" High Performance Polymers : Synthesis, Characterization and Chemical Modifications"

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By

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October 2013

To,

My Father, Late Mr. S. R. Singh

&

My Brother, Late Mr. Rajendra Singh

_____

Certificate of the Guide

Certified that the work incorporated in the thesis entitled "**High Performance Polymers: Synthesis, Characterization and Chemical Modifications**" submitted by **Mrs. Savita Kumari** was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in this thesis.

October, 2013

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Declaration by the Candidate

I hereby declare that all the experiments embodied in this thesis entitled **"High Performance Polymers: Synthesis, Characterization and Chemical Modifications"**, submitted for the degree of Doctor of Philosophy in Chemistry, to the University of Pune has been carried out by me at the Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division, National Chemical Laboratory, Pune, 411008, India, under the supervision of Dr. Prakash P. Wadgaonkar. The work is original and has not been submitted in part or full by me, for any degree or diploma to this or to any other University.

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Abstract

High performance polymers such as aromatic polyesters and aromatic polyamides are versatile classes of polymers covering a wide range of properties and applications. However, for more specific applications, many of these polymers are limited in scope because of the lack of functionality on the polymer backbone for further modification so as to tailor their properties. In general, to introduce functionalities within the polymers made by step-growth polymerization, two functionalization techniques are considered: chain-end or along the backbone of the polymers. The use of end-capping agent containing appropriate functional group for introduction of desired functional end group(s) leads to polymer chain terminations and reduces the molecular weight. On the other hand, the introduction of functional side groups by step-growth polymerization is in general not straightforward as the reaction conditions are much more drastic (high temperatures, vacuum). These strategies suffer from a few limitations, among which the synthesis of a specific building block for each application or the need to consider additional protecting and deprotecting steps, which restrict the possibilities for industrial manufacturing. Because of these limitations, the focus on the research about functionalization of polyesters and polyamides has been moving toward the use of the recently discovered click chemistry approach. Click chemistry, introduced by Sharpless and co-workers in 2001, has won a great deal of attention because of its high selectivity, quantitative yield, mild reaction conditions, and absence of by-products. The most popular click reactions are the copper(I)-catalyzed azide-alkyne click reaction and thiol-ene click reaction. During the last few years, click reactions have become a very powerful tool in polymer chemistry for functionalizing synthetic macromolecules and synthesizing a wide range of polymer architectures. Click chemistry modification has so far been applied mostly to aliphatic polymers such as polyesters, polyamides, polycarbonates, polyurethanes, etc. To the best of our knowledge, chemical modification of high performance polymers such as aromatic polyesters and aromatic polyamides have not been widely investigated.

Therefore, our research work was focused on a combination of step-growth polymerization and click chemistry to obtain, using a facile and universal route, a range of functionalized aromatic polyesters and polyamides.

The thesis has been divided into the following eight chapters.

Chapter 1 gives a brief review of literature on chemical modification of polymers with an emphasis on click chemistry modifications of polymers containing pendent functional groups.

Chapter 2 discusses scope and objectives of the present thesis.

Chapter 3: Synthesis and Characterization of Difunctional Monomers Containing Pendent Propargyloxy, Allyloxy, Azido Group or Pentadecyl Chain.

This section describes synthesis of monomers.

A. Synthesis of difunctional monomers containing pendent propargyloxy, allyloxy or azido group starting from 1,1,1-tris(4-hydroxyphenyl)ethane, 5-hydroxyisophthalic acid and 4,4'-bis(4-hydroxyphenyl)pentanoic acid.

    1.   1,1-Bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

    2.   5-(Propargyloxy)isophthalic acid

    3   5-(Propargyloxy)isophthaloyl chloride

    4   5-(Propargyloxy)-1,3-diisocyanatobenzene

    5   5-(Allyloxy)isophthalic acid

    6   5-(Allyloxy)isophthaloyl chloride

    7   5-(Allyloxy)-1,3-diisocyanatobenzene

    8   4,4'–(5-Azidopentane-2,2-diyl)diphenol

B. Synthesis of difunctional monomers containing pendent pentadecyl chain starting from 3-pentadecyl phenol, which in turn obtained from CNSL-a renewable resource material.

