly(ether sulfone) containing pendent furyl groups and bismaleimide. The film formed again after a solution casting process. This process could be repeated for at least twice with the obtained reprocessed film still being transparent and flexible. The recyclable behavior of cross-linked copoly(ether sulfone) was also investigated by stress-strain studies conducted on representative cross-linked copoly(ether sulfone) (PSU-2-BMI), first recycled (PSU-2-BMI1) and second recycled (PSU-2-BMI2). The data on mechanical properties is summarized in **Table 4a.7** and the stress-strain curves are presented in **Figure 4a.22**.

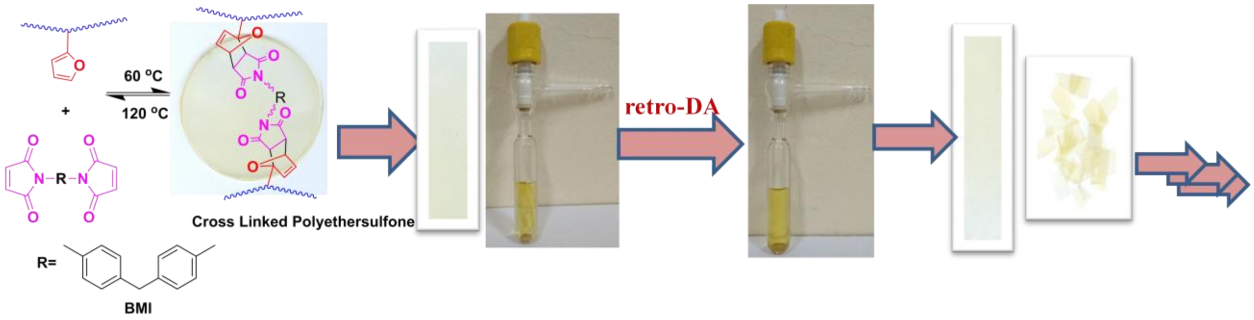


Figure 4a.21. Thermo-reversibility of cross-linked copoly(ether sulfone)s.

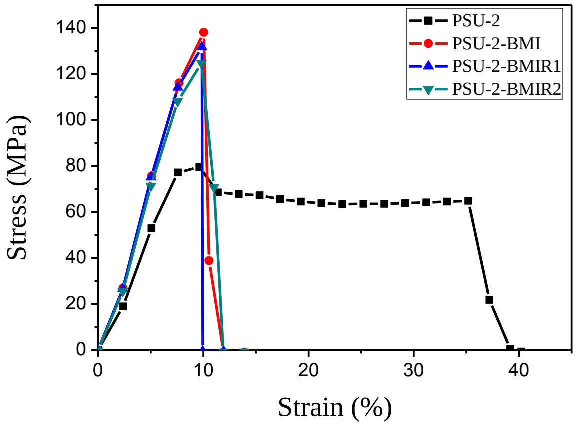


Figure 4a.22. Stress-strain curves of recycled cross-linked copoly(ether sulfone)s.

Table 4a.7. Mechanical properties of recycled copoly(ether sulfone)s

Copoly(ether sulfone)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PSU-2	1.11±0.03	79.5±0.3	35.2±4.2
PSU-2-BMI	1.54±0.06	138.2±0.7	10.0±2.1
PSU-2-BMIR1	1.54±0.04	134.7±0.5	9.9±3.4
PSU-2-BMIR2	1.46±0.04	132.6±0.9	9.8±1.5

These results indicated that mechanical properties of recycled polymers were closer to that of original cross-linked polymer. These data confirmed thermo-reversibility of Diels-Alder cross-linked copoly(ether sulfone).

4a.4 Conclusions

A new series of partially bio-based (co)poly(ether sulfone)s was synthesized by aromatic nucleophilic polycondensation of BPF and varying molar ratios of BPF and BPA with bis(4-fluorophenyl) sulfone. Inherent viscosity and number average molecular weights ($\overline{\mathrm{M_n}}$) of (co)poly(ether sulfone)s were in the range 0.92-1.47 dL/g and 91,300-1,31,000 g/mol, respectively, indicating formation of high molecular weight polymers. ^{13}C NMR spectral analysis of copoly(ether sulfone)s revealed the formation of random copolymers. (Co)poly(ether sulfone)s showed 10% weight loss in the temperature range 431-481 ^{o}C indicating their good thermal stability. T_g values of (co)poly(ether sulfone)s were in the range 179-189 ^{o}C and decreased with increase in the content of BPF. Tensile strength, Young's modulus and elongation at break, obtained from tensile testing of (co)poly(ether sulfone)s containing pendant furyl groups, were in the range 76.7-83.8 MPa, 1.02-1.18 GPa and 21.4-89.7 %, respectively indicating their suitability in structural applications. Subsequently, thermally reversible cross-linked poly(ether sulfone)s were prepared from the corresponding linear copoly(ether sulfone) containing pendant furyl groups by reactions with bismaleimides *via* Diels-Alder reaction. The formation of cross-linked poly(ether sulfone)s was demonstrated by gelation tests, solubility tests and DSC. The cross-linked PSU-2-BMI showed enhanced tensile strength and Young's modulus compared to parent copoly(ether sulfone) and was recycled two times without significant deterioration in these mechanical properties. This work is anticipated to open up new opportunities for preparation of recyclable high-performance thermosets from aromatic poly(ether sulfone)s.

4a.5 References

1. Sivaraman, K. M., Kellenberger, C., Pané, S., Ergeneman, O., Lühmann, T., Luechinger, N. A., Hall, H., Stark, W. J., Nelson, B. J. *Biomed. Microdevices*, 2012, **14**, 603–612.
2. Klein, E., Eichholz, E., Yeager, D. H. *J. Memb. Sci.*, 1994, **90**, 69–80.
3. Tomaszewska, M., Jarosiewicz, A. *Desalination*, 2004, **163**, 247–252.
4. Kraemer, S. Von, Puchner, M., Jannasch, P., Lundblad, A., Lindbergh, G. *J. Electrochem.*

Soc., 2006, **153**, 2077–2084.

5. Trisca-Rusu, C., Nechifor, A. C., Mihai, S., Parvu, C., Voicu, S. I., Nechifor, G. In *International Semiconductor Conference* IEEE 2009; 285–288.
6. Liu, J., Xu, Z., Li, X., Zhang, Y., Zhou, Y., Wang, Z., Wang, X. *Sep. Purif. Technol.*, 2007, **58**, 53–60.
7. Du, R., Zhao, J. *J. Memb. Sci.*, 2004, **239**, 183–188.
8. Nady, N., Franssen, M. C. R., Zuilhof, H., Eldin, M. S. M., Boom, R., Schroën, K. *Desalination*, 2011, **275**, 1–9.
9. Sikder, J., Pereira, C., Palchoudhury, S., Vohra, K., Basumatary, D., Pal, P. *Desalination*, 2009, **249**, 802–808.
10. Ohya, H., Shiki, S., Kawakami, H. *J. Memb. Sci.*, 2009, **326**, 293–302.
11. Wenz, L. M., Merritt, K., Brown, S. A., Moet, A., Steffee, A. D. *J. Biomed. Mater. Res.*, 1990, **24**, 207–215.
12. Sánchez, S., Pumera, M., Cabruja, E., Fàbregas, E. *Analyst*, 2007, **132**, 142–147.
13. Aerts, P. *J. Memb. Sci.*, 2000, **176**, 63–73.
14. Claes, L. *Biomed. Tech. Eng.*, 1989, **34**, 315–319.
15. Lufrano, F., Squadrito, G., Patti, A., Passalacqua, E. *J. Appl. Polym. Sci.*, 2000, **77**, 1250–1256.
16. Lufrano, F., Gatto, I., Staiti, P., Antonucci, V., Passalacqua, E. *Solid State Ionics*, 2001, **145**, 47–51.
17. Karlsson, L. *J. Memb. Sci.*, 2004, **230**, 61–70.
18. Manea, C., Mulder, M. *J. Memb. Sci.*, 2002, **206**, 443–453.
19. Shen, K., Hu, H., Wang, J., Liu, G. *Polymer*, 2017, **132**, 198–205.
20. Guiver, M. D., Robertson, G. P. *Macromolecules*, 1995, **28**, 294–301.
21. Gao, N., Zhang, S. *J. Appl. Polym. Sci.*, 2013, **128**, 1–12.
22. Zhang, X., Yue, B., Yan, L., Zeng, G., Tao, S. *Int. J. Hydrogen Energy*, 2016, **41**, 4740–4750.
23. Zhang, Q., Li, S., Zhang, S. *Chem. Commun.*, 2010, **46**, 7495.
24. Ghosh, A., Maji, S., Banerjee, S., Voit, B. *Polym. Adv. Technol.*, 2011, **22**, 794–801.
25. Awasthi, S., Kiran, V., Gaur, B. *Int. J. Hydrogen Energy*, 2017, **42**, 11710–11723.
26. Chauveau, E., Marestin, C., Mercier, R., Brunaux, A., Martin, V., Nogueira, R. P.,

Percheron, A., Roche, V., Waton, H. *J. Appl. Polym. Sci.*, 2015, **132**, 41890–41899.

27. Li, Z., Ding, J., Robertson, G. P., Guiver, M. D. *Macromolecules*, 2006, **39**, 6990–6996.
28. Wang, C., Li, N., Shin, D. W., Lee, S. Y., Kang, N. R., Lee, Y. M., Guiver, M. D. *Macromolecules*, 2011, **44**, 7296–7306.
29. Qi, Y., Ding, J., Day, M., Jiang, J., Callender, C. L. *Polymer*, 2006, **47**, 8263–8271.
30. Yi, Z., Zhu, L., Cheng, L., Zhu, B., Xu, Y. *Polymer*, 2012, **53**, 350–358.
31. Yu, Y., Wang, Y., Li, T., Liang, W., Li, C., Niu, W., Gao, L. *RSC Adv.*, 2017, **7**, 42468–42475.
32. Dizman, C., Tasdelen, M. A., Yagci, Y. *Polym. Int.*, 2013, **62**, 991–1007.
33. Ni, J., Zhao, C., Zhang, G., Zhang, Y., Wang, J., Ma, W., Liu, Z., Na, H. *Chem. Commun.*, 2011, **47**, 8943–8945.
34. Summers, G. J., Kasiama, M. G., Summers, C. A. *Polym. Int.*, 2016, **65**, 798–810.
35. Li, Y., Wang, X., Xie, M., Liu, X., Wang, C. *Int. J. Hydrogen Energy*, 2013, **38**, 16276–16285.
36. Luo, K., Li, J., Duan, G., Wang, Y., Yu, J., Zhu, J., Hu, Z. *Polymer*, 2018, **142**, 33–42.
37. Liu, Y.-L., Chen, Y.-W. *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
38. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
39. Hilf, J., Scharfenberg, M., Poon, J., Moers, C., Frey, H. *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
40. Varganici, C.-D., Ursache, O., Gaina, C., Gaina, V., Rosu, D., Simionescu, B. C. *Ind. Eng. Chem. Res.*, 2013, **52**, 5287–5295.
41. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. *Macromolecules*, 2013, **46**, 1794–1802.
42. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. *Polymer*, 2013, **54**, 5351–5357.
43. Chen, X. *Science*, 2002, **295**, 1698–1702.
44. Chen, X., Wudl, F., Mal, A. K., Shen, H., Nutt, S. R. *Macromolecules*, 2003, **36**, 1802–1807.
45. Liu, Y.-L., Hsieh, C.-Y. *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 905–913.
46. Yu, S., Zhang, R., Wu, Q., Chen, T., Sun, P. *Adv. Mater.*, 2013, **25**, 4912–4917.
47. Liu, Y.-L., Chuo, T.-W. *Polym. Chem.*, 2013, **4**, 2194–2205.
48. Tasdelen, M. A. *Polym. Chem.*, 2011, **2**, 2133.

49. Du, P., Wu, M., Liu, X., Zheng, Z., Wang, X., Sun, P., Joncheray, T., Zhang, Y. *New J. Chem.*, 2014, **38**, 770–776.
50. Becker, G., Marquetant, T. A., Wagner, M., Wurm, F. R. *Macromolecules*, 2017, **50**, 7852–7862.
51. Feng, L., Yu, Z., Bian, Y., Lu, J., Shi, X., Chai, C. *Polymer*, 2017, **124**, 48–59.
52. Irusta, L., Fernández-Berridi, M. J., Aizpurua, J. *J. Appl. Polym. Sci.*, 2017, **134**, 1–9.
53. Wei, Y., Du, X., Ma, X., Zhao, K., Zhang, S., Bai, Y. *Polym. Bull.*, 2017, **74**, 3907–3922.
54. Gaina, C., Gaina, V., Ciobanu, C. *J. Appl. Polym. Sci.*, 2009, **113**, 3245–3254.
55. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.
56. Kuhire, S. S., Nagane, S. S., Wadgaonkar, P. P. *EP Patent 3119750A1*, 2017.
57. Wang, H. M., Hsiao, S. H. *Polymer*, 2009, **50**, 1692–1699.
58. Mark, J. E. Physical Properties of Polymers Handbook, Springer, New York, 2007.
59. Hill, A. J., Tant, M. R. ACS Symposium Series; American Chemical Society: Washington, DC, 1999.
60. Shen, J., Caydamli, Y., Gurarslan, A., Li, S., Tonelli, A. E. *Polymer*, 2017, **124**, 235–245.
61. T. G. Fox *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
62. Toncelli, C., De Reus, D. C., Picchioni, F., Broekhuis, A. A. *Macromol. Chem. Phys.*, 2012, **213**, 157–165.
63. Wang, A., Niu, H., He, Z., Li, Y. *Polym. Chem.*, 2017, **8**, 4494–4502.
64. Polgar, L. M., van Duin, M., Broekhuis, A. A., Picchioni, F. *Macromolecules*, 2015, **48**, 7096–7105.
65. Canadell, J., Fischer, H., De With, G., van Benthem, R. A. T. M. *J. Polym. Sci. Part A Polym. Chem.*, 2010, **48**, 3456–3467.

Chapter-4b

(Co)poly(ether ether ketone)s Containing Pendant Furyl Groups: Synthesis, Characterization and Chemical Modifications

4b.1 Introduction

By virtue of their desirable properties such as high fracture strength, high modulus, and excellent solvent resistance, cross-linked aromatic polymers such as cyanate esters, epoxies, polybenzoxazines and bismaleimides are useful class of polymeric materials. Such polymers are employed in wide range of applications such as adhesives, coatings, printed circuit boards, electrical insulations, etc.[1–8] However, lack of recyclability is a major shortcoming of these systems. Once their desired application is completed, these hard-to-recycle cross-linked materials create major impact on environment.[9,10] It is, therefore, highly imperative to design and synthesize reversibly cross-linked polymers which are able to maintain cross-linked structure during application period and can undergo breaking of cross-linking at higher temperature to carry out their processability and recyclability.

The non-covalent linkages such as Van der Waals forces, ionic bonding, $\pi-\pi$ interactions, hydrogen bonding, etc,[11] are useful to create reversibly cross-linked polymeric networks. However, owing to their non-covalent nature, these polymeric materials are weak in nature. They cannot withstand high strain/temperature which is highly important property of cross-linked polymers. On the other hand, polymeric materials having reversible cross-linked network made up of covalent linkages are strong and exhibit excellent mechanical performance. Different strategies have been followed to form covalently bonded reversibly cross-linked polymers which include: a) introduction of cleavable linkages into monomers[12–16] b) utilization of monomers bearing functional groups such as cyclopentadiene,[17] anthracene,[18] paraformaldehyde-diamine,[19] fulvenes[20] or furan-maleimide, which can be cleaved effectively by the application of external stimuli. Of these, furan and maleimide functional groups are of great interest and have found wider applicability. To synthesize thermally reversible cross-linked polymers, furan-maleimide reaction is highly desirable because it undergoes coupling between maleimide and furan at ambient temperature forming cyclic adduct and breaking of the bonds in the temperature range 90-150 ^{o}C regenerating maleimide and furan.[21–23] This type of reaction is having benefits such as catalyst free nature, clean and can be repeated several times.[24] The literature reports reveal that furan-maleimide Diels-Alder reactions was employed for preparation of recyclable cross-linked polymeric materials such as polyamides,[25–27] polyurethanes,[28–31] epoxy resins,[32,33] polyesters,[34,35] polycarbonates,[36] etc. To the best of our knowledge, furan-maleimide Diels-Alder click reaction has not been studied with aromatic poly(ether ether ketone)s.

In this study, new poly(ether ether ketone) bearing pendant furyl groups was successfully synthesized by polycondensation of 4, 4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) with commercially available 4, 4′-difluorobenzophenone. A series of copoly(ether ether ketone)s were synthesized by polycondensation of different mole ratios of BPF and bisphenol-A (BPA) with 4,4′-difluorobenzophenone. The resulting (co)poly(ether ether ketone)s were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA), differential scanning calorimetric studies (DSC) and tensile testing. As a proof of concept, a representative copoly(ether ether ketone) (PEEK-2) was examined for cross-linking with 1,1’-(methylenedi-4,1-phenylene)bismaleimide (BMI) *via* Diels-Alder click reaction. Diels-Alder/retro Diels-Alder reaction was demonstrated by studies of sol-gel transition, solubility tests, DSC and stress-strain measurements.

4b.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC, XRD and tensile testing are given in **Chapter 2.**

4b.2.1 Synthesis of (co)poly(ether ether ketone)s bearing pendant furyl groups

A representative procedure for the synthesis of poly(ether ether ketone) is described below:

Into a 50 mL three-necked round bottom flask equipped with a nitrogen inlet, a Dean-Stark trap fitted with a reflux condenser and a magnetic stirring bar were charged BPF (1.0 g, 3.06 mmol), 4, 4′-difluorobenzophenone (0.67 g, 3.06 mmol), anhydrous potassium carbonate (0.64 g, 4.60 mmol), N,N-dimethylacetamide (10 mL) and toluene (10 mL). The reaction mixture was refluxed at 140 ^{o}C with stirring for 2 h and water was removed by azeotropic distillation with toluene. Toluene was removed by distillation, and the reaction mixture was heated at 155 °C for 7 h to obtain viscous polymer solution. The reaction mixture was cooled to room temperature, the viscous reaction mixture was poured into methanol (100 mL); the precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and reprecipitated into methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature for 24 h.

A similar procedure was followed for the synthesis of other (co)poly(ether ether ketone)s.

4b.2.2 Preparation of cross-linked copoly(ether ether ketone) films

To the solution of copoly(ether ether ketone) (PEEK-2) containing pendant furyl groups (200 mg) in chloroform (10 mL), a stoichiometric amount of bismaleimide, namely, 1, 1’-(methylenedi-1, 4-phenylene)bismaleimide (BMI) (furan/maleimide mol ratio = 1) was added. The mixture was stirred at 30 °C for 1 h and then the solution was poured into glass Petri-dish and the solvent was evaporated at room temperature to obtain a free-standing film. The film was kept at 60 °C in an oven for 36 h. The obtained cross-linked polymer film was used for further characterization.[27,35]

4b.2.3 Recyclability of cross-linked copoly(ether ether ketone) films

The cross-linked polymer films were heated in chloroform at 120 °C for 10 min in a pressure tube. The solution of polymer was poured into glass Petri-dish and solvent was allowed to evaporate off. After complete evaporation of solvent, film was kept at 60 °C in an oven for 36 h. Mechanical properties of cross-linked polymers were characterized by tensile testing. The same procedure was repeated twice and tensile data were measured.

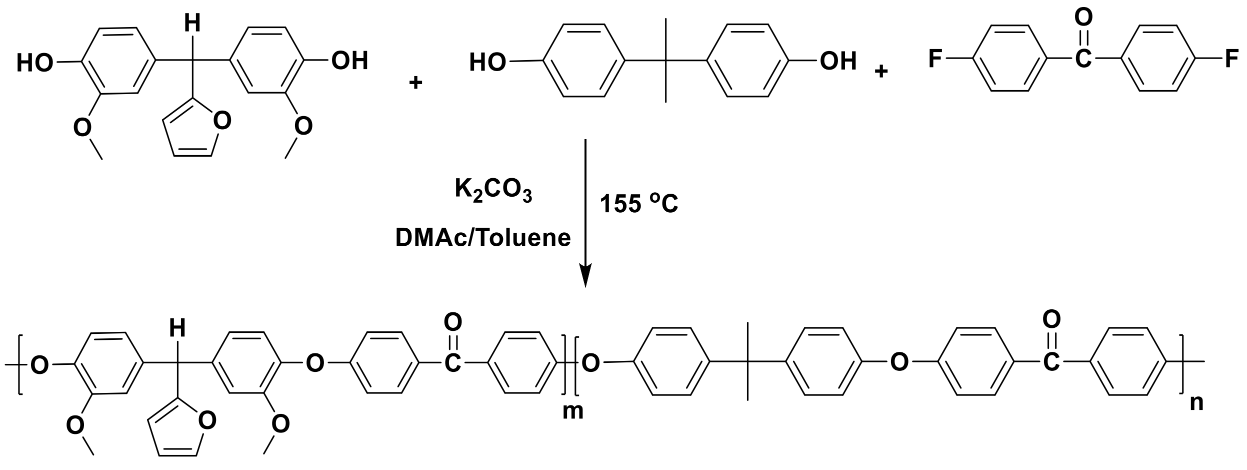
4b.2.4 Preparation of thermo-reversible cross-linked copoly(ether ether ketone) gel

Into a sample vial were taken copoly(ether ether ketone) (PEEK-2) containing pendant furyl groups (100 mg) and DMAc (1 mL). To the solution was added, a stoichiometric amount of bismaleimide (BMI) (furan/maleimide mol ratio = 1) in one lot. The sample vial was kept at 60 °C in an oven for 12 h. Cross-linking occurred and the system turned in to a gel. The polymer gel was thermally reversible and could be converted back to clear and fluid solution by heating at 120 °C for 10 min, during which the retro-DA reaction of furan-maleimide adduct occurred.

4b.3 Results and discussion

4b.3.1 Synthesis of (co)poly(ether ether ketone)s containing pendant furyl groups

New (co)poly(ether ether ketone)s containing pendant furyl groups were synthesized by aromatic nucleophilic polycondensation reaction of BPF or different mole ratios of BPF and BPA with 4,4′-difluorobenzophenone as shown in **Scheme 4b.1**.



Scheme 4b.1. Synthesis of (co)poly(ether ether ketone)s bearing pendant furyl groups.

Polymerization reaction conditions were similar to those described previously (**Chapter 4a**) for poly(ether sulfone)s. (Co)poly(ether ether ketone)s were isolated by precipitation into methanol. The results of polymerization reactions are summarized in **Table 4b.1**. Reasonably high molecular weight (co)poly(ether ether ketone)s were successfully synthesized with no evidence of cross-linking at final reaction temperature of 155 °C and reaction time of 7 h under nitrogen atmosphere.

Table 4b.1. Molar composition, inherent viscosity and molecular weight of (co)poly(ether ether ketone)s

(Co)poly(ether ether ketone)	BPF (mol%)	BPA (mol%)	η_{inh} (dL/g)[a]	Molecular Weight[b]		Dispersity
				$\overline{M_n}$	$\overline{M_w}$	
PEEK-1	100	00	0.74	33,600	75,400	2.2
PEEK-2	50	50	0.86	33,500	81,400	2.3
PEEK -3	30	70	0.78	34,600	70,300	2.0
PEEK -4	10	90	0.90	46,300	98,300	2.1

a: η_{inh} was measured with 0.5 % (w/v) solution of (co)poly(ether ether ketone) in chloroform at 30 °C±1 °C, b; Measured by GPC in chloroform using polystyrenes as calibration standard.

Inherent viscosities of (co)poly(ether ether ketone)s were in the range 0.74-0.90 dL/g indicating formation of reasonably high molecular weight polymers. Number average molecular weights ($\overline{M_n}$), obtained from gel permeation chromatography (GPC), were in the range 33,500-46,300 g/mol and dispersity values were in the range 2.0-2.3. Tough, transparent and flexible films of polymers could be cast from chloroform solutions of (co)poly(ether ether ketone)s and representative film of PEEK-1 is shown in **Figure 4b.1**.

Figure 4b.1. Film of poly(ether ether ketone) PEEK-1.

4b.3.2 Polymer solubility

(Co)poly(ether ether ketone)s were soluble at room temperature in solvents such as chloroform, dichloromethane, THF, DMAc and DMF. Solubility in common organic solvents of (co)poly(ether ether ketone)s offers opportunities for making films by casting, spin coating or dip coating. These (co)poly(ether ether ketone)s could be considered as excellent candidates for applications as membranes and in microelectronic devices where the combination of organo-solubility coupled with good thermal properties is desirable.

4b.3.3 Structural characterization

The chemical structures of (co)poly(ether ether ketone)s were confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The various functional groups present in poly(ether ether ketone) (PEEK-1), as studied through IR spectra, are marked in **Figure 4b.2**. The characteristic band of carbonyl group (C=O) appeared at 1661 cm^{-1} and the characteristic absorption band of aryl ether linkage (Ar-O-Ar) was observed at 1223 cm^{-1}. Furan ring breathing bands were observed at 1093 cm^{-1} and 1013 cm^{-1}, respectively.

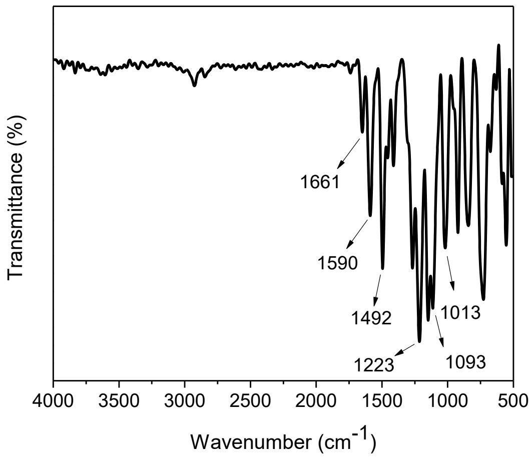


Figure 4b.2. IR spectrum of poly(ether ether ketone) PEEK-1.

^{1}H NMR spectrum of poly(ether ether ketone) containing pendant furyl groups (PEEK-1) is shown in **Figure 4b.3**.

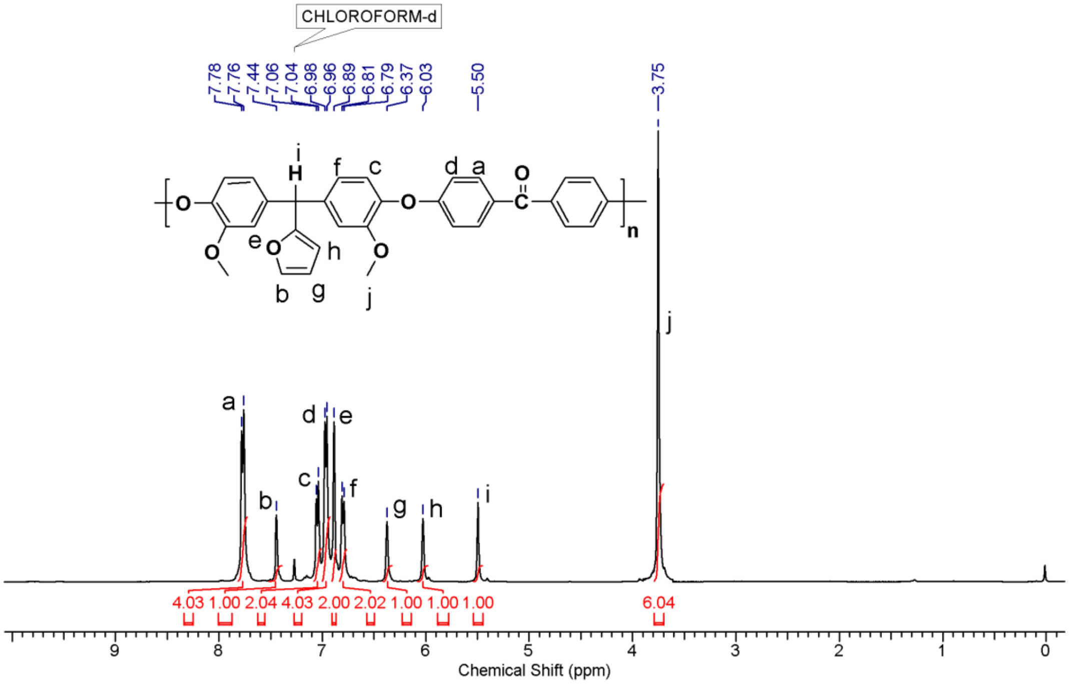


Figure 4b.3. ^{1}H NMR spectrum (in $CDCl_3$) of poly(ether ether ketone) PEEK-1.

The four protons *ortho* to carbonyl group appeared as a doublet at 7.77 δ ppm. The remaining aromatic protons *viz.*, protons *meta* to carbonyl group and aromatic protons of biphenol appeared as a multiplet over the range 6.79-7.06 δ ppm. The protons adjacent to the oxygen atom of furyl group exhibited a singlet at 7.44 δ ppm. Furyl protons labeled as “g” and “h” appeared as singlet at 6.37 and 6.03 δ ppm, respectively. Benzylic proton and methoxy group protons appeared as singlet at 5.50 δ ppm and 3.75 δ ppm, respectively.

^{13}C NMR spectrum of PEEK-1, along with assignments of the carbon atoms, is shown in **Figure 4b.4**. In ^{13}C NMR spectrum, a peak was observed at 194.2 δ ppm corresponding to carbonyl carbon.

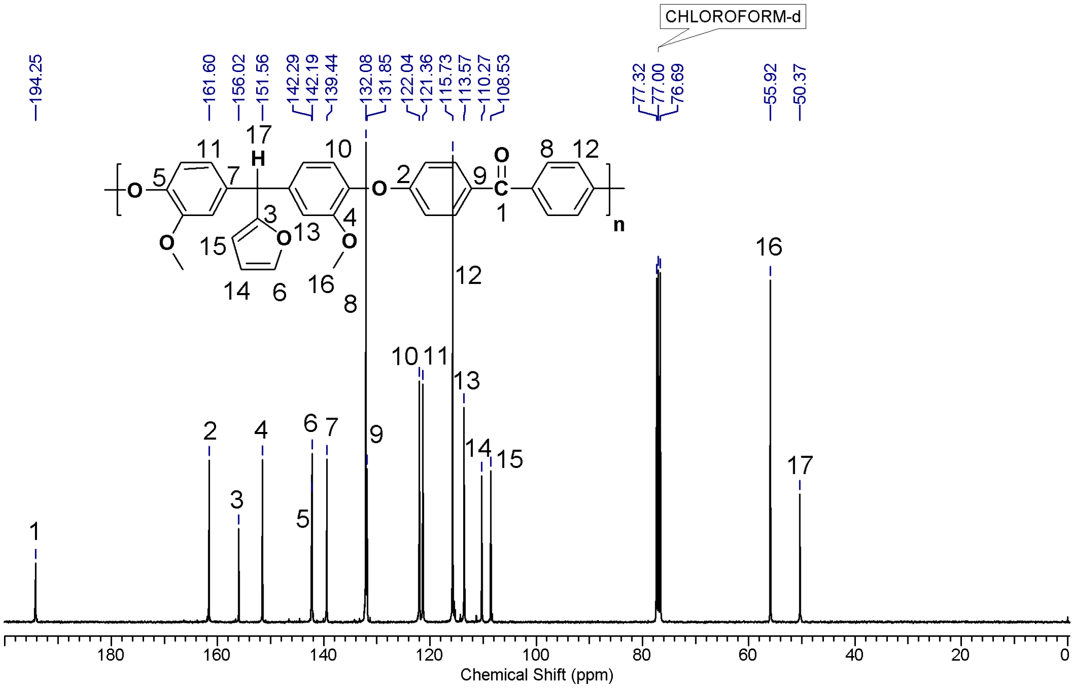


Figure 4b.4. ^{13}C NMR spectrum (in $CDCl_3$) of poly(ether ether ketone) PEEK-1.

Copoly(ether ether ketone)s possessing different content of furyl groups were obtained by using different molar ratios of BPF and BPA in the feed. The content of bisphenol containing pendant furyl group that was incorporated in copoly(ether ether ketone)s was determined from integrated intensity ratio of the peak for methoxy group “l” appeared at 3.74 δ ppm and the peak for methyl protons “m” of BPA appeared at 1.71 δ ppm in ^{1}H NMR spectra of copoly(ether ether ketone)s **(Figure 4b.5)**. As shown in **Table 4b.2**, the content of BPF incorporated in copoly(ether ether ketone)s correlated well with the amount taken for polymerization.

Thus, IR, ^{1}H NMR and ^{13}CNMR spectral data revealed the successful synthesis of (co)poly(ether ether ketone)s bearing pendant furyl groups. The spectral data of polymers endorsed stability of furyl moiety under the reaction conditions (155 °C/7 h, N_2 atmosphere) of preparation of (co)poly(ether ether ketone)s.

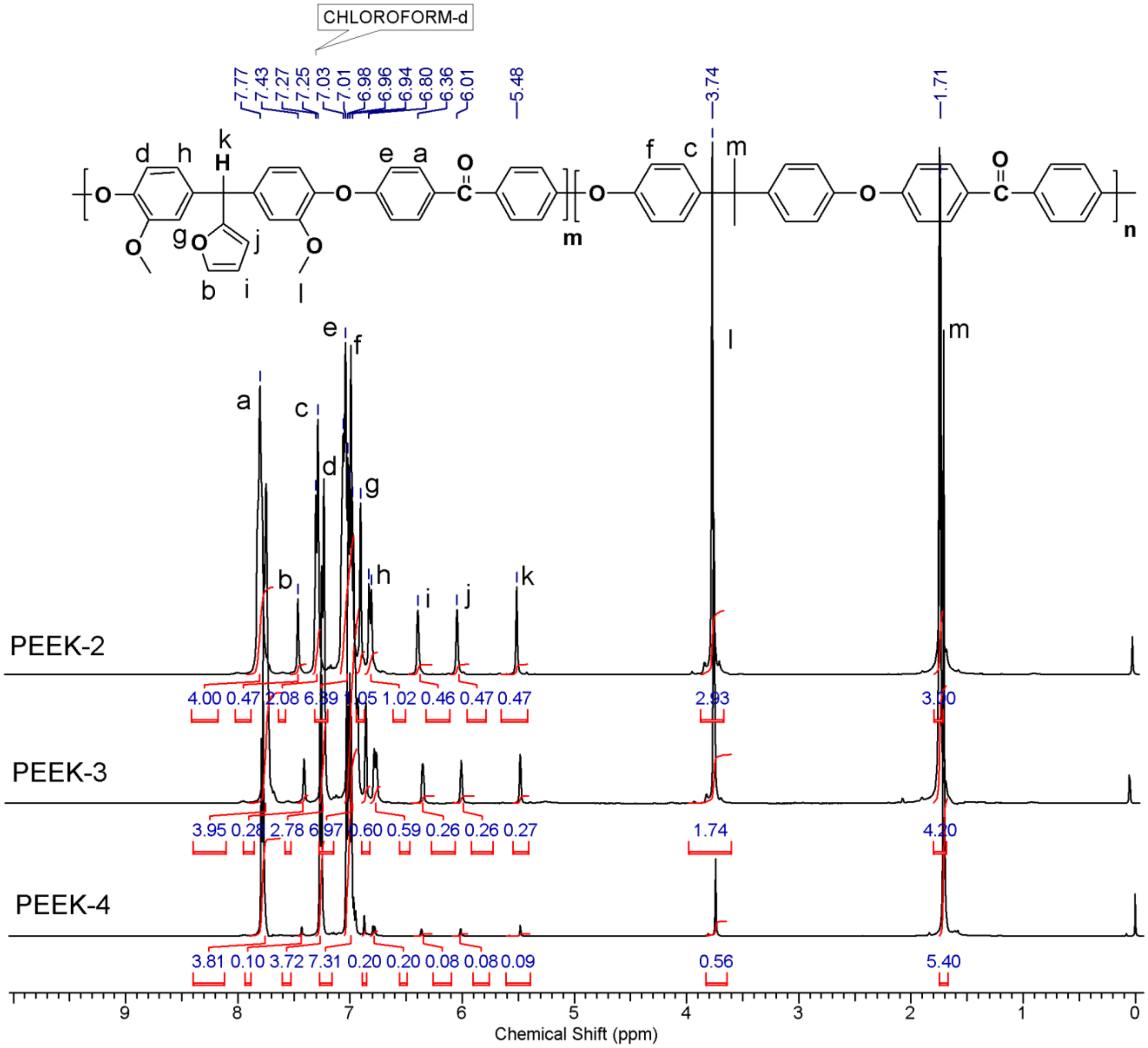
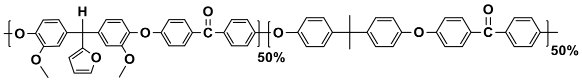
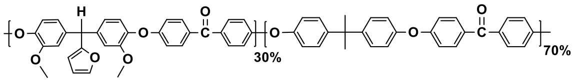
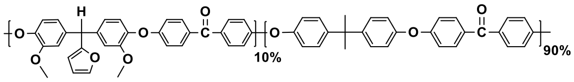


Figure 4b.5. ^{1}H NMR spectra (in CDCl$_3$) of copoly(ether ether ketone)s.

Table 4b.2. Molar composition of copoly(ether ether ketone)s determined by ^{1}H NMR spectra

Copoly(ether ether ketone)	Structure of copoly(ether ether ketone)	Feed BPF, mol %	Observed BPF, mol %
PEEK-2		50	48.9
PEEK-3		30	29.0
PEEK-4		10	9.3

The microstructure of copoly(ether ether ketone)s derived from copolymerization of BPA and BPF with 4,4′-difluorobenzophenone was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, the copolymerization of BPA and BPF is expected to lead to formation of random copolymer with following possibilities of enchainment of the two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 4b.6**). ^{13}C NMR spectra of copoly(ether ether ketone)s showed clear evidence not only for the random copoly(ether ether ketone) formation but also about the microstructural details as indicated by multiplicity of the signals.

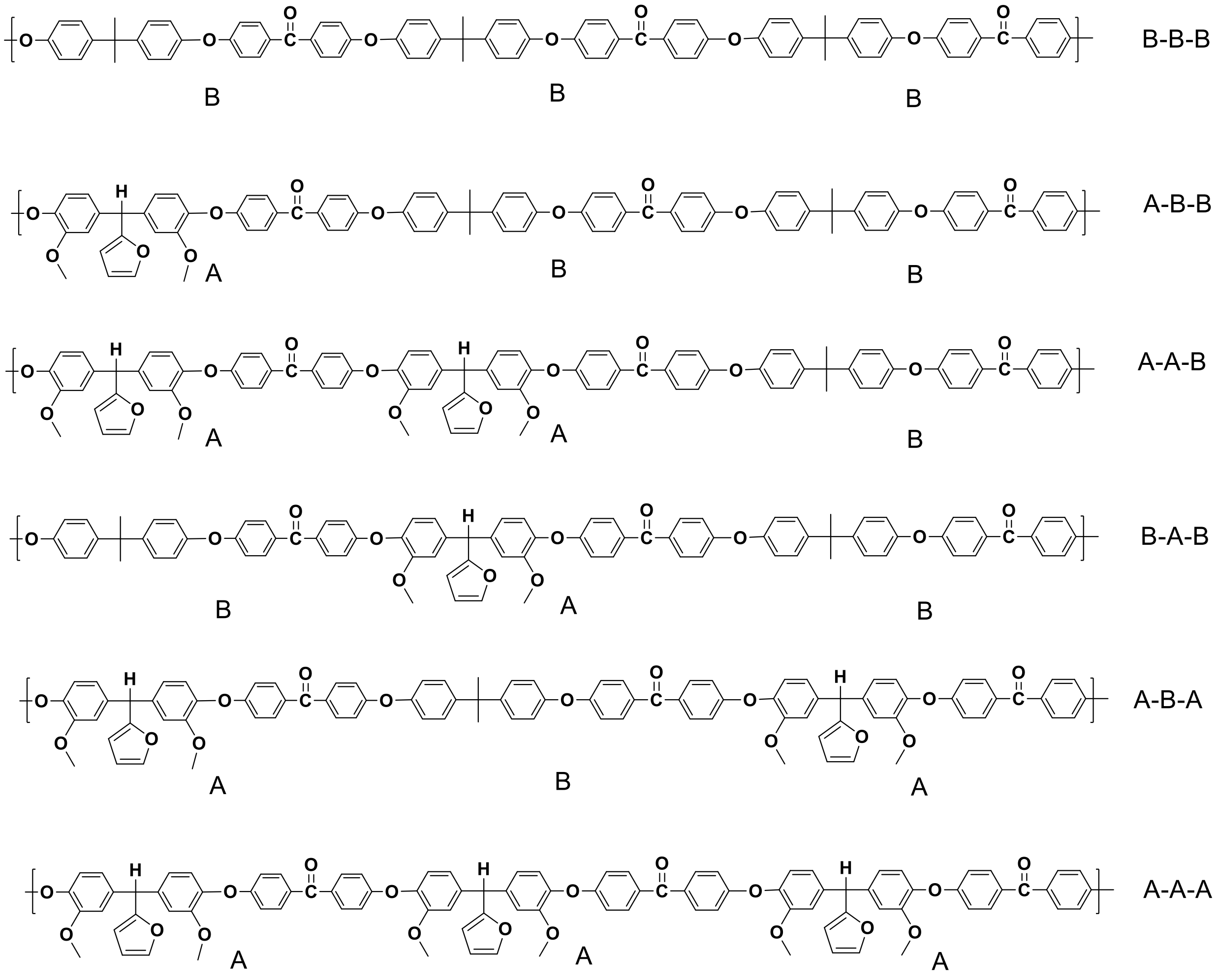


Figure 4b.6. Possible arrangements of BPF and BPA units in copoly(ether ether ketone)s.

The assignments of carbon atoms in ^{13}C NMR spectrum of PEEK-2, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 4b.7.**

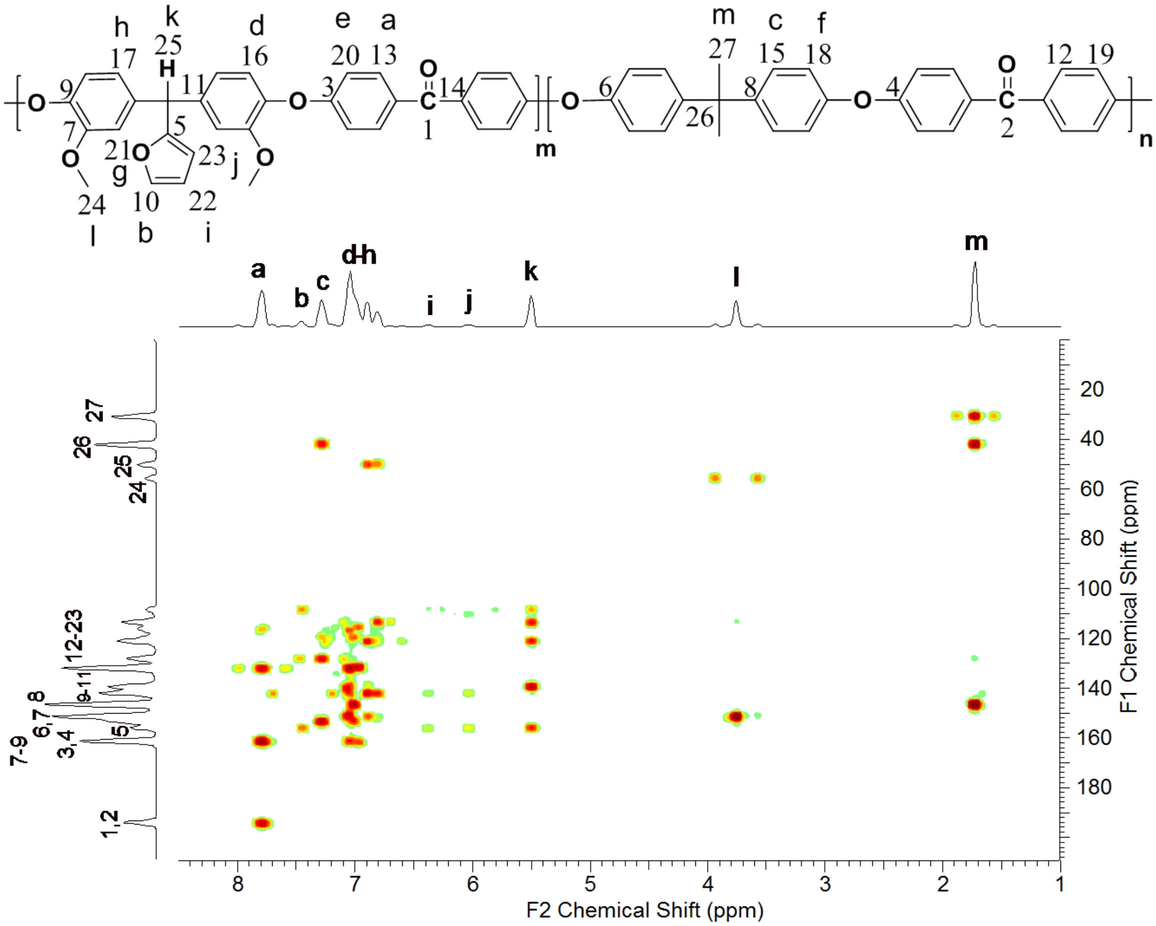


Figure 4b.7. HMBC spectrum (in $CDCl_3$) of PEEK-2.

^{13}C NMR spectrum of PEEK-2 (50:50 mol % of BPF:BPA) along with assignments of carbon atoms is presented in **Figure 4b.8.** For easy comparison, ^{13}C NMR spectra of homo-poly(ether ether ketone) PEEK-1 and copoly(ether ether ketone) PEEK-2 to PEEK-4 are also included in **Figure 4b.8**. It is interesting to note that the quaternary carbon labeled as “3A” and “4B” exhibited four distinct peaks at 161.32 δ ppm, 161.40 δ ppm, 161.60 δ ppm and 161.68 δ ppm for this particular copolymer. A comparison of the spectrum of PEEK-2 with that of PEEK-1 and PEEK-4 inferred that quaternary carbon peaks appeared at 161.60 δ ppm and 161.40 δ ppm originated from AAA and BBB arrangement of co-monomer units, respectively in copoly(ether ether ketone) while peaks at 161.32 δ ppm and 161.68 δ ppm correspond to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peak corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of PEEK-3 and PEEK-4.

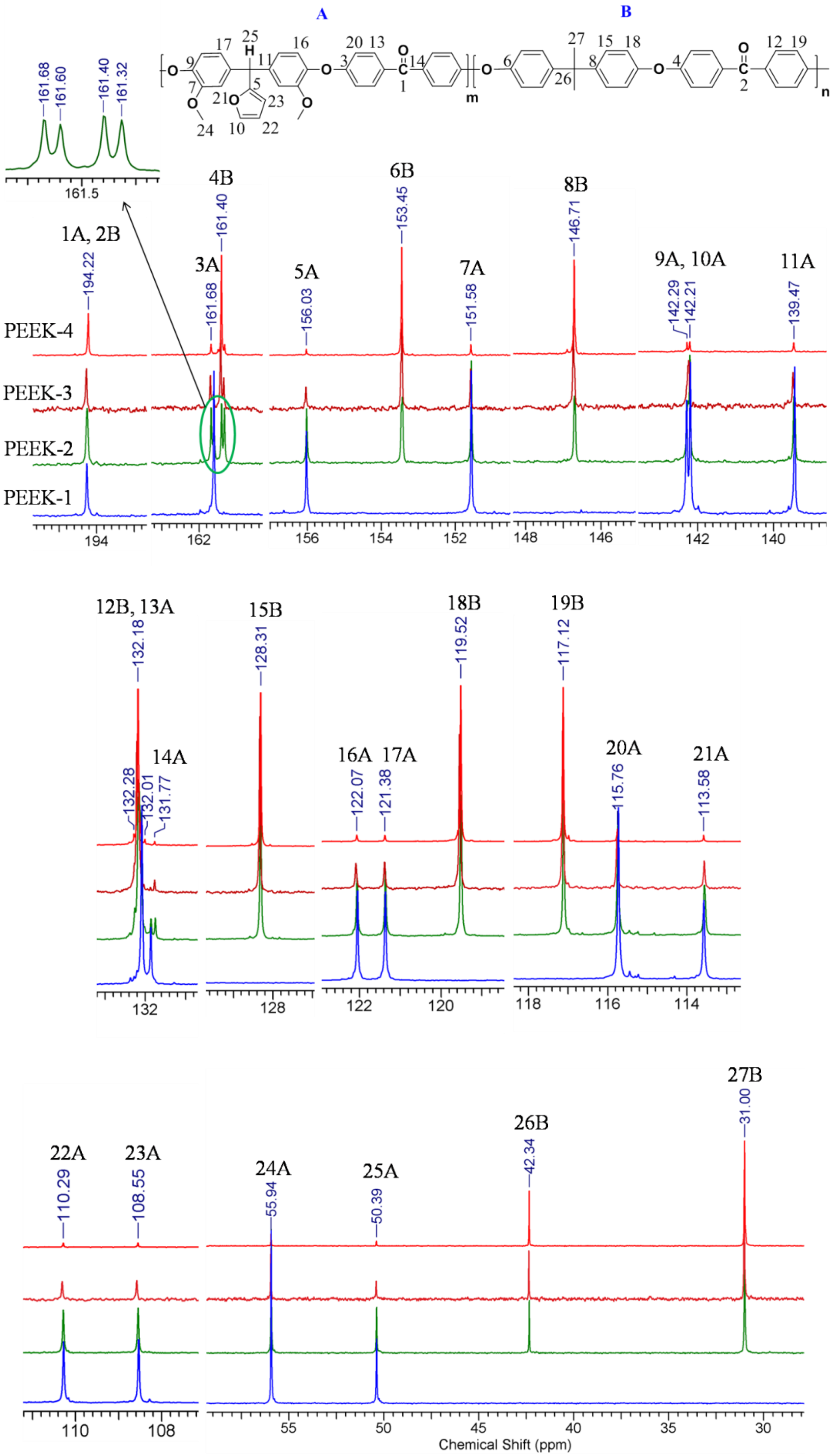


Figure 4b.8. ^{13}C NMR spectra (in CDCl$_3$) of (co)poly(ether ether ketone)s.

4b.3.4 X-Ray diffraction studies

The crystallinity of poly(ether ether ketone)s results in their insolubility and is dependent on the structure of both the starting materials i.e. bisphenol and aromatic dihalide. It is reported that polymers possessing substituents on the backbone and/or pendant side groups reduce crystallinity and bring about enhancement of solubility in common organic solvents.[37,38] Wide angle X-ray diffractograms of (co)poly(ether ether ketone)s are illustrated in **Figure 4b.9.** The patterns of (co)poly(ether ether ketone)s showed wide hump at 2θ = ~10-30°, which is an indication of their amorphous nature. The amorphous nature of (co)poly(ether ether ketone)s could be attributed to the presence of methoxy groups on polymer backbone and pendant furyl groups which interrupt polymer chain packing.

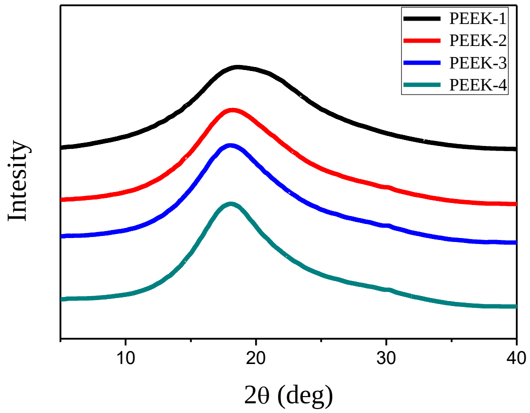


Figure 4b.9. X-Ray diffractograms of (co)poly(ether ether ketone)s.

4b.3.5 Thermal properties of (co)poly(ether ether ketone)s

The thermal properties of (co)poly(ether ether ketone)s were evaluated by thermogravimetric analysis (TGA) in nitrogen atmosphere. TG curves of (co)poly(ether ether ketone)s are shown in **Figure 4b.10A** and results are listed in **Table 4b.3**. The 10 % weight loss of poly(ether ether ketone)s was found in the range 429-464 °C indicating their good thermal stability. A representative DTG curve of copoly(ether ether ketone) PEEK-2 is reproduced in **Figure 4b.10B**. DTG curves of (co)poly(ether ether ketone)s indicated single stage degradation. The char yield at 800 °C of (co)poly(ether ether ketone)s in nitrogen atmosphere was found in the range 41-57 %. A comparison of % char yield data clearly revealed that char yield of copoly(ether ether ketone)s increased with increase in BPF content. The furyl groups possess aromatic character and thus contribute to the formation of char residue.[39]

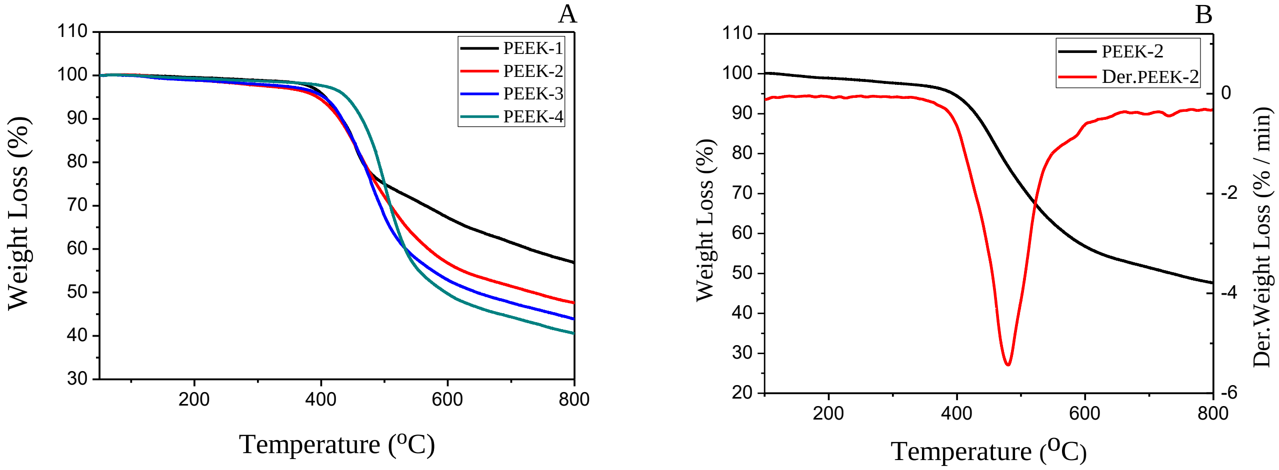


Figure 4b.10. A) TG curves of (co)poly(ether ether ketone)s; B) Representative TG and DTG curves of copoly(ether ether ketone) PEEK-2.

T_g values of (co)poly(ether ether ketone)s were determined by differential scanning calorimetry (DSC) under nitrogen with heating rate 10 °C/min (**Figure 4b.11**). No crystallization or melting transitions were observed over the studied temperature range (50-300 °C) in DSC studies for synthesized (co)poly(ether ether ketone)s. The results of T_g measurements are summarized in **Table 4b.3**. The T_g of BPF-based poly(ether ether ketone) was 152 °C which is lower than T_g of BPA-based poly(ether ether ketone) (157 °C).[40] In the series of copoly(ether ether ketone)s, T_g value decreased with increase in BPF content. This could presumably be due to the presence of pendant furyl groups and methoxy groups on aromatic rings which disrupt polymer chain packing.

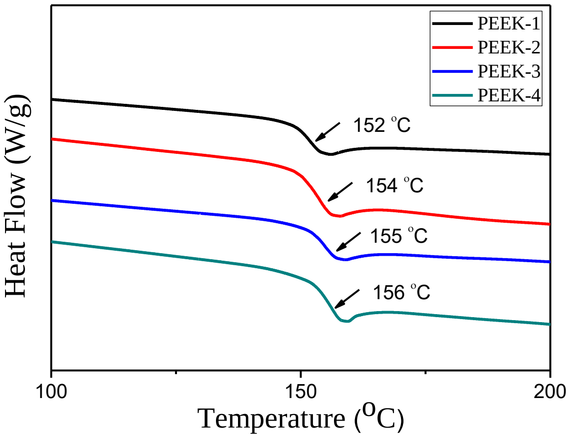
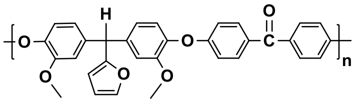
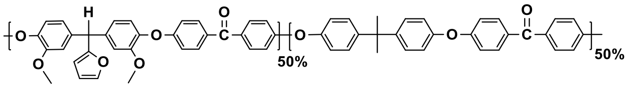
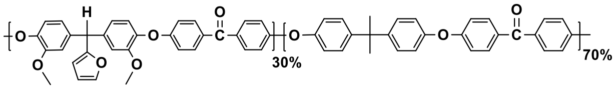
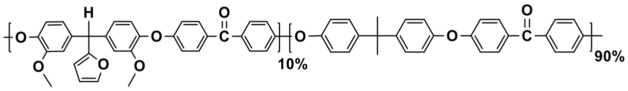
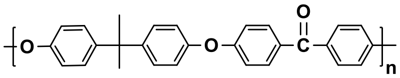


Figure 4b.11. DSC curves (co)poly(ether ether ketone)s.

Table 4b.3. Thermal properties of (co)poly(ether ether ketone)s

(Co)poly(ether ether ketone)	**Structure of (co)poly(ether ether ketone)**	**T_{10} (^{o}C)^{a}**	**Char Yield (%)^{b}**	**T_g (^{o}C)^{c}**
PEEK-1		429	57	152
PEEK-2		432	48	154
PEEK-3		432	44	155
PEEK-4		464	41	156
PEEK-BPA[d]		--	--	157[40]

a: 10 % weight loss on TGA thermograms at a heating rate of 10 °C/min under nitrogen atmosphere, b: char yield was measured at 800 °C, c: measured by DSC on second heating scan with heating rate of 10 °C/min under nitrogen atmosphere. d: Tg value of reference poly(ether ether ketone) was taken from literature.

4b.3.6 Mechanical properties of (co)poly(ether ether ketone)s

The mechanical properties of (co)poly(ether ether ketone)s were evaluated using poly(ether ether ketone)s films (thickness = 50-60 μm) that were prepared by casting from their chloroform solutions. The strain-stress curves of (co)poly(ether ether ketone)s are shown in **Figure 4b.12**. The average values of five repeated measurements are collected in **Table 4b.4**. (Co)poly(ether ether ketone)s exhibited high tensile strength in the range 84.2-88.4 MPa, Young’s modulus in the range 1.06-1.16 GPa and elongation in the range 9.2-10.0 % which qualify them to be useful as structural materials in several applications.

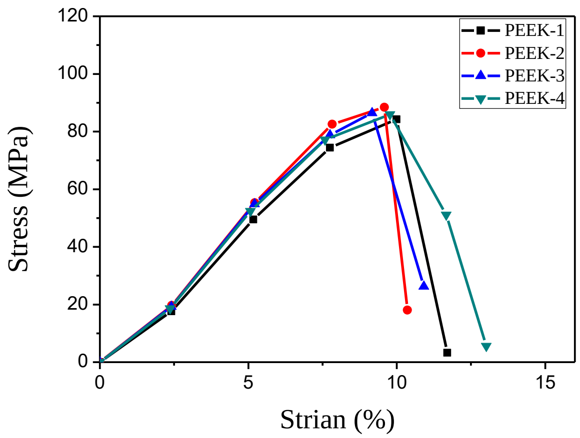
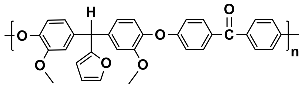
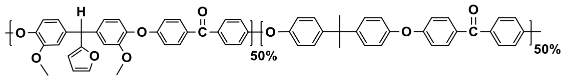
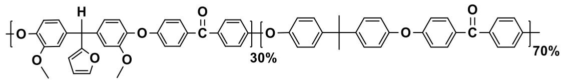
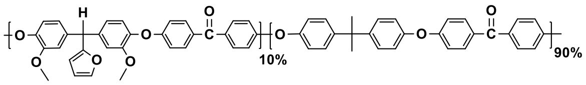


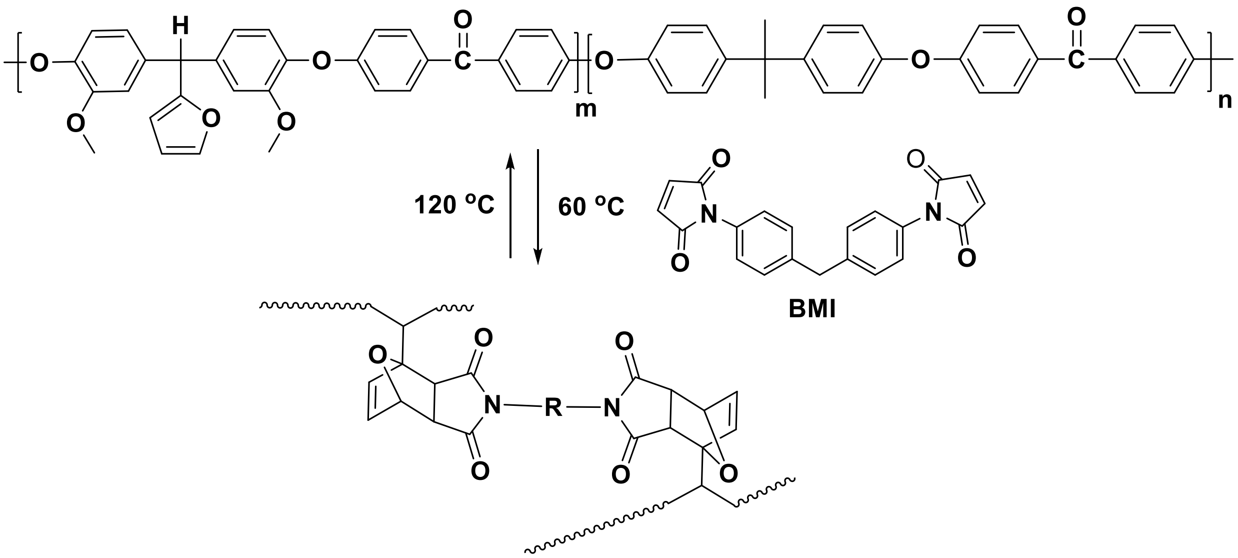
Figure 4b.12. Stress-strain curves of (co)poly(ether ether ketone)s.

Table 4b.4. Mechanical properties of (co)poly(ether ether ketone)s

(Co)poly(ether ether ketone)	**Structure of (co)poly (ether ether ketone)**	**Young's Modulus (GPa)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**
PEEK-1		1.06±0.10	84.2±0.3	10.0±2.4
PEEK-2		1.16±0.07	88.4±0.5	9.6±3.2
PEEK-3		1.11±0.04	86.4±0.1	9.2±2.1
PEEK-4		1.12±0.18	85.9±0.5	9.8±1.9

4b.3.7 Thermally–reversible cross-linked copoly(ether ether ketone) by Diels-Alder Chemistry

Thermally reversible cross-linked copoly(ether ether ketone) was prepared by reaction of copoly(ether ether ketone) (PEEK-2) bearing pendent furyl groups with 1,1'-(methylenedi-1,4-phenylene)bismaleimide (BMI) through Diels-Alder reaction as illustrated in **Scheme 4b.2**.



Scheme 4b.2. Preparation of thermally reversible cross-linked copoly(ether ether ketone).

On heating at 60 °C, copoly(ether ether ketone) containing pendent furyl groups underwent reaction with 1,1’-(methylenedi-4,1-phenylene)bismaleimide to obtain Diels-Alder adducts, leading to the formation of cross-linked copoly(ether ether ketone) denoted as PEEK-2-BMI. The cross-linked copoly(ether ether ketone) was characterized by solubility tests, sol-gel-sol transition, DSC and tensile measurements.[41]

4b.3.8 Thermal studies of cross-linked copoly(ether ether ketone)s

Thermo-reversibility of cross-linked copoly(ether ether ketone) (PEEK-2-BMI) was characterized by DSC analysis. DSC curves and data are illustrated in **Figure 4b.13** and **Table 4b.5**, respectively. PEEK-2-BMI revealed strong endothermic transition with maximum at 102 ^{o}C in the first heating cycle. The second heating cycle also showed endothermic transition at 113 ^{o}C for PEEK-2-BMI. Due to the fast heating rate (10 ^{o}C/min), complete retro Diels-Alder reaction did not occur in the time scale of first heating cycle and hence the endothermic transition was observed in the second heating cycle also. The cleavage of Diels-Alder adduct at slightly higher temperature in case of second heating cycle compared to the first heating cycle could presumably be attributed to retro Diels-Alder reaction of exo adduct. In general, exo adduct reverts at slightly higher temperature compared to endo adduct.[42] In the third heating cycle, endothermic transition was not detected indicating that complete cleavage of Diels-Alder adducts had occurred during the second heating cycle.

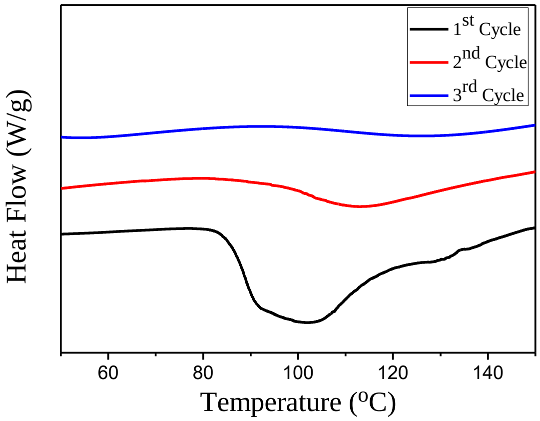


Figure 4b.13. DSC curves (first, second and third heating cycle) of cross-linked copoly (ether ether ketone) PEEK-2-BMI.

Table 4b.5. Decross-linking temperature and absorbed energy for retro Diels-Alder reaction

(Co)poly(ether ether ketone)	**1st Heating Cycle**		**2nd Heating Cycle**	
	T_{rDA} (°C)[a]	**ΔH (J/g)[b]**	**T_{rDA} (°C)[a]**	**ΔH (J/g)[b]**
PEEK-2-BMI	102	21	113	6

a: Temperature corresponding to retro Diels-Alder reaction; b: Absorbed energy for retro Diels-Alder reaction.

4b.3.9 Thermo-reversible gels *via* Diels-Alder reaction

Thermally induced Diels-Alder reaction between PEEK-2 and BMI was further evaluated in DMAc solvent, as shown in **Figure 4b.14**.

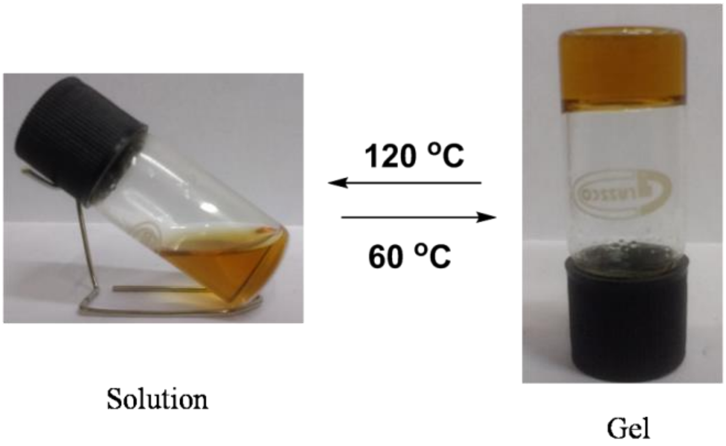


Figure 4b.14. Sol-gel transition of copoly(ether ether ketone)-based organogel.

The solution of a mixture of PEEK-2 and BMI (furan/maleimide mol ratio = 1) in DMAc was heated at 60 °C in a glass vial. An increase in viscosity of solution was observed. After 10 h, solution viscosity was so high that the gel did not flow even after inversion of vial (**Figure 4b.14**). The gel was heated at 120 °C for 10 min when the system turned into clear and low viscosity solution due to the decross-linking *via* retro Diels-Alder reaction. Upon cooling the solution to 60 °C, viscosity increased gradually and gel reformed completely on standing for 12 h. This could be explained by the re-formation of Diels-Alder adduct. This process was repeated three times, indicating thermo-reversible character of PEEK-2-BMI gel.

4b.3.10 Recycling of cross-linked copoly(ether ether ketone)s

The fractured specimens of PEEK-2-BMI, after tensile test measurements, were immersed in chloroform at room temperature. The samples were insoluble due to their cross-linked nature. The specimens gradually dissolved in chloroform when the temperature was raised to 120 °C in a sealed tube. At 120 °C, retro Diels-Alder reaction occurred resulting in the regeneration of poly(ether ether ketone) containing pendant furyl groups and BMI. The film was formed again by a solution casting process. This process could be repeated for at least two times with the obtained reprocessed film still being transparent and flexible. The recyclable behavior of cross-linked copoly(ether ether ketone) was also investigated by stress-strain studies conducted on representative cross-linked copoly(ether ether ketone) (PEEK-2-BMI), first recycled (PEEK-2-BMI1) and second recycled (PEEK-2-BMI2). The data on mechanical properties is summarized in **Table 4b.6** and the stress-strain curves are presented in **Figure 4b.16**.

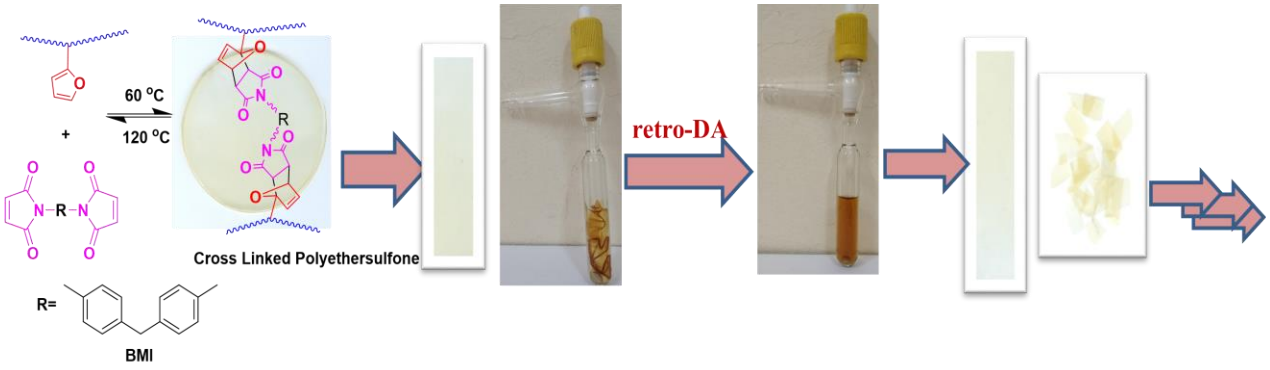


Figure 4b.15. Thermo-reversibility of cross-linked copoly(ether ether ketone).

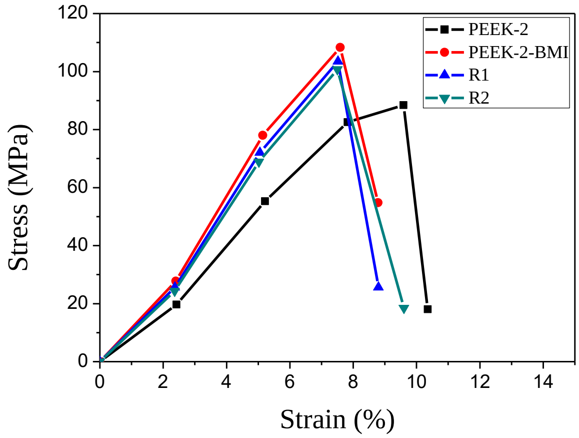


Figure 4b.16. Stress-strain curves of recycled cross-linked copoly(ether ether ketone)s.

The cross-linked copoly(ether ether ketone), PEEK-2-BMI, displayed higher Young's modulus and tensile strength and lower % elongation at break compared to parent copoly(ether ether ketone) PEEK-2. This is to be expected due to the formation of cross-linked network. The recycled copoly(ether ether ketone), PEEK-2-BMI1 and PEEK-2-BMI2, showed values of Young's modulus, tensile strength, and % elongation at break which are closer to the values of cross-linked copoly(ether ether ketone) (PEEK-2-BMI). These results demonstrated thermal reversibility of Diels-Alder cross-linked copoly(ether ether ketone).

Table 4b.6. Mechanical properties of recycled copoly(ether ether ketone)s

(Co)poly(ether ether ketone)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PEEK-2	1.16±0.07	88.4±0.5	9.6±3.2
PEEK-2-BMI	1.56±0.08	108.3±0.4	7.6±0.9
PEEK-2-BMIR1	1.52±0.04	104.5±0.7	7.5±1.3
PEEK-2-BMIR2	1.49±0.05	101.7±0.4	7.5±0.5

4b.4 Conclusions

A new aromatic poly(ether ether ketone) bearing pendant furyl groups was successfully synthesized by aromatic nucleophilic substitution polycondensation of BPF with commercially available 4, 4′-difluorobenzophenone. Copoly(ether ether ketone)s were synthesized by polycondensation of varying mole ratios of BPF and BPA with 4, 4′-difluorobenzophenone. The resulting (co)poly(ether ether ketone)s were readily soluble in organic solvents such as dichloromethane, chloroform, THF, DMAc, DMF, NMP and could be cast into tough, transparent and flexible films from chloroform solutions. The 10 % weight loss temperature of (co)poly(ether ether ketone)s was found in the range 429-464 °C, indicating their good thermal stability. T_g values of (co)poly(ether ether ketone)s were in the range 152-156 °C and decreased with increase in BPF content. A representative copoly(ether ether ketone) (PEEK-2) was cross-linked with BMI *via* Diels-Alder reaction to form cross-linked PEEK-2-BMI which showed improved mechanical properties and was recycled two times without significant loss of mechanical properties.

4b.5 References

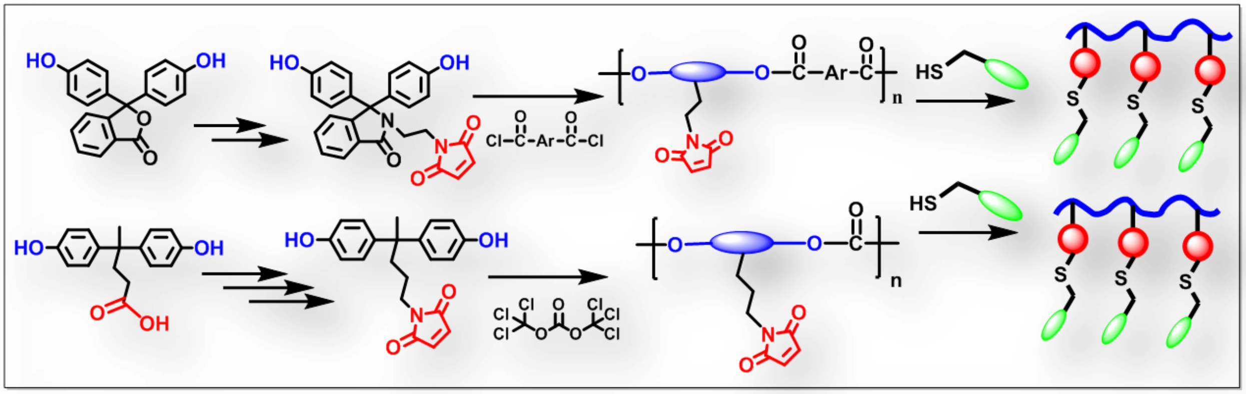
1. Crivello, J. V. *J. Polym. Sci. Polym. Chem. Ed.*, 1973, **11**, 1185–1200.
2. Auvergne, R., Caillol, S., David, G., Boutevin, B., Pascault, J.-P. *Chem. Rev.*, 2014, **114**, 1082–1115.
3. Pion, F., Ducrot, P.-H., Allais, F. *Macromol. Chem. Phys.*, 2014, **215**, 431–439.
4. Mantzaridis, C., Brocas, A.-L., Llevot, A., Cendejas, G., Auvergne, R., Caillol, S., Carlotti, S., Cramail, H. *Green Chem.*, 2013, **15**, 3091.
5. McCoy, J. D., Ancipink, W. B., Clarkson, C. M., Kropka, J. M., Celina, M. C., Giron, N. H., Hailesilassie, L., Fredj, N. *Polymer*, 2016, **105**, 243–254.
6. Vázquez, C. P., Joly-Duhamel, C., Boutevin, B. *Macromol. Chem. Phys.*, 2013, **214**, 1621–1628.
7. Kunnikuruvan, S., Parandekar, P. V., Prakash, O., Tsotsis, T. K., Nair, N. N. *Macromolecules*, 2017, **50**, 6081–6087.
8. Zhang, Z., Yu, R., Wang, F., Wang, J., Jiao, Y. *J. Appl. Polym. Sci.*, 2011, **122**, 2609–2615.
9. Polgar, L. M., van Duin, M., Broekhuis, A. A., Picchioni, F. *Macromolecules*, 2015, **48**, 7096–7105.
10. Wang, A., Niu, H., He, Z., Li, Y. *Polym. Chem.*, 2017, **8**, 4494–4502.
11. Suzuki, M., Hanabusa, K. *Chem. Soc. Rev.*, 2010, **39**, 455–463.
12. Buchwalter, S. L., Kosbar, L. L. *J. Polym. Sci. Part A Polym. Chem.*, 1996, **34**, 249–260.
13. Engelberg, P. I., Tesoro, G. C. *Polym. Eng. Sci.*, 1990, **30**, 303–307.

14. Ogino, K., Chen, J.-S., Ober, C. K. *Chem. Mater.*, 1998, **10**, 3833–3838.
15. Sastri, V. R., Tesoro, G. C. *J. Appl. Polym. Sci.*, 1990, **39**, 1439–1457.
16. Wang, L., Li, H., Wong, C. P. *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 3771–3782.
17. Kennedy, J. P., Castner, K. F. *J. Polym. Sci. Polym. Chem. Ed.*, 1979, **17**, 2055–2070.
18. Jones, J. R., Liotta, C. L., Collard, D. M., Schiraldi, D. A. *Macromolecules*, 1999, **32**, 5786–5792.
19. Garcia, J. M., Jones, G. O., Virwani, K., McCloskey, B. D., Boday, D. J., ter Huurne, G. M., Horn, H. W., Coady, D. J., Bintaleb, A. M., Alabdulrahman, A. M. S., Alsewailem, F., Almegren, H. A. A., Hedrick, J. L. *Science*, 2014, **344**, 732–735.
20. Boul, P. J., Reutenauer, P., Lehn, J.-M. *Org. Lett.*, 2005, **7**, 15–18.
21. Chen, X. *Science*, 2002, **295**, 1698–1702.
22. Franc, G., Kakkar, A. K. *Chem. - A Eur. J.*, 2009, **15**, 5630–5639.
23. Gandini, A., Silvestre, A., Coelho, D. *Polym. Chem.*, 2013, **4**, 1364–1371.
24. Gandini, A. *Prog. Polym. Sci.*, 2013, **38**, 1–29.
25. Liu, Y.-L., Chen, Y.-W. *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
26. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
27. Luo, K., Li, J., Duan, G., Wang, Y., Yu, J., Zhu, J., Hu, Z. *Polymer*, 2018, **142**, 33–42.
28. Varganici, C.-D., Ursache, O., Gaina, C., Gaina, V., Rosu, D., Simionescu, B. C. *Ind. Eng. Chem. Res.*, 2013, **52**, 5287–5295.
29. Du, P., Wu, M., Liu, X., Zheng, Z., Wang, X., Joncheray, T., Zhang, Y. *J. Appl. Polym. Sci.*, 2014, **131**, 40234–40241.
30. Irusta, L., Fernández-Berridi, M. J., Aizpurua, J. *J. Appl. Polym. Sci.*, 2017, **134**, 1–9.
31. Wei, Y., Du, X., Ma, X., Zhao, K., Zhang, S., Bai, Y. *Polym. Bull.*, 2017, **74**, 3907–3922.
32. Liu, Y.-L., Hsieh, C.-Y. *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 905–913.
33. Hu, F., La Scala, J. J., Sadler, J. M., Palmese, G. R. *Macromolecules*, 2014, **47**, 3332–3342.
34. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. *Polymer*, 2013, **54**, 5351–5357.
35. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. *Macromolecules*, 2013, **46**, 1794–1802.
36. Hilf, J., Scharfenberg, M., Poon, J., Moers, C., Frey, H. *Macromol. Rapid Commun.*, 2015, **36**, 174–179.

37. Wang, Z., Chen, T., Xu, J. *Macromolecules*, 2000, **33**, 5672–5679.
38. Liu, D., Yu, H., Wang, Z., Nie, Q. *Polym. Int.*, 2010, **59**, 937–944.
39. Wang, H. M., Hsiao, S. H. *Polymer*, 2009, **50**, 1692–1699.
40. Liao, J., Chu, Y., Wang, J., Zhou, M., Cao, Y. *J. Appl. Polym. Sci.*, 2015, **132**, 41289–41299.
41. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
42. Canadell, J., Fischer, H., De With, G., van Benthem, R. A. T. M. *J. Polym. Sci. Part A Polym. Chem.*, 2010, **48**, 3456–3467.

Chapter-5

Chemical Modification of Aromatic Polyesters and Polycarbonates *via* Maleimide-Thiol Click Reaction



Chapter-5a

(Co)polyesters Containing Pendant Maleimide Groups: Synthesis, Characterization and Chemical Modifications

5a.1 Introduction

Aromatic polyesters are an important class of high performance polymers which find broad range of applications in different areas such as coatings, automobiles, textiles, electronic industries, etc.[1,2] Even though aromatic polyesters are used in several industrial sectors, it is highly desirable to design polyesters possessing variable solubility characteristics, polarity, crystallinity and presence of reactive functional groups with capability to undergo efficient chemical reactions.[3–10]

The key monomers for synthesis of aromatic polyesters are bisphenols and aromatic diacids or their corresponding derivatives. A range of bisphenols and aromatic diacids with varying chemical structures have been utilized to obtain modified polyesters with enhanced mechanical, thermal and solubility characteristics.[4,11,12] As far as polyesters containing pendant reactive functional groups are concerned, limited examples have been reported. For instance, pendant functional groups such as carboxylic acid,[8] ester,[5] halogen,[13,14] cyano,[15] hydroxyl,[13] alkyne,[16] azido,[17] allyl[18], furyl[6] and maleimide[19] have been introduced into aromatic polyesters *via* use of appropriately substituted diacids or bisphenol monomer.

In this study, a new bisphenol containing pendant maleimide group, namely, N-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-MA) was synthesized starting from phenolphthalein. Aromatic polyesters containing pendant maleimide groups were synthesized by low temperature solution polycondensation of PPH-MA with aromatic diacid chlorides namely, isophthaloyl chloride (IPC), terephthaloyl chloride (TPC) and a mixture of IPC:TPC (50:50). Copolyesters were synthesized by polycondensation of various molar ratios of PPH-MA and bisphenol A with IPC. All the (co)polyesters were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetric studies (DSC). Subsequently, aromatic polyester with pendant maleimide groups was chemically modified by thiol-maleimide Michal addition reaction with two representative thiol compounds to yield post-modified polymers. Additionally, it was demonstrated that polyester containing pendant maleimide groups could be used to form insoluble cross-linked gels in the presence of multi-functional thiol cross-linker.

5a.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC and XRD are given in **Chapter 2**.

5a.2.1 Synthesis of bisphenol bearing pendant maleimide group

5a.2.1.1 Synthesis of N-aminoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone

Into a 500 mL three necked round bottom flask equipped with a mechanical stirrer, a gas inlet and a reflux condenser were placed phenolphthalein (25.0 g, 78.23 mmol) and 1, 2-diaminoethane (100 mL). The reaction mixture was stirred at 120 ^{o}C for 24 h. The excess of 1, 2-diaminoethane was removed by distillation under reduced pressure. The resulting residue was slowly poured into acidified cold water and the precipitated solid was separated by filtration. The obtained solid was dissolved in hot water and the solution was titrated with 10 % aqueous potassium hydroxide solution until pH 8. The solution was cooled to room temperature and the separated solid was collected by filtration. The product was purified by recrystallization from a mixture of ethanol and water (1:1, v/v).

Yield: 22.57 g (80 %); Melting point: 260 ^{o}C; IR (KBr): 3120, 1658 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_{6,}$ δ/ppm): 7.65 (d, 1 H), 7.50 (t, 1 H), 7.41 (t, 1 H), 7.34 (d, 1 H), 6.91 (d, 4 H), 6.69 (d, 4 H), 3.08- 3.34 (m, 6 H), 1.74-1.92 (m, 2 H); ^{13}C NMR (50 MHz, DMSO-d$_{6}$, δ/ppm): 167.1, 157.1, 151.5, 132.2, 130.7, 130.2, 129.0, 128.0, 123.6, 122.7, 115.3, 74.3, 56.0, 44.3; HRMS ESI^{+}: (M+Na)$^{+}$m/z calculated for $C_{22}H_{20}N_{2}O_{3}Na$: 383.1366, found: 383.1366.

5a.2.1.2 Synthesis of N-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone

Into a 500 mL two necked round bottom flask equipped with a mechanical stirrer, a gas inlet and a reflux condenser were placed N-aminoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (10.0 g, 27.76 mmol), maleic anhydride (5.45 g, 55.53 mmol) and glacial acetic acid (100 mL). The reaction mixture was stirred at 120 ^{o}C for 12 h. The reaction mixture was cooled to room temperature and was slowly poured into an ice cold-water. The solid product was collected by filtration. The product was dissolved in ethyl acetate (100 mL) and the solution was washed with water (3 x 100 mL). The ethyl acetate solution was dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed by evaporation under reduced pressure. The crude product was purified by column chromatography using pet ether:ethyl acetate (70:30, v/v) as an eluent to afford pure N-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone.

Yield: 6.90 g (56 %); Melting point: 288 °C; IR (KBr): 3426, 1707, 1662, 1402, 1123, 694 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ/ppm): 9.57 (br. s., 2 H), 7.68 (d, 1 H), 7.54 (t, 1 H), 7.44 (t, 1 H), 7.36 (d, 1 H), 6.92 (d, 4 H), 6.80 (s, 2 H), 6.71 (d, 4 H), 3.55 (t, 2 H), 2.99 (t, 2 H); ^{13}C NMR (50 MHz, DMSO-*d*$_6$, δ/ppm): 170.7, 167.6, 157.1, 151.6, 134.2, 132.3, 130.4, 129.7, 129.1, 128.0, 123.7, 122.9, 115.4, 74.5, 40.1, 35.2; HRMS ESI$^+$: (M+Na)$^+$m/z calculated for $C_{26}H_{20}N_2O_5Na$: 463.1264, found: 463.1260.

5a.2.2 Synthesis of (co)polyesters bearing pendant maleimide groups

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed N-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (1.0 g , 2.27 mmol), dichloromethane (7 mL), and triethylamine (0.90 mL, 6.49 mmol), and the solution was cooled to 0 °C. To the reaction mixture, the solution of isophthaloyl chloride (0.46 g, 2.27 mmol) in dichloromethane (10 mL) was added dropwise over a period of 20 min. The reaction mixture was stirred at 0 °C for 30 min followed by stirring at 25 °C for 1 h. The viscous reaction mixture was diluted with dichloromethane (5 mL), and the solution was poured slowly into methanol (200 mL) to precipitate the polymer. The precipitated polymer was isolated by filtration, washed with water (5 x 100 mL) followed by washing with methanol (2 x 50 mL) and dried under reduced pressure at room temperature for 12 h.

The other (co)polyesters were synthesized by similar procedure.

5a.2.3 Post-modification of polyester bearing pendant maleimide groups with 4-chlorothiophenol

To a Schlenk tube equipped with a magnetic stirring bar were added MAPES-1 (0.20 g, 0.35 mmol), 4-chlorothiophenol (0.10 g, 0.70 mmol), triethylamine (97.91 μL, 0.70 mmol) and dry dichloromethane (5 mL). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 24 h. The resultant polymer was purified by precipitation into methanol to remove triethylamine and the excess 4-chlorothiophenol. The modified polyester was isolated by filtration and dried at room temperature under reduced pressure for 8 h.

A similar procedure was followed for synthesis of other post-functionalized polyester.

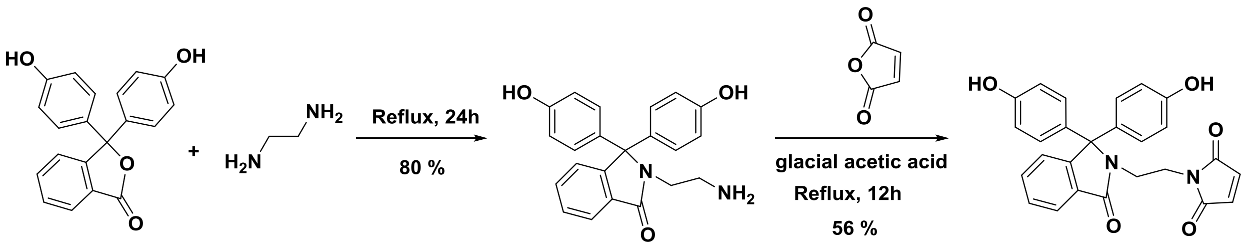
5a.2.4 Preparation of cross-linked polyester gel

Into a sample vial were taken polyester (MAPES-1) containing pendant maleimide groups (100 mg) and chloroform (1 mL). To the solution was added, a stoichiometric amount of pentaerythritol tetra(3-mercaptopropionate) (maleimide/thiol mol ratio = 1) and triethylamine (16.73 μL) at room temperature. The free standing gel material was obtained within few seconds.

5a.3 Results and discussion

5a.3.1 Monomer synthesis

Bisphenol containing pendant maleimide group was designed to be incorporated into aromatic polyesters by step-growth polymerization. **Scheme 5a.1** represents the route followed for the synthesis of *N*-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-MA) starting from phenolphthalein *via* two-step reaction pathway.



Scheme 5a.1. Synthesis of *N*-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone.

In the first step, N-aminoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone was synthesized by condensation of phenolphthalein and excess ethylenediamine. In the second step, N-aminoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone was reacted with maleic anhydride in acetic acid as a solvent under reflux conditions. The reaction was monitored by thin layer chromatography and the crude product was found to be a mixture of several compounds. From the crude product, PPH-MA was isolated by silica gel column chromatography with pet ether:ethyl acetate as an eluent and was characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

Figure 5a.1 represents IR spectrum of PPH-MA. The phenolic –OH band was observed at 3426 cm^{-1}. The strong carbonyl stretching bands at 1707 cm^{-1} and 1662 cm^{-1} could be attributed to maleimide and phthalimidine moieties, respectively. The characteristic bands of maleimide ring were observed at 1402, 1123 (C–N–C of maleimide) and 694 cm^{-1} (C=C of maleimide).

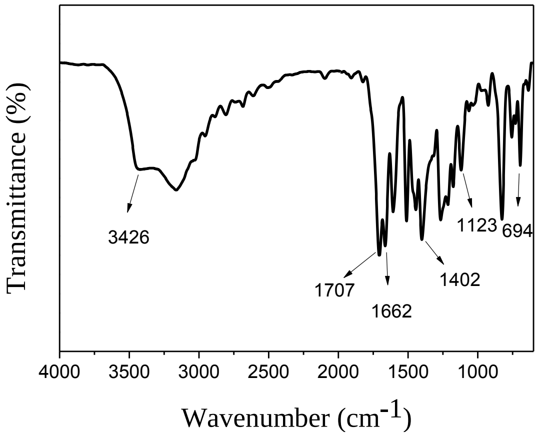


Figure 5a.1. IR spectrum of *N*-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone.

^{1}H NMR spectrum of PPH-MA is illustrated in **Figure 5a.2.** The characteristics peak of amine (–NH$_2$) proton at 3.20 δ ppm was disappeared, vinyl protons of maleimide were observed at 6.80 δ ppm which indicated the successful synthesis of the bisphenol containing pendant maleimide group. The spectral data for other protons were in good agreement with the proposed structure.

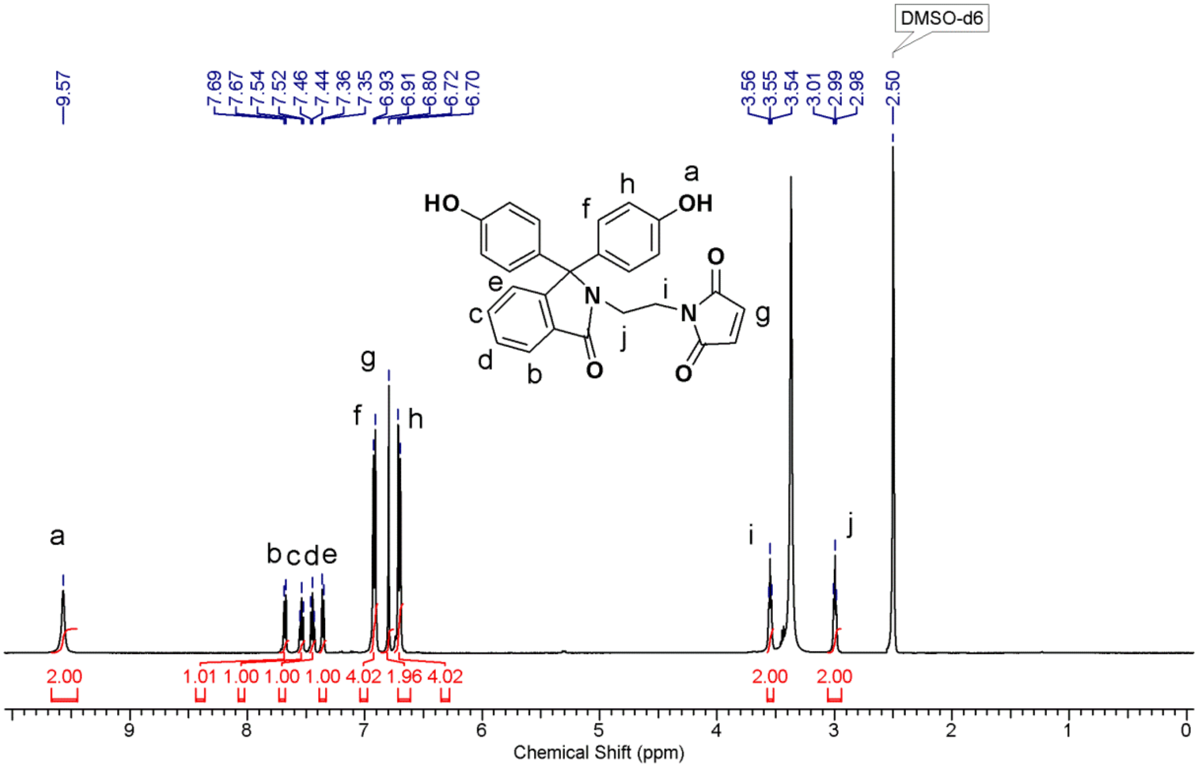


Figure 5a.2. ^{1}H NMR spectrum (in DMSO-d$_6$) of *N*-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone.

^{13}C NMR spectrum of PPH-MA **(Figure 5a.3)** was in accordance with the structure.

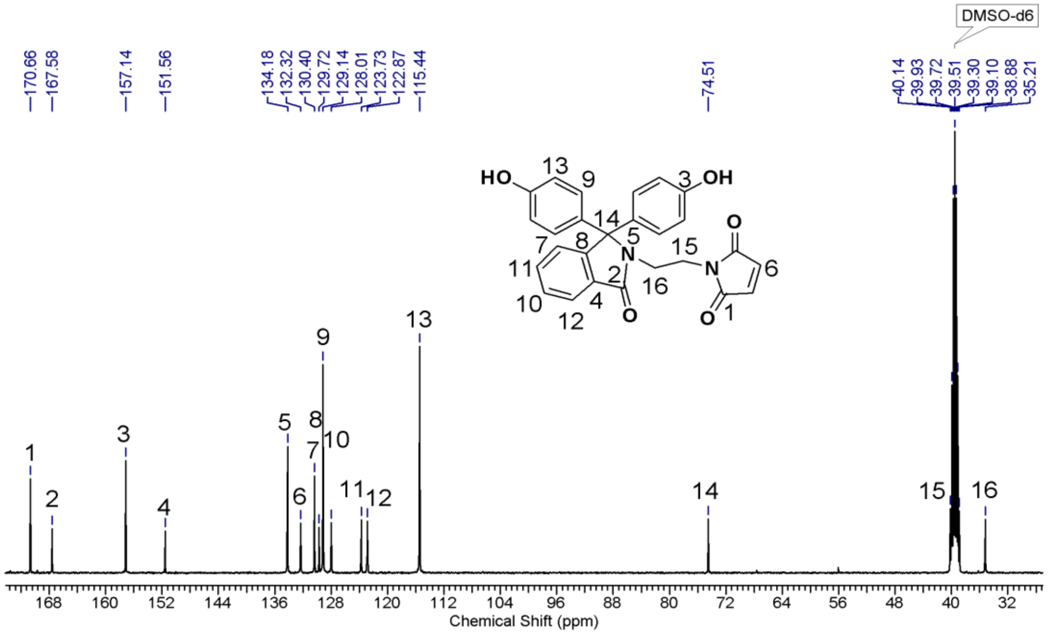


Figure 5a.3. ^{13}C NMR spectrum (in DMSO-d_6) of *N*-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone.

HRMS of PPH-MA is shown in **Figure 5a.4**. HRMS showed peak at 463.1260 corresponding to ([M+Na$^+$]) of PPH-MA **(**Calcd. ([M+Na]$^+$) for $C_{26}H_{20}N_2O_5Na$ =463.1264).