    9   2,4-Diazido-1-pentadecylbenzene

    10   1-Azido-4(4-azidophenoxy)-2-pentadecylbenzene

    11   4-(4-(Chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride

    12   *N*-(4-Amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Chapter 4 is sub-divided into two sections:

Chapter 4a: Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy Groups

This section describes:

i.   Synthesis of clickable aromatic polyester containing pendent propargyloxy groups by interfacial polycondensation of 5-(propargyloxy)isophthaloyl chloride with bisphenol A.

ii.   Synthesis of copolyesters by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, solubility tests, gel permeation chromatography (GPC), FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, TGA and DSC. This section also describes the curing studies of polyesters containing pendent propargyloxy groups in nonisothermal mode. The enthalpy of curing (ΔH) of polyesters was computed using DSC technique.

Chapter 4b: Chemical Modification of Polyesters Containing Pendent Propargyloxy Groups

This section deals with chemical modifications of polyester containing pendent propargyloxy groups by azide-alkyne click reaction using azides *viz*; 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene, azido-terminated polystyrene (PS-N$_3$) and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, PEG$_{550}$-N$_3$, PEG$_{1000}$-N$_3$). FT-IR, ^{1}H-NMR spectroscopy, GPC, contact angle measurements, UV-

Vis spectra and fluorescence measurement techniques were used to characterize the functionalized polyesters.

Chapter 5 is divided into two parts:

Chapter 5a: Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy Groups

This section describes:

i. Synthesis of polyesters containing pendent propargyloxy groups by polycondensation of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane with isophthaloyl chloride or terephthaloyl chloride.

ii. Synthesis of copolyester containing pendent propargyloxy groups by polycondensation of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane with a mixture of isophthaloyl chloride and terephthaloyl chloride.

iii. Synthesis of copolyesters containing pendent propargyloxy groups by polycondensation of a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and bisphenol A with isophthaloyl chloride.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies and TGA. This section also describes curing studies of these polyesters under nonisothermal mode using DSC. ΔH of polyesters was computed using DSC technique.

Chapter 5b: Synthesis and Characterization of Polyesters Containing Pendent Azido Groups

This section deals with:

i. Synthesis of polyesters containing pendent azido groups by polycondensation of 4,4'–(5-azidopentane-2,2-diyl)diphenol with isophthaloyl chloride or terephthaloyl chloride

ii. Synthesis of copolyester by polycondensation of 4, 4'–(5-azidopentane-2, 2-diyl)diphenol with a mixture of isophthaloyl chloride and terephthaloyl chloride.

iii. Synthesis of copolyesters by polycondensation of a mixture of 4,4'–(5-azidopentane-2,2-diyl)diphenol and 4, 4'-(1-phenylethane-1, 1-diyl)diphenol with isophthaloyl chloride.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, TGA and DSC. Copolyester containing 30 mol percent 4, 4'–(5-azidopentane-2, 2-diyl)diphenol monomer was modified with phenyl acetylene *via* azide-alkyne click reaction. FT-IR and ^{1}H-NMR spectroscopy was used to characterize the functionalized polyester.

Chapter 6 is divided into three sections:

Chapter 6a: Synthesis, Characterization and Curing Studies of Polyamides Containing Pendent Propargyloxy Groups

This section describes:

i.   Synthesis of polyamide containing pendent propargyloxy groups by polycondensation of 5-(propargyloxy)isophthaloyl chloride with 4,4'-oxydianiline.

i.   Synthesis of copolyamides by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with 4,4'-oxydianiline

Polyamides were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies. This section also describes the curing studies of polyamides containing pendent propargyloxy groups by DSC in nonisothermal mode. ΔH of polyamides was computed using DSC technique.

Chapter 6b: Chemical Modification of Polyamides Containing Pendent Propargyloxy Groups.

This chapter describes the chemical modification of polyamide containing pendent propargyloxy groups by azide-alkyne click reaction using azides *viz*; 1-(4-azidobutyl)pyrene, 9-(azidomethyl) anthracene and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, PEG$_{550}$-N$_3$, PEG$_{1000}$-N$_3$). The functionalized polyamides were characterized by FT-IR, ^{1}H-NMR spectroscopy, contact angle measurements, UV-Vis spectra, fluorescence measurement techniques, polarized optical microscopy (POM) and scanning electron microscopy (SEM) techniques

Chapter 6c: Synthesis and Characterization of Polyamides Containing Pendent Allyloxy Groups

This section deals with:

i.   Synthesis of polyamides containing pendent allyloxy groups by polycondensation of 5-(allyloxy)isophthalic acid and diamines, *viz*; 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylene dianiline and 4,4' (hexafluoroisopropylidene)dianiline.

ii. Synthesis of copolyamides containing varying mol percent 5-(allyloxy)isophthalic acid monomer by polycondensation of a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline.

Polyamides were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies.