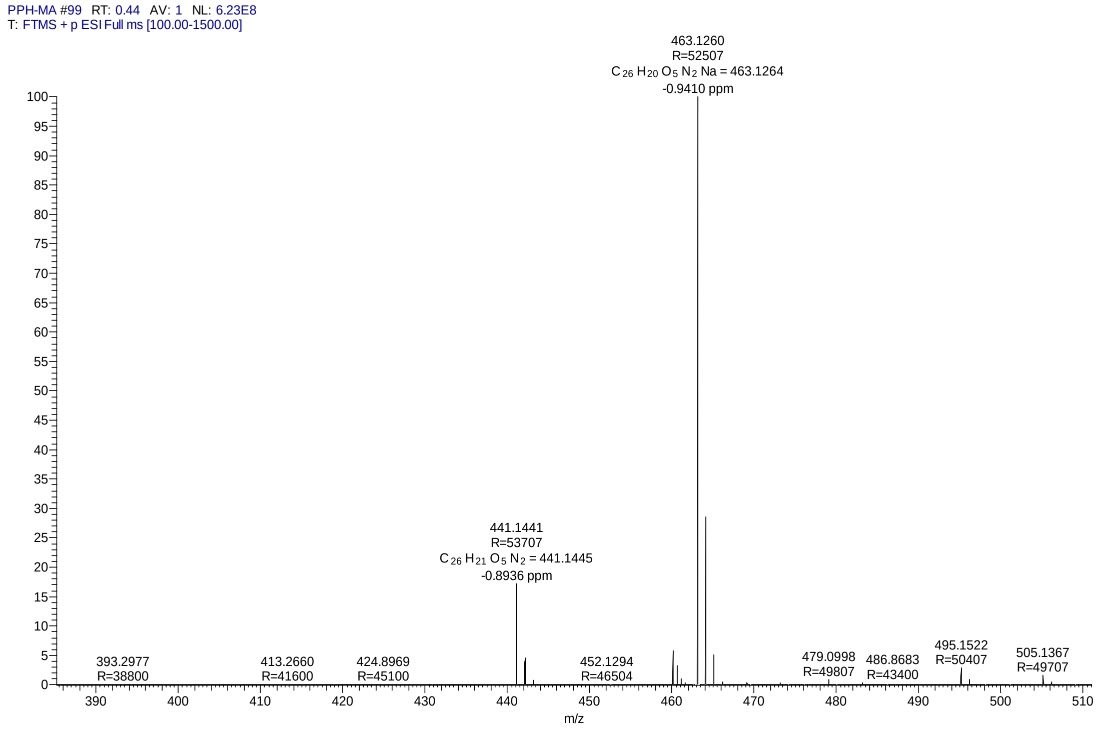
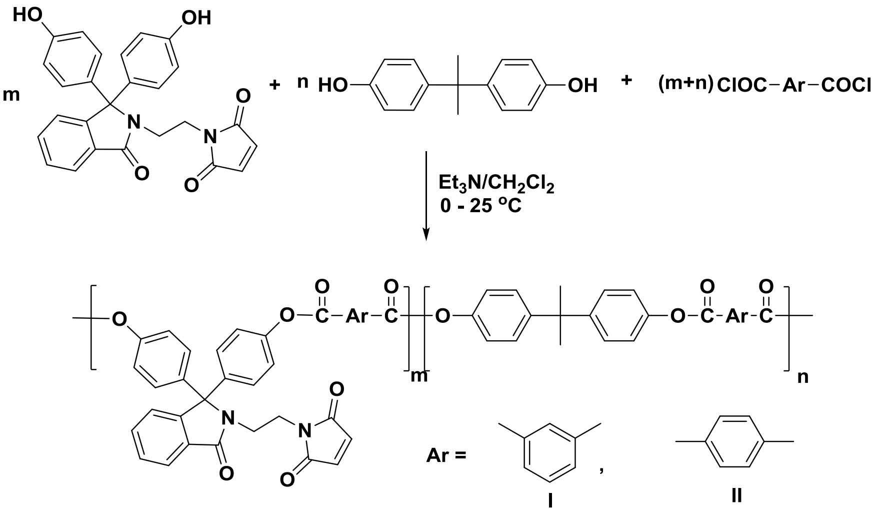


Figure 5a.4. HRMS of *N*-maleimidoethyl-3, 3-bis (4-hydroxyphenyl)-1-isobenzopyrrolidone.

5a.3.2 Synthesis of (co)polyesters bearing pendant maleimide groups

The widely used polymerization techniques for the preparation of aromatic polyesters from bisphenols and diacid chlorides are: interfacial polycondensation,[20,21] high-temperature solution polycondensation[22] and low-temperature solution polycondensation.[23,24] Generally, interfacial polycondensation is carried out under strongly alkaline conditions and high-temperature polycondensation requires temperature of 100 °C or above. It is known from the literature that maleimide group gets hydrolyzed in alkaline solution[25–27] and leads to cross-linking under higher temperature (on set temperature of cross-linking 200 °C).[28] Therefore, these two polymerization methods are not suitable for synthesis of aromatic polyesters containing pendant maleimide groups. Obviously, the low-temperature solution polycondensation technique was the method of choice for synthesis of polyesters containing pendant maleimide groups.

In this study, a series of aromatic polyesters containing pendant maleimide groups was synthesized by low-temperature solution polycondensation of PPH-MA or varying molar ratios of PPH-MA and BPA with aromatic diacid chlorides **(Scheme 5a.2).** The solution polymerization was carried out in dry dichloromethane using triethylamine as a base. The solution polymerization reactions proceeded smoothly in a homogenous manner. Notably, protection of maleimide group was not required. The polymerizations were generally conducted on a 1-2 g scale and gave nearly quantitative yields of isolated polyesters in all the cases. The results of synthesis of (co)polyesters bearing pendant maleimide groups are collected in **Table 5a.1**.



Scheme 5a.2. Synthesis of (co)polyesters bearing pendant maleimide groups.

The resulting (co)polyesters exhibited inherent viscosity (η_{inh}) in the range 0.52-0.97 dL/g indicating formation of medium to reasonably high molecular weight polyesters. This is also reflected in the results of measurements of molecular weights of polyesters by GPC **(Table 5a.1).** Number average molecular weights ($\overline{M_n}$) of polyesters with pendant maleimide groups were in the range 20,200 to 32,800 g/mol with dispersity values in the range 2.0 – 2.4.

Table 5a.1. Molar composition, inherent viscosity and molecular weight of (co)polyesters

(Co)polyester	**PPH-MA (mol%)**	**BPA (mol%)**	**IPC (mol%)**	**TPC (mol%)**	**η_{inh} (dL/g)^a**	**Molecular Weight^b**		**Dispersity**
						$\overline{M_n}$	$\overline{M_w}$	
MAPES-1	100	0	100	0	0.52	20,200	45,100	2.2
MAPES-2	100	0	0	100	0.62	25,100	56,600	2.2
MAPES-3	100	0	50	50	0.58	21,800	44,700	2.0
MAPES-4	30	70	100	0	0.97	32,800	76,400	2.3
MAPES-5	20	80	100	0	0.94	30,100	72,800	2.4
MAPES-6	10	90	100	0	0.83	27,800	63,500	2.3

a: η_{inh} was measured with 0.5 % (w/v) solution of (co)polyester in chloroform at 30 ± 0.1 ^{o}C, b: Measured by GPC in chloroform using polystyrene as calibration standard.

All these aromatic (co)polyesters were completely soluble at room temperature in organic solvents such as dichloromethane, chloroform, NMP, DMAc and DMF. Tough, transparent and flexible films of (co)polyesters bearing pendant maleimide groups could be cast from their solutions in chloroform. The representative film of polyester MAPES-1 is shown in **Figure 5a.5.**

Figure 5a.5. Film of polyester MAPES-1.

5a.3.3 Structural characterization

The formation of (co)polyesters containing pendant maleimide groups was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. IR spectrum of representative polyester MAPES-1 **(Figure 5a.6)** exhibited characteristic carbonyl absorption band of ester group at 1746 cm^{-1} and carbonyl absorption band of maleimide group appeared at 1707 cm^{-1}. The bands of maleimide group appeared at 1406, 1166 (C–N–C of maleimide) and 694 cm^{-1} (C=C of maleimide).

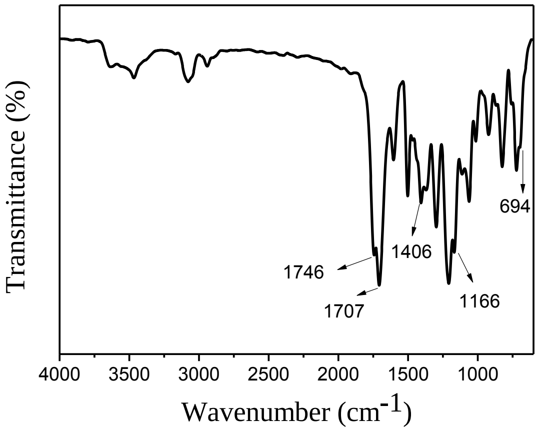


Figure 5a.6. IR spectrum of polyester MAPES-1.

As shown in **Figure 5a.7**, ^{1}H NMR spectrum of polyester MAPES-1 in CDCl$_3$ showed the a peak at 6.54 δ ppm corresponding to maleimide ring protons labeled as "j". The proton "a" flanked by ester carbonyl groups appeared as a singlet at 8.94 δ ppm. The protons "b" exhibited a doublet at 8.42 δ ppm. The proton "c" appeared as a doublet at 7.84 δ ppm. The proton "d" showed as a triplet at 7.66 δ ppm. The triplets appeared at 7.49 δ ppm and 7.42 δ ppm are assigned to aromatic protons labeled as "e" and "f", respectively. The proton *meta* to ester carbonyl groups labeled as "h" and the protons "g" are merged together and appeared at 7.31 δ ppm. The proton *ortho* to ester carbonyl groups marked as "i" exhibited a doublet at 7.23 δ ppm. The peaks appeared at 3.76 and 3.15 δ ppm are attributed to the methylene protons labeled as "k" and "l", respectively. The presence of peak corresponding to maleimide group in ^{1}H NMR spectrum of MAPES-1 with proper integration value endorsed the inertness of maleimide group in low temperature solution polycondensation reaction.

^{13}C NMR spectrum **(Figure 5a.8)** revealed a signal at 170.4 δ ppm corresponding to maleimide carbonyl as well as signals at 168.9 δ ppm reflecting carbonyl carbon of phthalimidine units. The signal of carbonyl carbon of ester linkage was observed at 163.8 δ ppm. The data corresponding to remaining carbon atoms were in good agreement with the proposed structure.

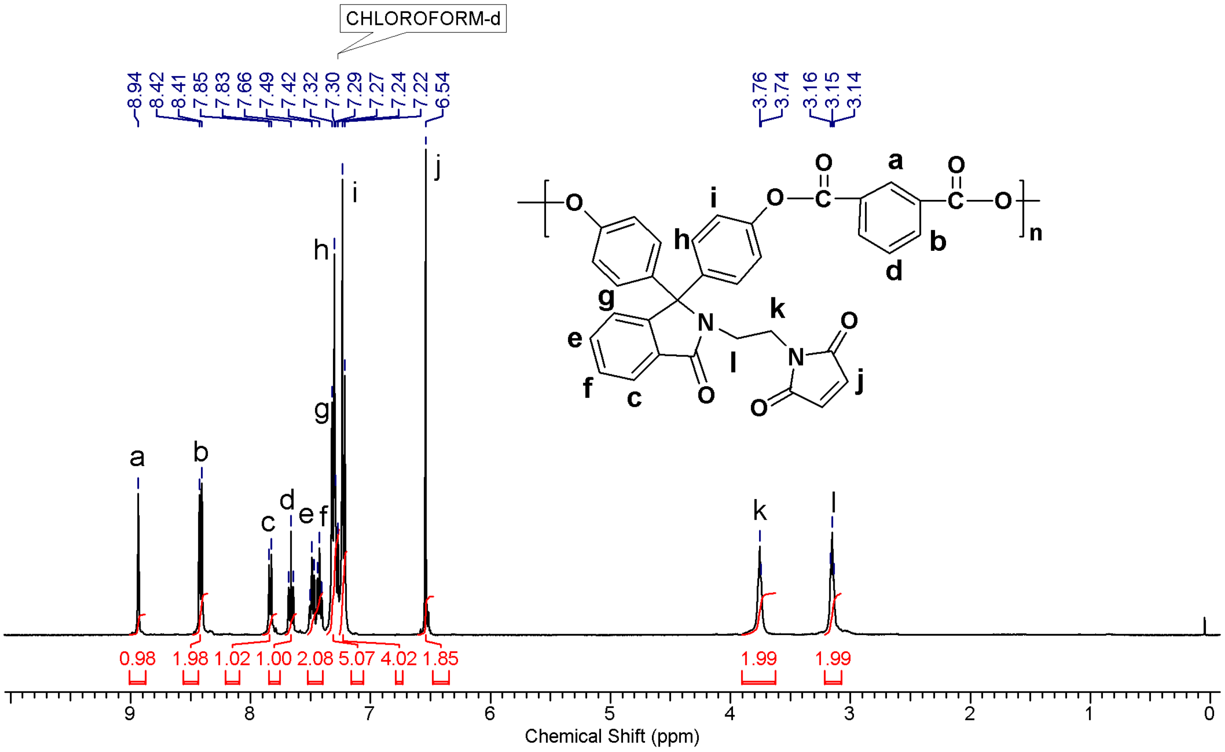


Figure 5a.7. ^{1}H NMR spectrum (in $CDCl_3$) of polyester MAPES-1.

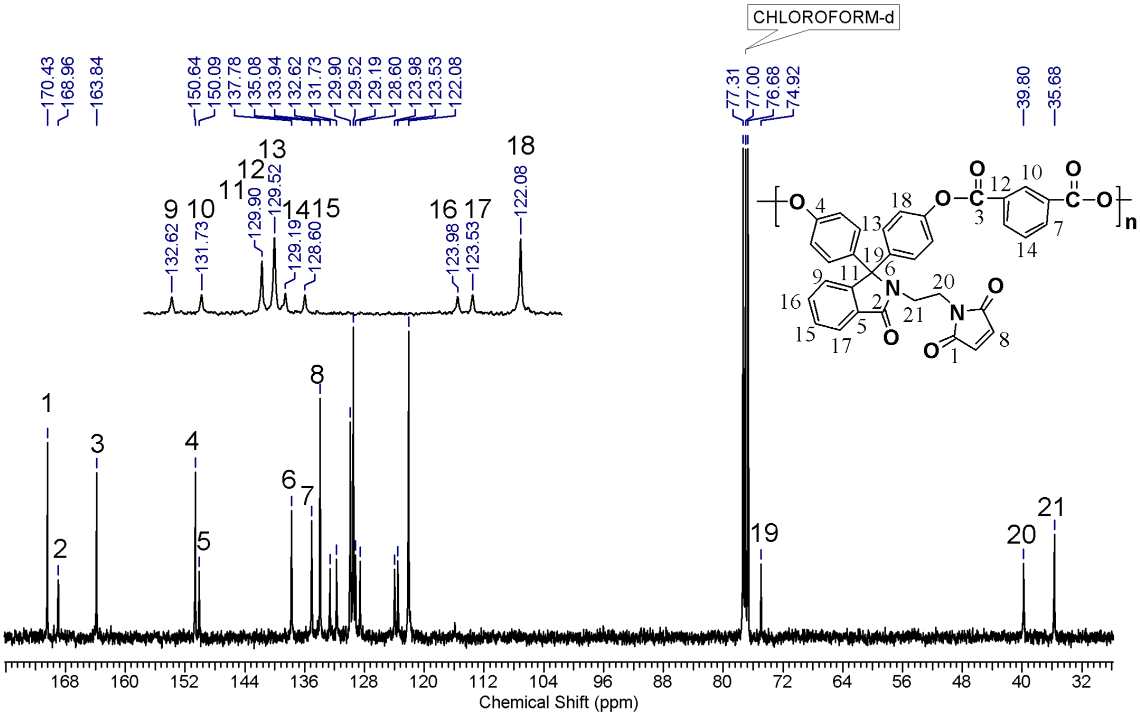


Figure 5a.8. ^{13}C NMR spectrum (in $CDCl_3$) of polyester MAPES-1.

The relative ratios of the two bisphenols, PPH-MA and BPA, incorporated into aromatic polyester backbone were calculated from their ^{1}H NMR spectra. For example, as shown in **Figure 5a.9**, in polymer MAPES-4 a nearly 1:1 incorporation of the two bisphenols was found by integrating the signal for methylene protons “m” appeared at 3.75 δ ppm, against methyl protons “o” corresponding to BPA appeared at 1.68 δ ppm. Thus, IR, ^{1}H NMR and ^{13}C NMR spectra nicely confirmed the synthesis of (co)polyesters with maleimide groups in pendant side chains.

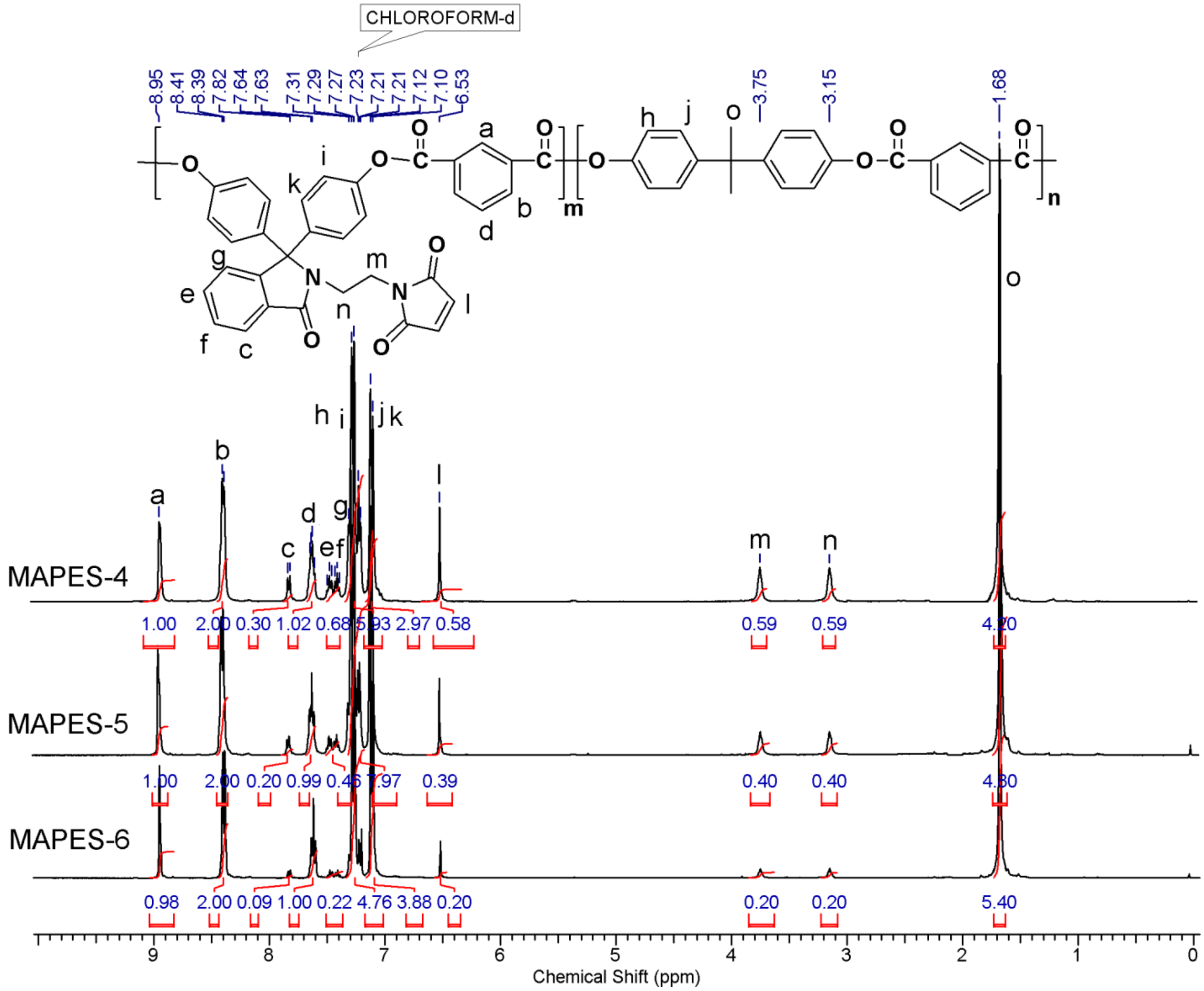
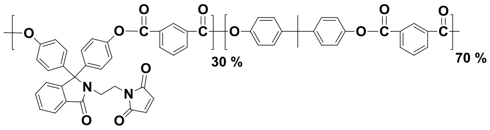
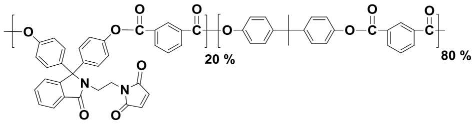
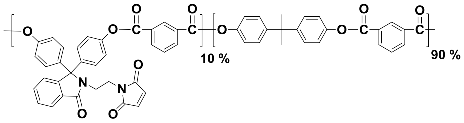


Figure 5a.9. ^{1}H NMR spectra (in $CDCl_3$) of copolyesters.

Table 5a.2. Molar composition of copolyesters determined by ^{1}H NMR spectra

Copolyester	Structure of copolyester	Feed PPH-MA, mol %	Observed PPH-MA, mol %
MAPES-4		30	29.5
MAPES-5		20	20.0
MAPES-6		10	10.0

The microstructure of copolyester derived from copolymerization of BPA and PPH-MA with IPC was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, the copolymerization of BPA and PPH-MA is expected to lead to formation of random copolymer with following possibilities of enchainment of the two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 5a.10**). ^{13}C NMR spectra of copolyesters showed clear evidence not only for the random copolyester formation but also about the microstructural details as indicated by the multiplicity of the signals.

The assignments of carbon atoms in ^{13}C NMR spectrum of MAPES-4, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 5a.11.**

^{13}C NMR spectrum of MAPSE-4 (30:70 mol % of PPH-MA:BPA) along with assignments of carbon atoms is presented in **Figure 5a.12.** For easy comparison, ^{13}C NMR spectra of homo-polyester MAPSE-1 and copolyesters MAPES-4 to MAPES-6 are also included in **Figure 5a.12**. It is interesting to note that the carbonyl carbon of ester linkage exhibited four distinct peaks at 163.85 δ ppm, 163.94 δ ppm, 164.15 δ ppm and 164.25 δ ppm for this particular copolymer. A comparison of the spectrum of MAPES-4 with that of MAPES-1 and MAPES-6 inferred that carbonyl peaks appeared at 163.85 δ ppm and 164.25 δ ppm originated from AAA and BBB arrangement of co-monomer units, respectively in copolyester while peaks at 163.94 δ ppm and 164.15 δ ppm correspond to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peak corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of MAPES-5 and MAPES-6.

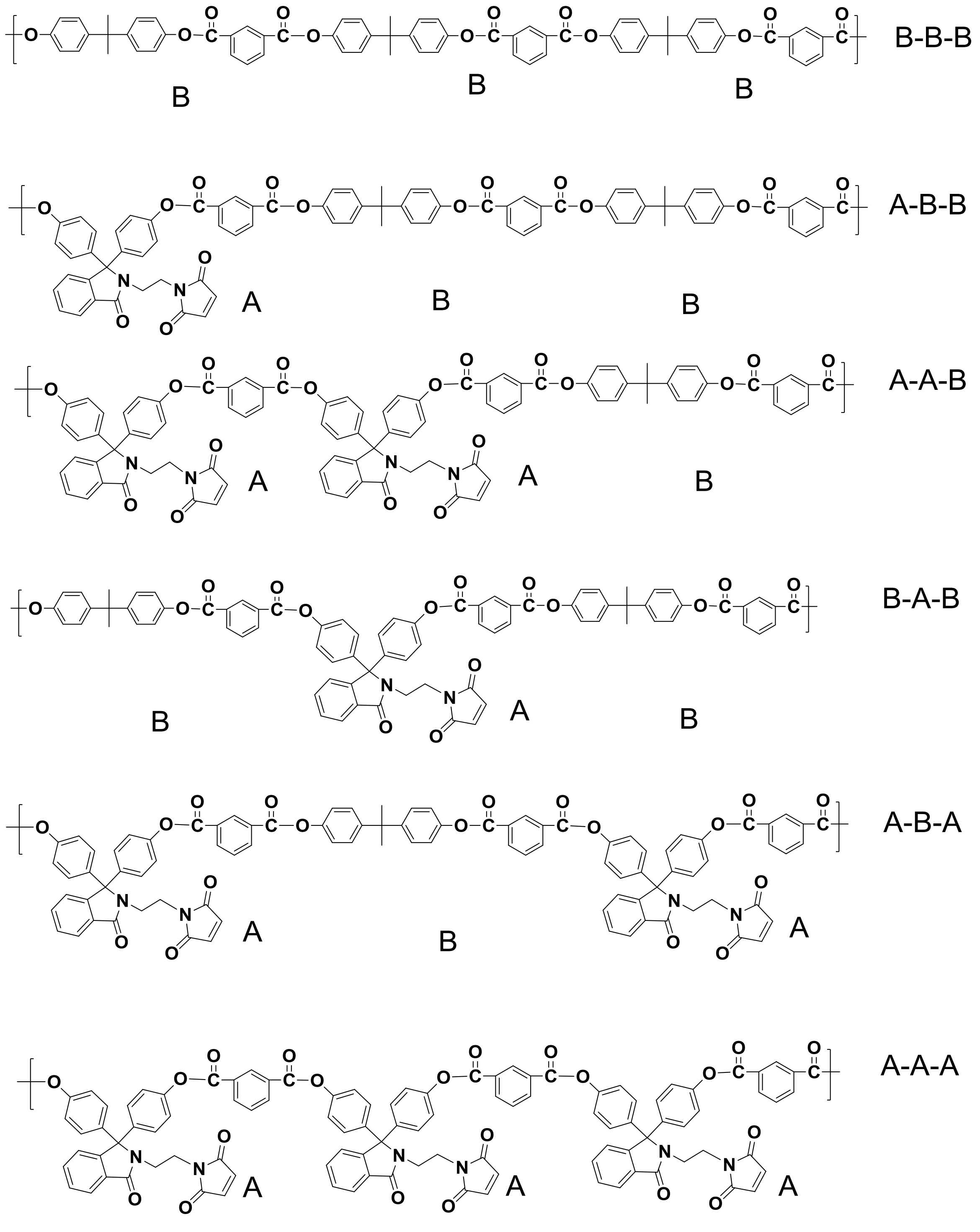


Figure 5a.10. Possible arrangements of PPH-MA and BPA units in copolyesters.

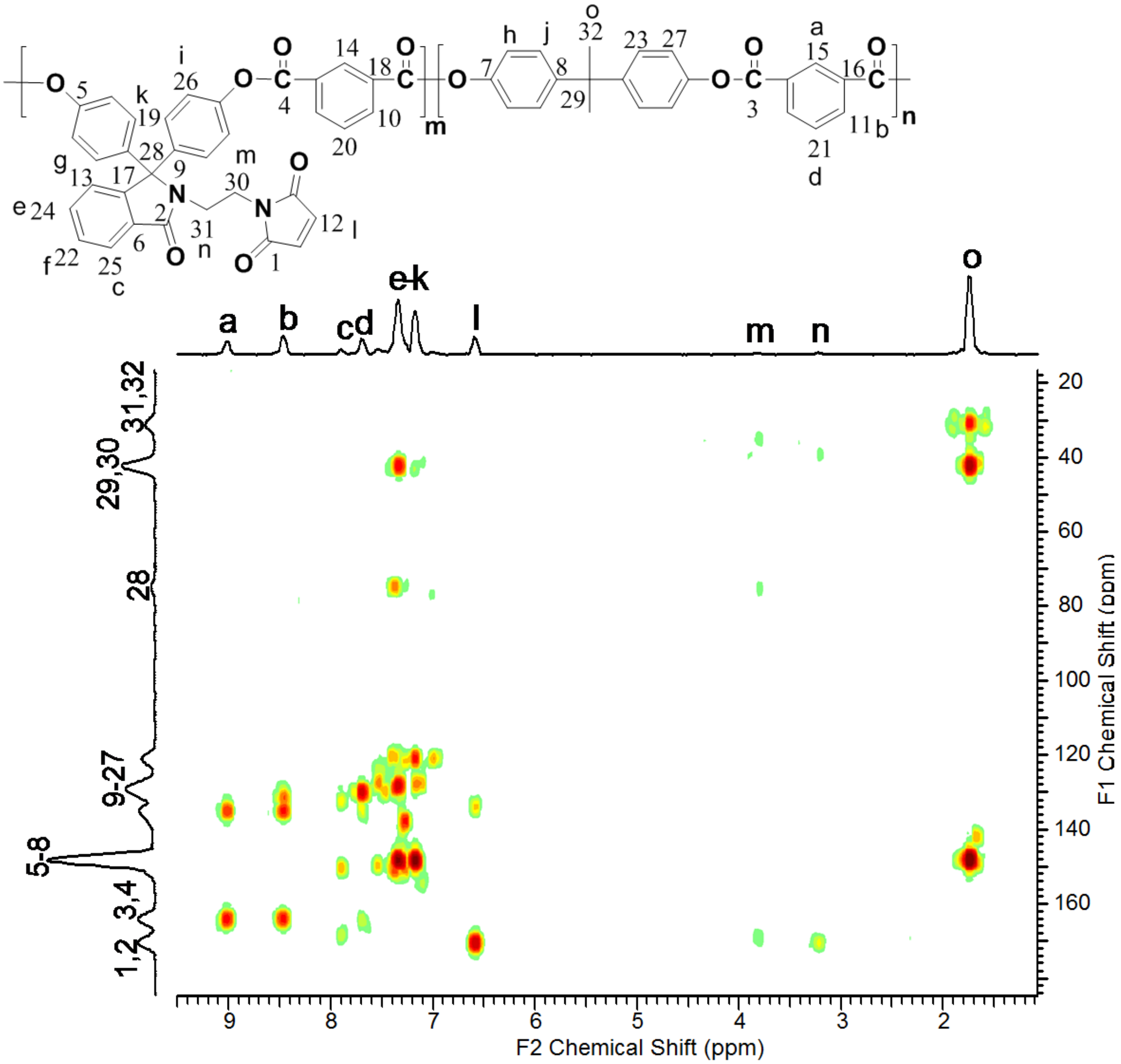


Figure 5a.11. HMBC spectrum (in $CDCl_3$) of MAPES-4.

Some of the other carbons in ^{13}C NMR spectrum of MAPES-4 also exhibited similar features as indicated in **Figure 5a.12**. It is also interesting to note that some of the carbon atoms of aromatic ring (for instance carbon atoms labeled as 7B and 8B) also showed more signals in copolyester which is likely to be due to the loss of symmetry upon formation of copolymer comprising of comonomer units enchained in the manner as shown in **Figure 5a.10** (A-A-B and A-B-B).

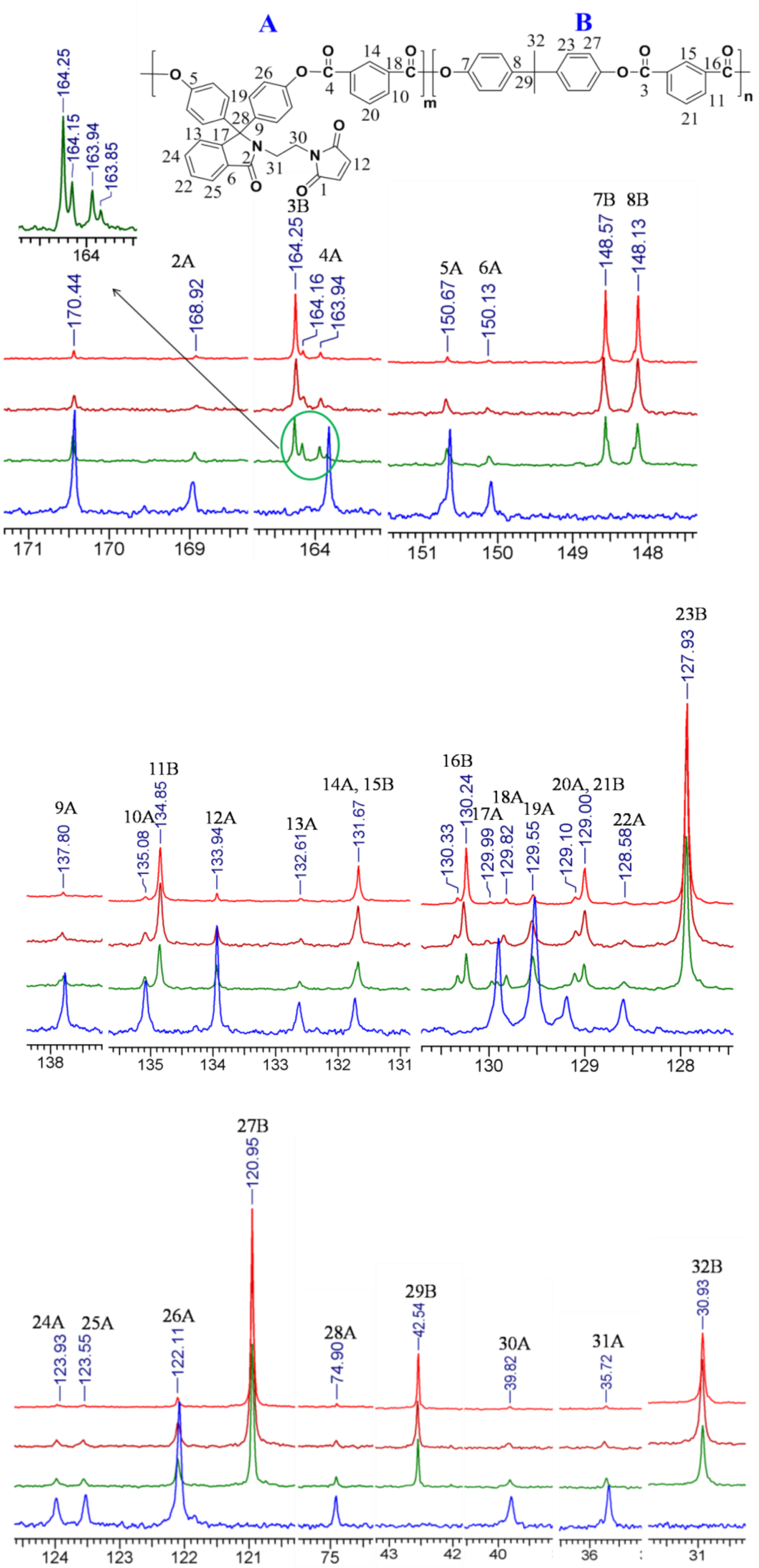


Figure 5a.12. ^{13}C NMR spectra (in $CDCl_3$) of (co)polyesters.

5a.3.4 X-Ray diffraction studies

The crystallinity of polyesters was examined by wide-angle X-ray diffraction patterns (**Figure 5a.13)**. Polyesters showed broad halo at about 2θ = ~10-30^{o} which indicated their amorphous nature. It is reasonable because incorporation of phthalimidine cardo units along with alkyl chain containing pendant maleimide groups on the polymer backbone disrupts the inter-chain interactions as well as the close packing of polymer chains. The amorphous nature of polyesters is reflected in their excellent solubility in organic solvents.

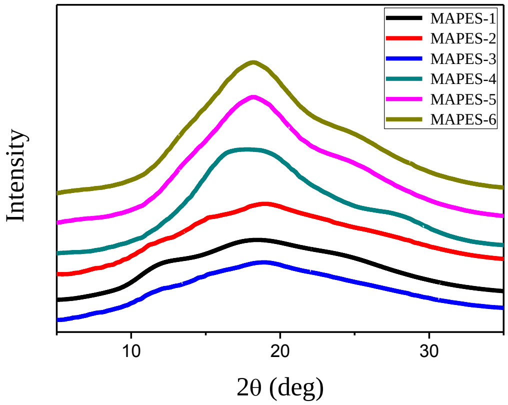


Figure 5a.13. X-Ray diffractograms of (co)polyesters.

5a.3.5 Thermal properties of (co)polyesters

The thermal stability of aromatic (co)polyesters was evaluated by TGA at a heating rate at 10 ^{o}C/min under nitrogen atmosphere.

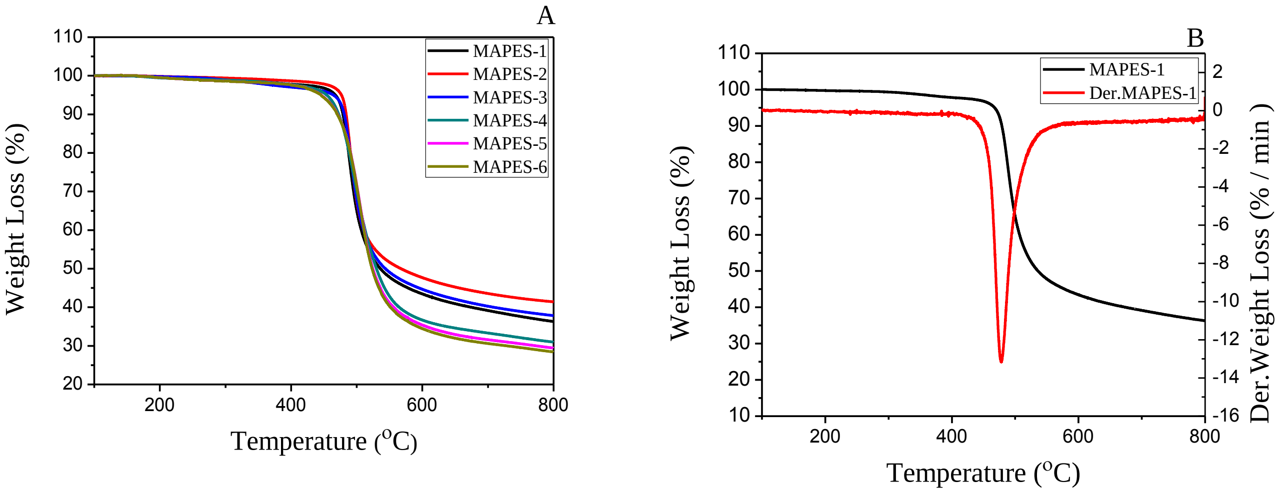
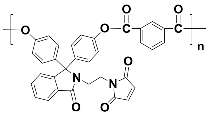
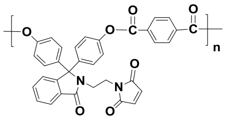
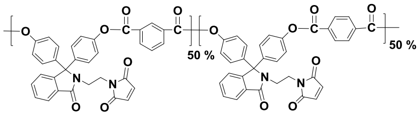
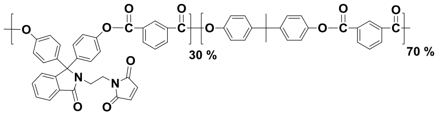
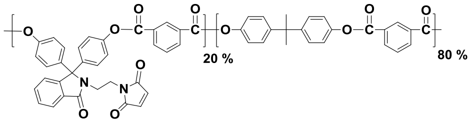
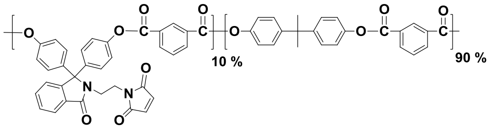


Figure 5a.14. A) TG curves of (co)polyesters; B) Representative TG and DTG curves of polyester MAPES-1.

TG curves of (co)polyesters are illustrated in **Figure 5a.14A. Figure 5a.14B** depicts representative thermogram (TG) and differential thermogram (DTG) curve of MAPES-1. The thermal properties of (co)polyesters are summarized in **Table 5a.3**. The temperature at 10 % weight loss (T_{10}) values for (co)polyesters were observed in the range 470-484 °C indicating their good thermal stability. The char yields of the (co)polyesters at 800 ^{o}C were in the range 29-41% and char yield tend to increase with the increase in the content of PPH-MA.

It is reported that maleimide group undergoes thermal cross-linking reactions at temperatures of 200 ^{o}C and above.[29] Furthermore, it is anticipated that aromatic polyesters based on PPH-MA, which contain rigid cardo phthalimidine moieties would exhibit T_g above 200 ^{o}C.[30] In view of these considerations, no efforts were made to determine T_g of synthesized (co)polyesters containing pendant maleimide groups by DSC analysis.

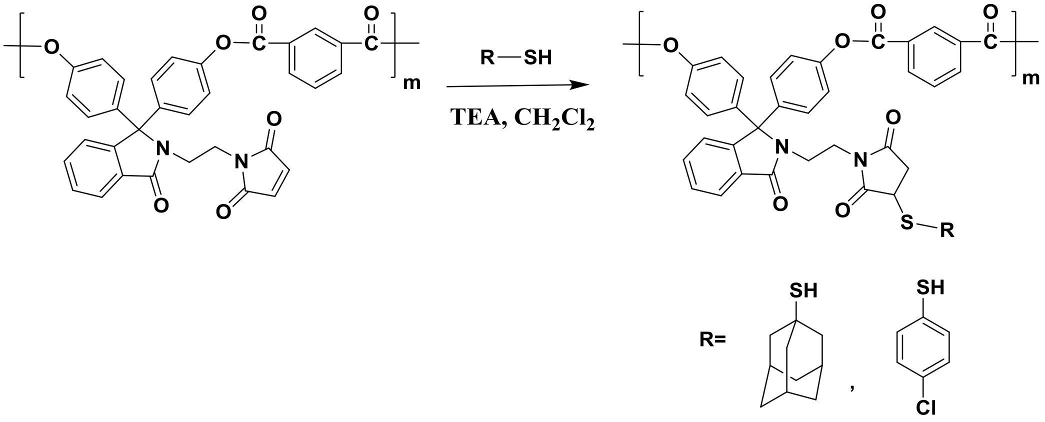
Table 5a.3. Thermal properties of (co)polyesters

(Co)polyester	**Structure of (Co)polyester**	**T_{10} (^{o}C)^{a}**	**Char Yield (%)^{b}**
MAPES-1		479	36
MAPES-2		484	41
MAPES-3		481	38
MAPES-4		473	31
MAPES-5		471	30
MAPES-6		470	29

a: 10 % Weight loss on TGA thermograms at a heating rate of 10 ^{o}C/min under nitrogen atmosphere, b: Char yield was measured at 800 ^{o}C, The net result of these structural modifications resulted into functional aromatic polyesters with excellent thermal properties, making them well suited for industrial applications where structurally rigid materials are required.

5a.3.6 Post-modification of polyester bearing pendant maleimide groups *via* thiol-maleimide click reaction

The post-modification of maleimide containing polyester was demonstrated *via* thiol-maleimide Michael type addition reactions with two different thiol-containing compounds, namely 4-chlorothiophenol (CTP) and 1-adamantanethiol (ADM). These thiols were chosen as representative examples for post-modification. Polyester MAPES-1 was post-functionalized with 2 equivalents of both the thiols *via* nucleophilic thiol-maleimide Michael addition click reaction catalyzed by Et_3N in dry dichloromethane at room temperature for 24 h **(Scheme 5a.3)**.



Scheme 5a.3. Click reaction of polyester MAPES-1 with 1-adamantanethiol and 4-chlorothiophenol.

^{1}H NMR spectrum of polyester obtained after chemical modification with 4-chlorothiophenol is illustrated in **Figure 5a.15**. ^{1}H NMR spectrum (**Figure 5a.15**) revealed complete disappearance of maleimide signal at 6.54 δ ppm, indicating complete conversion of these pendant groups. The proton signals corresponding to the succinimide ring were clearly observed, which is an indication the success of post-polymerization modification. Likewise, disappearance of maleimide proton signals and appearance of expected protons signals were also observed for Michael addition reaction of polyester bearing pendant maleimide groups with 1-adamantanethiol. Furthermore, no evidence of chain degradation was observed by GPC analysis (**Figure 5a.16**).

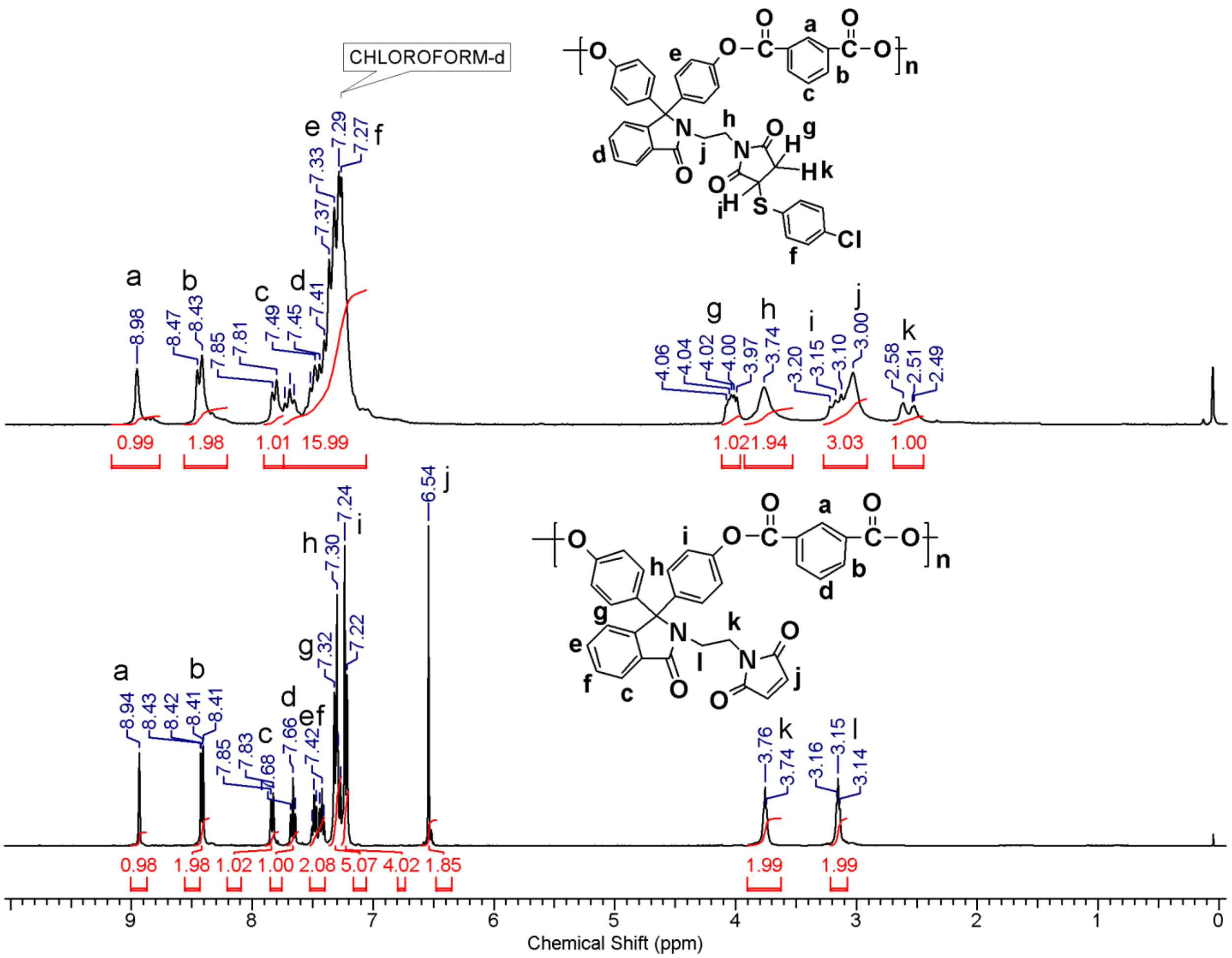


Figure 5a.15. ^{1}H NMR spectra (in $CDCl_3$) of polyester (MAPES-1) before (bottom) and after (top) thiol-maleimide Michael addition click reaction.

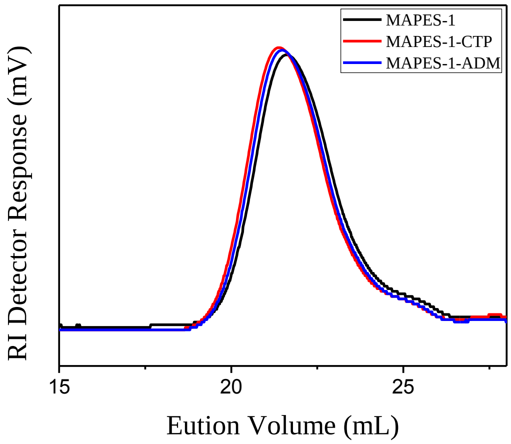


Figure 5a.16. GPC traces of MAPES-1, MAPES-1-CTP and MAPES-1-ADM.

5a.3.7 Gelation

Motivated by the success of post-polymerization modification, it was envisioned that thiol-maleimide reaction could be potentially utilized to cross-link maleimide bearing polymers to form network structure. To demonstrate this, tetrafunctional thiol *viz.*, pentaerythritol tetra(3-mercaptopropionate) was selected to perform cross-linking reaction with MAPES-1 in the presence of triethylamine as a base at room temperature. As depicted in **Figure 5a.17**, the gel was formed within few seconds under mild reaction condition using a molar ratio of maleimide to thiol of 1:1.

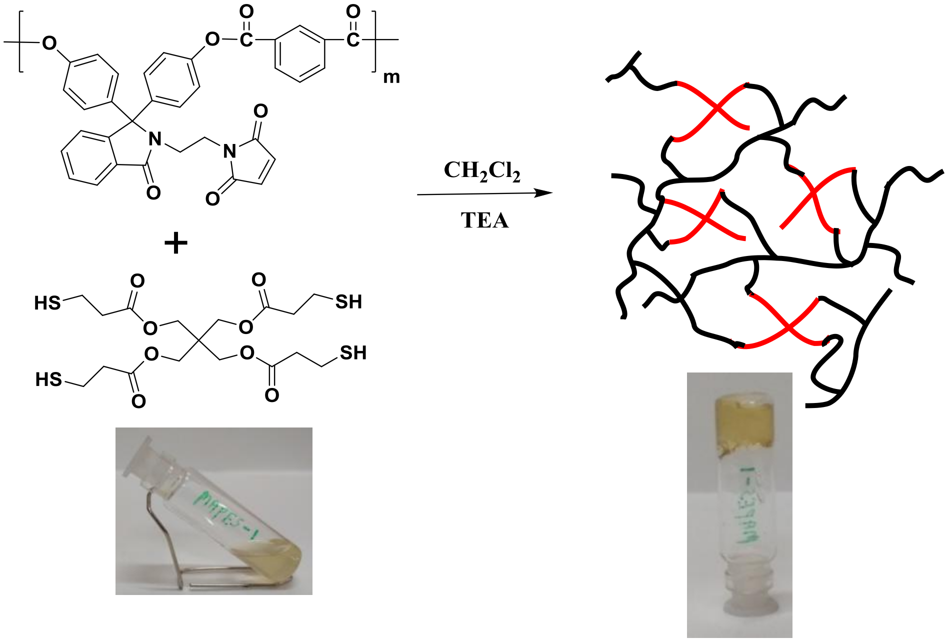


Figure 5a.17. Gel formation by cross-linking of MAPES-1 with pentaerythritol tetra(3-mercaptopropionate) *via* thiol-maleimide reaction.

5a.4 Conclusions

A new maleimide functionalized bisphenol *viz.,* N-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-MA) was successfully synthesized starting from commercially available phenolphthalein. A series of aromatic (co)polyesters containing pendant clickable maleimide groups was synthesized by low temperature solution polycondensation of PPH-MA and varying mixtures of PPH-MA and BPA with aromatic diacid chlorides. Inherent viscosities and number-average molecular weights of (co)polyesters containing pendant maleimide groups were in the range 0.52-0.97 dL/g and 20,200–32,800 g/mol, respectively. **(**Co)polyesters were soluble in chloroform, dichloromethane, THF, DMAc and DMF at room temperature. Tough, transparent and flexible films could be cast from solutions of (co)polyesters in chloroform. X-Ray diffractograms showed that polyesters containing pendant maleimide groups were amorphous in nature. Temperature of 10 % weight loss (T_{10}) for (co)polyesters were in the range 470-484 °C indicating their good thermal stability. Subsequently, the thiol-maleimide Michel reaction was employed to modify aromatic polyester by reaction of their pendant maleimide groups with 4-chlorothiophenol and 1-adamantanethiol. The quantitative conversion occurred without noticeable backbone degradation as confirmed by ^{1}H NMR spectroscopy and GPC, respectively. It was demonstrated that gel could be readily fabricated *via* thiol-maleimide click reaction from maleimide functionalized polyester MAPES-1 and pentaerythritol tetra(3-mercaptopropionate) as the multifunctional cross-linker.

5a.5 References

1. Olabisi, O. Handbook of thermoplastics, Marcel Dekker, 1997.
2. Margolis, J. M. Engineering thermoplastics : properties and applications, Dekker, 1985.
3. Gimeno, N., Martín-Rapún, R., Rodríguez-Conde, S., Serrano, J. L., Folcia, C. L., Pericás, M. A., Ros, M. B. *J. Mater. Chem.*, 2012, **22**, 16791–16800.
4. Zhang, P., Wu, L. B., Li, B. G. *Adv. Mater. Res.*, 2011, **239**–**242**, 2616–2619.
5. Tae-Dong, K., Hyun-Min, B., Kwang-Sup, L. *Bull. Korean Chem. Soc.*, 2002, **23**, 1031–1034.
6. Liu, J., Wang, L., Zhen, Z., Liu, X. *Colloid Polym. Sci.*, 2012, **290**, 1215–1220.
7. Bian, X.-C., Chen, L., Wang, J.-S., Wang, Y.-Z. *J. Polym. Sci. Part A Polym. Chem.*, 2010, **48**, 1182–1189.
8. Peng, C., Wu, J., Liu, J., Qiu, L., Liu, X., Bo, S., Zhen, Z. *Polym. Chem.*, 2013, **4**, 2703.
9. Ma, X., Niu, H., Cai, W., Xiao, T., Wang, C., Bai, X., Zhang, Y., Wang, W. *React. Funct. Polym.*, 2016, **108**, 63–70.
10. Honkhambe, P. N., Bhairamadgi, N. S., Biyani, M. V., Wadgaonkar, P. P., Salunkhe, M. M. *Eur. Polym. J.*, 2010, **46**, 709–718.
11. Choudhary, U., Mir, A. A., Emrick, T. *Macromolecules*, 2017, **50**, 3772–3778.
12. Dong, X., Chen, L., Duan, R.-T., Wang, Y.-Z. *Polym. Chem.*, 2016, **7**, 2698–2708.
13. Korshak, V. V., Vinogradova, S. V., Salazkin, S. N., Komarova, L. I. *Eur. Polym. J.*, 1974, **10**, 967–973.

14. Hsiao, S.-H., Chang, H.-Y. *J. Polym. Res.*, 1995, **2**, 99–108.
15. Yu, Y., Cai, M., Wang, T. *Mod. Appl. Sci.*, 2009, **3**.
16. Kumari, S. Ph.D. Thesis, Savitribai Phule Pune University, India, 2013.
17. Gerard, A. D., Urbain, L. L. *US Patent 3345171A*, 1967.
18. Choudhary, U., Mir, A. A., Emrick, T. *Macromolecules*, 2017, **50**, 3772–3778.
19. Serna, F. J., de Abajo, J., de la Campa, J. G. *Br. Polym. J.*, 1987, **19**, 453–458.
20. Preston, J. Interfacial Synthesis. Volume 2: Polymer Applications and Technology, California, 1977.
21. Kricheldorf, H. R. Handbook of polymer synthesis, CRC Press, 1991.
22. Jeong, H.-J., Iwasaki, K., Kakimoto, M., Imai, Y. *Polym. J.*, 1994, **26**, 379–385.
23. Morgan, P. W. *J. Polym. Sci. Part A*, 1964, **2**, 437–459.
24. Morgan, P. W. Condensation Polymers by Interfacial and Solution Methods, Ed., Interscience, 1965.
25. Barradas, R. G., Fletcher, S., Porter, J. D. *Can. J. Chem.*, 1976, **54**, 1400–1404.
26. Matsui, S., Aida, H. *J. Chem. Soc. Perkin Trans. 2*, 1978, **0**, 1277–1280.
27. Khan, M. N. *J. Pharm. Sci.*, 1984, **73**, 1767–1771.
28. Gaina, C., Gaina, V., Ciobanu, C. *J. Appl. Polym. Sci.*, 2009, **113**, 3245–3254.
29. Jin, S., Yee, A. F. *J. Appl. Polym. Sci.*, 1991, **43**, 1865–1874.
30. Vibhute, S. S., Joshi, M. D., Wadgaonkar, P. P., Patil, A. S., Maldar, N. N. *J. Polym. Sci. Part A Polym. Chem.*, 1997, **35**, 3227–3234.

Chapter-5b

(Co)polycarbonates Containing Pendant Maleimide Groups: Synthesis, Characterization and Chemical Modifications

5b.1 Introduction

In the endeavour of scientific community to fulfill the demands of functional polymers which are required to meet the benchmark set by modern society, researchers have been continuously proposing new macromolecular architectures. Due to their envisioned uses in different applications, polymers bearing pendant reactive functional groups along the main chain have attracted a great deal of attention.[1–4] The prominent methods for incorporation of reactive functional groups and thereby altering the polymer properties include: post-polymerization functionalization[5,6] and (co)polymerization of functional monomers.[7–11] Of these strategies, (co)polymerization of functional monomers offers a straightforward pathway to incorporate functional groups which allow desired polymer compositions and structures provided suitable monomers are available.[12,13] However, for incorporation of reactive functional groups such as hydroxyl,[12,14–16] amine,[17–19] carboxyl,[20–23] thiol, etc, tedious protection and post-polymerization deprotection methods need to be followed which sometimes involve use of heavy metal catalysts and eventually give low yields of functional polymers. The possibility of degradation of polymer backbone under aggressive reaction conditions also poses additional limitation for synthesis of well defined reactive functional polymers.

The monomers bearing pendant reactive functional group(s) which are orthogonal to polymerization reaction conditions while offering possibilities for post-polymerization functionalization without cumbersome protection/deprotection steps are highly desirable. To date, a range of ROP monomers and diols bearing pendant clickable functional groups e.g. allyl,[3,24–29] azido,[5,30,31] alkyne,[32–36] norbornene,[37,38] maleimide,[39–41] furyl,[42] anthryl[43] and active ester[44,45] have been reported for synthesis of aliphatic polycarbonates. With a notable exception of allyl functional groups, aromatic polycarbonates bearing pendant clickable groups have not been studied.[46–48]

In the present work, aromatic polycarbonates bearing pendant maleimide groups that could conveniently be post-functionalized by thiol-maleimide Michael type addition click reaction were targeted. Towards this end, a new bisphenol containing pendant maleimide group, namely, 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) was synthesized starting from 4, 4’-(5- azidopentane-2, 2-diyl) diphenol. Aromatic polycarbonate and copolycarbonates containing pendant maleimide groups were prepared, respectively, by solution polycondensation of BPA-MA or mixtures of varying ratios of BPA-MA and BPA with triphosgene. (Co)polycarbonates were characterized by inherent viscosity measurements, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Furthermore, post-polymerization modification of aromatic copolycarbonate containing pendant maleimide groups was demonstrated with two representative thiols. It was additionally demonstrated that herein synthesized polycarbonates can be used to form insoluble cross-linked gel in the presence of multi functional thiol cross-linker.

5b.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC and XRD are given in **Chapter 2**.

5b.2.1 Synthesis of bisphenol bearing pendant maleimide group

5b.2.1.1 Synthesis of 4, 4'-(5-aminopentane-2, 2-diyl) diphenol

Into a high-pressure glass reactor were added 4, 4'-(5-azidopentane-2, 2-diyl) diphenol (5.0 g, 16.83 mmol) and methanol (50 ml). 10 wt % Pd/C (0.5 g) was added into the reaction mixture and the hydrogenation reaction was carried out under H_2 pressure (60 psi) with shaking for 5 h. The reaction mixture was passed through Celite and the filtrate was concentrated in vacuum to obtain an off white solid. The crude product was recrystallized from a mixture of ethanol and water (1:1, v/v).

Yield: 4.50 g (82 %); Melting point- 164 ^{o}C; ^{1}H NMR (400 MHz, Methanol-d$_4$, δ/ppm): 7.04 (d, 4H), 6.70 (d, 4H), 2.60 (t, 2H), 2.06 (t, 2H), 1.57 (s, 3H), 127-1.38 (m, 2H); ^{13}C NMR (50 MHz, Methanol-d$_4$, δ/ppm): 156.1, 140.9, 129.1, 115.6, 44.2, 42.6, 40.5, 30.7, 28.2; HRMS ESI$^+$: $(M+Na)^+$m/z calculated for $C_{17}H_{21}NO_2Na$: 294.1470, found: 294.1462.

5b.2.1.2 Synthesis of 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol

Into a 500 mL two necked round bottom flask equipped with a mechanical stirrer, a gas inlet and a reflux condenser were placed 4, 4'-(5-aminopentane-2, 2-diyl) diphenol (6.0 g, 22.11 mmol), maleic anhydride (4.34 g, 44.22 mmol) and glacial acetic acid (200 mL). The reaction mixture was stirred at 120 ^{o}C for 12 h. The reaction mixture was cooled to room temperature and slowly poured into an ice cold-water. The solid product was collected by filtration. The product was dissolved in ethyl acetate (100 mL) and the ethyl acetate solution was washed with water (3 x

100 mL). The ethyl acetate solution was dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed by evaporation under reduced pressure. The crude product was purified by column chromatography using pet ether:ethyl acetate (70:30, v/v) as an eluent to afford 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol as a white powder.

Yield: 3.20 g (69 %); Melting point- 176 ^{o}C; IR (KBr): 3311, 1698, 1369, 1147, 692 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d$_6$, δ/ppm): 8.11 (s, 2H), 7.0 (d, 4H), 6.82 (s, 2 H), 6.73 (d, 4H), 3.45 (t, 2H), 2.07-2.03 (t, 2H), 1.53 (s, 3H), 1.40-1.36 (m, 2H); ^{13}C NMR (50 MHz, Acetone-d$_6$, δ/ppm): 171.7, 156.0, 141.5, 135.1, 129.0, 115.5, 45.2, 39.8, 38.7, 28.2, 25.1; HRMS ESI$^+$: (M+Na)$^+$m/z calculated for $C_{21}H_{21}NO_4Na$: 374.1363, found: 374.1361.

5b.2.2 Synthesis of (co)polycarbonates bearing pendant maleimide groups

Into a 100 mL three necked round bottom flask equipped with a nitrogen balloon, an addition funnel, and a magnetic stirrer were charged BPA-MA (1.0 g, 2.84 mmol) and dry dichloromethane (6 mL). The reaction mixture was cooled to 0 ^{o}C and the solution of triethylamine (1.19 mL, 8.53 mmol) in dry dichloromethane (3 mL) was added dropwise over a period of 10 min. To the reaction mixture, the solution of triphosgene (0.36 mg, 1.19 mmol) in dichloromethane (3 mL) was added dropwise and stirred at 0 ^{o}C for 15 min. The reaction mixture was allowed to warm to 25 ^{o}C and stirring was continued at that temperature for 4 h. The reaction mixture was neutralized with aqueous hydrochloric acid (2 M) and was extracted with dichloromethane (2 × 100 mL). The dichloromethane solution was washed with water (2 × 100 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure at 30 ^{o}C. The concentrated polymer solution was poured into methanol (1000 mL) and the precipitated polymer was filtered and washed with methanol. The polymer was dissolved in dichloromethane (10 mL) and reprecipitated into methanol (1000 mL), filtered and dried at 50 ^{o}C under reduced pressure for 12 h.

5b.2.3 Post-modification of polycarbonate bearing pendant maleimide groups with 4-chlorothiophenol

To a Schlenk tube equipped with a magnetic stirring bar were added PCMA-2 (0.10 g, 0.32 mmol), 4-chlorothiophenol (0.092 g, 0.63 mmol), triethylamine (88.10 μL, 0.63 mmol) and dry dichloromethane (5 mL). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 24 h. The resultant polymer was purified by precipitation into methanol to remove triethylamine and the excess 4-chlorothiophenol. The functionalized copolycarbonate was isolated by filtration and dried at room temperature under reduced pressure for 8 h.

A similar procedure was followed for synthesis of other post-functionalized polycarbonate.

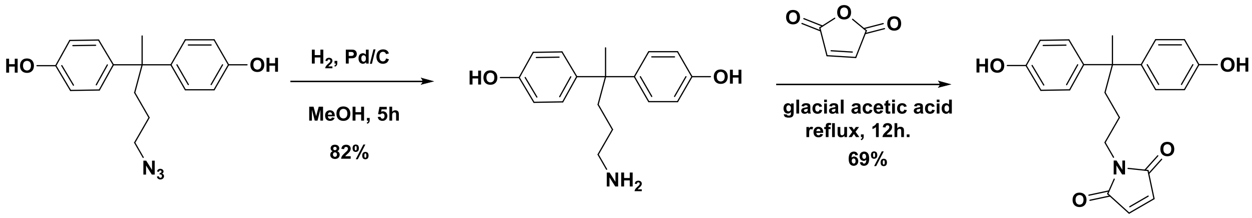
5b.2.4 Preparation of cross-linked polycarbonate gel

Into a sample vial were taken polycarbonate containing pendant maleimide groups PCMA-1 (100 mg) and chloroform (1 mL). To the solution was added, a stoichiometric amount of pentaerythritol tetra(3-mercaptopropionate) (maleimide/thiol mol ratio = 1) and triethylamine (25.31 μL) at room temperature. The free standing gel material was obtained within few seconds.

5b.3 Results and discussion

5b.3.1 Monomer synthesis

A new bisphenol containing pendant maleimide group *viz.*, 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) was obtained from 4, 4'-(5- azidopentane-2, 2-diyl) diphenol (synthesized in **Chapter-3**) and the synthetic route is illustrated in **Scheme 5b.1**.



Scheme 5b.1. Synthesis of 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol.

In the first step, the reduction of azido group in 4, 4'-(5 - azidopentane-2, 2- diyl) diphenol to obtain 4, 4'-(5-aminopentane-2, 2-diyl) diphenol was carried out using H_2 in the presence of 10% Pd/C as the catalyst in methanol as a solvent. In the second step, maleic anhydride was reacted with 4, 4'-(5-aminopentane-2, 2-diyl) diphenol in acetic acid to afford BPA-MA. The bisphenol containing pendant maleimide group is stable at least upto a year when stored in a refrigerator under dark conditions. The chemical structure of BPA-MA was confirmed by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

IR spectrum of BPA-MA is displayed in **Figure 5b.1**. The phenolic-OH band was observed at 3311 cm^{-1}. The characteristic bands of maleimide group were observed at 1698 cm^{-1} (C=O of maleimide), 1369, 1147 (C–N–C of maleimide), and 692 cm-1 (C=C of maleimide).

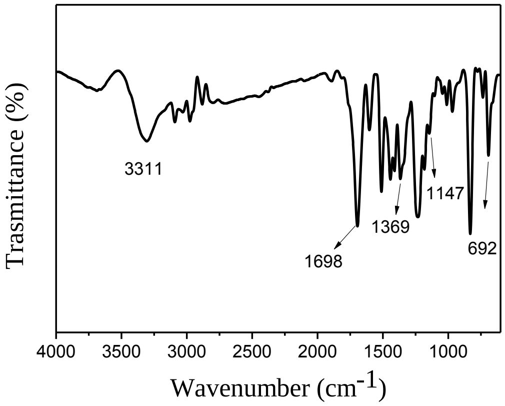


Figure 5b.1. IR spectrum of 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol.

^{1}H NMR spectrum of the BPA-MA is illustrated in **Figure 5b.2.** The phenolic -OH group appeared as a singlet at 8.11 δ ppm and four aromatic protons *meta* to phenolic -OH group appeared as a doublet at 7.0 δ ppm. The four aromatic protons *ortho* to phenolic -OH group appeared as a doublet at 6.73 δ ppm. The characteristic peak of vinyl protons “c” of maleimide appeared as a singlet at 6.82 δ ppm. Methylene protons “e” and “f” appeared as separate triplets at 3.45 δ ppm and 2.04 δ ppm, respectively. Methyl protons “g” appeared as a singlet at 1.53 δ ppm. Methylene protons “h” showed a multiplet over the range 1.36-140 δ ppm.

^{13}C NMR spectrum of BPA-MA along with assignments is shown in **Figure 5b.3**.

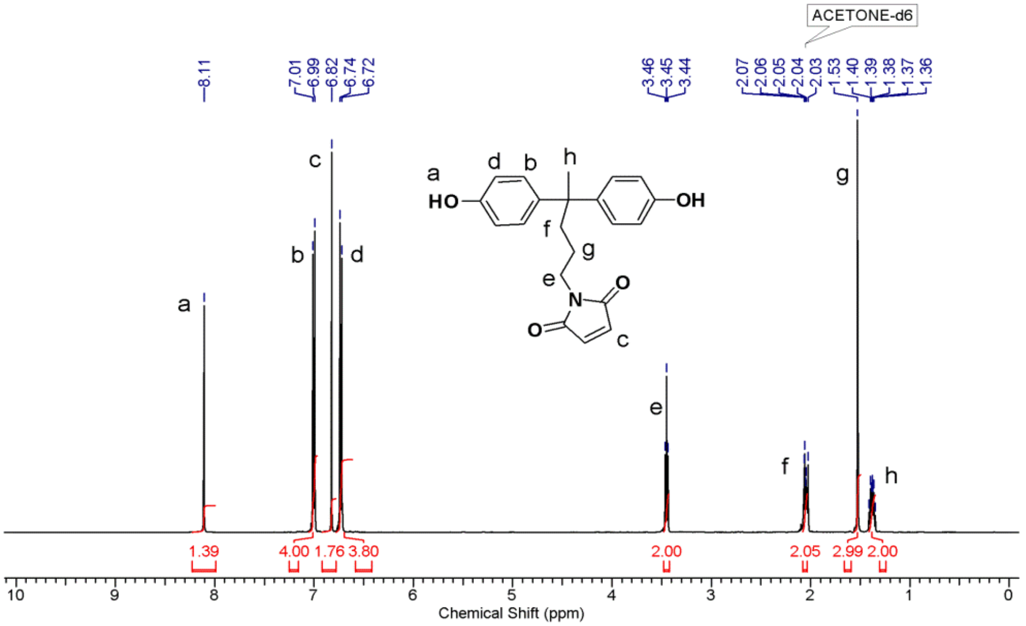


Figure 5b.2. ^{1}H NMR spectrum (in Acetone-d6) of 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol.

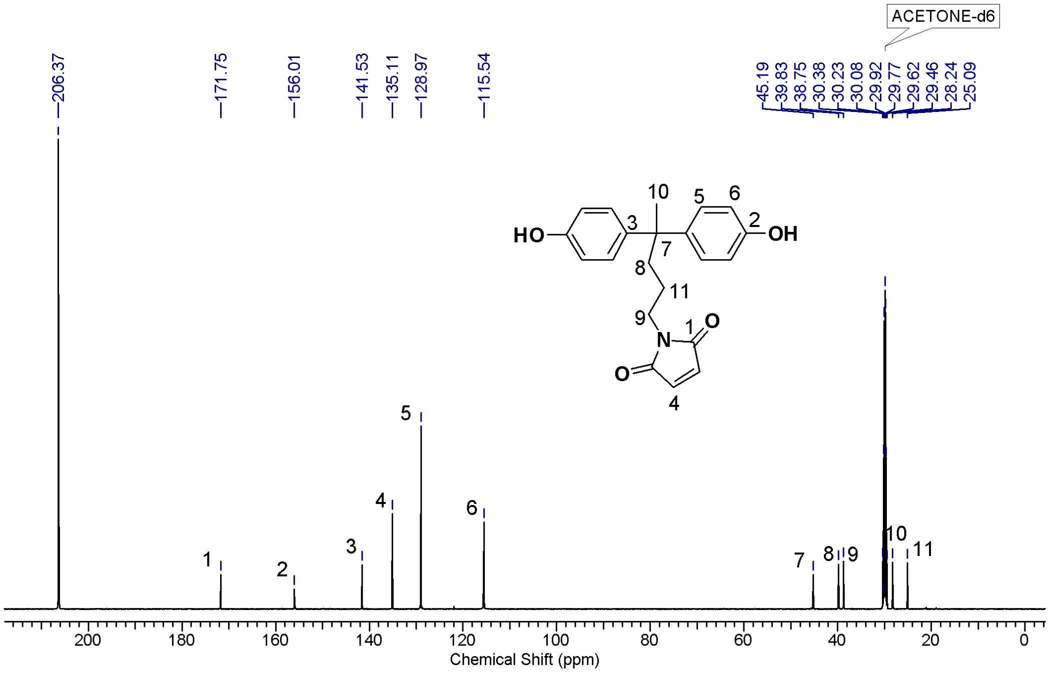


Figure 5b.3. ^{13}C NMR spectrum (in Acetone-d6) of 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol.

In HR-MS analysis (**Figure 5b.4**), the peak appeared at 374.1361 corresponding to ($[M+Na]^+$) of BPA-MA (cald. $[M+Na]^+$ for $C_{21}H_{21}NO_4Na$ =374.1363).

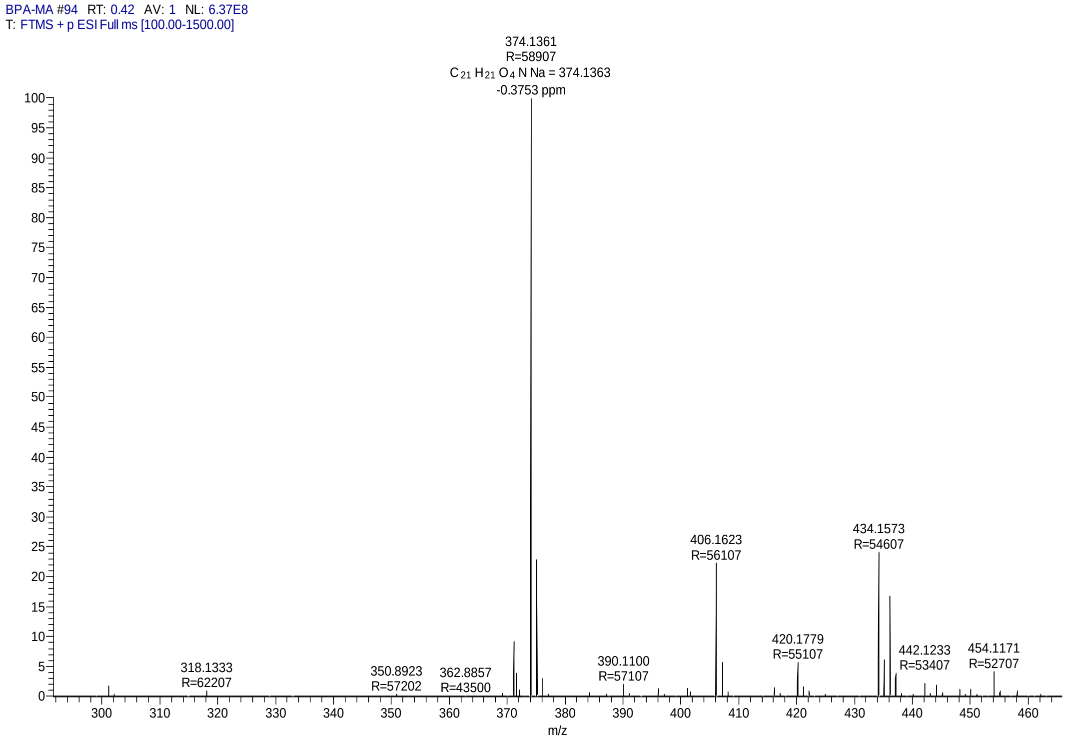
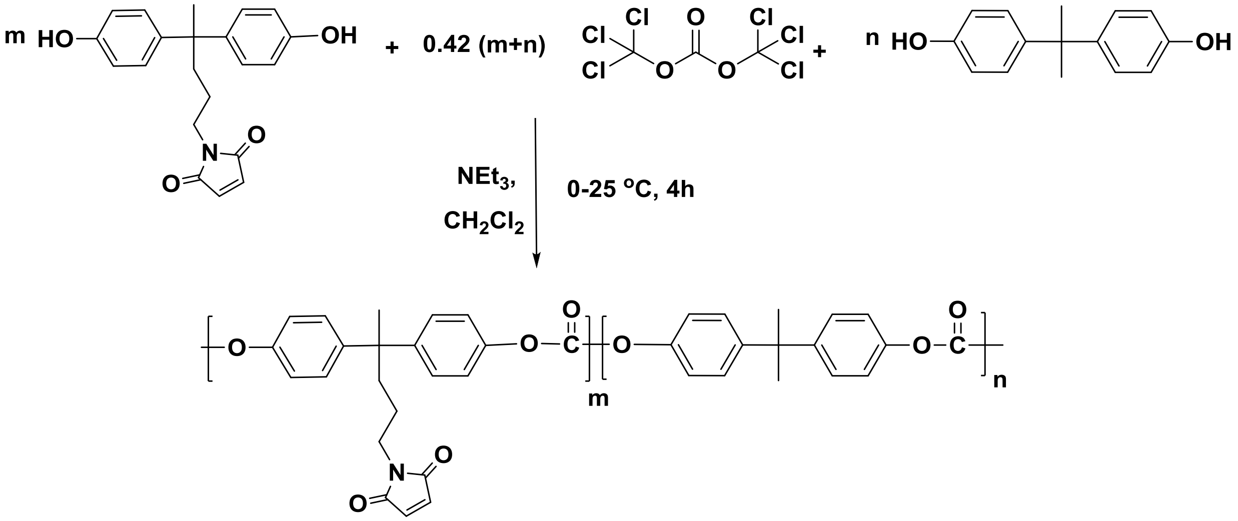


Figure 5b.4. HRMS of 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol.

5b.3.2 Synthesis of (co)polycarbonates bearing pendant maleimide groups

A series of aromatic (co)polycarbonates bearing pendant maleimide groups was synthesized by low-temperature solution polycondensation of BPA-MA or different molar ratios of BPA-MA and BPA with triphosgene **(Scheme 5b.2)**.



Scheme 5b.2. Synthesis of (co)polycarbonates bearing pendant maleimide groups.

(Caution: Special precaution should be taken while working with triphosgene. It is highly toxic by inhalation and ingestion; use of appropriate personal protective equipment is strongly recommended.) End capping agent was not used in polycarbonate synthesis. The molar stoichiometry of bisphenol:triphosgene employed was 1:0.42 which was based on the work of Boyles et al. who demonstrated the formation of high molecular weight polycarbonates under such stoichiometric conditions.[49] At the end of polymerization reactions, polycarbonates were isolated by precipitation in methanol and were purified by re-precipitation into excess methanol from chloroform solution. The polymerization using maleimide functional bisphenol was a clean reaction without any side reactions such as hydrolysis or cross-linking, yielding reasonably high molecular weight polycarbonates. The results of synthesis of (co)polycarbonates are summarized in **Table 5b.1**. Inherent viscosity (η_{inh}) values of (co)polycarbonates were in the range 0.46-0.66 dL/g and number average molecular weights ($\overline{M_n}$) of (co)polycarbonates were in the range 24,600 to 36,700 g/mol, which indicated that medium to reasonably high molecular weight polymers were obtained. The dispersity values were in the range 2.1-2.4, which is consistent with the results of a typical step growth polymerization.

Table 5b.1. Molar composition, inherent viscosity and molecular weight of (co)polycarbonates

(Co)polycarbonate	BPA-MA mol %	BPA mol %	η_{inh} [a] dL/g [a]	Molecular weight [b] $\overline{M_n}$	$\overline{M_w}$	Dispersity
PCMA-1	100	00	0.46	24,600	55,300	2.2
PCMA-2	50	50	0.54	25,100	60,400	2.4
PCMA-3	30	70	0.49	24,800	52,500	2.1
PCMA-4	10	90	0.59	32,400	69,000	2.1
PC-BPA	00	100	0.66	36,700	79,800	2.2

a: η_{inh} was measured with 0.5% (w/v) solution of (co)polycarbonate in chloroform at 30 ± 0.1 °C, b: Measured by GPC in chloroform using polystyrene as calibration standard.

Polycarbonates could be cast into transparent, tough and flexible films by casting from solution of polycarbonate in chloroform. Representative film of polycarbonate PCMA-1 is shown in **Figure 5b.5**.

Figure 5b.5. Film of polycarbonate PCMA-1.

5b.3.3 Structural characterization

The analysis data obtained from IR, ^{1}H NMR and ^{13}C NMR spectroscopy was used to support the formation of (co)polycarbonates. IR spectrum of representative aromatic polycarbonate PCMA-1 **(Figure 5b.6)** exhibited characteristic carbonyl absorption band of carbonate group at 1770 cm^{-1} and carbonyl absorption band of maleimide group appeared at 1703 cm^{-1}. The absorption bands at 1409, 1161, and 694 cm^{-1} correspond to maleimide group.

^{1}H NMR spectrum **(Figure 5b.7)** confirmed the expected structure of PCMA-1 primarily displaying the characteristic signals of maleimide functional groups as a singlet at 6.66 δ ppm. The singlet appeared at 7.17 δ ppm corresponds to aromatic protons labeled as "a". The methyl protons were observed as a singlet, representing three protons at 1.60 δ ppm. The signal of methylene protons "c" adjacent to maleimide group appeared as a triplet at 3.49 δ ppm. The methylene protons of pendant alkyl chain marked as "d" and "f" appeared at 2.08 and 1.40 δ ppm, respectively.

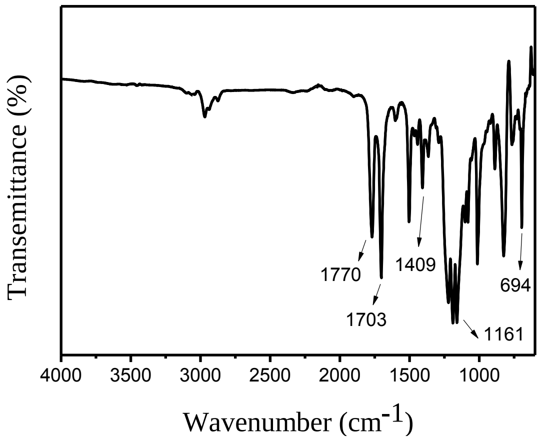


Figure 5b.6. IR spectrum of polycarbonate PCMA-1.

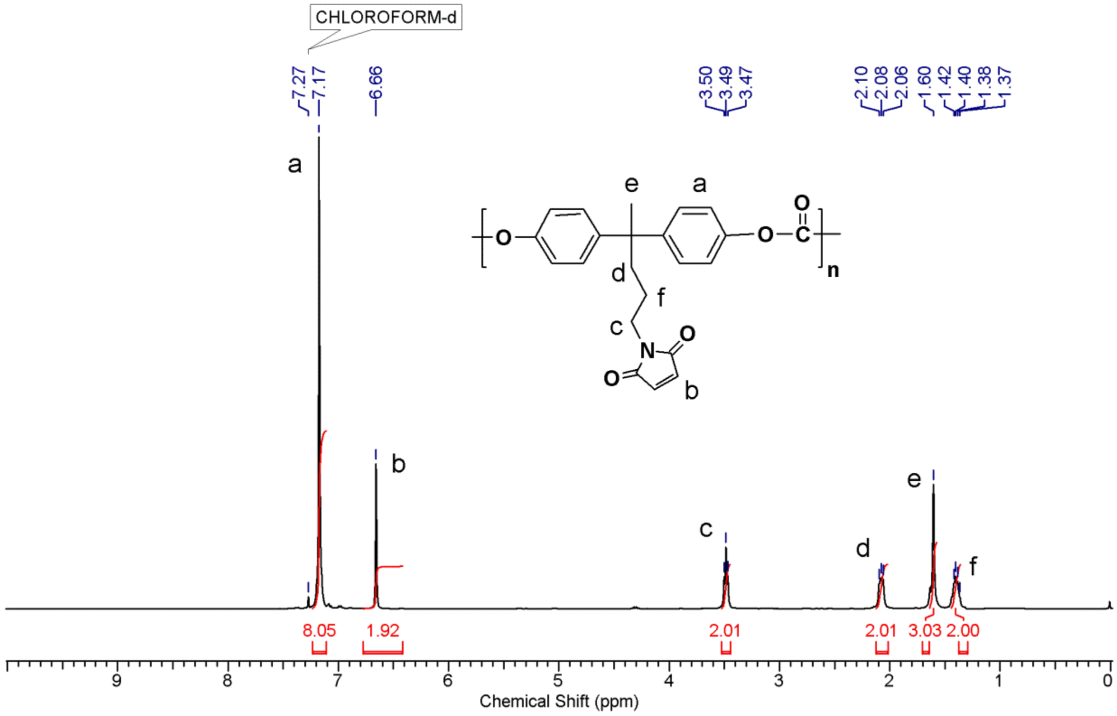


Figure 5b.7. ^{1}H NMR spectrum (in $CDCl_3$) of polycarbonate PCMA-1.

^{13}C NMR spectrum **(Figure 5b.8)** revealed a signal at 170.7 δ ppm corresponding to maleimide carbonyl as well as signal at 151.9 δ ppm reflecting the carbonyl carbon of carbonate linkage of polycarbonate. Assignment of remaining carbon atom is also depicted in **Figure 5b.8** and this spectrum agreed well with the proposed molecular structure of polycarbonate.

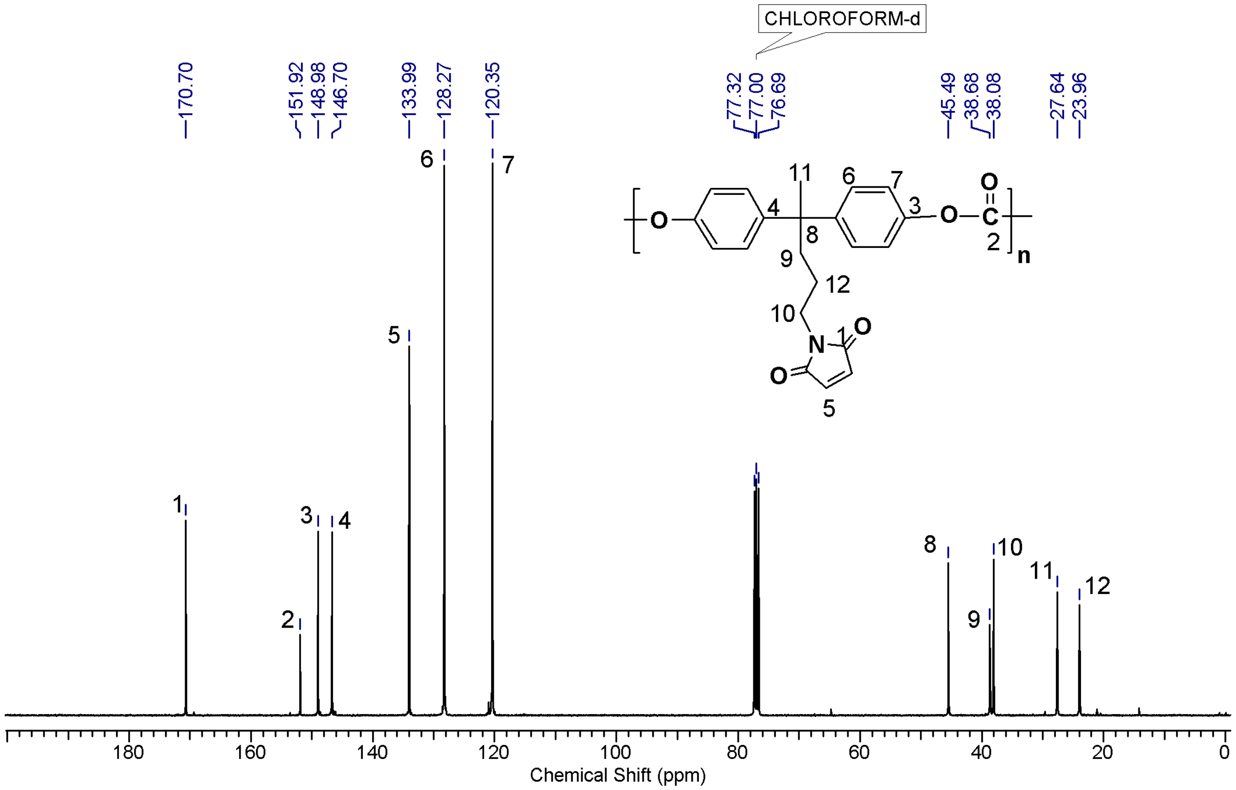


Figure 5b.8. ^{13}C NMR spectrum (in $CDCl_3$) of polycarbonate PCMA-1.

^{1}H NMR spectra of copolycarbonates in $CDCl_3$ are displayed in **Figure 5b.9**. ^{1}H NMR spectroscopy provided an easy method for determination of ratio of comonomers incorporated in the case of copolycarbonates. The relative integrated intensity ratio of signal appeared at 3.48 δ ppm, which corresponds to methylene protons adjacent to maleimide group, and that of signal appeared at 1.69 δ ppm corresponding to methyl protons of BPA units was used to determine molar ratio of BPA-MA and BPA. As reported in **Table 5b.2,** the experimental values determined from this relation were in excellent agreement with feed ratio of respective monomers used for polymerization reactions.

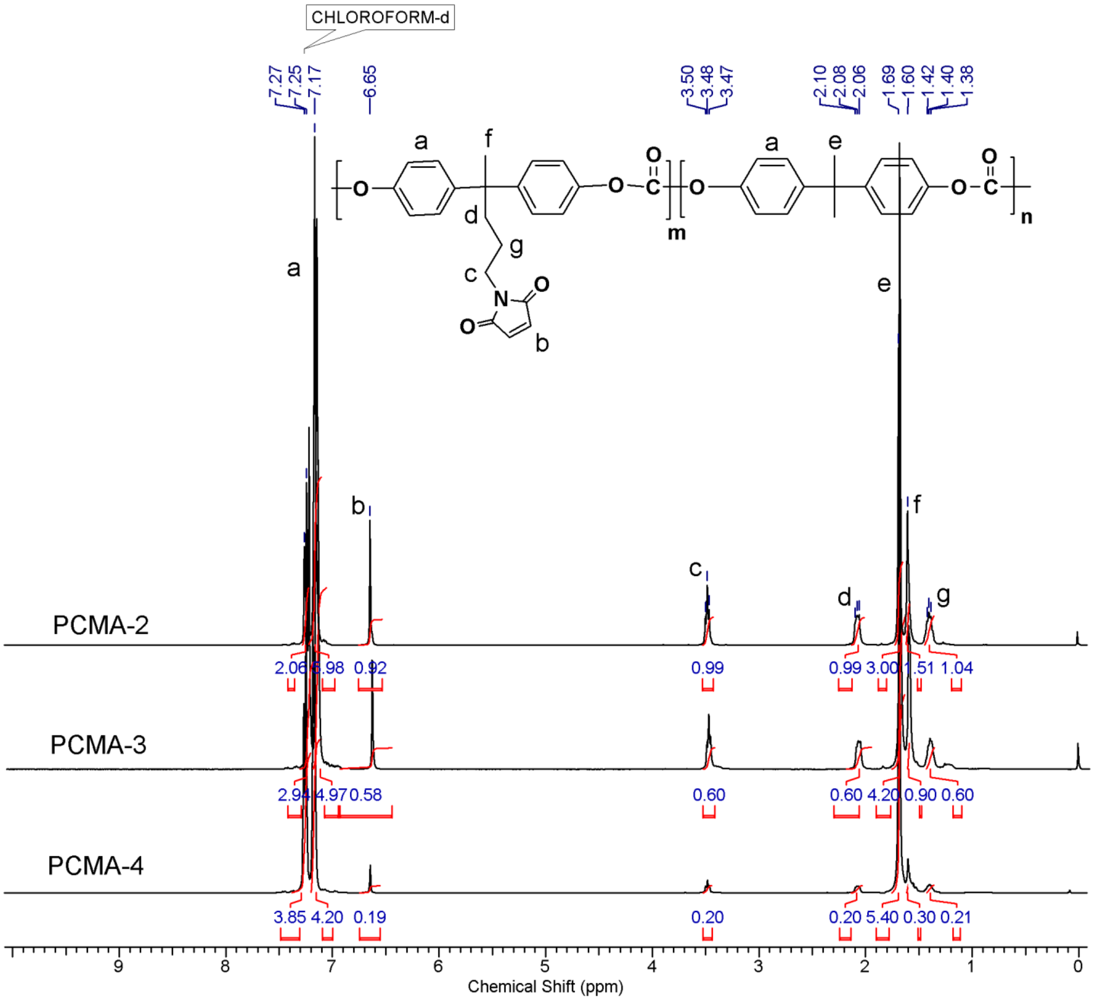
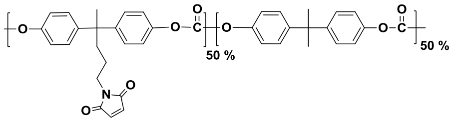
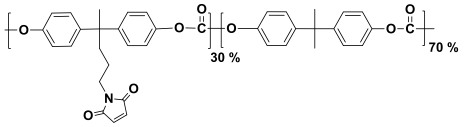
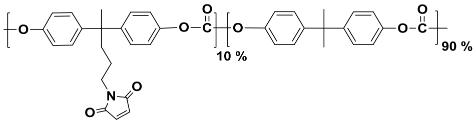


Figure 5b.9. ^{1}H NMR spectra of copolycarbonates.

Table 5b.2. Molar composition of copolycarbonates determined by ^{1}H NMR spectra

Copolycarbonate	**Structure of copolycarbonate**	**Feed BPA-MA, mol %**	**Observed BPA-MA, mol%**
PCMA-2		50	49.5
PCMA-3		30	30.0
PCMA-4		10	10

The microstructure of copolycarbonates derived from copolymerization of BPA and BPA-MA with triphosgene was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, the copolymerization of BPA and BPA-MA is expected to lead to formation of random copolymer with following possibilities of enchainment of the two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 5b.10**). ^{13}C NMR spectra of copolycarbonates showed clear evidence not only for the random copolycarbonate formation but also about the microstructural details as indicated by multiplicity of the signals.

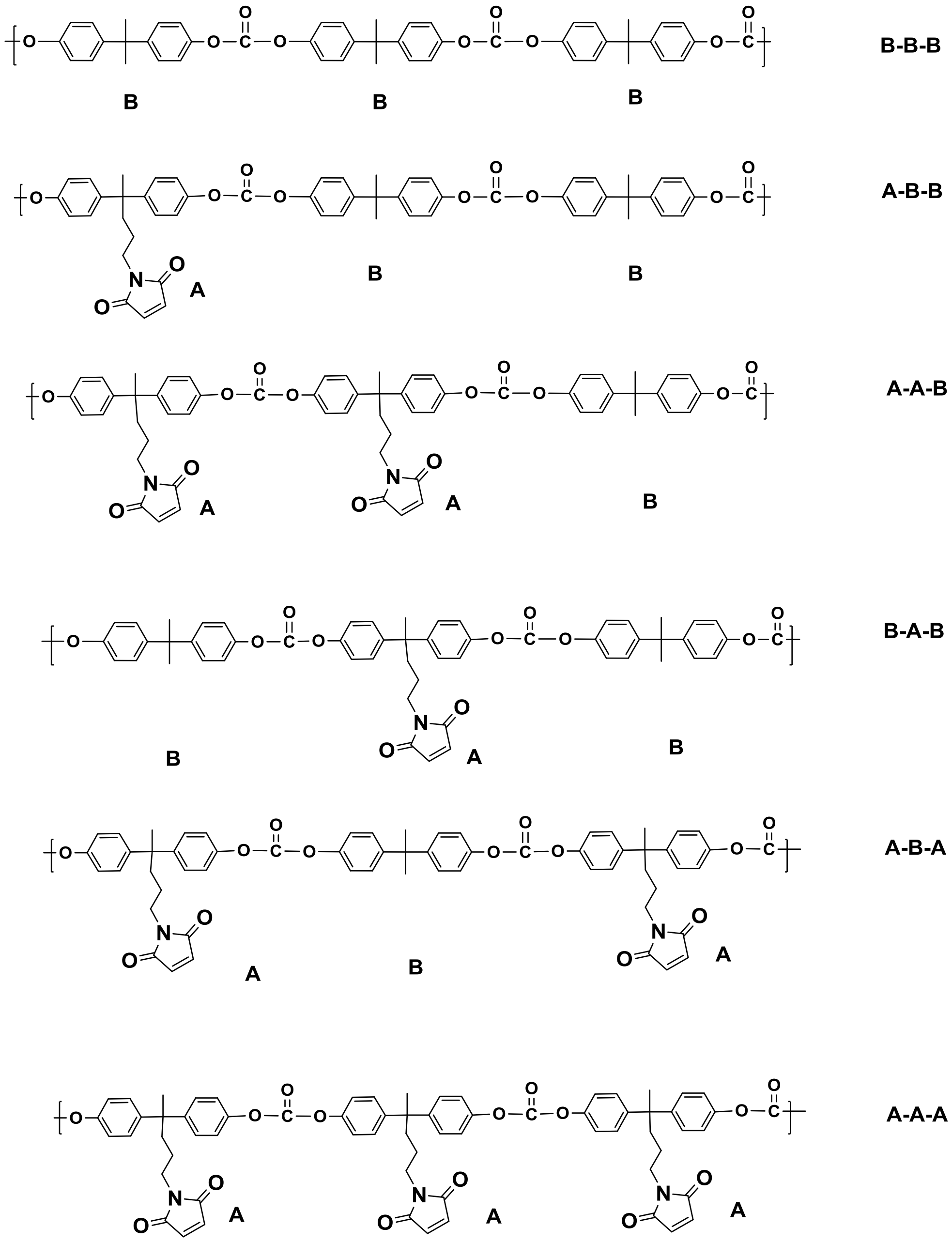


Figure 5b.10. Possible arrangements of BPA-MA and BPA units in copolycarbonates.

The assignments of carbon atoms in ^{13}C NMR spectrum of MAPC-2, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 5b.11.**

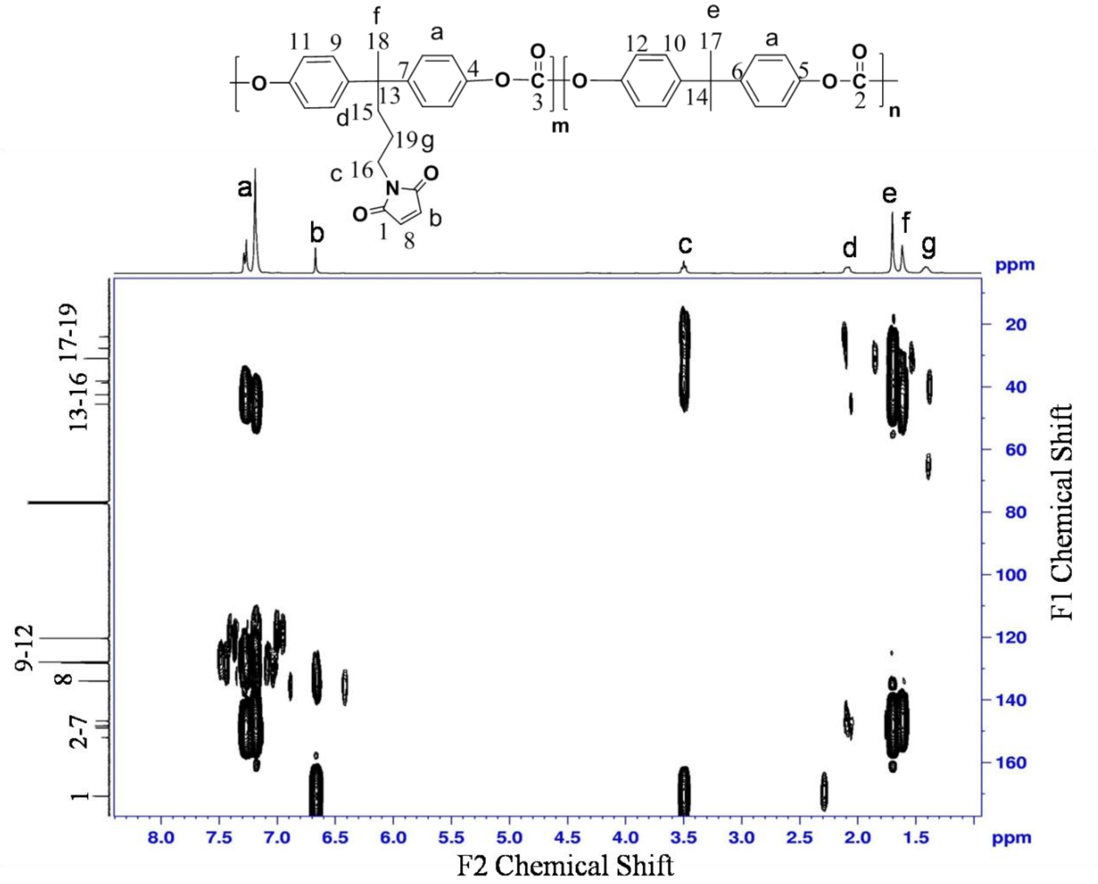


Figure 5b.11. HMBC spectrum (in CDCl$_3$) of MAPC-2.