Chapter 7: Synthesis, Characterization and Chemical Modification of Polyesters Containing Pendent Allyloxy Groups or Pentadecyl Chains

This chapter is divided into two sections:

Chapter 7a: Synthesis, Characterization and Chemical Modification of Polyesters Containing Pendent Allyloxy Groups

This section describes:

i. Synthesis of polyester containing pendent allyloxy groups by polycondensation of 5-(allyloxy)isophthaloyl chloride with bisphenol A.

ii. Synthesis of copolyester by polycondensation of a mixture of 5-(allyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy. This section also describes chemical modification of copolyester containing pendent allyloxy groups *via* thiol-ene click reaction using thiols *viz;* 1-butanethiol, 2-mercaptoethanol, 3-mercaptopropanoic acid and 11-marcaptoundecyl phosphoric acid. FT-IR and ^{1}H-NMR spectroscopy was used to characterize the functionalized polyesters.

Chapter 7b: Synthesis and Characterization of Polyesters Containing Pendent Pentadecyl Chains

This chapter describes:

i. Synthesis of polyesters containing pendent pentadecyl chains by polycondensation of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride with three bisphenols *viz.*, bisphenol-A, (hexafluoroisopropylidene)diphenol and 1,1'-bis(4-hydroxyphenyl)-1-phenylethane.

ii. Synthesis of copolyesters by polycondensation of a mixture of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and IPC or 4-(4-(chlorocarbonyl)-phenoxy)-2-pentadecylbenzoyl chloride and TPC with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, DSC and TGA.

Chapter 8 summarizes the results and describes salient conclusions of the investigations reported in this thesis.

Glossary

HPP	High performance polymer
PA	Polyamide
PES	Polyester
BTEAC	Benzyltriethyl ammonium chloride
PEG	Polyethylene glycol
PMDETA	*N,N',N'',N'''*-pentamethyldiethylenetriamine
PS	Polystyrene
LAH	Lithium aluminium hydride
NMP	1-Methyl-2-pyrrolidinone
TPP	Triphenyl phosphite
BPA	2,2-Bis(4-hydroxyphenyl)propane or bisphenol-A
CNSL	Cashew nut shell liquid
DMAc	*N,N*-Dimethylacetamide
DMF	*N,N*-Dimethylformamide
THF	Tetrahydrofuran
DCM	Dichloromethane
CDCl$_3$	Deuterated chloroform
DMSO- d6	Deuterated dimethylsulfoxide
GPC	Gel permeation chromatography
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
WAXD	Wide angle X-ray diffraction

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Chapter 1

Introduction and Literature Survey

1.1 Introduction

These are exciting times to be a synthetic polymer chemist! Today, practitioners have more tools than ever available to design and synthesize complex macromolecules and advanced materials. During the past 20 years, a significant amount of core research in polymer chemistry has focused on the development of polymerization methodology that provides the straightforward preparation of (co)polymers with predetermined molecular masses, narrow molecular mass distributions, advanced architectures, tunable properties, i.e., 'smart' (co)polymers, and, but to a site-specific functionalization.[1-3] Indeed, with the discovery and development of the suite of controlled radical polymerization techniques (stable free radical polymerization, reversible addition–fragmentation chain transfer (RAFT) radical polymerization, atom transfer radical polymerization,[4] tellurium-mediated radical polymerization) as well as advances in more techniques such as, but not limited to, ring opening metathesis polymerization, *N*-carboxyanhydride polymerization and quasi-living cationic polymerization today synthetic polymer chemists have the ability to readily prepare novel functional (co)polymers with a degree of control that could barely be imagined just a few years ago.[5-9] However, for all the merits and the versatility of such techniques there are still challenges in the direct preparation of functional polymers. For example, certain desirable target functionality may be incompatible with a given polymerization technique such as hydroxyl and amine. Although advances in controlled/living radical polymerization and catalytic polymerization techniques have improved the issue of functional group tolerance, there are still a number of functional groups that cannot be introduced by direct polymerization approaches using current polymerization techniques.[10] In such instances, polymer chemists are often forced to employ post-polymerization modification reactions in order to obtain the target (co)polymer. This may be a straightforward deprotection of a protected functional group, or something more elaborate such as a coupling-type reaction or bioconjugation to convert a linear polymer into a (co)polymer with a more advanced architecture such as a star polymer for example.[11-13] While such post-polymerization reactions are not new, such an approach is often not considered ideal because of the typical non-quantitative nature of such modification reactions.[14] The importance of this cannot be understated since the presence, quantity, and distribution of newly introduced functionality will have a clear and defining effect on the chemical, physical, and mechanical properties of the final material.[15, 16] So, any post-polymerization modification reaction should be facile, site selective, rapid and quantitative.

Polymers bearing chemically reactive functional groups provide versatile and powerful tools for polymer chemists and serve as reactive modular platforms for the subsequent elaboration of a broad range of functional polymers. Reactive polymers are often synthesized directly from monomers containing functionality that is inert to the polymerization conditions, but that can be used for post-functionalization to introduce additional functionality and/or modify further the physicochemical properties of the resulting polymers.[15, 17] This approach to polymer synthesis and design brings with it a number of potential advantages. First, it can provide straightforward route

to the synthesis of functional polymers which may be difficult to access by direct polymerization of a given functional monomer. Second, the use of these polymers as 'reactive' templets can provide rapid access to diverse range of polymer structure and obviate the need to synthesize and polymerize new class of functional monomers. In this context, synthetic approaches based on the post-polymerization functionalization of a common reactive template can also provide platform to design libraries of polymers with similar molecular weight and molecular weight distributions, and can thus facilitate identification of new polymers. Finally, the incorporation of reactive polymers into other macromolecular architectures (e.g. crosslinked, assemblies, thin films, etc.) provides opportunities to design surfaces, interfaces and other materials that might be difficult (or impossible) to fabricate by direct incorporation of other functional polymers (e.g. by post-fabrication treatment with functionality that might hinder or otherwise not survive conditions used during fabrication)

Post-polymerization functionalization is an attractive strategy for the synthesis of highly functionalized polymers and can be used to overcome limited functional group tolerance. This approach is based on the polymerization of monomers possessing functional handles on the side-chains that are tolerant to the polymerization conditions but highly selective and reactive to undergo subsequent functionalization reactions with their complimentary coupling partners bearing the desired functionalities. To afford well-defined functional polymers, this strategy requires highly efficient functionalization transformations that proceed quantitatively in an orthogonal fashion with high fidelity and selectivity under mild reaction conditions. This can be achieved by employing click reactions. Many research groups have utilized click reactions in the post-polymerization modification to synthesize highly functionalized polymers. Click chemistry has emerged as the coupling chemistry of choice for post-polymerization functionalization of polymers that allows the incorporation of functionalities that are otherwise not compatible with specific polymerization techniques. The concept of click chemistry represents an ideal way for the preparation of tailor-made macromolecular architectures.[18] Utilizing the different approaches (post-modification and clickable monomer) different types of highly functional polymers are accessible and can act as building blocks for the preparation of more complex structures.

The term click chemistry was first introduced by K. Barry Sharpless and coworkers in 2001,[19-21] who defined click chemistry as a group of reactions that….

1. Must be modular.
2. Wide in scope.
3. Give very high yields.
4. Generate only inoffensive by products that can be removed by nonchromatographic methods.
5. Be stereospecific (but not necessarily enantioselective).
6. The required process characteristics include simple reaction conditions (ideally, the process should be insensitive to oxygen and water).

7. Readily available starting materials and reagents, the use of no solvent or a solvent that is benign (such as water) or easily removed, and simple product isolation.

8. Purification, if required, must be by nonchromatographic methods, such as crystallization or distillation.

9. The product must be stable under physiological conditions.

This exciting concept seems to perfectly answer the needs of modern scientists working in research areas as diverse as macromolecular chemistry or materials science, molecular biology, drug design, etc.