^{13}C NMR spectrum of MAPC-2 (50:50 mol % of BPA-MA:BPA) along with assignments of carbon atoms is presented in **Figure 5b.12.** For easy comparison, ^{13}C NMR spectra of homo-polycarbonate MAPC-1 and copolycarbonates MAPC-2 to MAPC-4 are also included in **Figure 5b.12**. It is interesting to note that the carbonyl carbon of carbonate linkage exhibited three distinct peaks at 151.95 δ ppm, 152.03 δ ppm and 152.11 δ ppm for this particular copolycarbonate. A comparison of the spectrum of MAPC-2 with that of MAPC-1 and MAPC-4 inferred that carbonyl peaks appeared at 151.95 δ ppm and 152.11 δ ppm originated from AAA and BBB arrangement of co-monomer units, respectively in copolycarbonate while a peak at 152.03 δ ppm corresponds to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peak corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of PCMA-3 and PCMA-4.

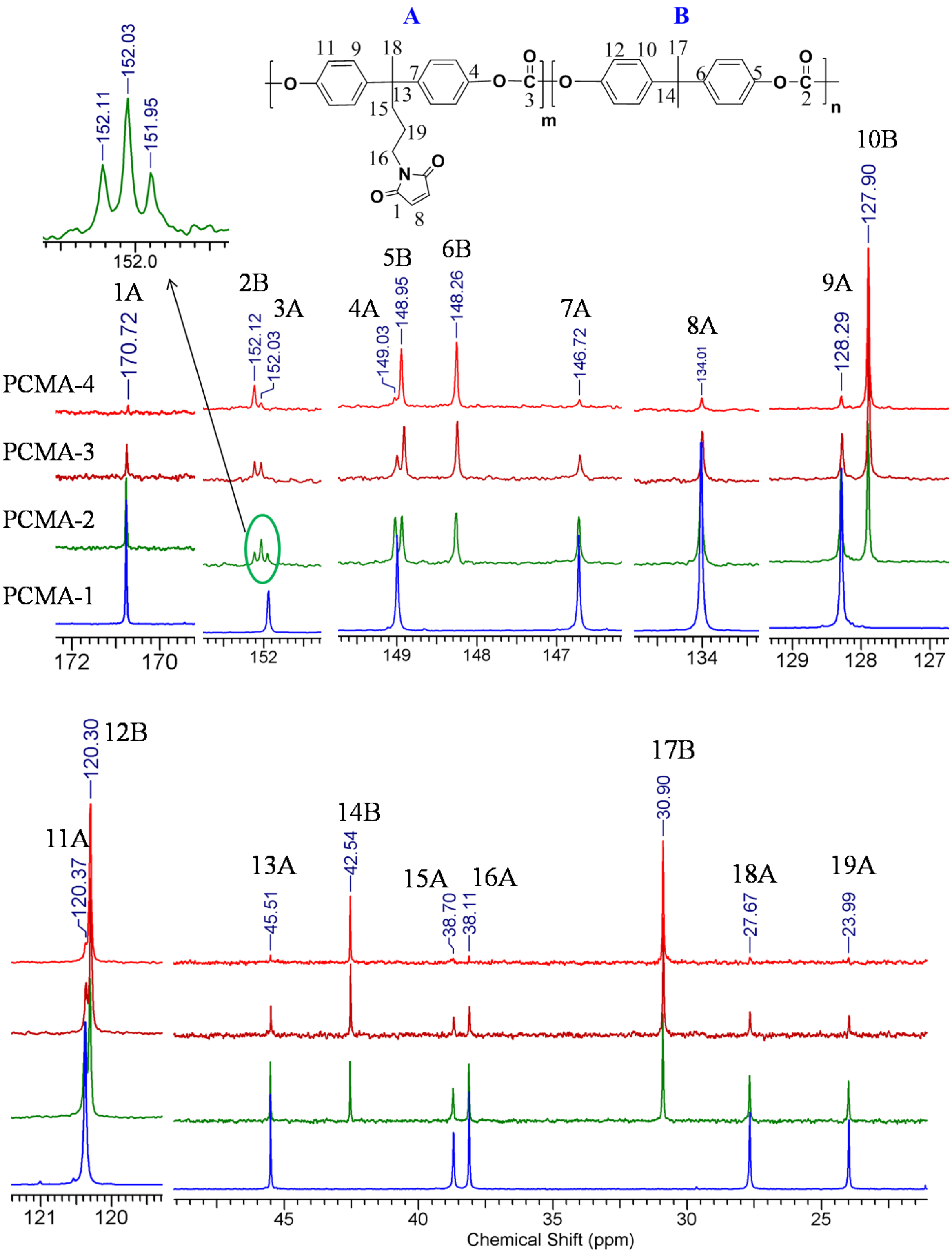


Figure 5b.12. ^{13}C NMR spectra of (co)polycarbonates.

5b.3.4 X-Ray diffraction studies

The crystallinity of aromatic (co)polycarbonates containing pendant maleimide groups was determined by wide-angle-X-ray diffraction (WAXD) studies (**Figure 5b.13)**. A broad halo at around 2θ = 10-30 °C indicated that (co)polycarbonates are amorphous in nature.

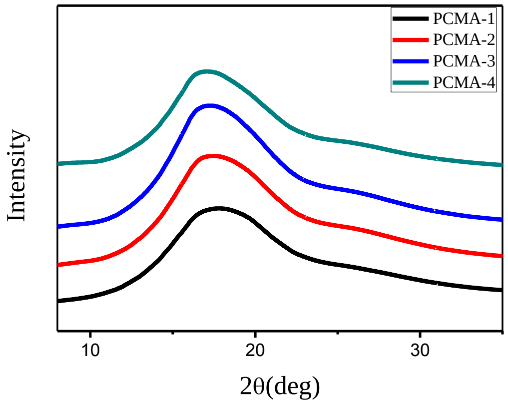


Figure 5b.13. X-Ray diffractograms of (co)polycarbonates.

5b.3.5 Thermal properties of (co)polycarbonates

The thermal behavior of (co)polycarbonates was analyzed using TGA at a heating rate of 10 °C/min under nitrogen atmosphere. TG curves of (co)polycarbonates are illustrated in **Figure 5b.14A**. A representative thermogram (TG) and differential thermogram (DTG) curve of MAPC-1 reproduced in **Figure 5b.14B**. The thermal properties of (co)polycarbonates are summarized in **Table 5b.3**.

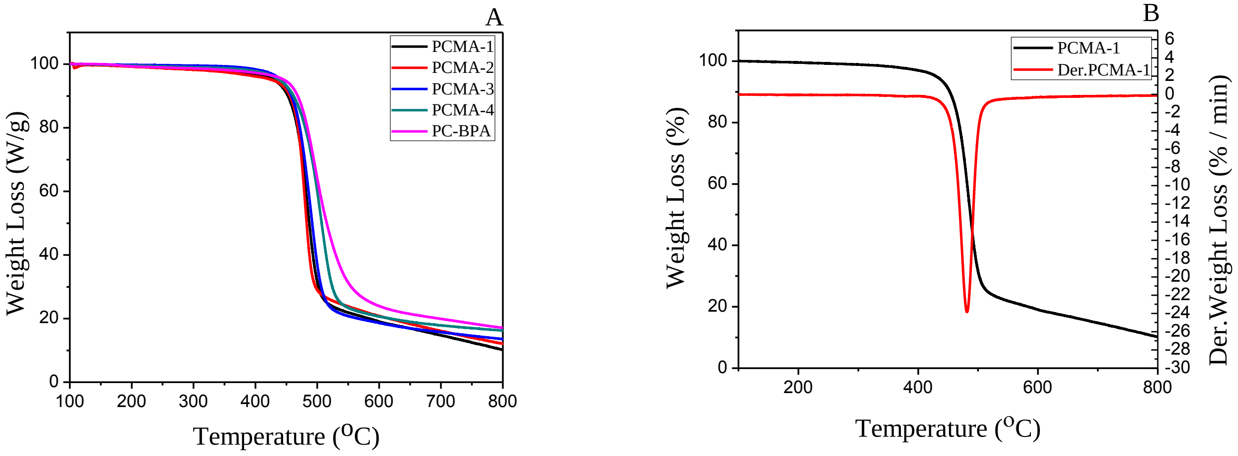


Figure 5b.14. A) TG curves of (co)polycarbonates; B) Representative TG and DTG curves of polycarbonates PCMA-1.

The 10 % weight loss temperature of these (co)polycarbonates was in the range 452-462 ^{o}C which indicated their high thermal stability. A comparison of T_{10} value of BPA-MA based polycarbonate (PCMA-1) (452 ^{o}C) with that of T_{10} value of BPA-based polycarbonate (PC-BPA) (468 ^{o}C) indicated that the former showed lower T_{10} value by 16 ^{o}C. The lower T_{10} value of polycarbonate bearing pendant maleimide groups could be ascribed to the presence of thermally labile alkyl chain. In the series of copolycarbonates, decrease in T_{10} value was observed with increase in the content of BPA-MA. The % char yield values at 800 ^{o}C of (co)polycarbonates were in the range 10-17 and char yield values tend to decrease with the increase in BPA-MA content.

Differential scanning calorimetry (DSC) was used for determination of glass transition temperatures (T_g) of (co)polycarbonates. The T_g values were calculated from second heating scans of polycarbonate samples at a heating rate of 10 °C/min. DSC curves for (co)polycarbonates are depicted in **Figure 5b.15** and data is collected in **Table 5b.3**. Polycarbonate based on BPA-MA showed T_g at 127 ºC which is lower than T_g value of BPA-polycarbonate (147 ºC) by 20 ^{o}C. This clearly results from presence of pendant alkyl chains which are responsible for decrease in intermolecular interaction which in turn results in lowering of T_g. Copolycarbonates containing varying mole percent incorporation of BPA-MA showed T_g values in the range 135 ºC-145 ºC and the values tend to decrease with increase in mol % incorporation of BPA-MA.

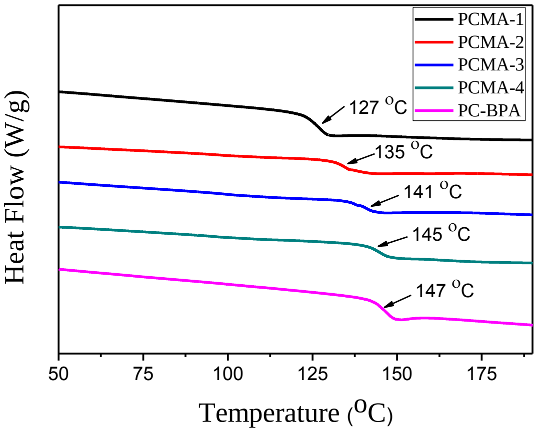
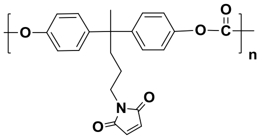
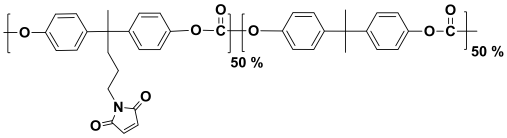
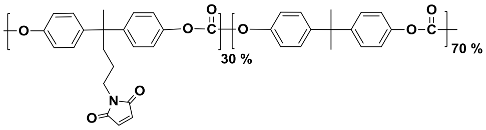
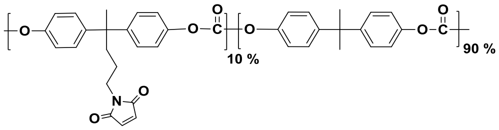
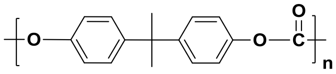


Figure 5b.15. DSC curves of (co)polycarbonates.

Table 5b.3. Thermal properties of (co)polycarbonates

(Co)polycarbonate	**Structure of (co)polycarbonate**	**T_{10} (°C)^a**	**Char Yield (%)^b**	**T_g (°C)^c**
PCMA-1		452	10	127
PCMA-2		456	12	135 (134.4)^d
PCMA-3		458	14	141 (138.5)^d
PCMA-4		462	16	145 (143.8)^d
PC-BPA		468	17	147

a: 10 % Weight loss on TGA thermograms at a heating rate of 10 °C/min under nitrogen atmosphere, b: Char yield was measured at 800 °C, c: Measured by DSC on second heating scan with heating rate of 10 °C/min under nitrogen atmosphere, d: T_g values calculated by Fox equation.

The experimental T_g values of copolycarbonates were compared to the theoretical T_g values calculated by Fox equation.[50,51]

$$\frac{1}{T_{gc}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Where, T_{gc} is T_g of copolycarbonates and T_{g1} and T_{g2} are T_g values of homo-polycarbonates derived from BPA-MA and BPA, respectively (i.e. T_{g1}=127 °C, T_{g2}=147 °C). W_1 and W_2 represent weight fractions of BPA-MA and BPA in copolycarbonates. The 1/T_g of (co)polycarbonates were plotted against % weight fraction of BPA-MA (**Figure 5b.16).** T_g value obtained from the DSC exhibited nearly a linear relationship with weight % BPA-MA. The calculated T_g values are included in **Table 5b.3.**

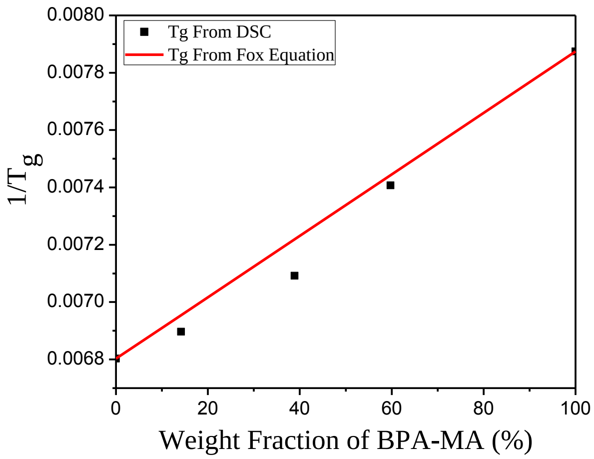
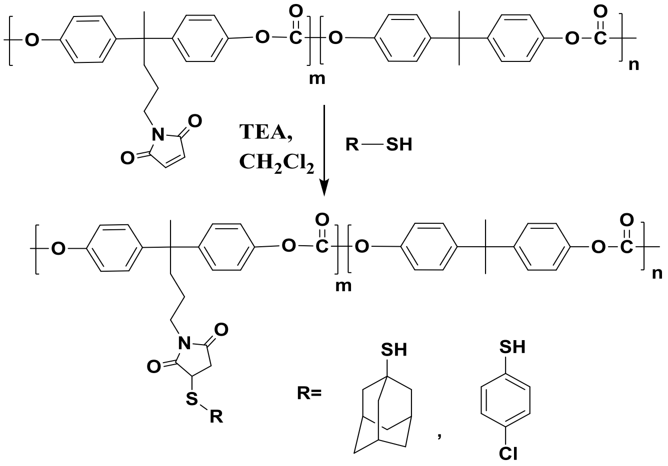


Figure 5b.16. $1/T_g$ as a function of weight % of BPA-MA in copolycarbonates.

5b.3.6 Post-modification of polycarbonate *via* thiol-maleimide Michael type addition reaction

The chemical modification of polycarbonate bearing pendant maleimide groups was demonstrated *via* thiol-maleimide Michael type addition reaction with two different thiol-containing compounds, namely 4-chlorothiophenol (CTP) and 1-adamantanethiol (ADM). These thiols were chosen as representative examples for post-modification. Copolycarbonate PCMA-2 was post-functionalized with 2 equivalents of both the thiols *via* nucleophilic thiol-maleimide Michael addition click reaction catalyzed by Et_3N in dry dichloromethane at room temperature for 24 h **(Scheme 5b.3)**.



Scheme 5b.3. Click reaction of copolycarbonate PCMA-2 with 1-adamantanethiol and 4-chlorothiophenol.

^{1}H NMR spectrum of copolycarbonate obtained after chemical modification with 4-chlorothiophenol is depicted in **Figure 5a.15**.

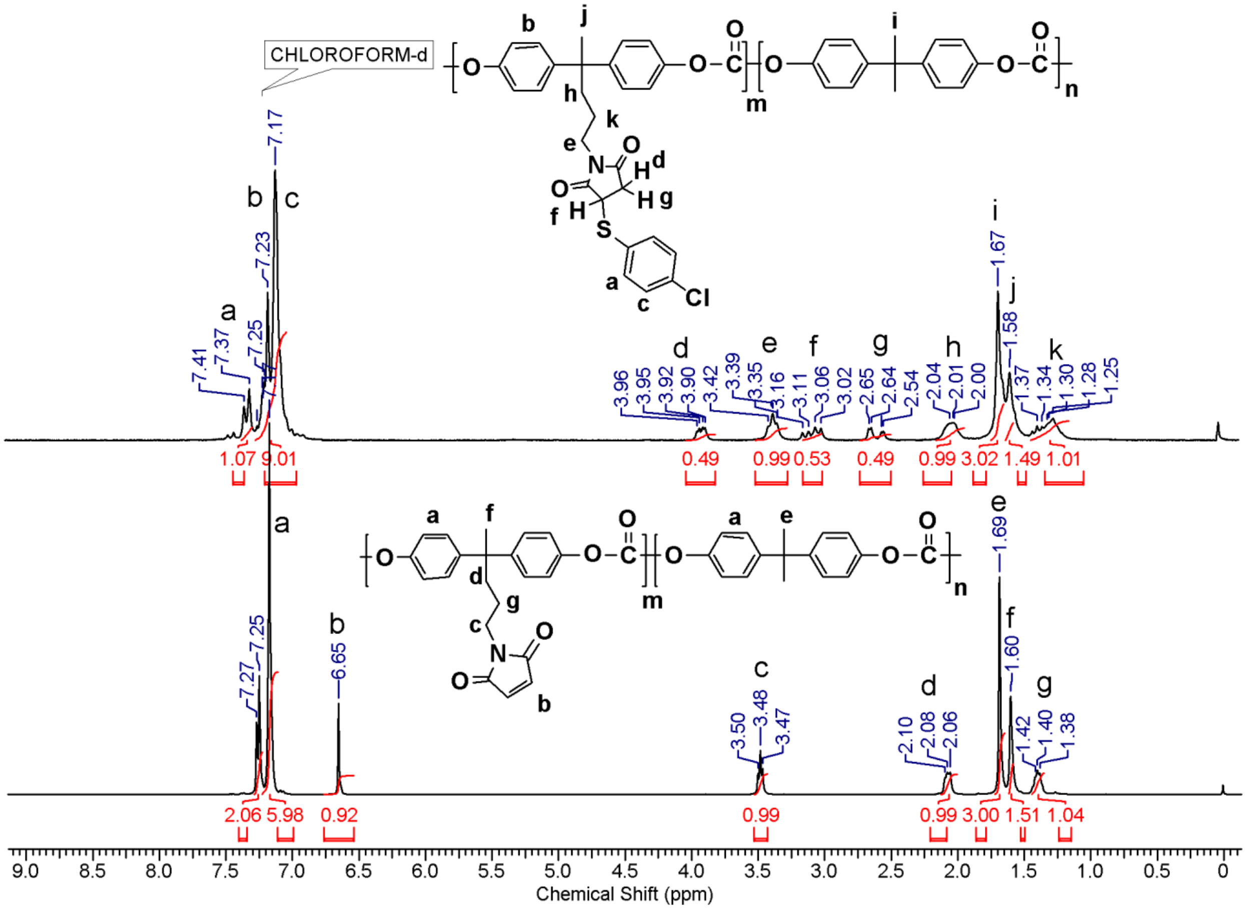


Figure 5b.17. ^{1}H NMR spectra (in $CDCl_3$) of copolycarbonate PCMA-2 before (bottom) and after (top) thiol-maleimide Michael addition click reaction.

Evaluation of the ^{1}H NMR spectrum of copolycarbonate functionalized with 4-chlorothiophenol exhibited that the characteristic maleimide double bond signal at 6.65 δ ppm disappeared and peaks corresponding to aromatic protons of 4-chlorothiophenol appeared at 7.39 δ ppm **(Figure 5b.17)**. The proton signals from the newly formed succinimide ring are clearly assignable, which is an indication the success of post-polymerization modification. Similarly, disappearance of maleimide proton signals and appearance of expected protons signals were also observed for the 1-adamantanethiol Michael addition reaction. Furthermore, no evidence of chain degradation was observed by GPC analysis (**Figure 5b.18**).

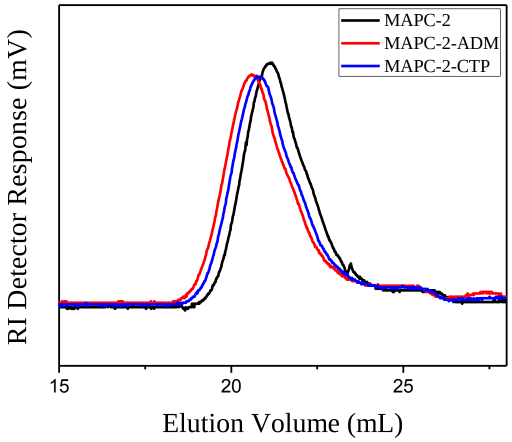


Figure 5b.18. GPC traces of MAPC-2, MAPC-2-ADM and MAPC-2-CTP.

5b.3.7 Gelation

To test the feasibility of thiol-maleimide cross-linking reaction, as a representative example, a solution of polycarbonate MAPC-1(100 mg/mL) in dichloromethane was combined with pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and triethylamine as base at room temperature. As demonstrated in **Figure 5b.19**, the gel was formed within few seconds under mild reaction condition using a molar ratio of maleimide to thiol of 1:1.

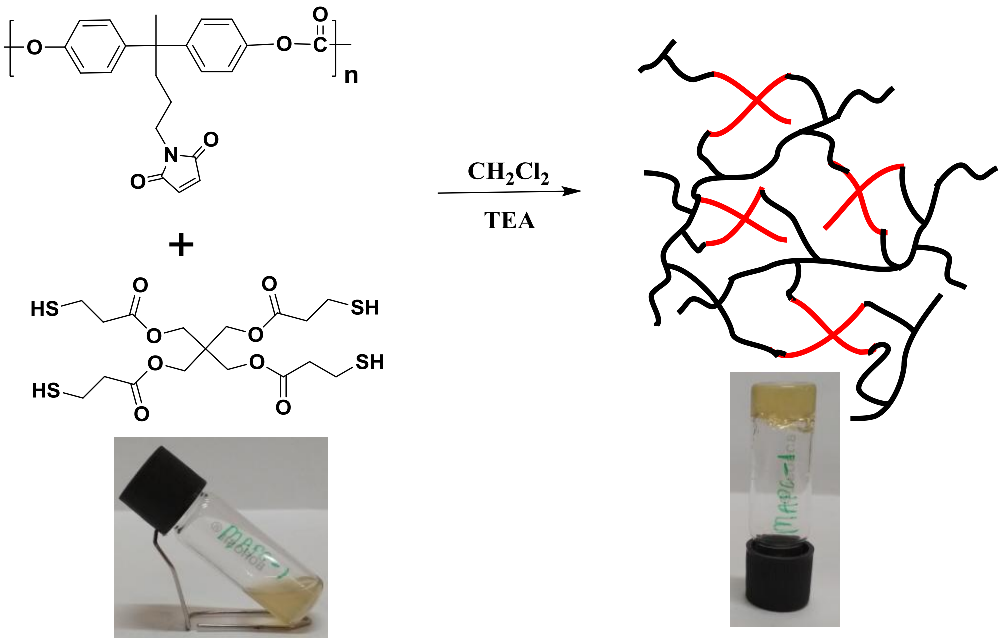


Figure 5b.19. Gel formation by cross-linking of MAPC-1 with pentaerythritol tetra(3-mercaptopropionate) *via* thiol-maleimide reaction.

5b.4 Conclusions

In this study, a new maleimide functionalized bisphenol, namely, 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) was successfully synthesized as an A_2 monomer starting from 4, 4'-(5 -azidopentane-2, 2-diyl) diphenol. A series of aromatic (co)polycarbonates bearing pendant clickable maleimide groups was synthesized using triphosgene as carbonyl source *via* solution polymerization. Inherent viscosities and number average molecular weights of (co)polycarbonates containing pendant maleimide groups were in the range 0.46-0.66 dL/g and 24,600-36,700 g/mol, respectively, indicating the formation of reasonably high molecular weight polymers. Polycarbonates could be cast into tough, transparent and flexible films from chloroform solutions. The T_{10} values for (co)polycarbonates were in the range 452-462 °C indicating their high thermal stability. The lowering of T_g in polycarbonates (127-145 °C) could be attributed to the presence of packing disruptive pendant alkyl chain containing maleimide group. Subsequently, post-polymerization modification of pendant maleimide groups in polycarbonate by thiol-maleimide Michael type addition click reaction under mild reaction conditions with two representative thiols led to the isolation of modified aromatic polycarbonates The quantitative transformation occurred without backbone degradation as observed by ^{1}H NMR spectroscopy and GPC, respectively. Additionally, it was demonstrated that gel could be readily produced *via* thiol-maleimide Michael addition reaction from maleimide functionalized polycarbonate and thiol cross-linker. Aromatic polycarbonates bearing pendant maleimide groups represent versatile precursors for synthesis of modified polycarbonates possessing interesting functional groups with the use of appropriate functionally substituted thiol reagents.

5b.5 References

1. Pelet, J. M., Putnam, D. *Pharm. Res.*, 2013, **30**, 362–376.
2. Cooley, C. B., Trantow, B. M., Nederberg, F., Kiesewetter, M. K., Hedrick, J. L., Waymouth, R. M., Wender, P. A. *J. Am. Chem. Soc.*, 2009, **131**, 16401–16403.
3. Thomas, A. W., Dove, A. P. *Macromol. Biosci.*, 2016, **16**, 1762–1775.
4. Tempelaar, S., Mespouille, L., Coulembier, O., Dubois, P., Dove, A. P. *Chem. Soc. Rev.*, 2013, **42**, 1312–1336.
5. Ono, R. J., Liu, S. Q., Venkataraman, S., Chin, W., Yang, Y. Y., Hedrick, J. L. *Macromolecules*, 2014, **47**, 7725–7731.

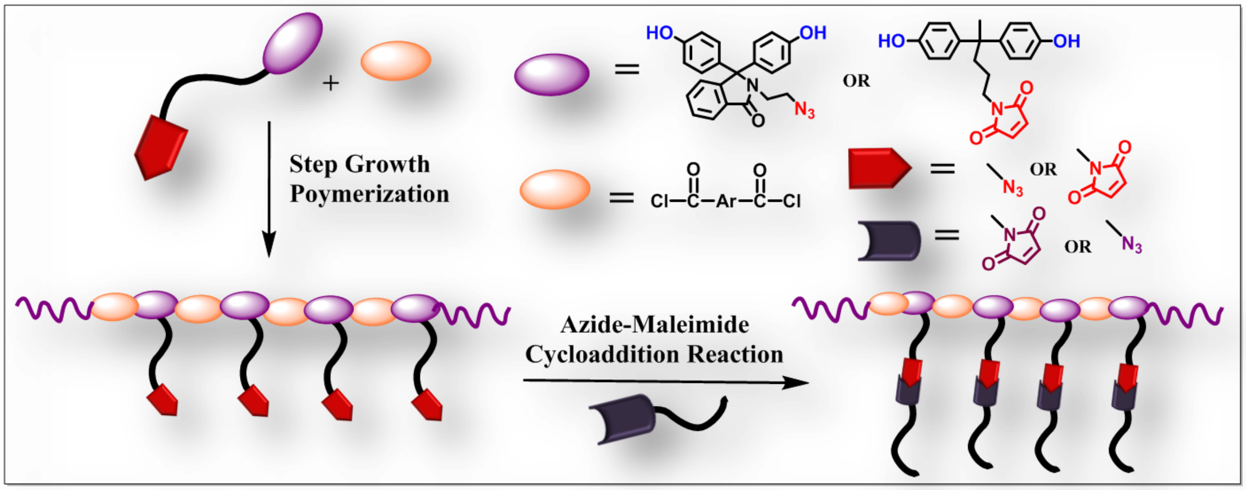
6. Liu, Y.-L., Chen, Y.-W. *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
7. Lu, J., Shoichet, M. S. *Macromolecules*, 2010, **43**, 4943–4953.
8. Jang, H., Joo, H., Sutradhar, S. C., Banik, N., Ha, J., Yoo, J., Choi, K., Ryu, T., Kim, W. *Mater. Lett.*, 2016, **180**, 170–174.
9. Chen, W., Yang, H., Wang, R., Cheng, R., Meng, F., Wei, W., Zhong, Z. *Macromolecules*, 2010, **43**, 201–207.
10. Fournier, D., Du Prez, F. *Macromolecules*, 2008, **41**, 4622–4630.
11. Choi, J., Moon, D. S., Jang, J. U., Yin, W. Bin, Lee, B., Lee, K. J. *Polymer*, 2017, **116**, 287–294.
12. Trollsås, M., Lee, V. Y., Mecerreyes, D., Löwenhielm, P., Möller, M., Miller, R. D., Hedrick, J. L. *Macromolecules*, 2000, **33**, 4619–4627.
13. Gerhardt, W. W., Noga, D. E., Hardcastle, K. I., García, A. J., Collard, D. M., Weck, M. *Biomacromolecules*, 2006, **7**, 1735–1742.
14. Zhang, X., Mei, H., Hu, C., Zhong, Z., Zhuo, R. *Macromolecules*, 2009, **42**, 1010–1016.
15. Vandenberg, E. J., Tian, D. *Macromolecules*, 1999, **32**, 3613–3619.
16. Hu, X., Liu, S., Chen, X., Mo, G., Xie, Z., Jing, X. *Biomacromolecules*, 2008, **9**, 553–560.
17. Venkataraman, S., Veronica, N., Voo, Z. X., Hedrick, J. L., Yang, Y. Y. *Polym. Chem.*, 2013, **4**, 2945.
18. Sanda, F., Kamatani, J., Endo, T. *Macromolecules*, 2001, **34**, 1564–1569.
19. Hu, X., Chen, X., Xie, Z., Cheng, H., Jing, X. *J. Polym. Sci. Part A Polym. Chem.*, 2008, **46**, 7022–7032.
20. Faccini, M., Balakrishnan, M., Torosantucci, R., Driessen, A., Reinhoudt, D. N., Verboom, W. *Macromolecules*, 2008, **41**, 8320–8323.
21. Al-Azemi, T. F., Bisht, K. S. *Macromolecules*, 1999, **32**, 6536–6540.
22. Kimura, Y., Shirotani, K., Yamane, H., Kitao, T. *Macromolecules*, 1988, **21**, 3338–3340.
23. Pounder, R. J., Dove, A. P. *Biomacromolecules,* 2010, **11**, 1930–1939.
24. Tempelaar, S., Mespouille, L., Dubois, P., Dove, A. P. *Macromolecules,* 2011, **44**, 2084–2091.
25. Kühling, S., Keul, H., Höcker, H. *Makromol. Chemie*, 1990, **191**, 1611–1622.
26. Olsén, P., Odelius, K., Albertsson, A.-C. *Macromolecules*, 2014, **47**, 6189–6195.
27. Łukaszczyk, J., Jaszcz, K., Kuran, W., Listoś, T. *Macromol. Biosci.*, 2001, **1**, 282–289.

28. Olofsson, K., Malkoch, M., Hult, A. *J. Polym. Sci. Part A Polym. Chem.*, 2016, **54**, 2370–2378.
29. He, F., Wang, Y.-P., Liu, G., Jia, H.-L., Feng, J., Zhuo, R.-X. *Polymer*, 2008, **49**, 1185–1190.
30. Xu, J., Prifti, F., Song, J. *Macromolecules*, 2011, **44**, 2660–2667.
31. Zhang, X., Zhong, Z., Zhuo, R. *Macromolecules*, 2011, **44**, 1755–1759.
32. Li, T., Jing, X., Huang, Y. *Polym. Adv. Technol.*, 2011, **22**, 1266–1271.
33. Tempelaar, S., Barker, I. A., Truong, V. X., Hall, D. J., Mespouille, L., Dubois, P., Dove, A. P. *Polym. Chem.*, 2013, **4**, 174–183.
34. Han, Y., Shi, Q., Hu, J., Du, Q., Chen, X., Jing, X. *Macromol. Biosci.*, 2008, **8**, 638–644.
35. Hu, D., Peng, H., Niu, Y., Li, Y., Xia, Y., Li, L., He, J., Liu, X., Xia, X., Lu, Y., Xu, W. *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 750–760.
36. Hilf, J., Frey, H. *Macromol. Rapid Commun.*, 2013, **34**, 1395–1400.
37. Williams, R. J., Barker, I. A., O'Reilly, R. K., Dove, A. P. *ACS Macro Lett.*, 2012, **1**, 1285–1290.
38. Murayama, M., Sanda, F., Endo, T. *Macromolecules*, 1998, **31**, 919–923.
39. Onbulak, S., Tempelaar, S., Pounder, R. J., Gok, O., Sanyal, R., Dove, A. P., Sanyal, A. *Macromolecules*, 2012, **45**, 1715–1722.
40. Voo, Z. X., Khan, M., Xu, Q., Narayanan, K., Ng, B. W. J., Bte Ahmad, R., Hedrick, J. L., Yang, Y. Y. *Polym. Chem.*, 2016, **7**, 656–668.
41. Xing, D., Ma, L., Gao, C. *Macromol. Biosci.*, 2014, **14**, 1429–1436.
42. Hilf, J., Scharfenberg, M., Poon, J., Moers, C., Frey, H. *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
43. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.
44. Engler, A. C., Chan, J. M. W., Coady, D. J., O'Brien, J. M., Sardon, H., Nelson, A., Sanders, D. P., Yang, Y. Y., Hedrick, J. L. *Macromolecules*, 2013, **46**, 1283–1290.
45. Sanders, D. P., Fukushima, K., Coady, D. J., Nelson, A., Fujiwara, M., Yasumoto, M., Hedrick, J. L. *J. Am. Chem. Soc.*, 2010, **132**, 14724–14726.
46. Mollah†, M. S. I., Seo†, D. W., Islam, M. M., Lim, Y. D., Cho, S. H., Shin, K. M., Kim, J. H., Kim, W. G. *J. Macromol. Sci. Part A Pure Appl. Chem.*, 2011, **48**, 400–408.

47. Xin, Y., Sakamoto, J., van der Vlies, A. J., Hasegawa, U., Uyama, H. *Polymer*, 2015, **66**, 52–57.
48. Wacker, K. T., Kristufek, S. L., Lim, S.-M., Kahn, S., Wooley, K. L. *RSC Adv.*, 2016, **6**, 81672–81679.
49. Boyles, D. A., Filipova, T. S., Bendler, J. T., Longbrake, G., Reams, J. *Macromolecules*, 2005, **38**, 3622–3629.
50. T. G. Fox *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
51. Cheah, K., Cook, W. D. *Polym. Eng. Sci.*, 2003, **43**, 1727–1739.

Chapter-6

Post-Modification of Aromatic (Co)polyesters *via* Azide-Maleimide Cycloaddition Reaction



Chapter-6a

(Co)polyesters Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modifications

6a.1 Introduction

Polymers containing pendant azido groups have attracted a great deal of attention as azido group is capable of undergoing the celebrated CuAAC click reaction allowing access to modified polymers. Additionally, azido group can be transformed into amines, triazenes, etc, making possible the introduction of such functionalities into polymers.[1,2] Both the post-functionalization and functional monomer approaches have been put to use to obtain a range of aliphatic and aromatic polymers. Examples of such polymeric systems include: polycarbonates,[3–15] polyesters,[16–23] polyurethanes,[24–30] polyamides,[31–38] poly(ether sulfone)s[39–45] and poly(ether ether ketone)s.[46]

The objective of present study was to synthesize a bisphenol bearing pendant azido group, namely, 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (PPH-N_3), starting from phenolphthalein which is a commercially available, inexpensive and bench-top chemical. Aromatic polyesters were synthesized by low temperature solution polycondensation of PPH-N_3 with aromatic diacid chlorides *viz.*, isophthalic acid chloride (IPC) and terephthalic acid chloride (TPC). Copolyesters were synthesized by polycondensation of varying mole ratios of PPH-N_3 and bisphenol-A with isophthaloyl chloride. (Co)polyesters were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetric studies (DSC). Furthermore, representative aromatic polyester containing pendant azido groups was post-modified by metal-free 1, 3-dipolar cycloaddition click reaction with two maleimides.

6a.2 Experimental

Details about materials used in the study and experimental techniques such as IR, ^{1}H, ^{13}C NMR HRMS spectroscopy, inherent viscosity, GPC, TGA, DSC and XRD are given in **Chapter 2**.

6a.2.1 Synthesis of bisphenol bearing pendant azido group

6a.2.1.1 Synthesis of 2-(2-hydroxyethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one

Into a 500 mL three necked round bottom flask equipped with a mechanical stirrer, a gas inlet and a condenser were charged phenolphthalein (5.0 g, 15.70 mmol) and 2-aminoethanol (10.55 g, 172.80 mmol). The reaction mixture was refluxed for 24 h. Excess of 2-aminoethanol was distilled out under reduced pressure, and the residue was poured into ice-cold water to obtain a white precipitate. The crude product was recrystallized from a mixture of ethanol and water (30:70, v/v) to afford 2-(2-hydroxyethyl)-3, 3-bis(4-hydroxyphenyl)isoindolin-1-one as white crystals.

Yield: 4.70 g (83 %); Melting point: 254 ^{o}C; IR (KBr): 3023, 1668 cm^{-1}; ^{1}H NMR (200 MHz, Acetone-d$_6$, δ/ppm): 8.55 (br.s, 2H), 7.75 (d, 1H), 7.55 (t, 1H), 7.47 (t, 1H), 7.40 (d, 1H), 7.08 (d, 4H), 6.84 (d, 4H), 3.95 (t, 1H), 3.55 (t, 2H), 3.02 (q, 2H); ^{13}C NMR (50 MHz, Acetone-d$_6$, δ/ppm): 169.5, 158.3, 153.0, 133.1, 132.4, 131.5, 130.3, 129.0, 124.7, 123.9, 116.4, 76.0, 60.6, 45.1; HRMS ESI^{+}: (M+Na)$^{+}$m/z calculated for $C_{22}H_{19}NO_4Na$: 484.1206, found: 484.1201.

6a.2.1.2 Synthesis of 2-(2-bromoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one

Into a 250 mL two necked round-bottom flask fitted with a magnetic stirring bar were added 2-(2-hydroxyethyl)-3,3-bis(4-hydroxyphenyl)isoindolin-1-one (7.0 g, 19.38 mmol) and dry THF (60 mL) and the solution was cooled to 0 $^{\circ}$C. To the reaction mixture were added carbon tetrabromide (7.71 g, 23.26 mmol) and triphenyl phosphine (6.10 g, 23.26 mmol) and the reaction mixture was stirred at room temperature for 2 h. THF was evaporated under reduced pressure and the reaction mixture was washed with water (2 x 50 ml) and extracted into dichloromethane (100 mL). The dichloromethane solution was washed with saturated brine solution (3 x 50 mL) and dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether: ethyl acetate (70:30, v/v) as an eluent to afford 2-(2-bromoethyl)-3,3-bis(4-hydroxyphenyl) isoindolin-1-one as a white solid.

Yield: 7.14 g (87 %); Melting point: 258 ^{o}C; IR (KBr): 1662 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d$_6$, δ/ppm): 8.64 (br. s, 2H), 7.77 (d, 1H), 7.55 (t, 1H), 7.48 (t, 1H), 7.42 (d, 1H), 7.09 (d, 4H), 6.86 (d, 4H), 3.79 (t, 2H), 2.64 (t, 2H); ^{13}C NMR (50 MHz, Acetone-d$_6$, δ/ppm): 168.5, 158.5, 152.6, 133.4, 132.3, 131.2, 130.1, 129.1, 124.8, 124.0, 116.5, 75.5, 43.7, 27.8; HRMS ESI^{+}: (M+Na)$^{+}$m/z calculated for $C_{22}H_{18}BrNO_3Na$: 448.0342, found: 448.0336.

6a.2.1.3 Synthesis of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one

Into a 100 mL single necked round bottom flask fitted with a magnetic stirring bar were added 2-(2-bromoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (6.0 g, 1.45 mmol) and N, N-dimethylformamide (60 ml). Sodium azide (4.89 g, 70.70 mmol) was added to the solution and the reaction mixture was stirred for 24 h at room temperature. DMF was removed by distillation under reduced pressure. The reaction mixture was dissolved in ethyl acetate (100 mL) and the solution was washed with water (3 x 50 mL). The ethyl acetate solution was washed with saturated brine solution (3 x 50 mL), separated, dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using pet ether:ethyl acetate (80:20, v/v) to afford 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one as a white solid.

Yield: 4.9 g (90 %); Melting point: 198 ^{o}C; IR (KBr): 3190, 2096, 1652 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d$_6$, δ/ppm): 8.64 (br. s, 2H), 7.77 (d, 1H), 7.56 (t, 1H), 7.47 (t, 1H), 7.44 (d, 1H), 7.10 (d, 4H), 6.86 (d, 4H), 3.66 (t, 2H), 2.68 (t, 2H); ^{13}C NMR (50 MHz, Acetone-d$_6$, δ/ppm): 168.8, 158.4, 152.8, 133.3, 132.3, 131.2, 130.2, 129.02, 124.7, 124.0, 116.4, 75.7, 48.8, 40.6; HRMS ESI^{+}: (M+Na)$^{+}$m/z calculated for $C_{22}H_{18}N_4O_3Na$: 409.1271, found: 409.1266.

6a.2.2 Synthesis of (co)polyesters bearing pendant azido groups

A representative procedure for synthesis of polyesters is described below.

Into a 100 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (1.0 g , 2.58 mmol), dichloromethane (7 mL), and triethylamine (1.03 mL, 7.37 mmol), and the solution was cooled to 0 ^{o}C. To the reaction mixture, the solution of isophthaloyl chloride (0.53 g, 2.58 mmol) in dichloromethane (10 mL) was added dropwise over a period of 20 min. The reaction mixture was stirred at 0 ^{o}C for 30 min followed by stirring at 25 ^{o}C for 1 h. The viscous reaction mixture was diluted with dichloromethane (5 mL), and the solution was poured slowly into n-hexane (50 mL) to precipitate the polymer. The precipitated polymer was isolated by filtration, washed with water (5 x 100 mL) followed by washing with methanol (2 x 50 mL) and dried under reduced pressure at room temperature for 12 h.

The other (co)polyesters were synthesized by similar procedure.

6a.2.3 Post-modification of polyester bearing pendant azido groups with N-methylmaleimide

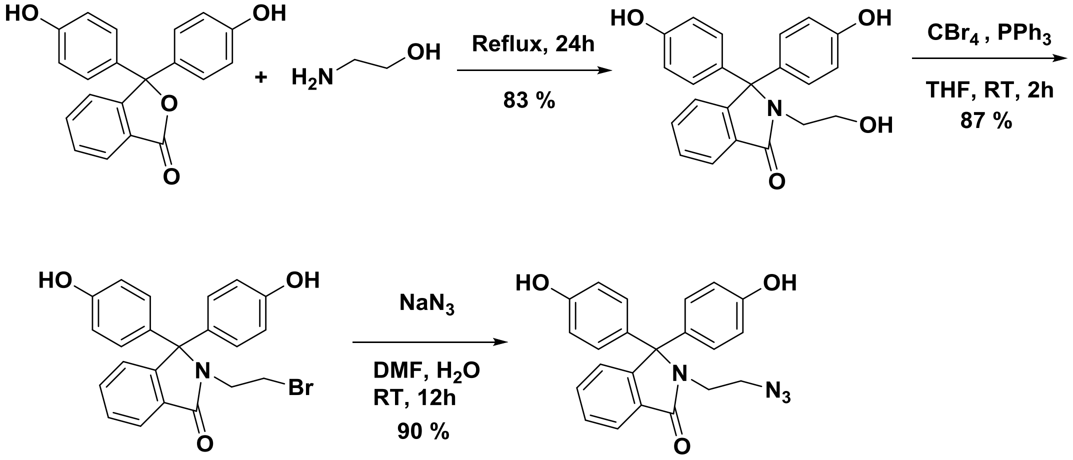
To a Schlenk tube equipped with a magnetic stirring bar were added AZPES-4 (0.20 g, 0.39 mmol), N-methylmaleimide (0.087 g, 0.78 mmol) and dry chloroform (5 mL). The reaction mixture was stirred at 60 ^{o}C under nitrogen atmosphere for 24 h. The resultant polymer was purified by precipitation into methanol to remove the excess N-methylmaleimide. The functionalized polyester was isolated by filtration and dried at room temperature under reduced pressure for 8 h.

A similar procedure was followed for synthesis of other post-functionalized polyester.

6a.3 Results and discussion

6a.3.1 Monomer synthesis

A new bisphenol containing pendant azido group, namely, 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (PPH-N_3), was synthesized starting from commercially available phenolphthalein *via* simple organic transformations (**Scheme 6a.1)**.



Scheme 6a.1. Synthesis of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one.

In the first step, phenolphthalein was reacted with excess of ethanolamine to afford 2-(2-hydroxyethyl)-3, 3-bis(4-hydroxyphenyl)isoindolin-1-one. Further, bromination of 2-(2-hydroxyethyl)-3, 3-bis(4-hydroxyphenyl)isoindolin-1-one using carbon tetrabromide as a brominating agent in the presence of triphenyl phosphine under Apple reaction conditions afforded 2-(2-bromoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one. Finally, the conversion of 2-(2-bromoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one into PPH-N_3 was accomplished by nucleophilic substitution reaction of bromide group using sodium azide in the presence of DMF as a solvent. The chemical structure of bisphenol monomer PPH-N_3 was confirmed by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

IR spectrum **(Figure 6a.1)** of PPH-N_3 showed characteristic absorption bands at 2096 cm^{-1} and 1652 cm^{-1} corresponding to azido and carbonyl stretching, respectively. ^{1}H NMR spectrum of PPH-N_3 is presented in **Figure 6a.2**. The peak at 8.64 δ ppm was assigned to phenolic proton ‘a’.

The protons *meta* to phenolic -OH labeled as “f” exhibited a doublet at 7.10 δ ppm and protons *ortho* to phenolic -OH appeared as a doublet at 6.86 δ ppm. The peaks in the range 7.42-7.78 δ ppm are assigned to aromatic protons of phthalimidine ring. The methylene protons labeled as “h” and “i” exhibited two separate triplets at 3.66 δ ppm and 2.68 δ ppm, respectively.

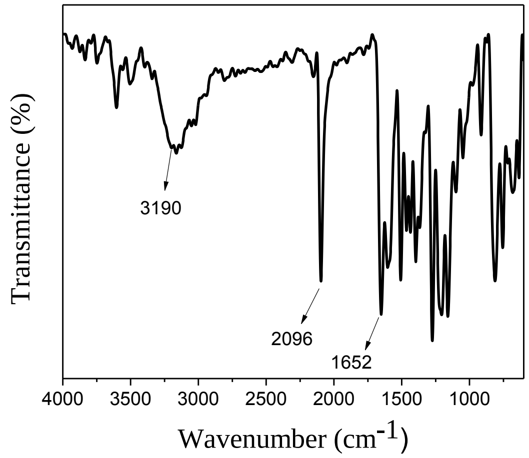


Figure 6a.1. IR spectrum of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one.

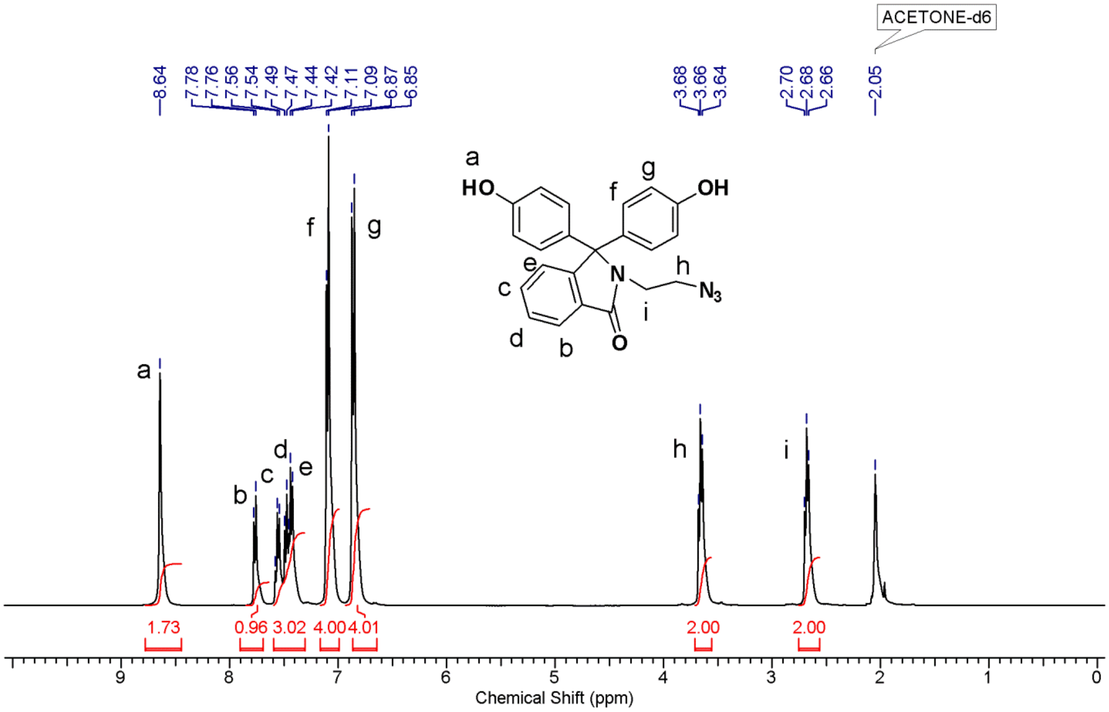


Figure 6a.2. ^{1}H NMR spectrum (in Acetone-d_6) of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one.