The most common examples that meet the criteria for click chemistry include the following classes of chemical transformations (**Scheme1.1**)
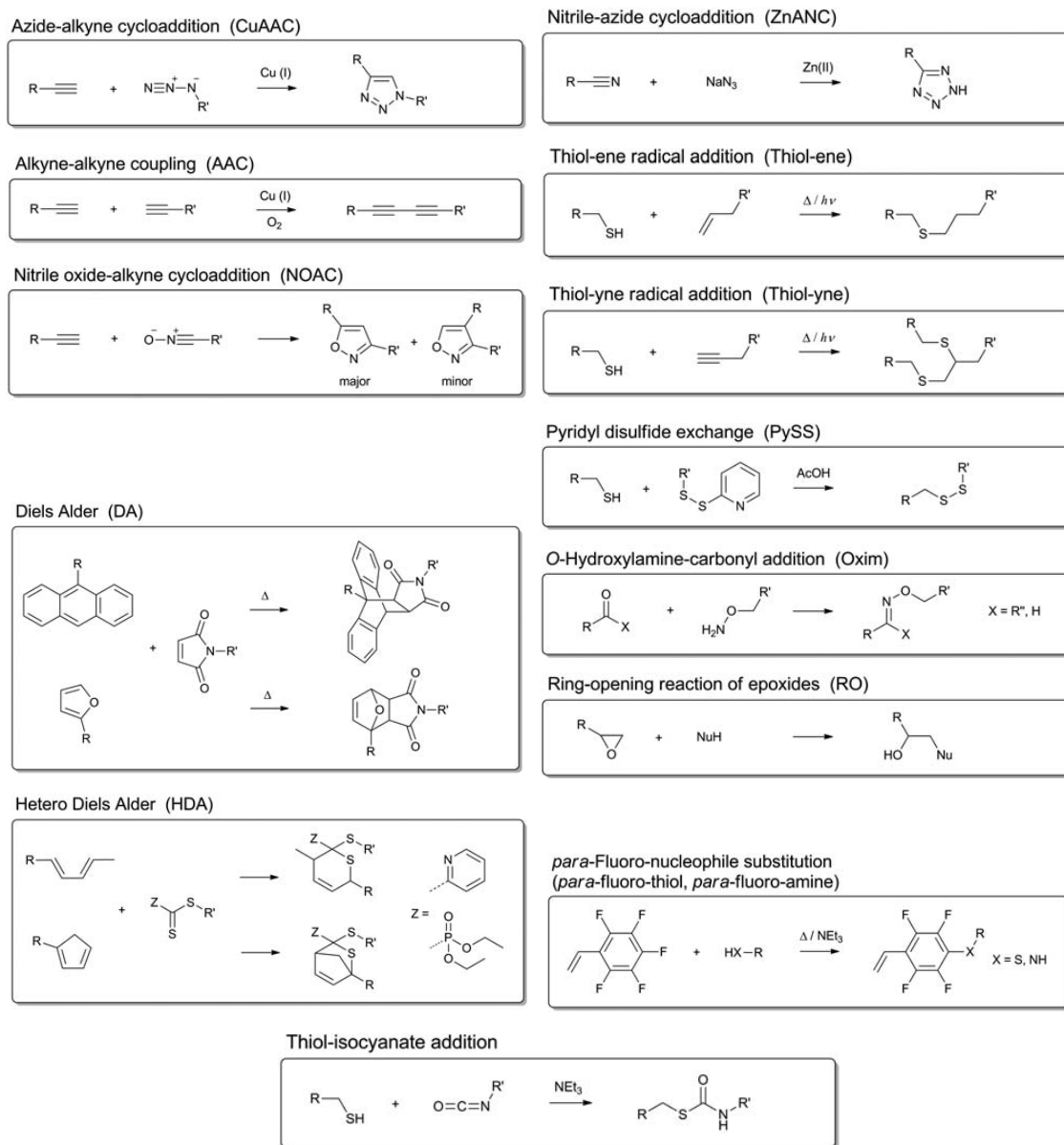
Scheme 1.1 Click chemistry strategies[21]

Copper (I)-catalyzed azide-alkyne cycloaddition and thiol-ene coupling click reaction have attracted much attention. Both these reactions were used in the present research work and are briefly discussed in this chapter.

1.2 Azide-alkyne click reaction

Of all currently identified click reactions, the heteroatom cycloaddition class of reaction is the most reliable and versatile category. Within this category, the copper catalyzed azide-alkyne cycloaddition (CuAAC) of azides and alkynes is known for being an "ideal" click reaction. The CuAAC represents a versatile method to modify polymers under mild conditions with a high tolerance for already existing functional groups and can be achieved with many sources of Cu(I) catalysts and solvents, including aqueous. The CuAAC reaction of terminal alkynes is completely selective in the formation of the 1,4-disubstituted triazoles (**Scheme 1.2**) with a variety of Cu(I) catalysts or precursors of Cu(I) catalysts.[22]

Scheme 1.2 Copper catalyzed azide-alkyne click reaction

The basic mechanism of copper catalyzed azide-alkyne click reaction is presented in **Scheme 1.3.**
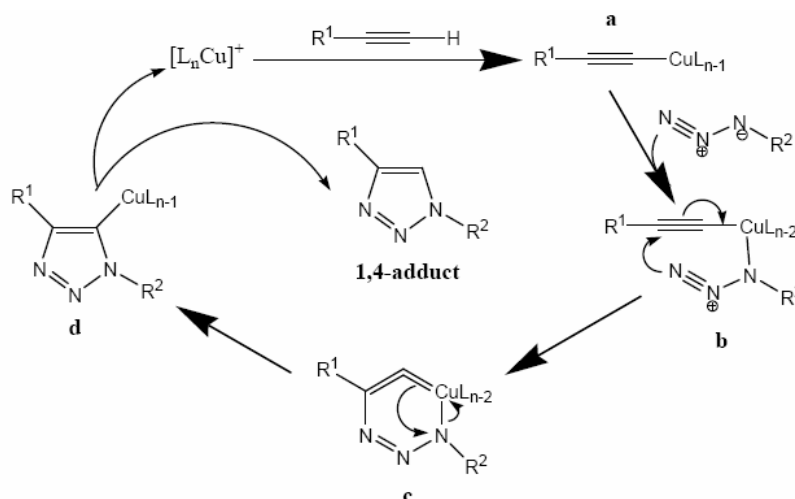
Scheme 1.3 Mechanism of copper catalyzed azide-alkyne click reaction[22]