^{13}C NMR spectrum of PPH-N_3 along with the assignments is shown in **Figure 6a.3**.

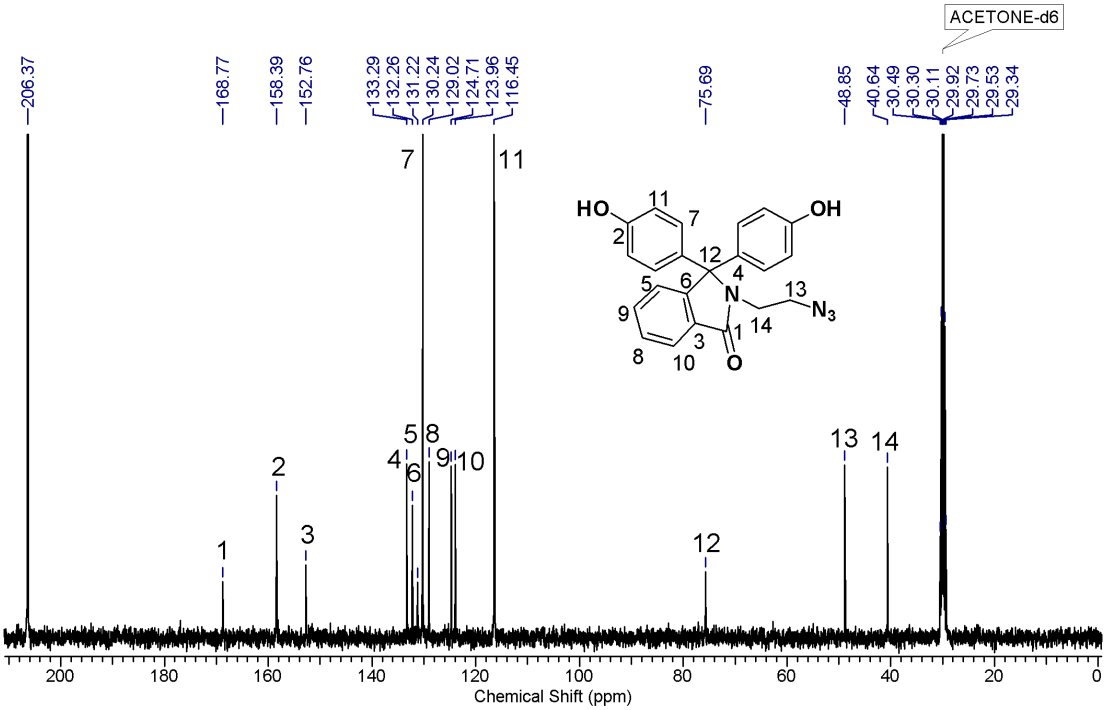


Figure 6a.3. ^{13}C NMR spectrum (in Acetone-d$_6$) of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one.

Furthermore, HRMS (**Figure 4**) analysis of PPH-N$_3$ showed peak at 409.1266 corresponding to ([M+Na]$^+$) of PPH-N$_3$ (calcd. ([M+Na]$^+$) for $C_{22}H_{18}N_4O_3Na$ = 409.1271).

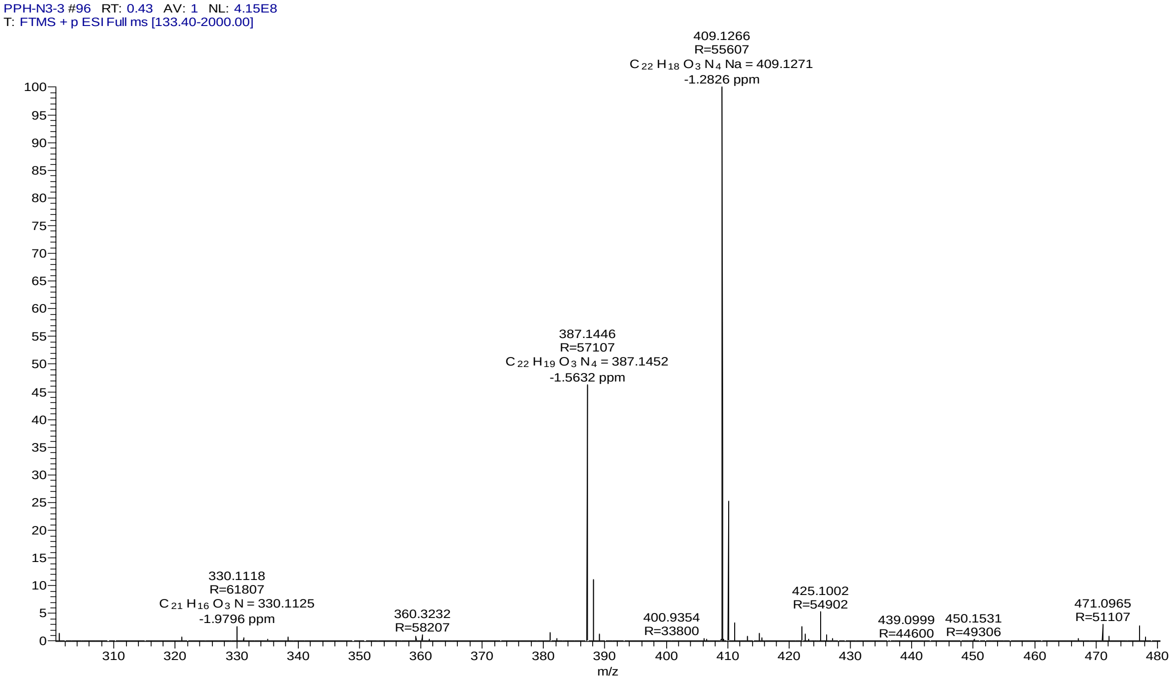
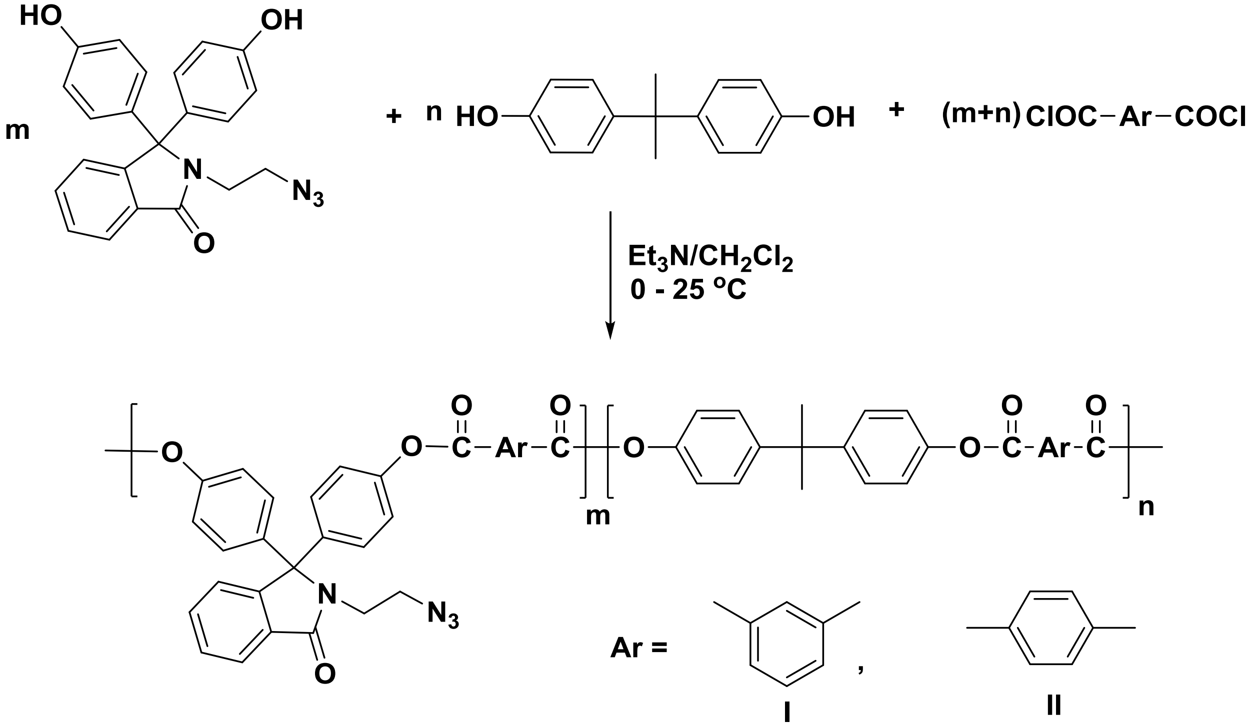


Figure 6a.4. HRMS of 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one.

PPH-N_3 was found to be stable when stored at low temperature under nitrogen atmosphere at least for a year as was evidenced from ^{1}H NMR spectrum of the sample recorded after one year of its preparation.

6a.3.2 Synthesis of (co)polyesters bearing pendant azido groups

In the present work, a series of aromatic (co)polyesters bearing pendant azido groups was synthesized by low-temperature solution polycondensation of PPH-N_3 or different molar composition of PPH-N_3 and BPA with aromatic diacid chlorides (**Scheme 6a.2)**.



Scheme 6a.2. Synthesis of (co)polyesters bearing pendant azido groups.

The reactions were carried out in dry dichloromethane using triethylamine as a base. The solution polymerization was carried out at low temperature (0 to 25 °C) and is particularly suitable as at that temperature azido group is stable and there is no risk of its decomposition.[47] The results of the synthesis of aromatic (co)polyesters are given in **Table 6a.1**. Polyesters bearing pendant azido groups were isolated as white fibrous materials with inherent viscosity and number average molecular weights ($\overline{M_n}$) in the range 0.50-0.79 dL/g and 16,700-28,200 g/mol, respectively. The dispersity values for (co)polyesters were in the range 2.1-2.6, which is typical of a step growth polymerization reaction.

Table 6a.1. Molar composition, inherent viscosity and molecular weight of (co)polyesters

(Co)polyester	**PPH-N_3 (mol%)**	**BPA (mol%)**	**IPC (mol%)**	**TPC (mol%)**	**η_{inh} (dL/g)^a**	**Molecular Weight^b**		**Dispersity**
						$\overline{M_n}$	$\overline{M_w}$	
AZPES-1	100	0	100	0	0.50	16,700	39,100	2.3
AZPES-2	100	0	0	100	0.60	22,400	48,600	2.1
AZPES-3	100	0	50	50	0.51	18,200	38,500	2.1
AZPES-4	50	50	100	0	0.55	21,900	51,800	2.3
AZPES-5	30	70	100	0	0.58	23,800	62,100	2.6
AZPES-6	10	90	100	0	0.79	28,200	69,800	2.4

a: η_{inh} was measured with 0.5 % (w/v) solution in chloroform at 30 ± 0.1 ^oC, b: Measured on GPC in chloroform; polystyrene was used as the calibration standard.

All the polyesters exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, DMAc and DMF. The excellent solubility of polyesters could be attributed to incorporation of cardo phthalimidine units as well as pendant aliphatic side chains. Transparent, tough and flexible films could be cast from their chloroform solutions. The representative film of polyester AZPES-1 is shown in **Figure 6a.5**.

Figure 6a.5. Film of polyester AZPES-1.

6a.3.3 Structural characterization

The chemical structures of (co)polyesters containing pendant azido groups prepared as shown in **Scheme 6a.1** were confirmed by IR, ^1H NMR and ^{13}C NMR spectroscopy. As shown in **Figure**

6a.6, IR spectrum of AZPES-1 revealed the strong absorption band of azido functional group at 2102 cm^{-1}, which confirmed that azido functional groups were retained during polyesterification reaction. The other characteristic bands which appeared at 1746 and 1698 cm^{-1} are assigned to stretching vibration of carbonyl of ester linkage and phthalimidine moiety, respectively.

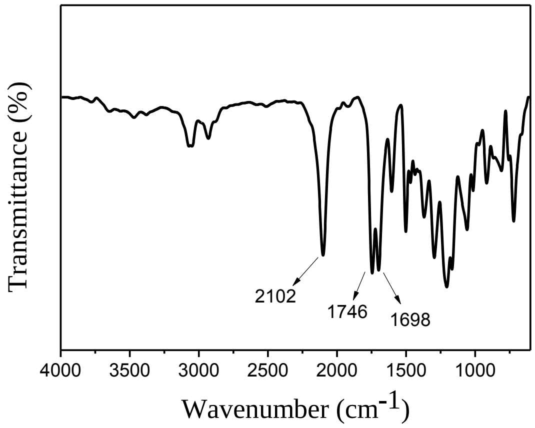


Figure 6a.6. IR spectrum of polyester AZPES-1.

Figure 6a.7 depicts ^{1}H NMR spectrum of polyester containing pedant azido groups (AZPES-1).

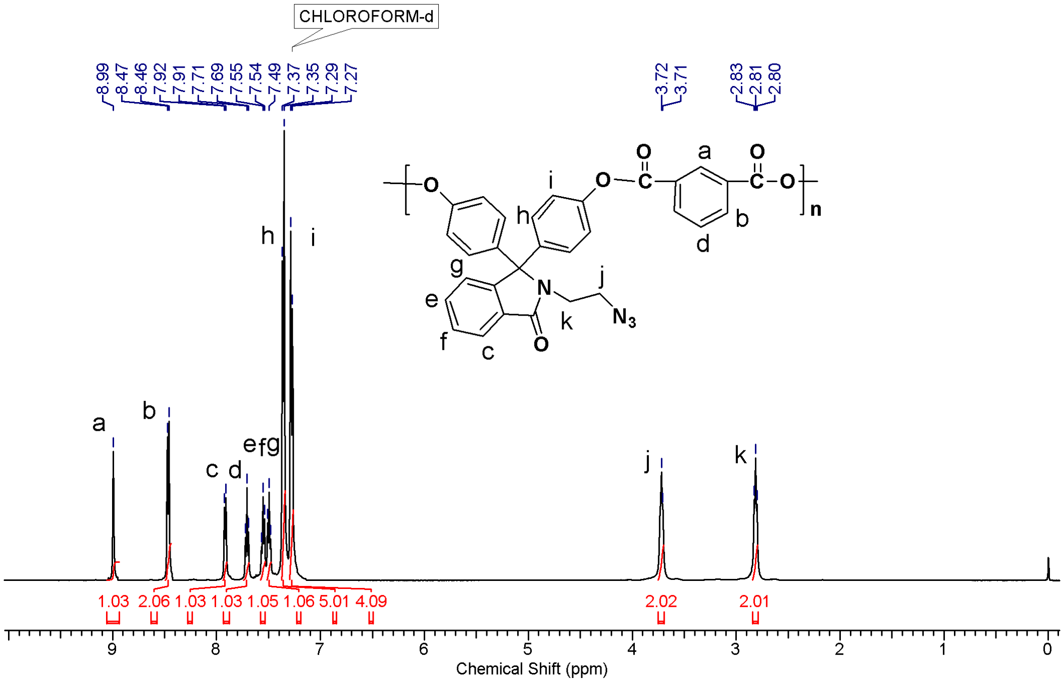


Figure 6a.7. ^{1}H NMR spectrum in $CDCl_3$) of polyester AZPES-1.

The proton “a” flanked by ester carbonyl groups appeared as a singlet at 8.99 δ ppm. The protons “b” exhibited a doublet at 8.47 δ ppm. The proton “c” appeared as a doublet at 7.92 δ ppm. The proton “d” showed as a triplet at 7.71 δ ppm. The triplets appeared at 7.55 δ ppm and 7.49 δ ppm are assigned to aromatic protons labeled as “e” and “f”, respectively. The proton *meta* to ester carbonyl groups labeled as “h” and protons “g” are merged together and appeared at 7.36 δ ppm. The proton *ortho* to ester carbonyl groups marked as “i” exhibited a doublet at 7.28 δ ppm. The peaks appeared at 3.72 and 2.81 δ ppm are attributed to methylene protons labeled as “j” and “k”, respectively.

^{13}C NMR spectrum of polyester AZPES-1 exhibited the signals at 168.6 and 163.8 δ ppm which correspond to carbonyl carbon of phthalimidine and ester linkage, respectively. Assignment of remaining carbons is depicted in **Figure 6a.8** and spectrum agreed well with the proposed molecular structure.

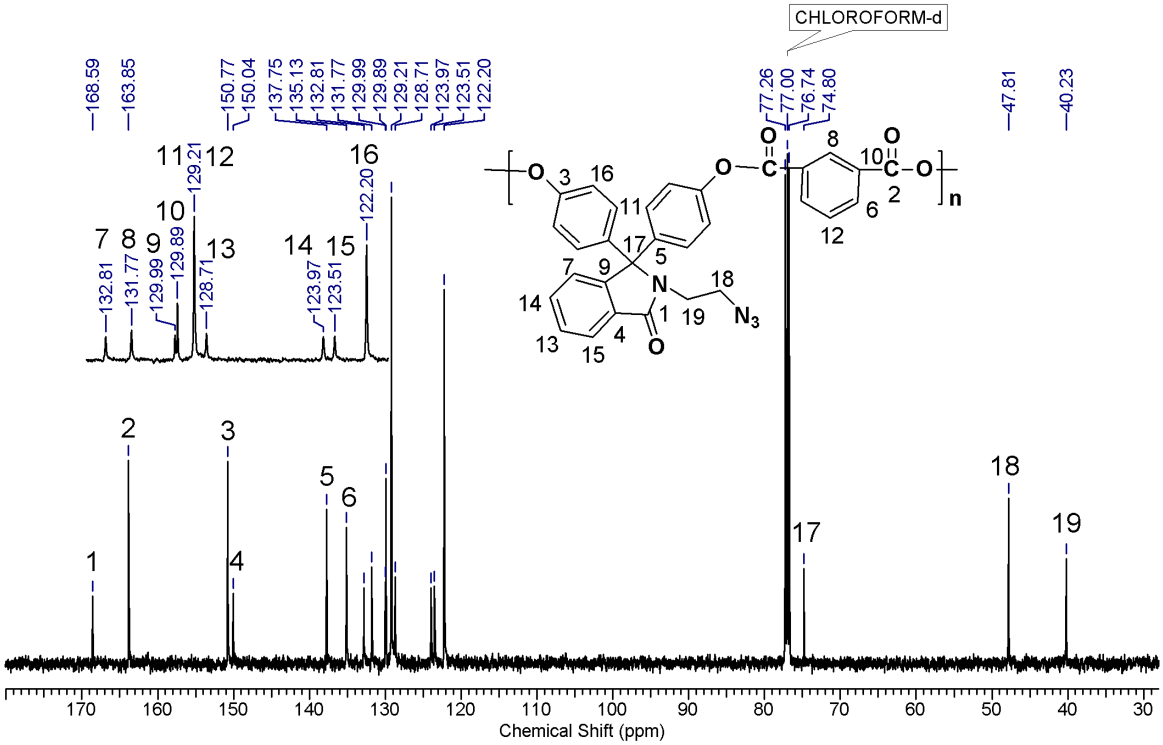


Figure 6a.8. ^{13}C NMR spectrum (in $CDCl_3$) of polyester AZPES-1.

The composition of bisphenols incorporated in copolyesters was determined by integrating the peak for methyl group “n” of BPA appeared at 1.73 ppm and peak for methylene protons “l” adjacent to azido group observed at 3.72 ppm in ^{1}H NMR spectra of copolyesters **(Figure 6a.9)**. From the results depicted in **Table 6a.2**, the content of PPH-N_3 incorporated in copolyesters correlated well to the feed content. Thus, IR, ^{1}H NMR and ^{13}C NMR spectroscopic data indicated successful synthesis of aromatic (co)polyesters bearing pendant azido groups.

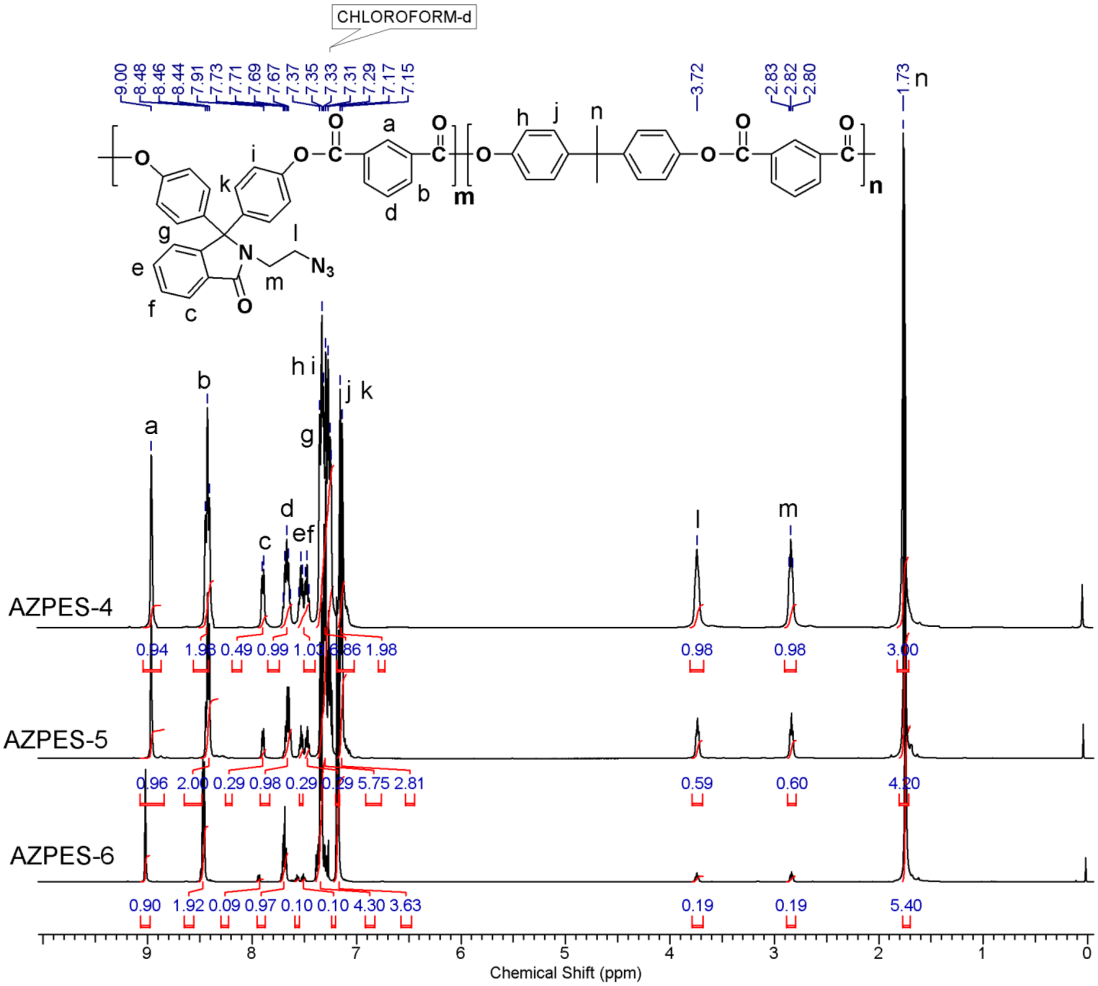
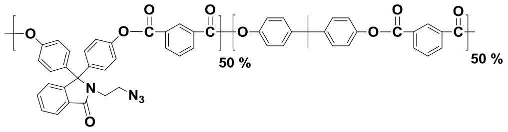
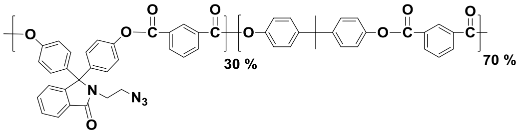
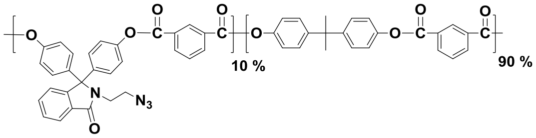


Figure 6a.9. ^{1}H NMR spectra (in $CDCl_3$) of copolyesters.

Table 6a.2. Molar composition of copolyesters determined by ^{1}H NMR spectra

Copolyester	**Structure of copolyester**	**Feed PPH-N_3, mol %**	**Observed PPH-N_3, mol %**
AZPES-4		50	49.0
AZPES-5		30	29.5
AZPES-6		10	9.5

The microstructure of copolyesters derived from copolymerization of PPH-N_3 and BPA with IPC was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, copolymerization of BPA and PPH-N_3 is expected to lead to formation of random copolyesters with following possibilities of enchainment of the two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 6a.10**). ^{13}C NMR spectra of copolyesters showed clear evidence not only for the random copolyester formation but also about the microstructural details as indicated by the multiplicity of the signals.

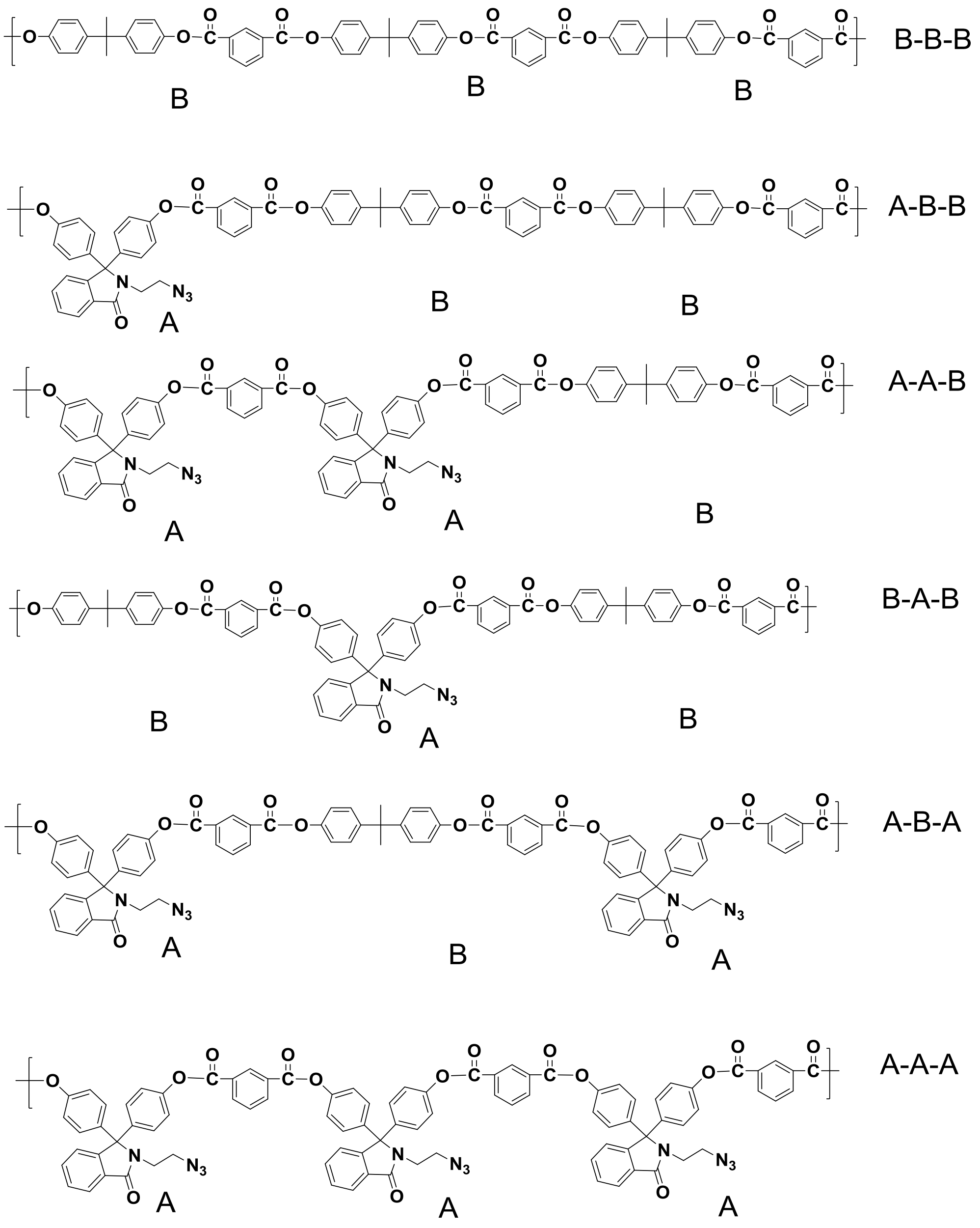


Figure 6a.10. Possible arrangements of PPH-N_3 and BPA units in copolyesters.

The assignments of carbon atoms in ^{13}C NMR spectrum of AZPES-4, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 6a.11.**

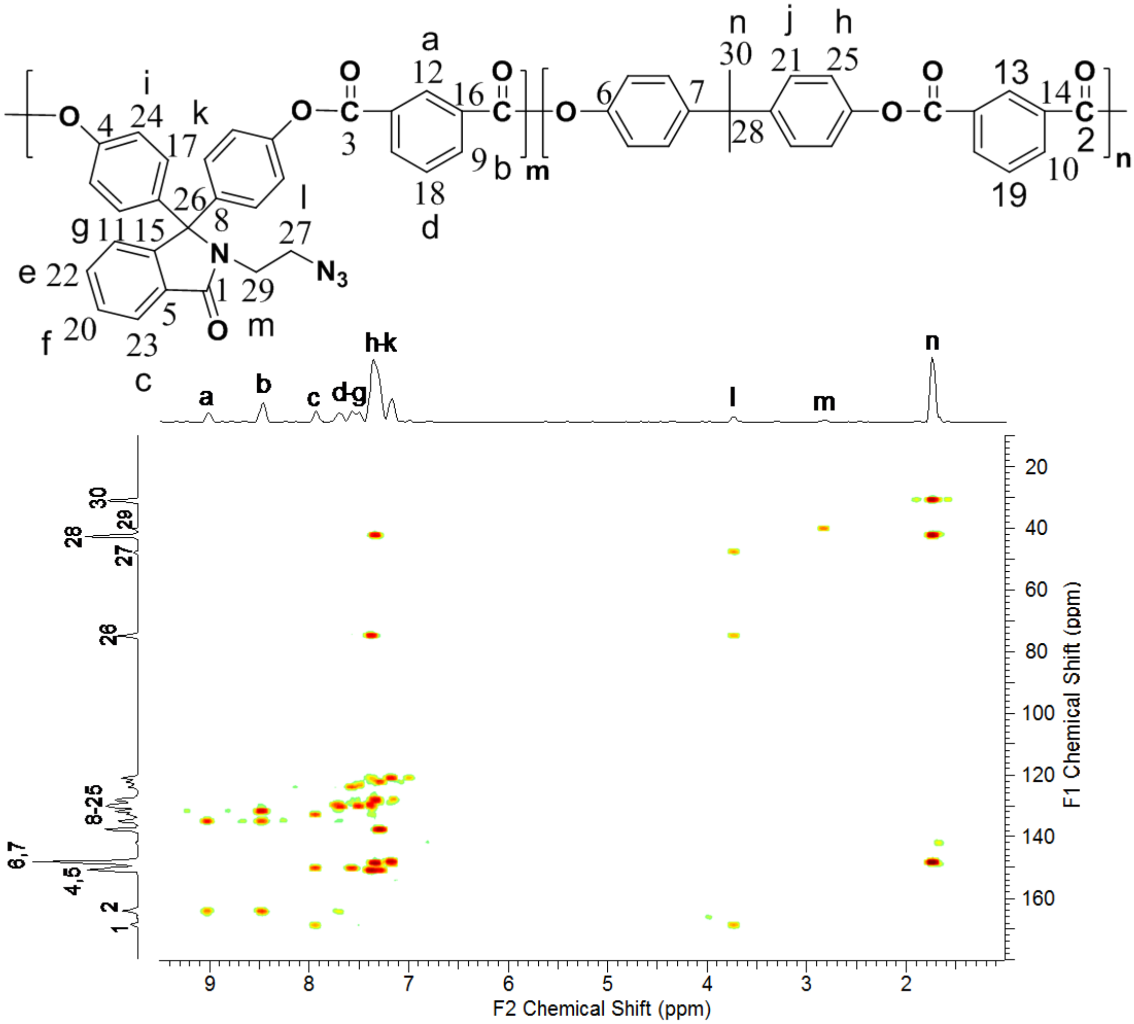
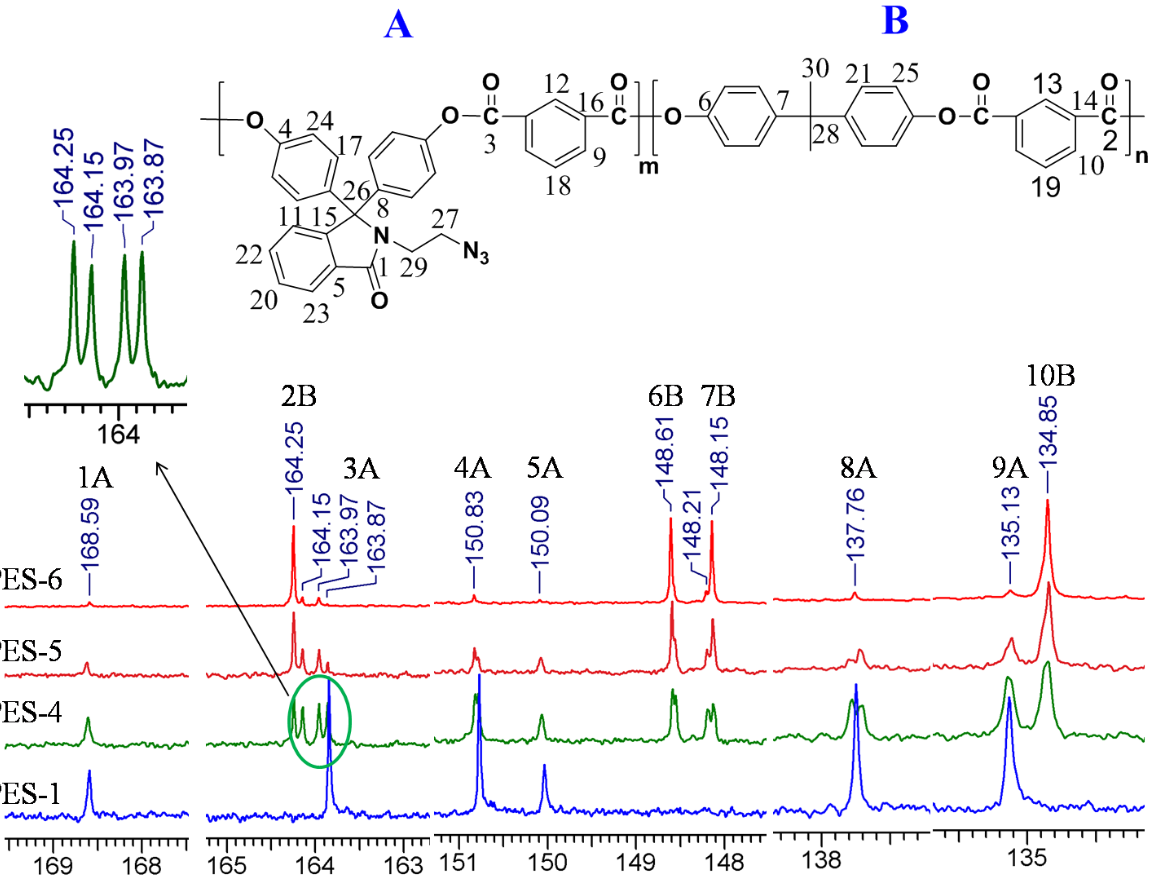


Figure 6a.11. HMBC spectrum (in $CDCl_3$) of AZPES-4.

^{13}C NMR spectrum of AZPSE-4 (50:50 mol % of PPH-N_3:BPA) along with assignments of carbon atoms is presented in **Figure 6a.12.** For easy comparison, ^{13}C NMR spectra of homo-polyester AZPSE-1 and copolyesters AZPES-4 to AZPES-6 are also included in **Figure 6a.12**. It is interesting to note that the carbonyl carbon of ester linkage exhibited four distinct peaks at 163.87 δ ppm, 163.97 δ ppm, 164.15 δ ppm and 164.25 δ ppm for this particular copolymer. A comparison of the spectrum of AZPES-4 with that of AZPES-1 and AZPES-6 inferred that carbonyl peaks appeared at 163.87 δ ppm and 164.25 δ ppm originated from AAA and BBB arrangement of co-monomer units, respectively in copolyester while peaks at 163.97 δ ppm and 164.15 δ ppm correspond to BAB/ABA/BBA/AAB arrangement of co-monomer units. The intensity of peaks corresponding to BAB/ABA/BBA/AAB arrangement of co-monomer units was found to vary with composition of comonomers and was not clearly distinguishable in case of AZPES-5 and AZPES-6.

Some of the other carbon atoms in ^{13}C NMR spectrum of AZPES-4 also exhibited similar features as indicated in **Figure 6a.12**. It is also interesting to note that some of the carbon atoms of aromatic ring (for instance carbon atoms labeled as 4A, 6B, 7B and 8A) also showed more signals in copolyester which is likely to be due to the loss of symmetry upon formation of copolymer comprising of comonomer units enchained in the manner as shown in **Figure 6a.10**.



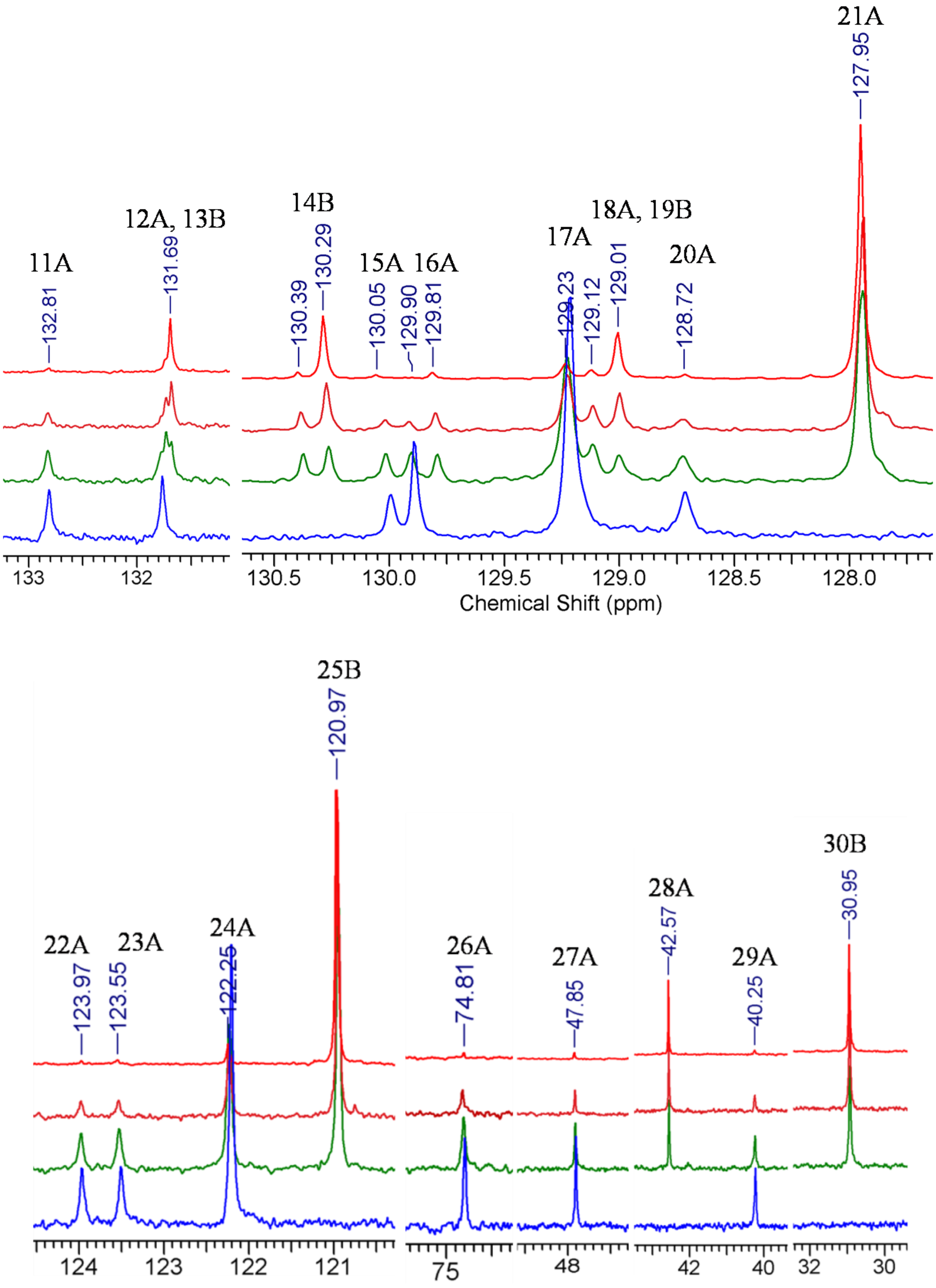


Figure 6a.12. ^{13}C NMR spectra (in $CDCl_3$) of (co)polyesters.

6a.3.4 X-Ray diffraction studies

X-Ray diffraction patterns (**Figure 6a.13)** for aromatic polyesters containing pendant azido groups exhibited broad halo at around 2θ = ~ 19^{o} which could be mainly because of the presence of cardo phthalimidine groups and alkyl chain containing pendant azido groups on polymer backbone, which disrupt the close packing of polymer chains making them amorphous. This was reflected in their improved solubility in common organic solvents.

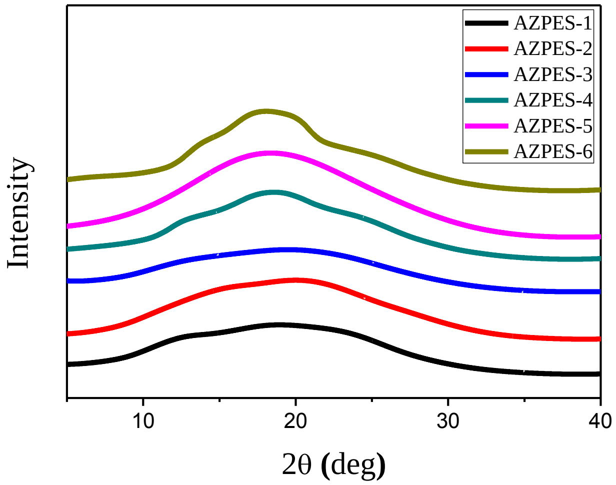


Figure 6a.13. X-Ray diffractograms of (co)polyesters.

6a.3.5 Thermal properties of (co)polyesters

The thermal properties of aromatic (co)polyesters containing pendant azido groups were examined by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate 10 °C/min (**Figure 6a.14A)**. A representative thermogram (TG) and differential thermogram (DTG) curve of AZPES-1 presented in **Figure 6a.14B**. The thermal decomposition of polyesters containing pendant azido groups was found to take place in three steps. The first step of decomposition occurred in the temperature range 200–283 °C with a mass loss of around 7.1 %, which corresponds to the theoretical mass loss due to release of nitrogen by decomposition of azido groups. Similar observations have been reported in the literature for thermal decomposition of polymers containing pendant azido groups[48,49]. The second and the third stage of weight loss could presumably be attributed to degradation of alkyl side chain and polymer backbone, respectively.

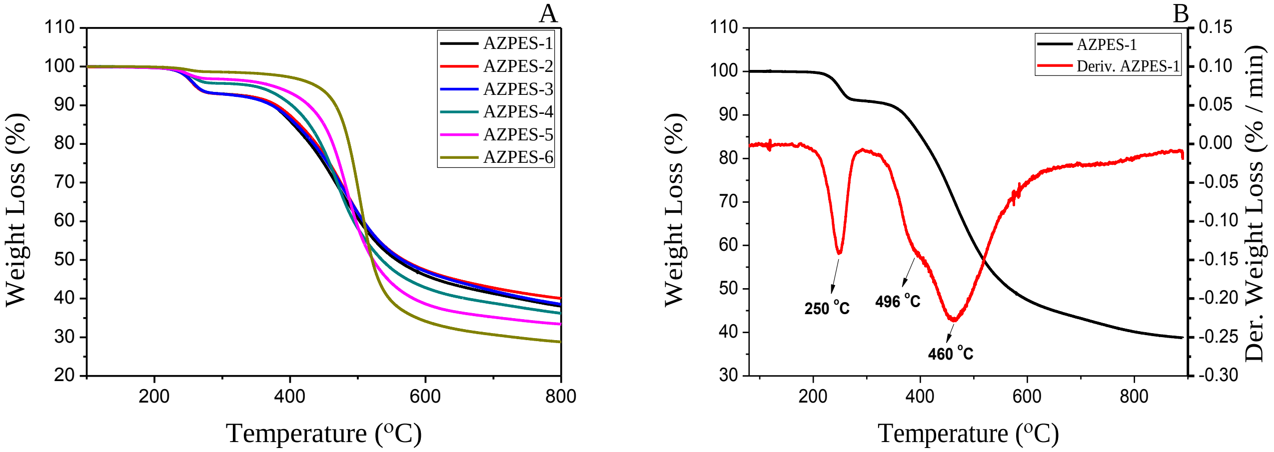


Figure 6a.14. A) TG curves of (co)polyesters; B) Representative TG and DTG curves of polyester AZPES-1.

The glass transition temperature (T_g) values of aromatic (co)polyesters containing cardo phthalimidine groups are anticipated to be rather high (>200 ^oC). It is known in the literature that azido functional group decomposes (>200 ^oC) into highly reactive nitrene intermediate, which can subsequently form intra- and intermolecular bonds with neighboring polymer backbone to produce network structure.[48,49] Furthermore, TG analysis of synthesized (co)polyesters containing pendant azido groups indicated degradation of pendant azido groups starting at 200 ^oC (**Figure 6a.14**). In view of these considerations, it was impractical to determine T_g of synthesized (co)polyesters containing pendant azido groups by DSC analysis.

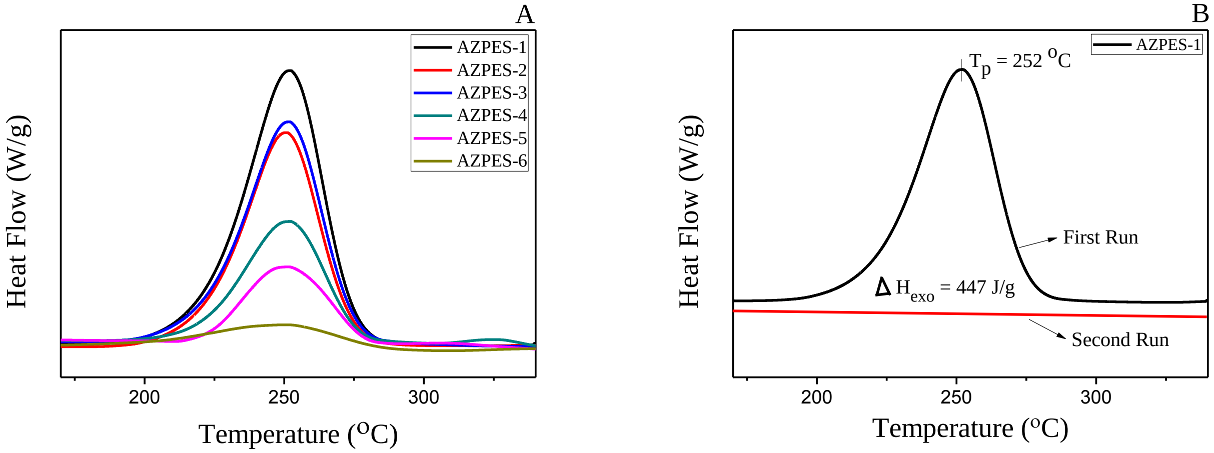


Figure 6a.15. Exothermic heat flow during azide decomposition: A) The first heating cycle of (co)polyesters; B) Representative first and second heating cycle of polyester AZPES-1.

The thermal decomposition and cross-linking involving degradation of azido groups was studied by DSC analysis. **Figure 6a.15B** shows DSC profile of AZPES-1 homo-polyester. It was observed that AZPES-1 exhibited an intense exothermic peak with a peak maximum at 252 °C during the first heating scan. The peak is attributed to the decomposition of azide moiety with concomitant occurrence of cross-linking reactions leading to the formation of a network structure.[50] In the second heating scan, no exothermic peak was observed which indicated completion of decomposition and cross-linking reactions during the first heating scan recorded upto 300 °C. As shown in **Figure 6a.15** and from the results summarized in **Table 6a.3**, it was observed that the value of ΔH_{exo} was found to increase with the increase in content of PPH-N_3 in (co)polyesters. A plot of energy released *vs.* mol % PPH-N_3 content in (co)polyesters showed a linear relationship (**Figure 6a.16)**.