First, the alkyne coordinates to the Cu(I) and displaces one of the Cu ligands, creating a copper acetylide species (**a**). In the second step, the azide replaces another Cu ligand forming intermediate **b**. The ring closure is initiated by an attack on the C_2-carbon of the copper acetylide by the nitrogen in **b**, resulting in the formation of the unusual copper (II) metallacycle intermediate (**c**). The intermediate **c** contracts to a five membered heterocycle (**d**) and proteolysis releases the 1,4- adduct, completing the catalytic cycle.[23]

CuAAC Click chemistry led to its widespread application in all fields of polymer chemistry over the last few years, and more than 1000 research articles including many reviews have been published on CuAAC since the Sharpless and co-workers publications of 2002.[24-26] CuAAC Click chemistry has been extensively used in the polymer research field for the preparation of functional polymers, block copolymers, hyperbranched polymers and so on.[6, 11, 27, 28]

A drawback of the CuAAC post-polymerization modification reaction is that removal of the copper catalyst can be demanding, as it can form complexes with the triazole ring, which hampers the solubility of the functionalized polymer.[29] An attractive, copper-free functionalization strategy is the strain-promoted azide alkyne cycloaddition.

1.3 Thiol-ene click reaction

The anti-Markovnikov's addition of thiols to alkenes is usually mediated by a radical source or by ultraviolet (UV) irradiation.[30] One of the earliest systematic studies regarding the post-polymerization modification of polybutadiene *via* radical thiol addition was reported by Serniuk and coworkers in 1948.[31] They proposed that only the vinyl groups generated by 1,2-addition of butadiene units (i.e., pendent vinyl groups) were functionalized, which was later confirmed by Romani and coworkers.[32] Since these early studies, thiol–ene post polymerization modification has developed into a powerful synthetic tool.[33, 34]

Due to the toxicity of copper and the potential danger inherent of working with azides, a growing interest has risen in thiol-ene chemistry, which is copper and azide-free.[35, 36] The radical addition of a thiol, R-SH, across a C=C bond, i.e., hydrothiolation, under certain conditions is commonly referred to as a thiol-ene reaction– a highly efficient method used for polymerizations (functional polymers, dendrimers, hydrogel etc.), curing reactions, grafting reactions, surface modification and for the modification of polymers.[15, 37, 38]

The basic radical mechanism for the thiol-ene click reaction is presented in **Scheme 1.4**
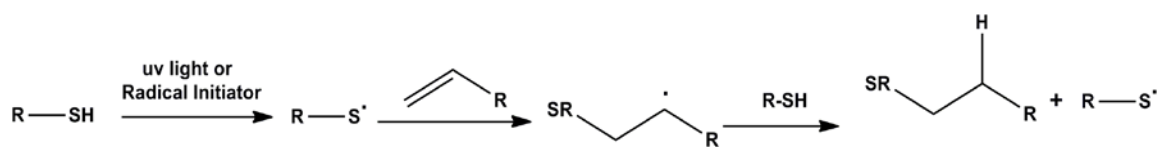
Scheme 1.4 The radical based thiol-ene mechanism[39]

The thiyl radical is generated either thermally or photochemically in the presence of an ene. In fact, sunlight can be used as an effective tool to initiate the reaction. The thiyl radical adds across the C=C bond, with anti-Markovnikov's orientation, yielding a carbon-centered radical that undergoes a chain transfer event with a second molecule of thiol to yield the addition product with concurrent regeneration of a thiyl radical. This is a classical radical chain reaction with initiation, propagation and, of course, possible termination events involving radical-radical coupling reactions.[40] In recent years, significant effort has been expended toward polymer functionalization using thiol–ene free-radical reactions.[41, 42]

The versatility of click reaction for polymer synthesis has been exemplified in many reports and review articles.[13, 43-52] Several excellent reviews have appeared in the field of

functional polymers—often addressing the side chain modification possibilities associated with a specific polymerization protocol.[1, 27, 35, 41, 44, 50, 53-71] The click chemistry modification of polymers such as aliphatic polyesters, aliphatic polyamides, aliphatic polycarbonates and aliphatic polyurethanes containing various pendent groups such as propargyloxy, allyloxy, or azido groups prepared either by step-growth polymerization or by ring opening polymerization have been extensively reviewed.[8, 17, 23, 42, 72-85] The chemical modification of aromatic polyethersulfones and poly(2,6-dimethylphenylene oxide) containing pendent azido groups *via* click chemistry approach has been described in the literature.[64, 86, 87]

1.4 Click chemistry approach for chemical modification of polymers

Currently, two strategies have been widely used for the modification of polymers (i) post-modification approach and (ii) functional monomer approach (**Scheme1.5**).
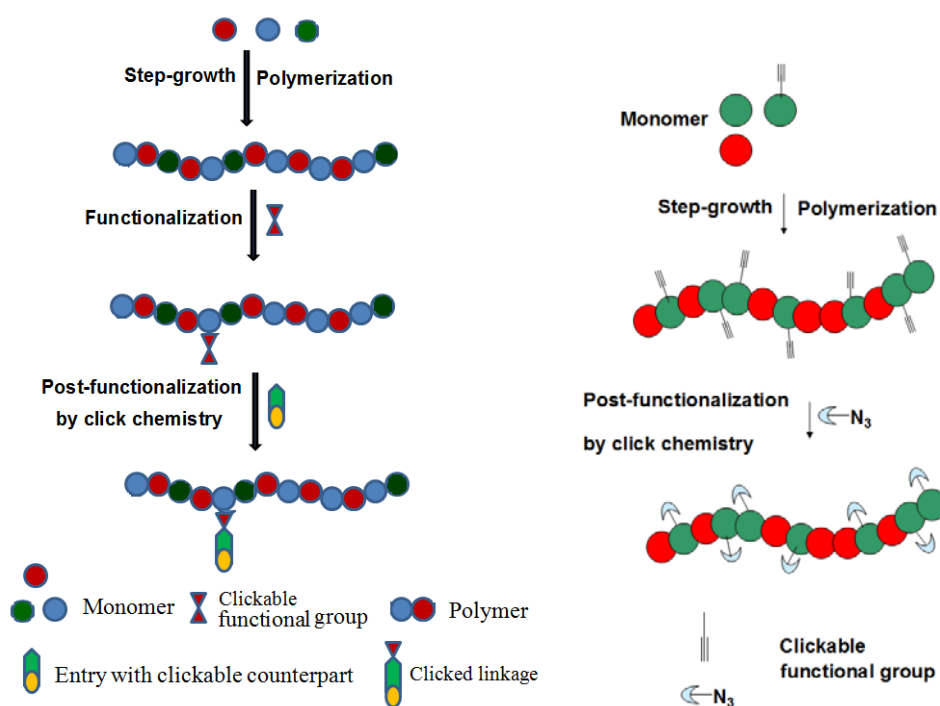
Scheme 1.5 Chemical modification of polymers *via* (i) Post-modification approach (ii) Functional monomer approach

1.4.1 Post-modification approach
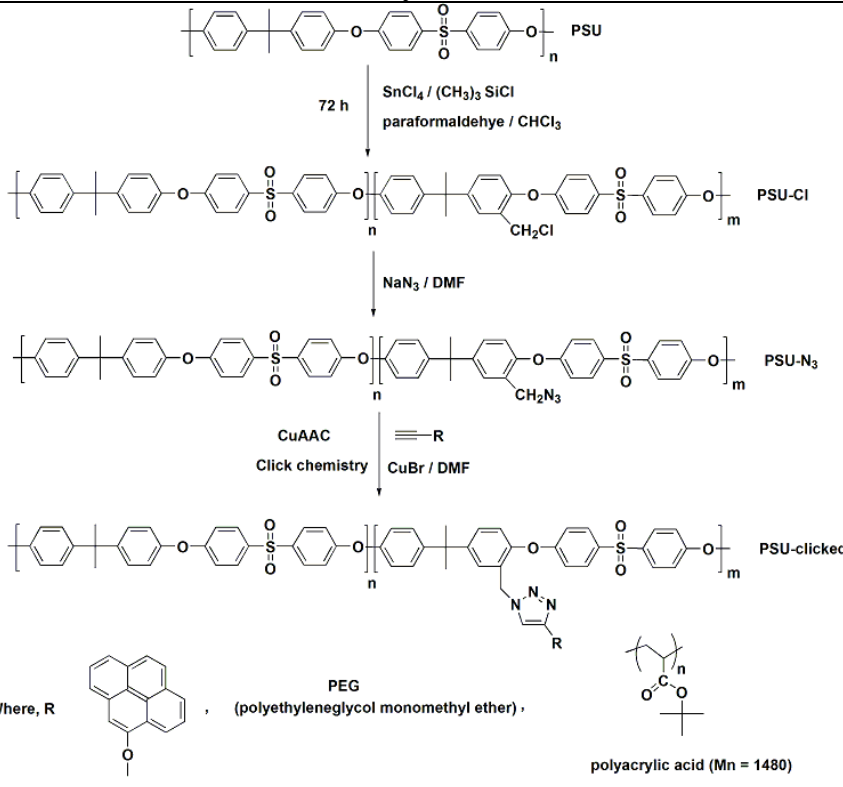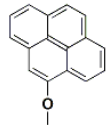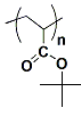
In recent years, the main scientific and applied interest is focused not only on the synthesis of new types of polymeric materials but also on the modification of existing polymers to alter their properties to meet requirements for new applications. In this case, modification as well as clicking is carried out at the polymer.[64, 86]