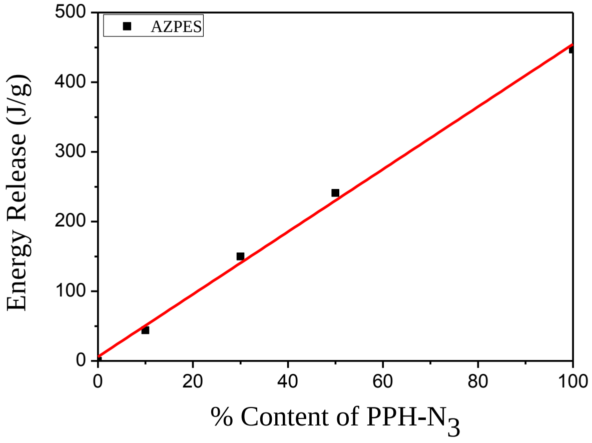
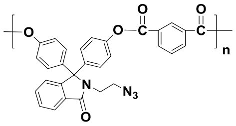
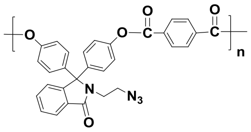
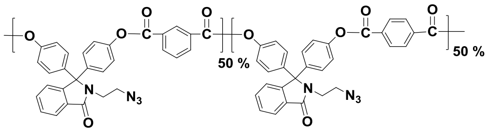
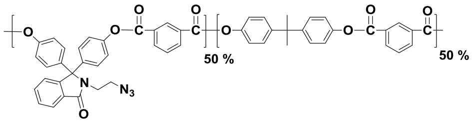
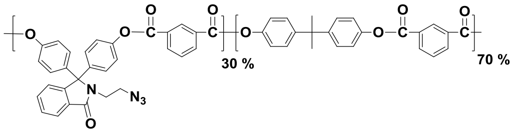
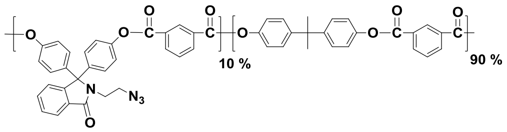


Figure 6a.16. A plot of energy released *vs.* mol % PPH-N_3 content in (co)polyester.

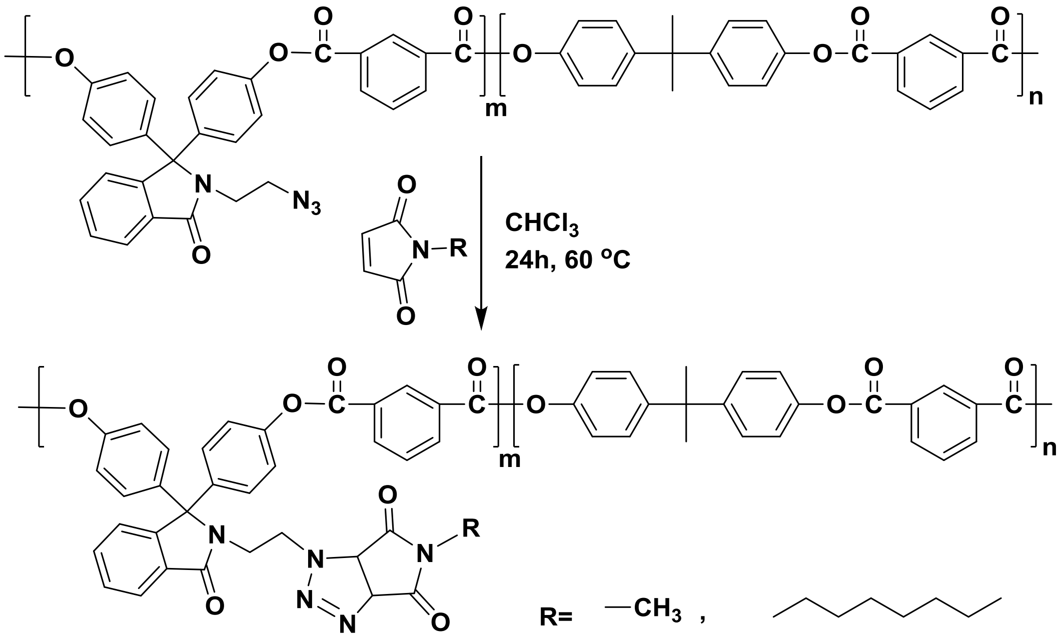
Table 6a.3. DSC data of aromatic (co)polyesters

(Co)polyester	**(Co)polyester**	**T_p (°C)^a**	ΔH_{exo} **(J/g)^b**
AZPES-1		252	447
AZPES-2		252	342
AZPES-3		252	350
AZPES-4		252	241
AZPES-5		251	150
AZPES-6		251	44

a: The exothermic peak temperature; b: Heat of reaction measured by DSC at a heating rate of 10 °C/min in nitrogen.

6a.3.6 Post-modification of copolyester using metal-free azide-maleimide cycloaddition reaction

Aromatic (co)polyester bearing pendant azido groups could be used to react with two different maleimides, namely, N-methylmaleimide (NMI) and N-hexylmaleimide (NHM) *via* metal-free dipolar azide-maleimide cycloaddition reaction. These maleimide containing moieties were chosen as representative examples for post-modification of aromatic polyester. Polyester (AZPES-4) was post-modified with 2 equivalent of different maleimides per azido group *via* metal-free azide-maleimide cycloaddition click reaction in dry chloroform at 60 °C for 24 h **(Scheme 6a.3)**.



Scheme 6a.3. Click reactions of copolyester AZPES-4 with N-methylmaleimide and N-hexylmaleimide.

After the azide-maleimide click reaction, IR analysis was carried out to check the successful completion of click reaction, the azido group stretching band at 2103 cm^{-1} disappeared and a new stretching band appeared at 1714 cm^{-1} which corresponds to carbonyl group of triazole adduct, as shown in **Figure 6a.17**.

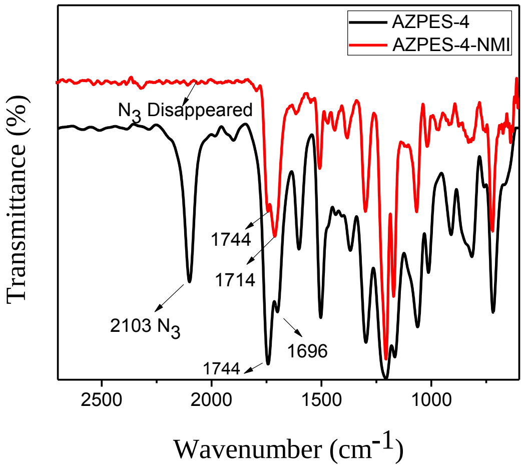


Figure 6a.17. IR spectra of copolyester AZPES-4 before (bottom) and after (top) azide-maleimide cycloaddition reaction.

^{1}H NMR spectrum of polyester obtained after post-modification by 1, 3-dipolar cycloaddition click reaction with N-methylmaleimide is illustrated in **Figure 6a.18**.

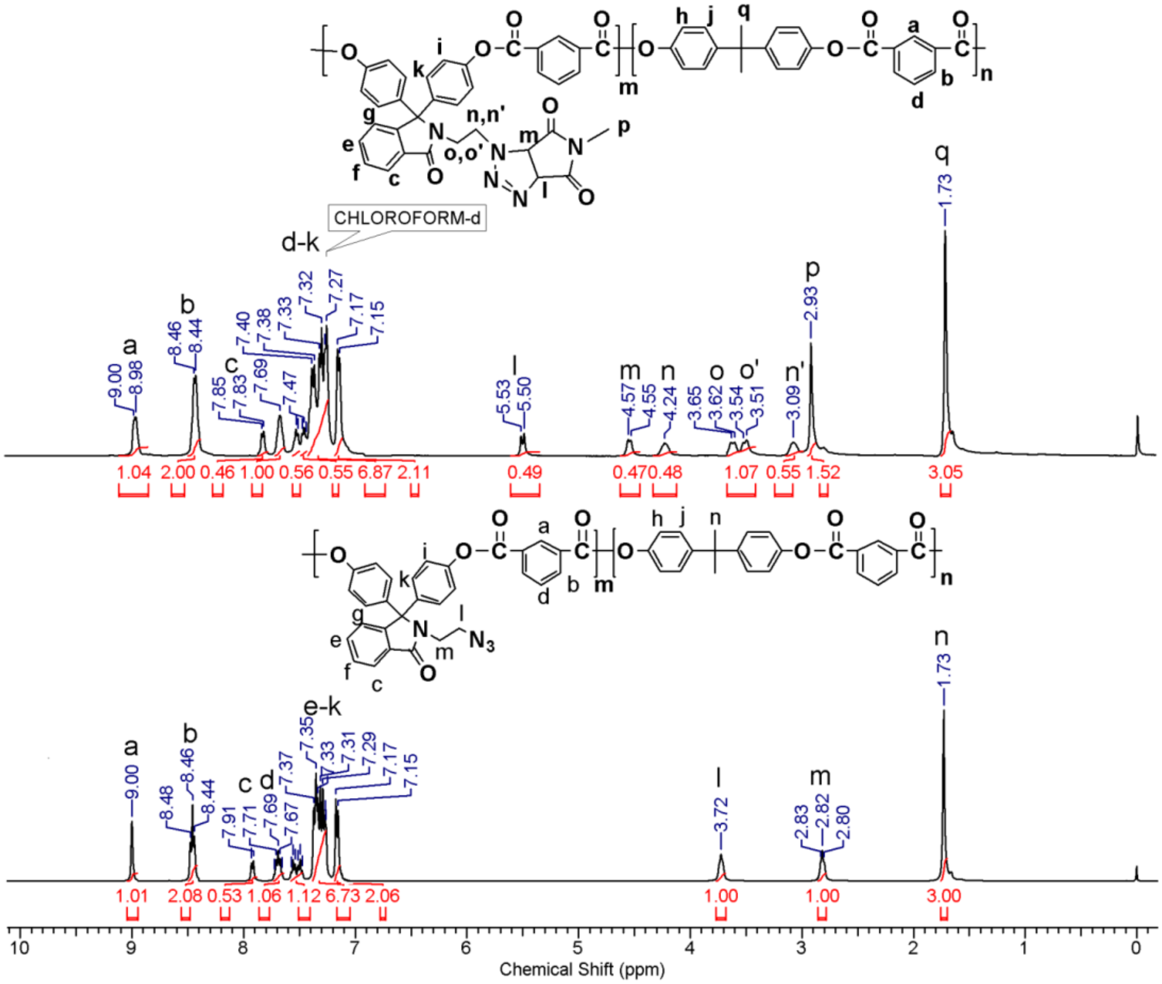


Figure 6a.18. ^{1}H NMR spectrum (in $CDCl_3$) of copolyester AZPES-4 before (bottom) and after (top) azide-maleimide cycloaddition reaction.

^{1}H NMR spectrum clearly indicated appearance of a new set of signals at 5.52 δ ppm, 4.56 δ ppm and 2.93 δ ppm which are associated with product formed by reaction of N-methylmaleimide with azido groups. The assignments of other protons are indicated in **Figure 6a.18**. Likewise, ^{1}H NMR spectrum of product obtained by reaction of copolyester AZPES-4 with N-hexylmaleimide indicated quantitative reaction and was in good agreement with the structure of modified copolyester.

A comparison of GPC traces (**Figure 6a.19)** of modified polyesters with that of parent polyester indicated that there was no chain degradation**.**

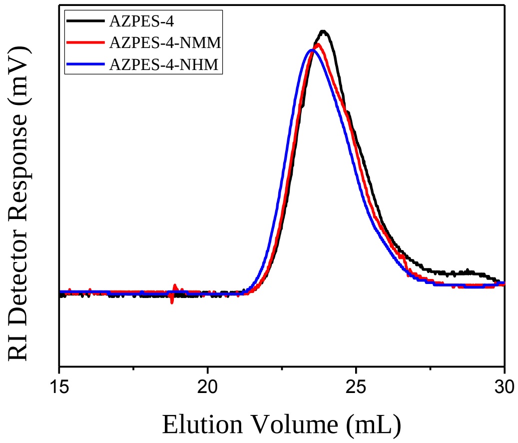


Figure 6a.19. GPC traces of AZPES-4, AZPES-4-NMM and AZPES-4-NHM.

6a.4 Conclusions

A new bisphenol bearing pendant azido group, namely, 2-(2-azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (PPH-N_3) was successfully synthesized starting from commercially available phenolphthalein. Aromatic (co)polyesters containing pendant azido groups were prepared from PPH-N_3 and two aromatic diacid chlorides and their 50:50 mol % mixture by low temperature solution polycondensation technique. Copolyesters were also synthesized by utilizing different molar proportions of PPH-N_3 and BPA with IPC. Inherent viscosities and number-average molecular weights of azido functionalized aromatic (co)polyesters were in the range 0.50-0.79 dL/g and 16,700–28,200 g/mol, respectively. The thermal decomposition of polyesters containing pendant azido groups was found to be take place in three steps. The first step of the decomposition which occurred in the temperature range 200–283 °C was attributed to decomposition of azido groups. The second and the third stage of decomposition could be presumably due to degradation of alkyl side chain and the polyester backbone, respectively. The curing reactions of polyesters involving azido groups were studied by DSC in nonisothermal mode and ΔH_{exo} values of curing reactions were observed in the range 44-447 J/g. A linear increase in ΔH_{exo} values was observed with increase in the content of azido functional groups in copolyesters. Subsequently, the metal-free 1, 3-dipolar cycloaddition click reaction was utilized to modify aromatic polyester by reaction of their pendant azido groups with two representative maleimides. As a result of this approach, properties of aromatic polyesters could be altered *via* the appropriate choice of maleimide compound.

6a.5 References

1. Trigo-López, M., Pablos, J. L., García, F. C., Serna, F., García, J. M. *J. Polym. Sci. Part A Polym. Chem.*, 2014, **52**, 1469–1477.
2. Bräse, S., Gil, C., Knepper, K., Zimmermann, V. *Angew. Chem. Int. Ed.*, 2005, **44**, 5188–5240.
3. Xu, J., Prifti, F., Song, J. *Macromolecules*, 2011, **44**, 2660–2667.
4. Zhang, X., Zhong, Z., Zhuo, R. *Macromolecules*, 2011, **44**, 1755–1759.
5. Ono, R. J., Liu, S. Q., Venkataraman, S., Chin, W., Yang, Y. Y., Hedrick, J. L. *Macromolecules*, 2014, **47**, 7725–7731.
6. Hilf, J., Frey, H. *Macromol. Rapid Commun.*, 2013, **34**, 1395–1400.
7. Tempelaar, S., Barker, I. A., Truong, V. X., Hall, D. J., Mespouille, L., Dubois, P., Dove, A. P. *Polym. Chem.*, 2013, **4**, 174–183.
8. Dai, Y., Zhang, X., Xia, F. *Macromol. Rapid Commun.*, 2017, **38**, 1700357.
9. Hilf, J., Scharfenberg, M., Poon, J., Moers, C., Frey, H. *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
10. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.
11. Onbulak, S., Tempelaar, S., Pounder, R. J., Gok, O., Sanyal, R., Dove, A. P., Sanyal, A. *Macromolecules*, 2012, **45**, 1715–1722.
12. Islam, M. M., Seo, D.-W., Jang, H.-H., Lim, Y.-D., Shin, K. M., Kim, W.-G. *Macromol. Res.*, 2011, **19**, 1278–1286.
13. Chen, W., Yang, H., Wang, R., Cheng, R., Meng, F., Wei, W., Zhong, Z. *Macromolecules*, 2010, **43**, 201–207.
14. Olsén, P., Odelius, K., Albertsson, A.-C. *Macromolecules*, 2014, **47**, 6189–6195.
15. Thomas, A. W., Dove, A. P. *Macromol. Biosci.*, 2016, **16**, 1762–1775.
16. El Habnouni, S., Darcos, V., Garric, X., Lavigne, J.-P., Nottelet, B., Coudane, J. *Adv. Funct. Mater.*, 2011, **21**, 3321–3330.
17. Billiet, L., Fournier, D., Du Prez, F. *J. Polym. Sci. Part A Polym. Chem.*, 2008, **46**, 6552–6564.
18. Jiang, X., Vogel, E. B., Smith, M. R., Baker, G. L. *Macromolecules*, 2008, **41**, 1937–1944.

19. Jazkewitsch, O., Mondrzyk, A., Staffel, R., Ritter, H. *Macromolecules*, 2011, **44**, 1365–1371.
20. Babinot, J., Renard, E., Langlois, V. *Macromol. Rapid Commun.*, 2010, **31**, 619–624.
21. Shibata, Y., Tanaka, H., Takasu, A., Hayashi, Y. *Polym. J.*, 2011, **43**, 272–278.
22. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. *Macromolecules*, 2013, **46**, 1794–1802.
23. Choudhary, U., Mir, A. A., Emrick, T. *Macromolecules*, 2017, **50**, 3772–3778.
24. Basko, M., Bednarek, M., Billiet, L., Kubisa, P., Goethals, E., Du Prez, F. *J. Polym. Sci. Part A Polym. Chem.*, 2011, **49**, 1597–1604.
25. Garg, K., Chatterjee, D., Wadgaonkar, P. P. *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 1008–1020.
26. Fournier, D., Du Prez, F. *Macromolecules*, 2008, **41**, 4622–4630.
27. Choi, J., Moon, D. S., Jang, J. U., Yin, W. Bin, Lee, B., Lee, K. J. *Polymer*, 2017, **116**, 287–294.
28. Varganici, C.-D., Ursache, O., Gaina, C., Gaina, V., Rosu, D., Simionescu, B. C. *Ind. Eng. Chem. Res.*, 2013, **52**, 5287–5295.
29. Agar, S., Durmaz, H., Gunay, U. S., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 521–527.
30. Billiet, L., Gok, O., Dove, A. P., Sanyal, A., Nguyen, L.-T. T., Du Prez, F. E. *Macromolecules*, 2011, **44**, 7874–7878.
31. Billiet, L., Hillewaere, X. K. D., Du Prez, F. E. *Eur. Polym. J.*, 2012, **48**, 2085–2096.
32. Trigo-López, M., Barrio-Manso, J. L., Serna, F., García, F. C., García, J. M. *Macromol. Chem. Phys.*, 2013, **214**, 2223–2231.
33. Diakoumakos, C. D., Mikroyannidis, J. A. *Eur. Polym. J.*, 1995, **31**, 761–767.
34. Liu, Y.-L., Chen, Y.-W. *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
35. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
36. Luo, K., Li, J., Duan, G., Wang, Y., Yu, J., Zhu, J., Hu, Z. *Polymer*, 2018, **142**, 33–42.
37. Bandyopadhyay, P., Banerjee, S. *Ind. Eng. Chem. Res.*, 2014, **53**, 18273–18282.
38. Du, S., Wang, W., Yan, Y., Zhang, J., Tian, M., Zhang, L., Wan, X. *Chem. Commun.*, 2014, **50**, 9929–9931.
39. Dizman, C., Altinkok, C., Tasdelen, M. A. *Des. Monomers Polym.*, 2017, **20**, 293–299.

40. Zhang, X., Yue, B., Yan, L., Zeng, G., Tao, S. *Int. J. Hydrogen Energy*, 2016, **41**, 4740–4750.
41. Yang, Y., Miao, L., Hu, J., Liu, G., Tu, Y., Lin, S., Liu, F., Li, F., Wu, Y., Zhang, G., Zou, H. *J. Mater. Chem. A*, 2014, **2**, 10410–10423.
42. Shen, K., Hu, H., Wang, J., Liu, G. *Polymer*, 2017, **132**, 198–205.
43. Tie, W., Zhong, Z., Li, L., Zhang, A., Shen, F., Lee, M.-H., Li, X.-D. *Eur. Polym. J.*, 2012, **48**, 2070–2075.
44. Ni, J., Zhao, C., Zhang, G., Zhang, Y., Wang, J., Ma, W., Liu, Z., Na, H. *Chem. Commun.*, 2011, **47**, 8943–8945.
45. Summers, G. J., Kasiama, M. G., Summers, C. A. *Polym. Int.*, 2016, **65**, 798–810.
46. Qi, Z., Gong, C., Liang, Y., Li, H., Wu, Z., Feng, W., Wang, Y., Zhang, S., Li, Y. *Int. J. Hydrogen Energy*, 2015, **40**, 9267–9277.
47. Laridon, U. L., Antwerp, W., Delzenne, G. *US Patent 3345171A*, 1967.
48. Varma, I. K., Choudhary, V., Gaur, B., Lochab, B., Oberoi, S., Chauhan, R. *J. Appl. Polym. Sci.*, 2006, **101**, 779–786.
49. Gaina, C., Gaina, V., Ionita, D. *Polym. Int.*, 2011, **60**, 296–303.
50. Albuszis, M., Roth, P. J., Pauer, W., Moritz, H.-U. *Polym. Chem.*, 2016, **7**, 5414–5425.

Chapter-6b

(Co)polyesters Containing Pendant Maleimide Groups Based on Bisphenol Derived from Levulinic Acid: Synthesis, Characterization and Chemical Modifications

6b.1 Introduction

Polymers bearing pendant maleimide groups are attractive scaffolds for chemical modifications as maleimide group undergoes a set of interesting reactions such as furan-maleimide Diels-Alder reaction,[1–3] anthracene-maleimide Diels-Alder reaction,[4,5] thiol-maleimide Michael addition reaction,[6–12] metal-free azide-maleimide 1,3-dipolar cycloaddition click reaction[13,14] and cross-linking under photochemical and thermal conditions.[15–17] Thus, the chemistry of maleimide functional group has been widely exploited in material and biological sciences.[7,11]

The pendant maleimide groups have been introduced into several polymers which include: polyesters,[18,19] polyurethanes,[3,15,20,21] polycarbonates,[7,11] polyamides[22–27] and polyketones.[28]

In the present work, new aromatic polyesters bearing pendant maleimide groups were synthesized by solution polycondensation of 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) with isophthalic acid chloride (IPC), terephthalic acid chloride (TPC) and a mixture of TPC and IPC (50:50 mol %). Copolyesters were also prepared by polycondensation of varying mixtures of BPA-MA and bisphenol-A (BPA) with IPC. (Co)polyesters were characterized by inherent viscosity measurements, FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Subsequently, post-polymerization functionalization of aromatic polyester containing pedant maleimide groups was demonstrated by carrying out metal-free 1, 3-dipolar azide-maleimide cycloaddition click reaction with two azido compounds *viz.*, (azidomethyl)benzene (Bz-N_3) and 1-(azidomethyl)-pyrene (Py-N_3).

6b.2 Experimental

Details about materials used in the study and experimental techniques such as FT-IR, ^{1}H, ^{13}C NMR spectroscopy, inherent viscosity, GPC, TGA, DSC and XRD are given in **Chapter 2.**

6b.2.1 Synthesis of (co)polyesters bearing pendant maleimide groups

A representative procedure for synthesis of polyesters is described below.

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed 4, 4’-(5-maleimidopentane-2, 2-diyl) diphenol (1.0 g, 2.84 mmol), dichloromethane (7 mL), and triethylamine (1.13 mL, 8.12 mmol), and the solution was cooled to 0 ^{o}C. To the reaction mixture, the solution of isophthaloyl chloride (0.58 g, 2.84 mmol) in dichloromethane (10 mL) was added dropwise over a period of

20 min. The reaction mixture was stirred at 0 °C for 30 min and at 25 °C for 1 h. The viscous reaction mixture was diluted with dichloromethane (5 mL), and the solution was poured slowly into n-hexane (50 mL) to precipitate the polymer. The precipitated polymer was isolated by filtration, washed with water (5 x 100 mL) followed by washing with methanol (2 x 50 mL) and dried at 50 °C/1 mm Hg for 20 h.

The other (co)polyesters were synthesized by similar procedure.

6b.2.2 Post-modification of maleimide functionalized polyester with 1-(azidomethyl)pyrene

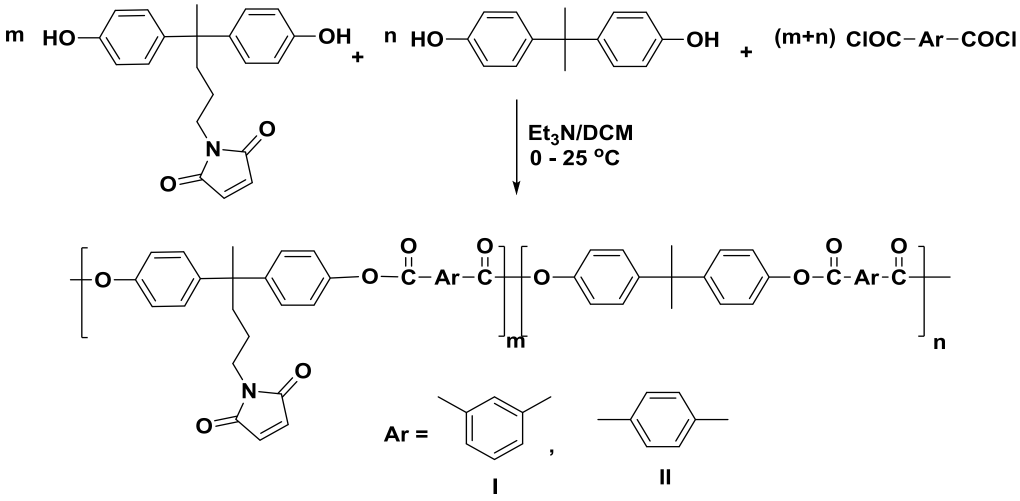
To a Schlenk tube equipped with a magnetic stirring bar were added MAPES-4 (0.20 g, 0.48 mmol), 1-(azidomethyl)pyrene (0.25 g, 0.96 mmol) and dry chloroform (5 mL). The reaction mixture was stirred at 60 °C under nitrogen atmosphere for 24 h. The resultant polymer was purified by precipitation into methanol to remove excess 1-(azidomethyl)pyrene. The functionalized polyester was isolated by filtration and dried at room temperature under reduced pressure for 8 h.

A similar procedure was followed for synthesis of other post-functionalized polyester.

6b.3 Results and discussion

6b.3.1 Synthesis (co)polyesters bearing pendant maleimide groups

A new series of (co)polyesters bearing pendant maleimide groups was synthesized from BPA-MA or different mole ratios of BPA-MA and BPA with aromatic diacid chlorides by low-temperature solution polycondensation as shown in **Scheme 6b.1**.



Scheme 6b.1. Synthesis of (co)polyesters bearing pendant maleimide groups.

The reaction conditions were similar to those described in chapter 5a for synthesis of polyesters containing pendant maleimide groups. The polymerization reactions were carried out on a 1-2 g scale and gave almost quantitative yields of isolated polymers. Inherent viscosities of (co)polyesters were in the range 0.50-0.76 dL/g. Number average molecular weights ($\overline{M_n}$), obtained from gel permeation chromatography (GPC), were in the range 17,700-32,100 g/mol and dispersity values were in the range 2.1-2.5. These data indicated formation of moderate to reasonably high molecular weight (co)polyesters. The results of polymerization reactions are summarized in **Table 6b.1**.

Table 6b.1. Molar composition, inherent viscosity and molecular weight of (co)polyesters

(Co)polyester	**BPA-MA (mol%)**	**BPA (mol%)**	**IPC (mol%)**	**TPC (mol%)**	**η_{inh} (dL/g)**[a]	**Molecular Weight**[b]		**Dispersity**
						$\overline{M_n}$	$\overline{M_w}$	
MAPES-1	100	0	100	0	0.53	19,400	42,900	2.2
MAPES-2	100	0	0	100	0.66	24,500	53,200	2.1
MAPES-3	100	0	50	50	0.50	17,700	45,100	2.5
MAPES-4	30	70	100	0	0.70	25,900	62,500	2.4
MAPES-5	20	80	100	0	0.73	29,600	65,600	2.2
MAPES-6	10	90	100	0	0.76	32,100	71,200	2.2

a: η_{inh} was measured with 0.5 % (w/v) solution in chloroform at 30 ± 0.1 °C, b: Measured on GPC in chloroform using polystyrene as calibration standard.

(Co)polymers exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, DMAc and DMF at room temperature. Tough, transparent and flexible films could be cast from chloroform solutions of (co)polyesters. A representative film of polyester MAPES-1 is shown in **Figure 6b.1.**

Figure 6b.1. Film of polyester MAPES-1.

6b.3.2 Structural characterization

The chemical structures of synthesized (co)polyesters were elucidated on the basis of FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. FT-IR spectrum of aromatic polyester MAPES-1 **(Figure 6b.2)** presented the absorption bands of ester linkage and imide carbonyl at 1742 and 1706 cm^{-1}, respectively. The bands at 1409, 1165, and 694 cm^{-1} are characteristic of maleimide group.

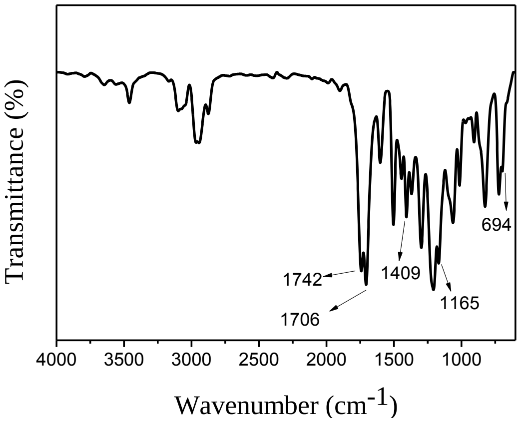


Figure 6b.2. FT-IR spectrum of polyester MAPES-1.

^{1}H NMR spectrum **(Figure 6b.3)** confirmed the expected structure of MAPES-1 primarily displaying the characteristic signals of maleimide functional group at 6.69 δ ppm. The proton “a” flanked by ester carbonyl groups appeared as a singlet at 9.0 δ ppm. The protons “b” exhibited a doublet at 8.45 δ ppm. The proton “c” exhibited a triplet at 7.69 δ ppm. The protons *meta* to ester carbonyl groups labeled as “d” exhibited a doublet at 7.26 δ ppm and the proton *ortho* to ester carbonyl groups marked as “e” exhibited a doublet at 7.17 δ ppm. The methyl protons were observed as a singlet, representing three protons at 1.66 δ ppm. The signal of methylene protons of alkane moiety attached to maleimide group appeared as a triplet at 3.52 δ ppm. The methylene protons of pendant alkyl chain labeled as “h” and “j” appeared at 2.12 and 1.45 δ ppm, respectively.

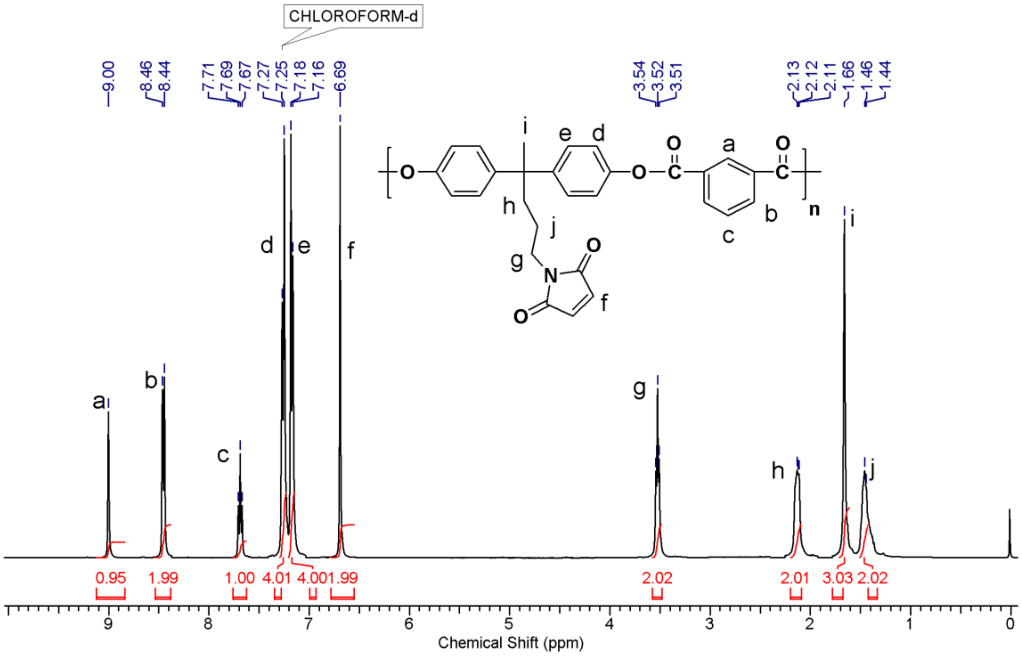


Figure 6b.3. ^{1}H NMR spectrum (in $CDCl_3$) of polyester MAPES-1.

^{13}C NMR spectrum **(Figure 6b.4)** exhibited a signal at 170.7 δ ppm corresponding to maleimide carbonyl as well as signals appeared at 164.1 δ ppm representing carbonyl carbon of ester linkage in the polymer backbone. Assignment of remaining carbon atoms is also depicted in **Figure 6b.4** and the spectrum agreed well with proposed molecular structure of polyester.

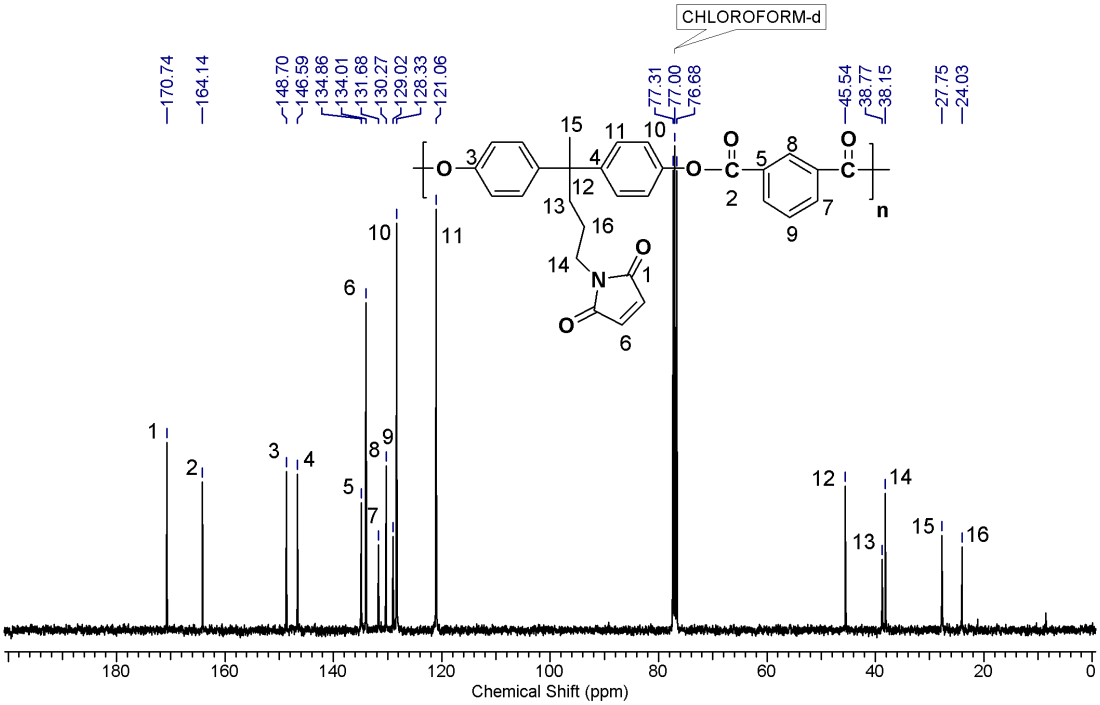


Figure 6b.4. ^{13}C NMR spectrum (in $CDCl_3$) of polyester MAPES-1.

The content of bisphenol containing pendant maleimide group that was incorporated in aromatic copolyester was determined by integrating the peak for methylene protons “i” appeared at 3.53 δ ppm and the peak for methyl protons “k” of BPA appeared at 1.74 δ ppm in ^{1}H NMR spectra of copolyesters **(Figure 6b.5)**. As shown in **Table 6b.2**, these data revealed that content of BPA-MA and BPA monomers in copolyesters was in good agreement with that of the corresponding feed.

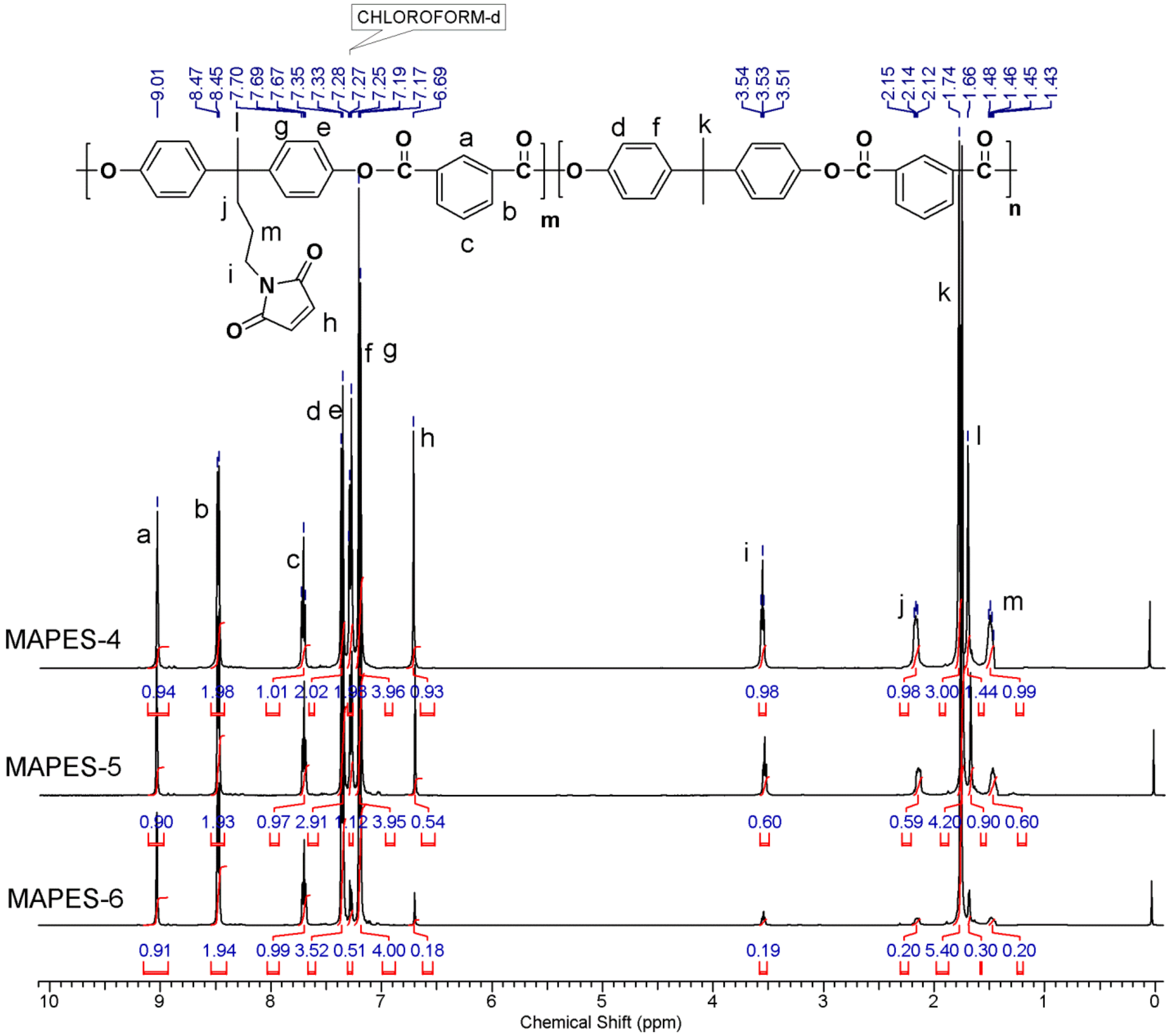
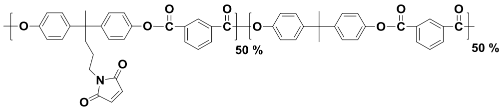
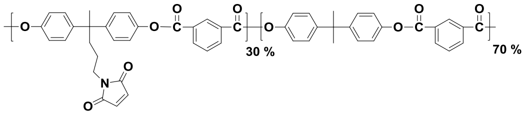
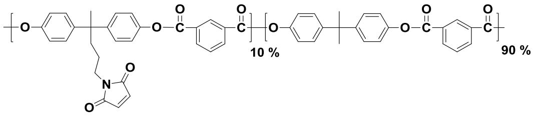


Figure 6b.5. ^{1}H NMR spectra (in $CDCl_3$) of copolyesters.

Table 6b.2. Molar composition of copolyesters determined by ^{1}H NMR spectra

Copolyester	Structure of copolyester	Feed BPA-MA, mol %	Observed BPA-MA, mol %
MAPES-4		50	49.0
MAPES-5		30	30.0
MAPES-6		10	9.5

The microstructure of copolyesters derived from copolymerization of BPA and BPA-MA with IPC was studied by ^{13}C NMR spectroscopy. Under the employed experimental conditions, the copolymerization of BPA and BPA-MA is expected to lead to formation of random copolyesters with following possibilities of enchainment of two bisphenol moieties wherein three adjacent monomer units are considered (**Figure 6b.6**).

The assignments of carbon atoms in ^{13}C NMR spectrum of MAPES-4, as a representative example, were confirmed by heteronuclear multiple bond correlation spectroscopy (HMBC). HMBC spectrum along with assignments is reproduced in **Figure 6b.7.**

^{13}C NMR spectrum of MAPES-4 (50:50 mol % of BPA-MA:BPA) along with assignments of carbon atoms is presented in **Figure 6b.8.** For easy comparison, ^{13}C NMR spectra of homo-polyester MAPES-1 and copolyesters MAPES-4 to MAPES-6 are also included in **Figure 6b.8**. Unlike in case of ^{13}C NMR spectra of copolyesters based on PPH-MA (**Chapter 5a**) and PPH-N_3 (**Chapter 6a**), wherein four peaks were observed corresponding to ester carbonyl carbon (at 163.85 δ ppm, 163.94 δ ppm, 164.15 δ ppm and 164.25 δ ppm, and at 163.87 δ ppm, 163.97 δ ppm, 164.15 δ ppm and 164.25 δ ppm, respectively), only two peaks were observed for ester carbonyl carbon (at 164.15 δ ppm, 164.25 δ ppm) in the case of MAPES-4. The lesser number of peaks corresponding to carbonyl carbon in case of copolyesters containing pendant maleimide groups could be attributed to the structural resemblance of BPA-MA and BPA.

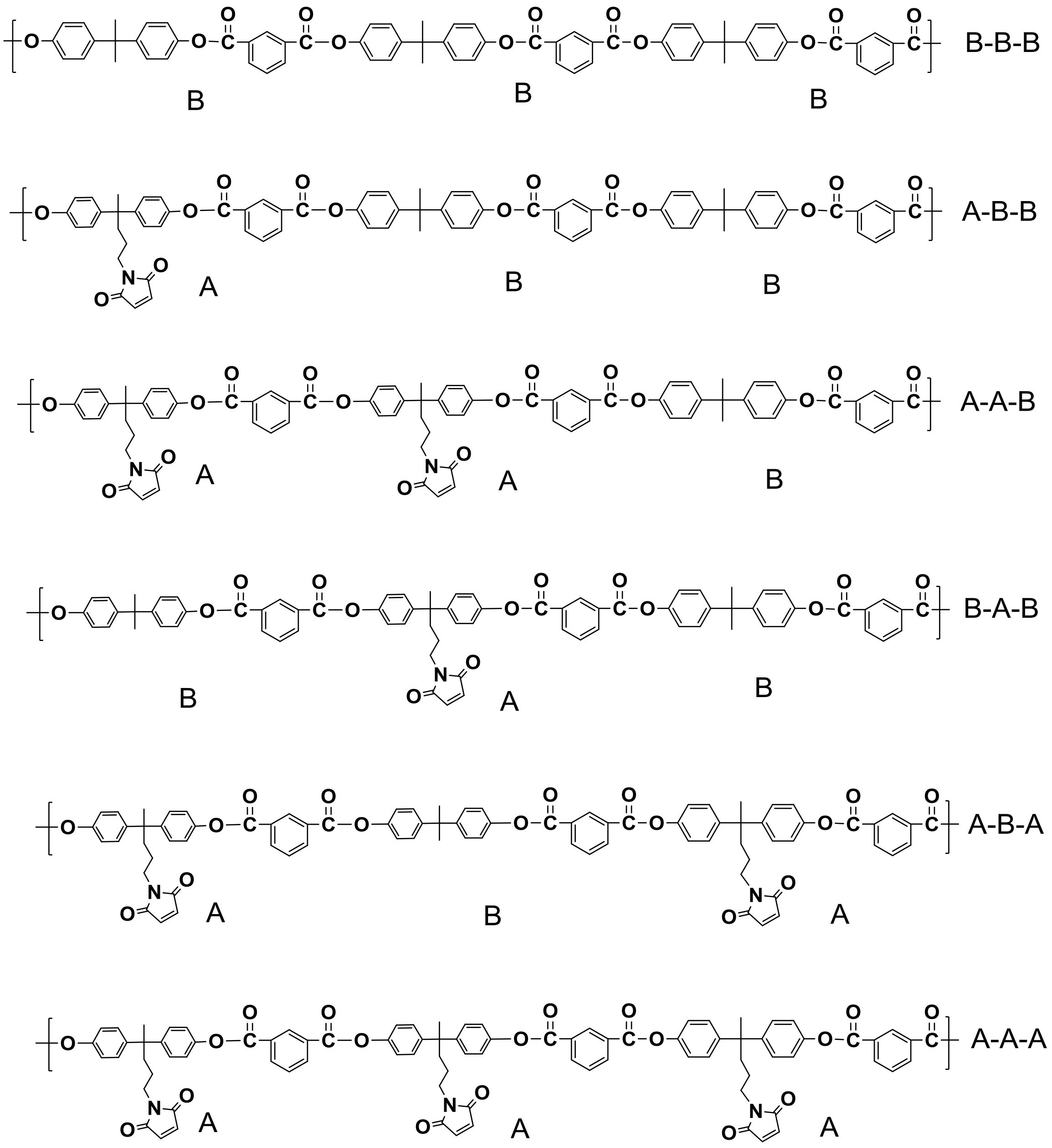


Figure 6b.6. Possible arrangements of BPA-MA and BPA units in copolyesters.

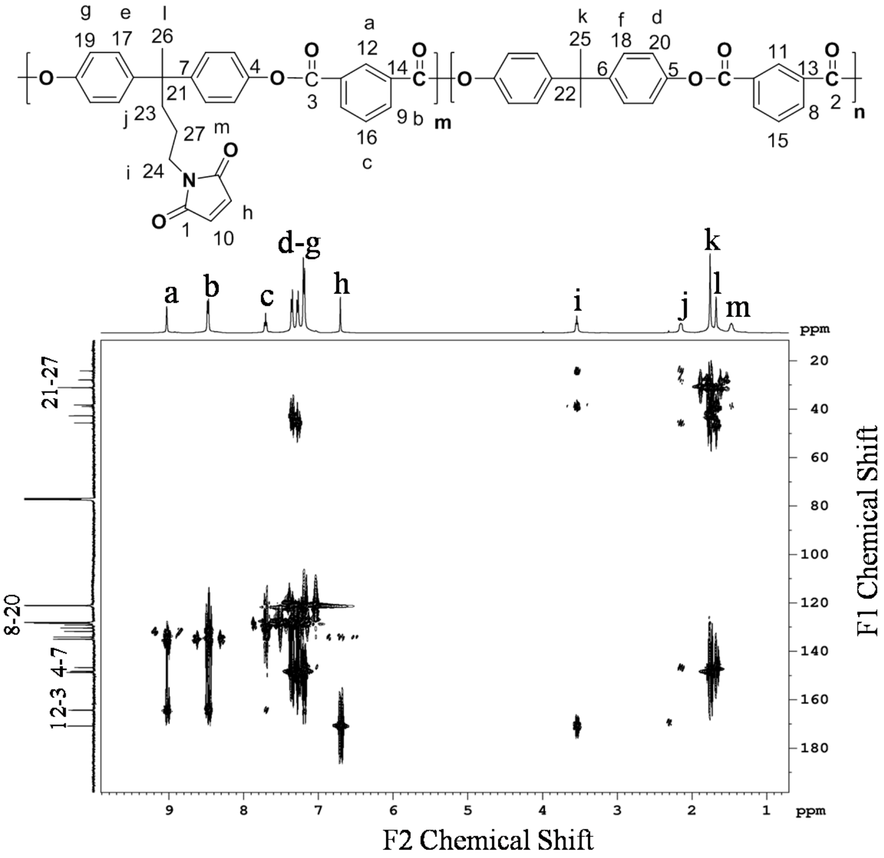
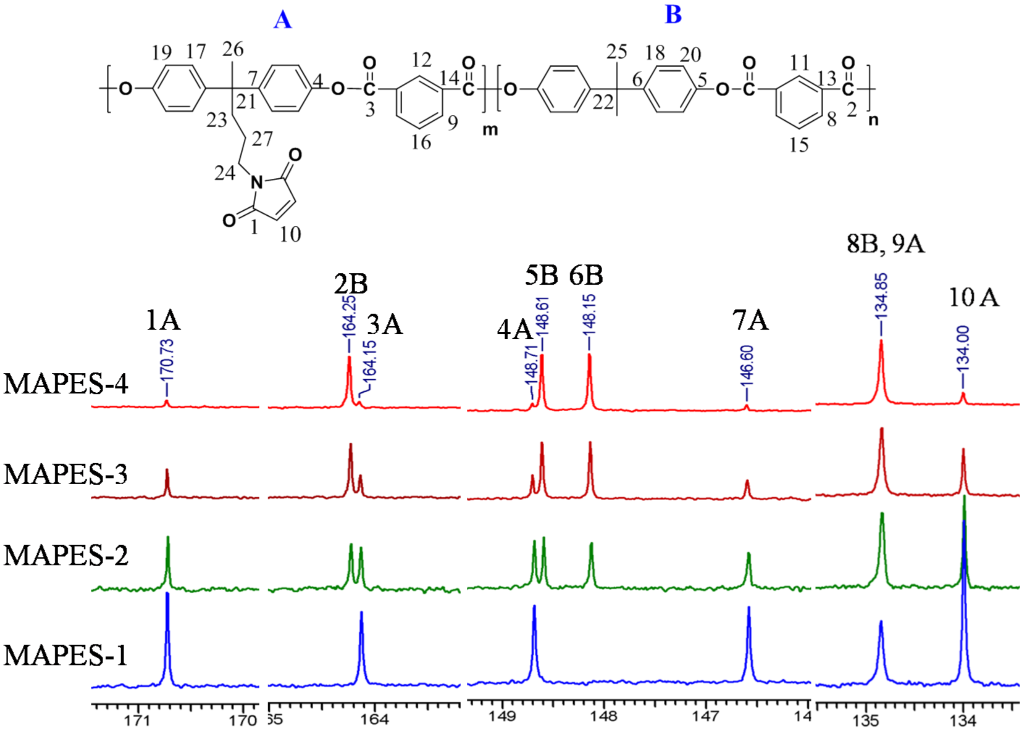


Figure 6b.7. HMBC spectrum (in $CDCl_3$) of MAPES-4.



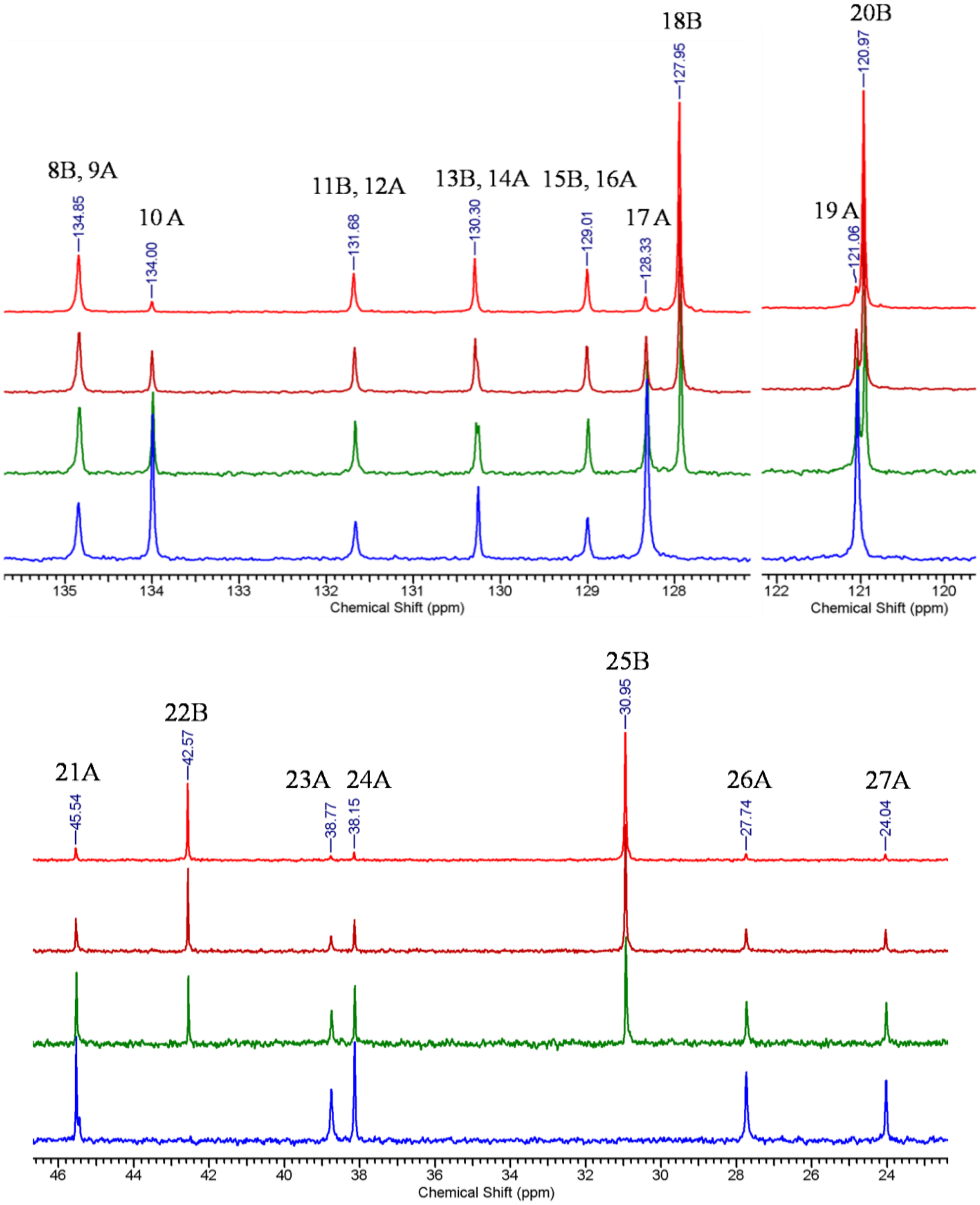


Figure 6b.8. ^{13}C NMR spectra (in $CDCl_3$) of copolyesters.

6b.3.3 X-Ray diffraction studies

The crystallinity of aromatic polyesters containing pendant maleimide groups was evaluated by wide angle X-ray diffraction studies (WAXD). X-Ray diffractograms of aromatic polyesters are reproduced in **Figure 6b.9**. All the aromatic polyesters revealed broad halo over 2θ range of ~10-35^{o}. This clearly indicated that the introduction of alkyl chain containing pendant maleimide groups into polymer backbone hindered the chain packing resulting in amorphous nature of these aromatic polyesters, which is also reflected in their enhanced solubility.

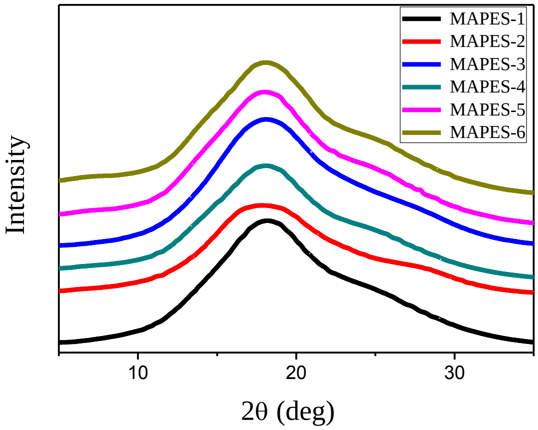


Figure 6b.9. X-Ray diffractograms of (co)polyesters.

6b.3.4 Thermal properties of (co)polyesters

The thermal stability of (co)polyesters containing pendant maleimide groups was evaluated by thermogravimetric analysis at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. TG curves of (co)polyesters are illustrated in **Figure 6b.10A, Figure 6b.10B** contains representative thermogram (TG) and differential thermogram (DTG) curve of MAPES-1. The thermal behavior data of polyesters is summarized in **Table 6b.3**. The temperature at 10% weight loss (T_{10}) of (co)polyesters was in the range of 464-468 ^{o}C indicating their good thermal stability. The char yield of (co)polyesters at 800 ^{o}C was found in the range 24-28 %. The data clearly indicated that char yield in the series of copolyesters decreased with increase in content of BPA-MA.

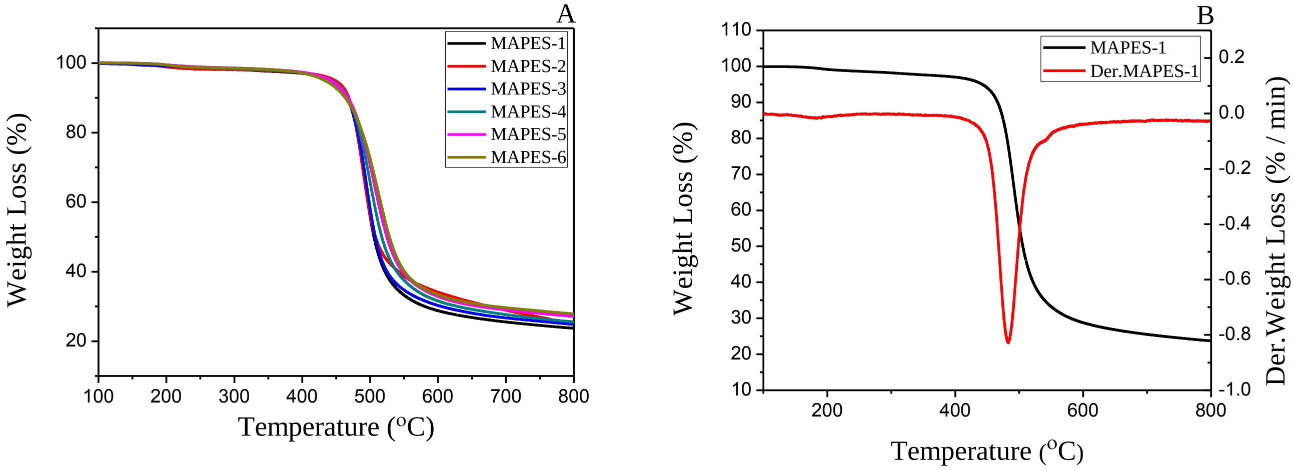


Figure 6b.10. A) TG curves of (co)polyesters; B) Representative TG and DTG curves of polyester MAPES-1.

Glass transition temperature (T_g) of polyesters was evaluated by differential scanning calorimetry (DSC) from second heating scans at a heating rate of 10 °C/min **(Figure 6b.11)**. It is reported in the literature that upon heating at temperature higher than 190 °C, maleimide groups undergo cross-linking reaction *via* free radical mechanism[15,29]. Therefore, aromatic (co)polyesters containing pendant maleimide groups were heated only upto 190 °C in DSC measurements. T_g values are summarized in **Table 6b.3**. DSC curves of polyesters MAPES-1, MAPES-2 and MAPES-3 obtained from second heating scan showed T_g at 142 °C, 166 °C and 154 °C, respectively. A comparison of this data with literature T_g values of polyesters from BPA-TPC, (210 °C) BPA-IPC (181 °C) and BPA-TPC+IPC (197 °C)[30] indicated that there is a drop in glass transition temperature of polyesters by the incorporation of pendant alkyl chain with maleimide groups. Copolyesters showed T_g values in the range 162 °C-178 °C and the values tend to decrease with increase in mol % incorporation of BPA-MA.

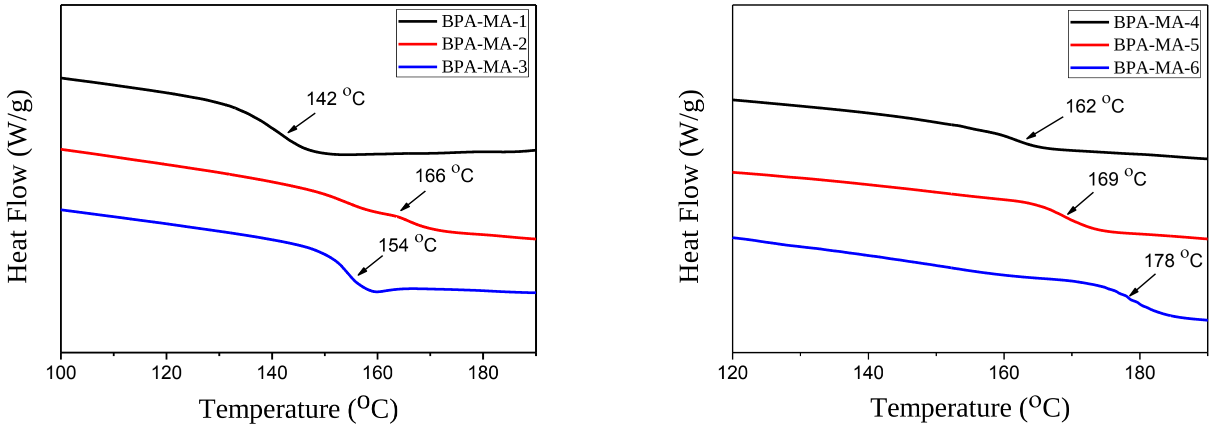


Figure 6b.11. DSC curves of (co)polyesters.

The experimental T_g values of polyesters were compared to the theoretical T_g values calculated by Fox equation.[31]

$$\frac{1}{T_{gc}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Where, T_{gc} is the T_g of copolyesters and T_{g1} and T_{g2} are T_g of homo-polyesters derived from BPA-MA and BPA, respectively (i.e. T_{g1}=142 °C, T_{g2}=181 °C). W_1 and W_2 represent weight fractions of BPA-MA and BPA in the copolyesters. The $1/T_g$ of (co)polyesters were plotted against weight fraction of BPA-MA in % and the plot is shown in **Figure 6b.12.** The T_g value obtained from DSC exhibited a nearly linear relationship with weight % BPA-MA. The calculated T_g are summarized in **Table 6b.3.**

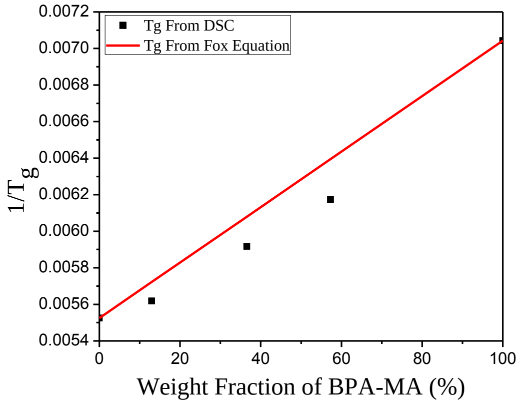
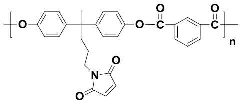
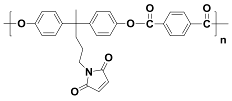
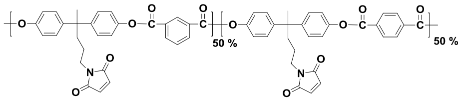
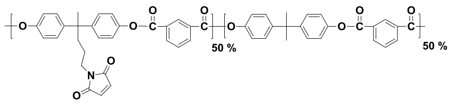
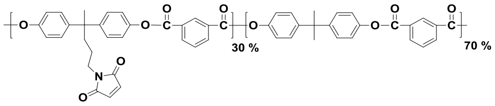
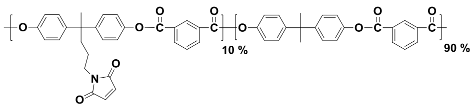


Figure 6b.12. $1/T_g$ as a function of weight % of BPA-MA in copolyesters.

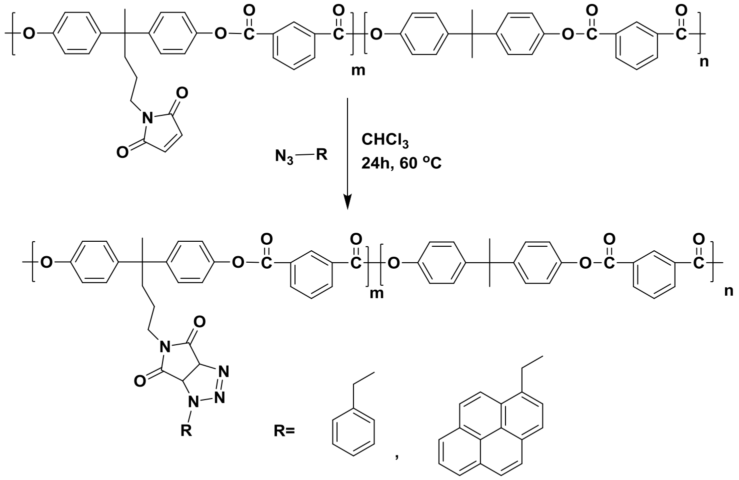
Table 6b.3. Thermal properties of (co)polyesters

(Co)polyester	**Structure of (Co)polyester**	**T_{10} (^{o}C)^{a}**	**Char Yield (%)^{b}**	**T_g (^{o}C)^{c}**
MAPES-1		466	24	142
MAPES-2		468	25	166
MAPES-3		466	25	154
MAPES-4		467	26	162 (156.4)^{d}
MAPES-5		467	27	169 (164.5)^{d}
MAPES-6		464	28	178 (174.8)^{d}

a: 10 % Weight loss on TGA thermograms at a heating rate of 10 ^{o}C/min under nitrogen atmosphere, b: Char yield was measured at 800 ^{o}C, c: Measured by DSC on second heating scan with heating rate of 10 ^{o}C /min under nitrogen atmosphere, d: T_g values calculated by Fox equation.

6b.3.5 Post-modification of copolyester using metal-free azide-maleimide cycloaddition reaction

The post-functionalization of polyester bearing pendant maleimide groups was demonstrated by metal-free 1, 3- dipolar azide-maleimide cycloaddition click reaction with two representative azido compounds, namely, Py-N_3 and Bz-N_3. **(Scheme 6b.3)**.



Scheme 6b.2. Click reactions of copolyester MAPES-4 with (azidomethyl)benzene and 1-(azidomethyl)-pyrene.

^{1}H NMR spectrum of polyester obtained after chemical modification by 1,3-dipolar cycloaddition click reaction with Py-N_3 is depicted in **Figure 6b.13**. ^{1}H NMR spectrum revealed complete disappearance of maleimide signal at 6.69 δ ppm, indicating complete conversion of these pendant groups. The assignments of other protons are indicated in **Figure 6b.13**. Similarly, disappearance of maleimide proton signals and appearance of expected protons signals were also observed for azide-maleimide cycloaddition reaction of polyester containing pendant maleimide groups MAPES-4 with Bz-N_3. Furthermore, no evidence of chain degradation was observed by GPC analysis (**Figure 6b.14**).

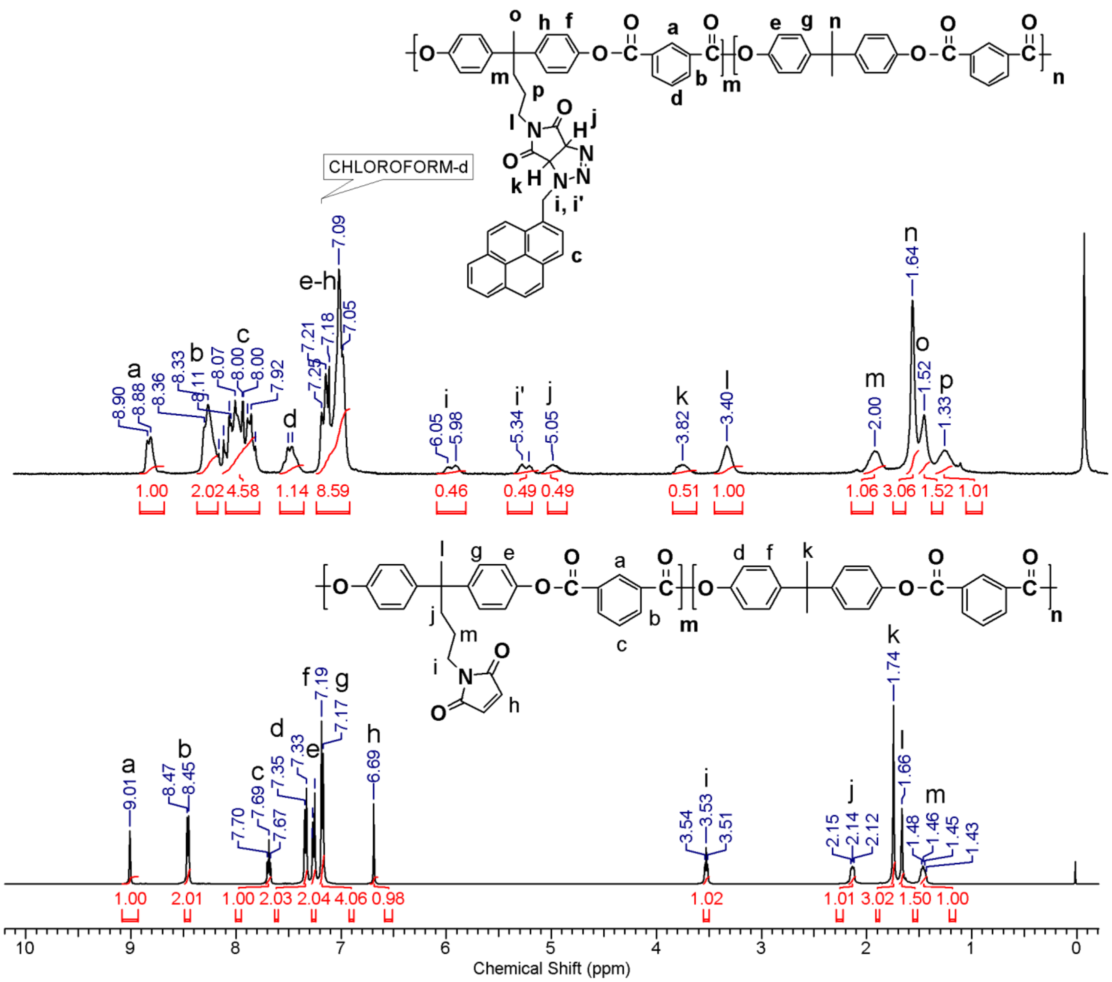


Figure 6b.13. ^{1}H NMR spectrum (in $CDCl_3$) of copolyester MAPES-4 before (bottom) and after (top) azide-maleimide cycloaddition reaction.

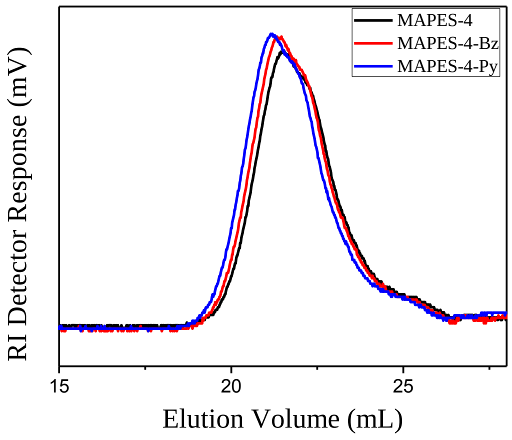


Figure 6b.14. GPC traces of MAPES-4, MAPES-4-Bz and MAPES-4-Py.

Copolyester MAPES-4 was functionalized with Py-N_3 *via* azide-maleimide cycloaddition reaction to yield MAPES-4-Py. UV-Vis spectra of MAPES-4 and MAPES-4-Py were recorded (**Figure 6b.15**).

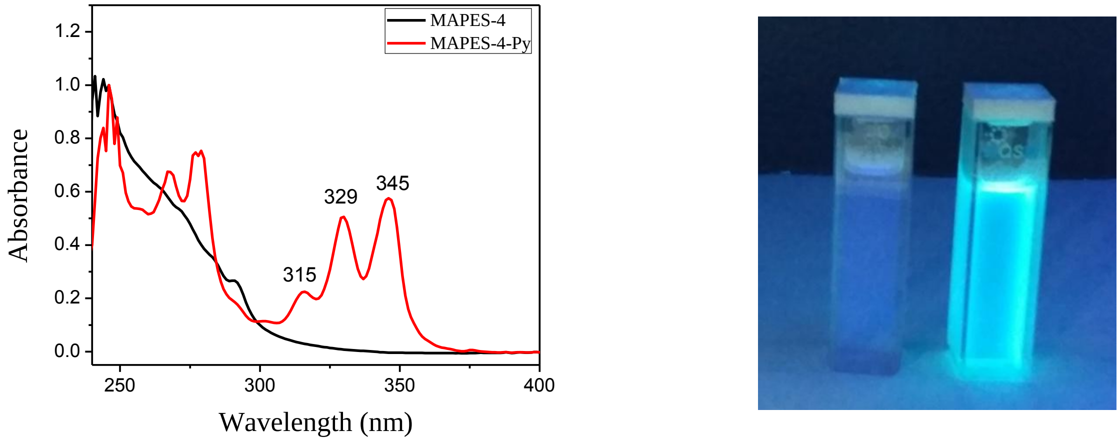


Figure 6b.15. UV-Vis spectra of MAPES-4 Py along with that of MAPES-4.

Three bands appeared at 315 nm, 329 nm and 345 nm in UV-Vis spectrum of MAPES-4-Py corresponding to typical pyrene vibronic bands (at 314 nm, 328 nm and 345 nm).[32] As expected, UV-Vis spectrum of MAPES-4 did not display any bands corresponding to pyrene vibronic bands. This result indicated that pyrene moiety was chemically bound to modified copolyester.

6b.4 Conclusions

New maleimide functionalized aromatic (co)polyesters were successfully synthesized by low temperature solution polycondensation of BPA-MA and different compositions of BPA-MA and bisphenol-A with aromatic diacid chlorides. Number average molecular weights of (co)polyesters were in the range 17,700-32,100 g/mol, indicating formation of moderate to reasonably high molecular weight polymers. Tough, transparent and flexible films of (co)polyesters could be cast from chloroform solutions. T_g and T_{10} values of the polyesters were in the range 142-178 °C and 464-468 °C, respectively. The feasibility of 1, 3 dipolar azide-maleimide cycloaddition click reaction on pendant maleimide groups was demonstrated by reactions with two representative azido group containing compounds. The metal-free click reaction proceeded quantitatively without affecting polyester backbone, which was confirmed by ^1H NMR spectroscopy and GPC analysis.

6b.5 References

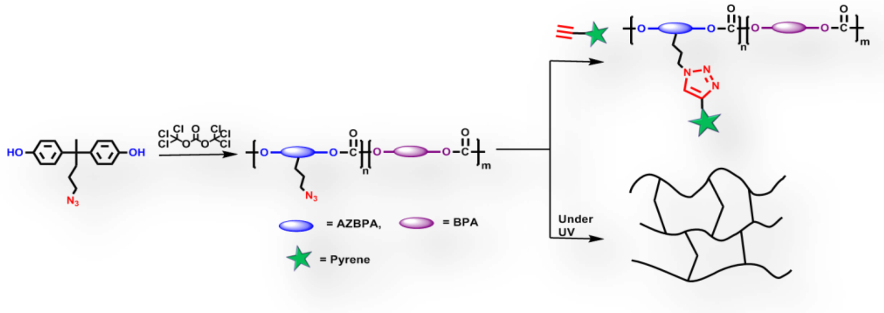
1. Arunbabu, D., Noh, S. M., Nam, J. H., Oh, J. K. *Macromol. Chem. Phys.*, 2016, **217**, 2191–2198.
2. Kötteritzsch, J., Stumpf, S., Hoeppener, S., Vitz, J., Hager, M. D., Schubert, U. S. *Macromol. Chem. Phys.*, 2013, **214**, 1636–1649.
3. Varganici, C.-D., Ursache, O., Gaina, C., Gaina, V., Rosu, D., Simionescu, B. C. *Ind. Eng. Chem. Res.*, 2013, **52**, 5287–5295.
4. Gacal, B., Durmaz, H., Tasdelen, M. a, Hizal, G., Tunca, U., Yagci, Y., Demirel, A. L. *Macromolecules*, 2006, **39**, 5330–5336.
5. Dag, A., Aydin, M., Durmaz, H., Hizal, G., Tunca, U. *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4476–4483.
6. Billiet, L., Gok, O., Dove, A. P., Sanyal, A., Nguyen, L.-T. T., Du Prez, F. E. *Macromolecules*, 2011, **44**, 7874–7878.
7. Onbulak, S., Tempelaar, S., Pounder, R. J., Gok, O., Sanyal, R., Dove, A. P., Sanyal, A. *Macromolecules*, 2012, **45**, 1715–1722.
8. Yang, H., Li, X., Lan, Y., Tian, T., Cui, J., Zhu, T., Shen, D., Li, G. *J. Mater. Chem. C*, 2013, **1**, 6120–6128.
9. Arslan, M., Gevrek, T. N., Lyskawa, J., Szunerits, S., Boukherroub, R., Sanyal, R., Woisel, P., Sanyal, A. *Macromolecules*, 2014, **47**, 5124–5134.
10. Yilmaz, I. I., Arslan, M., Sanyal, A. *Macromol. Rapid Commun.*, 2012, **33**, 856–862.
11. Xing, D., Ma, L., Gao, C. *Macromol. Biosci.*, 2014, **14**, 1429–1436.
12. Pounder, R. J., Stanford, M. J., Brooks, P., Richards, S. P., Dove, A. P. *Chem. Commun.*, 2008, 5158–5160.
13. Zhu, H.-Z., Wang, G., Wei, H.-L., Chu, H.-J., Zhu, J. *Macromol. Res.*, 2016, **24**, 793–799.
14. Varma, I. K., Choudhary, V., Gaur, B., Lochab, B., Oberoi, S., Chauhan, R. *J. Appl. Polym. Sci.*, 2006, **101**, 779–786.
15. Gaina, C., Gaina, V., Ciobanu, C. *J. Appl. Polym. Sci.*, 2009, **113**, 3245–3254.
16. Stevens, M. P., Jenkins, A. D. *J. Polym. Sci. Polym. Chem. Ed.*, 1979, **17**, 3675–3685.
17. Decker, C., Bianchi, C. *Polym. Int.*, 2003, **52**, 722–732.
18. Serna, F. J., de Abajo, J., de la Campa, J. G. *Br. Polym. J.*, 1987, **19**, 453–458.
19. Dong, X., Chen, L., Duan, R.-T., Wang, Y.-Z. *Polym. Chem.*, 2016, **7**, 2698–2708.

20. Yu, S., Zhang, R., Wu, Q., Chen, T., Sun, P. *Adv. Mater.*, 2013, **25**, 4912–4917.
21. Lin, C., Sheng, D., Liu, X., Xu, S., Ji, F., Dong, L., Zhou, Y., Yang, Y. *Polymer*, 2017, **127**, 241–250.
22. De Abajo, J., De Santos, E. *Angew. Makromol. Chemie*, 1983, **111**, 17–27.
23. Bandyopadhyay, P., Banerjee, S. *Ind. Eng. Chem. Res.*, 2014, **53**, 18273–18282.
24. Liu, Y.-L., Lee, H.-C. *J. Polym. Sci. Part A Polym. Chem.*, 2006, **44**, 4632–4643.
25. Liu, Y.-L., Chen, Y.-W. *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
26. Liu, Y.-L., Hsieh, C.-Y., Chen, Y.-W. *Polymer*, 2006, **47**, 2581–2586.
27. Liu, Y.-L., Li, S.-H., Lee, H.-C., Hsu, K.-Y. *React. Funct. Polym.*, 2006, **66**, 924–930.
28. Mikroyannidis, J. A. *J. Polym. Sci. Part A Polym. Chem.*, 1990, **28**, 669–677.
29. Jin, S., Yee, A. F. *J. Appl. Polym. Sci.*, 1991, **43**, 1865–1874.
30. Snehalata, B. Ph.D. Thesis, Savitribai Phule Pune University, India, 2007.
31. Fox, T. G. *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
32. Zhao, C., Wu, D., Lian, X., Zhang, Y., Song, X., Zhao, H. *J. Phys. Chem. B*, 2010, **114**, 6300–6308.

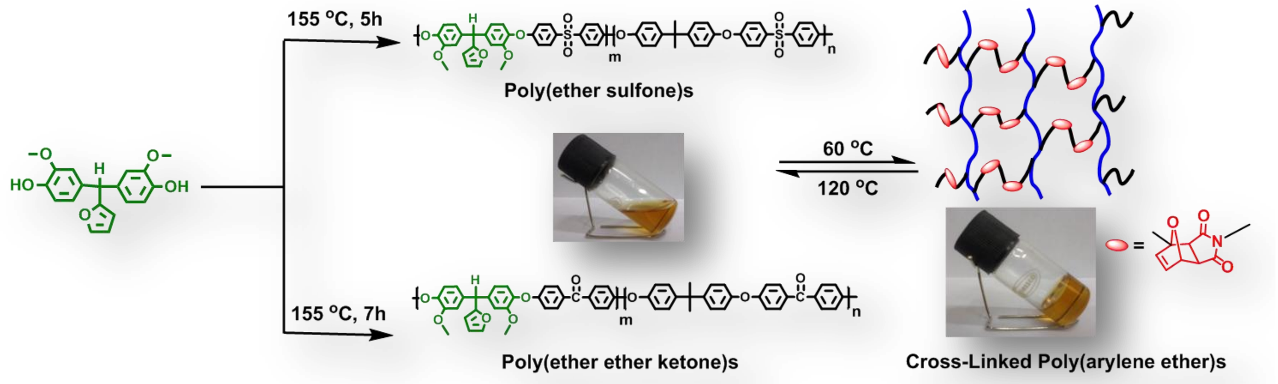
Chapter-7

Summary and Conclusions

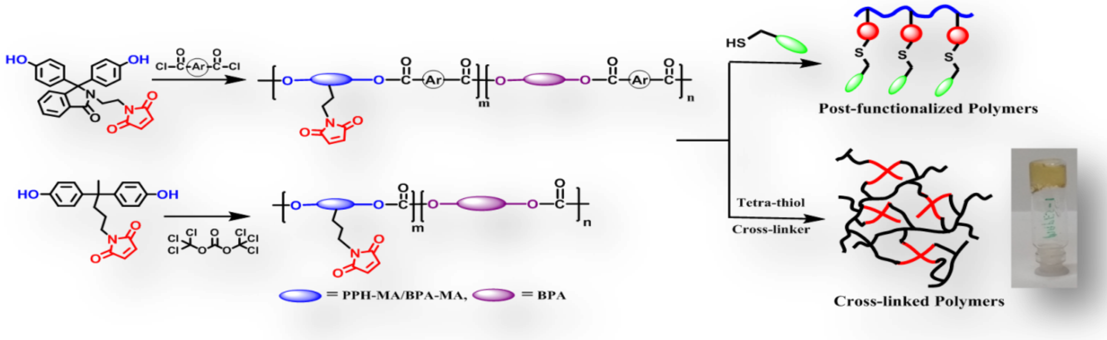
Chapter 3



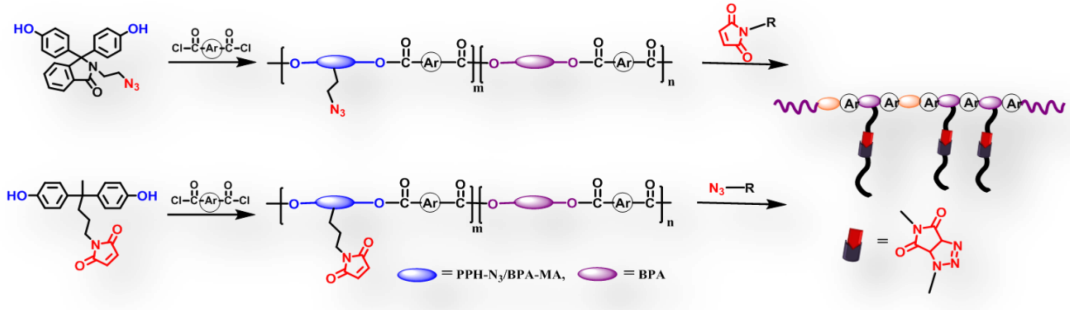
Chapter 4



Chapter 5



Chapter 6



7.1 Summary

The overall objective of the research work was to design and synthesize aromatic step-growth polymers containing pendant clickable groups *via* functional monomer approach and to demonstrate the feasibility of chemical modification of synthesized polymers using appropriate click reactions. To achieve the set targets, a total of five bisphenol monomers bearing pendant clickable functional groups such as azido, maleimide or furyl were synthesized. Of these, four bisphenols were synthesized for the first time. The utility of these bisphenol monomers for synthesis of a range of step-growth polymers such as aromatic polyesters, polycarbonates, poly(ether sulfone)s and poly(ether ether ketone)s was demonstrated under certain reaction conditions taking into consideration thermal and chemical stability of the clickable functional group involved.

A new bisphenol containing pendant azido group, namely, 4, 4’-(5-azidopentane-2, 2-diyl) diphenol (AZBPA) was successfully synthesized starting from commercially available 4, 4’-bis (4-hydroxyphenyl) pentanoic acid. Aromatic polycarbonate containing pendant azido groups was synthesized by solution polycondensation of AZBPA with triphosgene. Copolycarbonates possessing pendant azido groups were also synthesized by utilizing different molar proportions of AZBPA and BPA with triphosgene. The chemical structures of polycarbonates were confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. By analyzing triad sequence distribution using expanded ^{13}C NMR spectra, it was found that random copolycarbonates were formed. Number-average molecular weights of (co)polycarbonates were in the range 35,400–42,200 g/mol. Glass transition temperature (T_g) values of (co)polycarbonates were observed in the range 106-143 °C and T_g values decreased with increase in content of AZBPA in copolycarbonates. ΔH_{exo} of curing reactions of polycarbnates studied by DSC in nonisothermal mode was observed in the range 93-877 J/g. The increase in ΔH_{exo} was observed with increase in the content of azido functional groups in (co)polycarbonates. The feasibility of CuAAC reaction on pendant azido groups was demonstrated by reaction with 1-[(2-propynyloxy)methyl]pyrene. With CuBr/Et_3N as the catalyst system, click reaction proceeded quantitatively without affecting the polycarbonate backbone. The complete conversion of pendant azide functionalities to triazoles was confirmed by IR and ^{1}H NMR spectral analysis. Thus, polycarbonates possessing pendant azido groups represent interesting precursors for synthesis of polycarbonates containing a range of functional groups *via* azide-alkyne click reaction with appropriate alkynes. By taking advantage of the presence of photo-cleavable azido functionality, photo-crosslinking of aromatic polycarbonates bearing pendant azido groups was carried out under UV irradiation to obtain cross-linked polycarbonates possessing enhanced thermal and mechanical properties.

A fully bio-based bisphenol bearing pendant furyl group, namely, 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) was synthesized by reaction of furfural and guaiacol- both of which are derived from lignocellulose. BPF was successfully utilized for synthesis of a new series of partially bio-based (co)poly(ether sulfone)s by aromatic nucleophilic substitution polycondensation with bis(4-fluorophenyl) sulfone. The high molecular weight (co)poly(ether sulfone)s were obtained which could be formed into tough, transparent and flexible films from chloroform solutions. ^{13}C NMR spectral analysis of (co)poly(ether sulfone)s revealed the formation of random copolymers. (Co)poly(ether sulfone)s showed 10% weight loss in the temperature range 431-481 ^{o}C indicating their good thermal stability. T_g values of (co)poly(ether sulfone)s were in the range 179-189 ^{o}C and decreased with the increase in the content of BPF. Tensile strength, Young's modulus and elongation at break, obtained from tensile testing of (co)poly(ether sulfone)s containing pendant furyl groups, were in the range 76.7-83.8 MPa, 1.02-1.18 GPa and 21.4-89.7 %, respectively indicating their suitability in structural applications. Subsequently, thermally reversible cross-linked poly(ether sulfone)s were prepared from the corresponding linear polymers containing pendant furyl groups by reaction with bismaleimides *via* Diels-Alder reaction. The formation of cross-linked poly(ether sulfone)s was demonstrated by gelation tests, DSC and tensile measurements. The cross-linked PSU-2-BMI showed improved mechanical properties and was recycled two times without significant deterioration of mechanical properties.

A new series of aromatic (co)poly(ether ether ketone)s bearing pendant furyl groups was successfully synthesized by aromatic nucleophilic substitution polycondensation of BPF or mixtures of BPF and BPA with commercially available 4,4′-difluorobenzophenone. Reasonably high molecular weight, film forming (co)poly(ether ether ketone)s were obtained. (Co)poly(ether ether ketone)s were readily soluble at room temperature in organic solvents such as dichloromethane, chloroform, THF, DMAc, DMF and NMP. The observed bisphenol composition, as determined from ^{1}H NMR spectra, of copoly(ether ether ketone)s matched well with the feed composition. With the triad sequence distribution analysis using expanded ^{13}C NMR spectra, random enchainment of bisphenol units was observed for copoly(ether ether ketone)s. The broad halo over 2θ ≈ 10–30º was observed for (co)poly(ether ether ketone)s in the wide angle X-ray diffraction patterns which revealed their amorphous nature. The 10 % weight loss temperature of (co)poly(ether ether ketone)s was found in the range 429-464 °C, indicating their good thermal stability. Glass transition temperatures (T_g) of (co)poly(ether ether ketone)s were in the range 152-156 °C. Furthermore, copoly(ether ether ketone) (PEEK-2) was cross-linked with 1, 1'-(methylenedi-4, 1-phenylene)bismaleimide *via* Diels-Alder reaction to form cross-linked PEEK-2-BMI which could be thermally recycled by taking advantage of retro-Diels Alder reaction. The cross-linked PEEK-2-BMI showed improved mechanical properties and was recycled two times without significant loss of mechanical properties.

A new maleimide functionalized bisphenol, namely, N-maleimidoethyl-3, 3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-MA) was readily synthesized starting from commercially available phenolphthalein. A series of aromatic (co)polyesters containing pendant clickable maleimde groups was synthesized from PPH-MA or varying mixtures of PPH-MA and BPA and aromatic diacid chlorides by low temperature solution polycondensation method. Inherent viscosities and number-average molecular weights of (co)polyesters containing pendant maleimide groups were in the range 0.52-0.97 dL/g and 20,200–32,800 g/mol, respectively. **(**Co)polyesters were soluble in chloroform, dichloromethane, THF, DMAc and DMF at room temperature. Tough, transparent and flexible films could be cast from solutions of (co)polyesters in chloroform. X-Ray diffractograms showed that polyesters containing pendant maleimide groups were amorphous in nature. Temperatures of 10 % weight loss (T_{10}) for (co)polyesters were in the range 470-484 °C indicating their good thermal stability. Subsequently, thiol-maleimide Michael reaction was employed to modify aromatic polyester by reaction of their pendant maleimide groups with 4-chlorothiophenol and 1-adamantanethiol. ^{1}H NMR spectra and GPC analysis of post-modified polyesters confirmed quantitative chemical reactions and absence of backbone degradation, respectively. Furthermore, it was demonstrated that gel could be readily fabricated *via* thiol-maleimide click reaction of maleimide functionalized polyester MAPES-1 and pentaerythritol tetra(3-mercaptopropionate) as the cross-linker.

A new maleimide functionalized bisphenol, *viz.*, 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) was conveniently synthesized as an A_2 monomer starting from 4, 4'- (5 - azidopentane-2, 2- diyl) diphenol. A series of aromatic (co)polycarbonates bearing pendant maleimide groups was synthesized from BPA-MA or varying compositions of BPA-MA and bisphenol A and triphosgene as carbonyl source *via* solution polymerization. Notably, maleimide functionalized polycarbonates were obtained without the need for additional protection and deprotection steps. Inherent viscosities and number average molecular weights of (co)polycarbonates containing pendant maleimide groups were in the range 0.46-0.66 dL/g and 24,600-36,700 g/mol, respectively, indicating the formation of reasonably high molecular weight polymers. Polycarbonates could be cast into tough, transparent and flexible films from chloroform solutions. The T_{10} values for (co)polycarbonates were in the range 452-462 °C indicating their high thermal stability. The lowering of T_g in polycarbonates (127-145 °C) could be attributed to the presence of packing disruptive pendant alkyl chain containing maleimide group. Subsequently, post-polymerization modification of pendant maleimide groups in polycarbonate backbone by thiol-maleimide Michael type addition click reaction under mild reaction conditions with two representative thiols was demonstrated. The post-modification reactions were quantitative and free from any side reactions as indicated by ^{1}H NMR spectroscopy and GPC analysis. Additionally, it was demonstrated that gel could be readily produced *via* thiol-maleimide Michael addition reaction from maleimide functionalized polycarbonate and a thiol cross-linker. Aromatic polycarbonate bearing pendant maleimide groups provide interesting opportunities for chemical modifications with a range of commercially available thiols of divergent chemical structures.

2-(2-Azidoethyl)-3, 3-bis(4-hydroxyphenyl) isoindolin-1-one (PPH-N_3) was successfully synthesized starting from commercially available phenolphthalein. Aromatic polyesters containing pendant azido groups were prepared by low temperature solution polycondensation of PPH-N_3 with aromatic diacid chlorides. Copolyesters were also synthesized by utilizing different molar proportions of PPH-N_3 and BPA with IPC. Reasonably high molecular weight, organo-soluble and film forming (co)polyesters of amorphous nature were obtained. The thermal decomposition of polyesters containing pendant azido groups was found to be take place in three steps. The first step of decomposition which occurred in the temperature range 200-283 °C was attributed to decomposition of azido groups. The second and the third stage of decomposition could be presumably due to degradation of alkyl side chain and the polyester backbone, respectively. The curing reactions of polyesters involving azido groups were studied by DSC in nonisothermal mode and ΔH_{exo} values of curing reactions were observed in the range 44-447 J/g. A linear increase in ΔH_{exo} values was observed with increase in the content of azido functional groups in copolyesters. Subsequently, the feasibility of post-modification of copolyesters bearing pendant azido groups by metal-free 1, 3-dipolar cycloaddition click reaction with two representative maleimides, namely, N-methylmaleimide and N-hexylmaleimide was demonstrated. In both the cases, the quantitative reaction occurred without any backbone degradation as revealed by IR and ^{1}H NMR spectroscopy and GPC analysis.

A series of new (co)polyesters bearing pendant maleimide groups was synthesized by low temperature solution polycondensation of 4, 4'-(5-maleimidopentane-2, 2-diyl) diphenol (BPA-MA) or varying ratios of BPA-MA and bisphenol-A with aromatic diacid chlorides. Number average molecular weights of (co)polyesters were in the range 17,700-32,100 g/mol, indicating formation of moderate to reasonably high molecular weight polymers. Tough, transparent and flexible films of (co)polyesters could be cast from chloroform solutions. T_g and T_{10} values of polyesters were in the range 142-178 °C and 464-468 °C, respectively. The feasibility of 1, 3 dipolar azide-maleimide cycloaddition click reaction on pendant maleimide groups present in copolyester was demonstrated by reactions with two representative azides. The catalyst-free chemical modification reactions proceeded in quantitative manner.

7.2 Future perspectives

The present work based on design and synthesis of bisphenols bearing pendant clickable groups and aromatic step-growth polymers such as polycarbonates, polyesters, poly(ether sulfone)s and poly(ether ether ketone)s has opened up many prospects for the future work.

- The present work which deals with synthesis of bisphenol monomers possessing pendant clickable groups has broadened the range of monomers available for synthesis of functionalized aromatic step-growth polymers which can be subsequently post-functionalized by employing appropriate click reactions.
- By using the synthetic strategies devolved in this work, it is possible to expand the repertoire of bisphenols bearing pendant clickable groups. For instance, a range of clickable groups such as cyclopentadiene, alkyne, alkene, anthracenyl, norbornene, indole, etc could be introduced into bisphenol monomers by use of appropriate reagent for reactions with 4, 4'-bis (4-hydroxyphenyl) pentanoic acid and phenolphthalein.
- The present work on post-modification of synthesized step-growth polymers containing pendant functional groups was focused on demonstration of reactivity of functional groups with appropriate model compounds. The findings suggest that these polymers are

valuable precursors for synthesis of polymers with set of desired properties by appropriate choice of low molecular weight reagent/prepolymer for chemical modifications.

- Synthesis of functional copolyesters or copolycarbonates can be carried out from a combination of bisphenols bearing pendant (protected) maleimide or furyl groups with suitable comonomers (diacid chlorides or phosgene) and the resulting polymers containing maleimide and furyl groups pendant to the same polymer chain could be further self cross-linked *via* Diels-Alder click reaction.
- Polyesters and polycarbonates containing pendant maleimide groups can be utilized for the preparation of cross-linked materials under UV and thermal treatments.
- The concept of polymer blending is of paramount importance due to improvement of specific properties of polymers involved in the blending process. The synthesized polymers containing pendant maleimide groups can be blended chemically with polymers containing pendant furyl groups *via* Diels-Alder click reaction and blends are anticipated to exhibit enhanced physico-chemical properties.

List of Patents

- **Samadhan S. Nagane,** Prakash S. Sane, Bhausaheb V. Tawade, Prakash P. Wadgaonkar, 2, 2′-bis (4-hydroxyphenyl) alkyl azides and process for the preparation thereof, *US Patent 9562004 B*2**,** 2017**.**
- **Samadhan S. Nagane,** Sachin S. Kuhire, Prakash P. Wadgaonkar, Bisphenols containing pendant 'clickable maleimide group and polymers therefrom, *US Patent 20180009788 A1*, 2018**.**
- Sachin S. Kuhire, **Samadhan S. Nagane,** Prakash P. Wadgaonkar, Pendant furyl containing bisphenols, polymers therefrom and a process for the preparation thereof, *EP 3119750 A1*, 2017**.**

List of Publications

- **Samadhan S. Nagane** and Prakash P. Wadgaonkar, (Co)polycarbonates Containing Pendant Azido Groups: Synthesis, Characterization and Chemical Modifications, *Journal of Polymer Science, Part A: Polymer Chemistry*, *(Manuscript communicated).*
- **Samadhan S. Nagane** and Prakash P. Wadgaonkar, Thermally Reversible Cross-linked (Co)poly(arylene ether)s *via* Furan-Maleimide Diels-Alder Reaction, *(Manuscript under preparation).*
- **Samadhan S. Nagane** and Prakash P. Wadgaonkar, Synthesis, Characterization and Chemical Modifications of Aromatic Polycarbonates *via* Maleimide-Thiol Click Reaction, *(Manuscript under preparation).*

- Sachin S. Kuhire, **Samadhan S. Nagane** and Prakash P. Wadgaonkar, Poly(ether urethane)s from aromatic diisocyanates based on lignin-derived phenolic acids**,** *Polymer International*, 66, (2017), 882-866.
- Prakash S. Sane, Bhausaheb V. Tawade, Indravadan Parmar, Savita Kumari, **Samadhan Nagane** and Prakash P. Wadgaonkar, A Facile Strategy for Synthesis of α, α'-Heterobifunctionalized Poly(e-caprolactone)s and Poly(methyl methacrylate)s Containing ''Clickable''Aldehyde and Allyloxy Functional Groups Using Initiator Approach, *Journal of Polymer Science, Part A: Polymer Chemistry*, 51 (2013), 2091–2103.