The clickable polymers act as basic modules for further functionalization reactions to engineer more complex architectures.[78] A survey of literature revealed that a few aromatic polymers such as polyethersulfones (PSU) or poly(2,6-dimethylphenylene oxide) (PPO) were post-functionalized *via* post-modification approach using click chemistry.[35, 64, 86-89] The post-

functionalization method for the synthesis of functional polyether sulfones overcomes problems related to the limited functional-group tolerance encountered in direct polymerization. Sulfonation, halomethylation and lithiation are the most frequently applied methods that can be used to introduce functional groups into the polyethersulfone structures. Although the post-functionalization method allows the synthesis of various functional polyethersulfones that cannot be prepared by direct polymerization, it also encounters some problems such as the insufficient efficiency of the reaction in installing functional groups and undesirable and detrimental side reactions arising from the harsh reaction conditions. Consequently, the selection of a mild and efficient synthetic route is an important issue for the preparation of functionalized polyethersulfones. For this purpose, commercially available PSU was converted to azido-functionalized polymer (PSU-N$_3$) by successive chloromethylation and azidation processes. Then the clickable counterpart was successfully reacted with PSU-N$_3$ by click chemistry to yield modified polyethersulfone.

The reports on post-functionalization of aromatic polyethersulfones and poly(2,6-dimethyl phenylene oxide) containing pendent clickable functional groups *via* post-modification approach using click reaction are summarized in **Table 1.1.**

Table 1.1 Post-functionalization of aromatic step-growth polymers *via* post-modification approach

Sr.No.	Polymer	Reference
1		64, 86, 87

2		35, 90
3		88

AC	TPSF	R1	R2
1	1	H	CH_2OH
2	2	$COOC_2H_5$	$COOC_2H_5$
3	3	H	$-CH_2-O-C_6H_4-(CH_2)_8-CH_3$
-	4	COOH	COOH

4		89

1.4.2 Clickable monomer approach
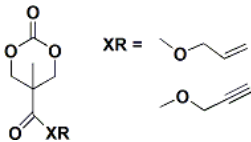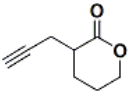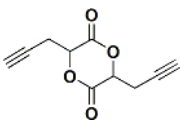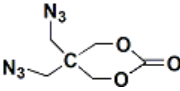
By using functional monomers with clickable moiety, clickable polymers can be achieved to construct various functional polymers clicking post to the polymerization.[58, 91, 92] This approach relies on the design of monomers whose functional groups are orthogonal to polymerization reactions. As a requirement the clickable functionality present in monomer must be inert towards the polymerization conditions but should allow a quantitative conversion in a subsequent reaction step yielding a broad range of desired functional polymers without affecting the polymer backbone. Moreover, most functional monomers are not commercially available and have to be

synthesized prior to the polymerization. Monomers containing propargyl, allyl or azido functional groups are the prominent examples of monomers used for synthesis of clickable polymers.[16] These clickable groups can withstand certain polymerization conditions and can be conveniently transformed afterwards. These groups have the distinct advantage of not requiring a protection or deprotection during the polymerization.[29, 93]

         Clickable monomer can be used to synthesize pendent functionalized polymers that can be easily modified *via* click chemistry. Thereby, the clickable monomer can be homopolymerized or copolymerized to obtain versatile random-, block-, comb polymers containing clickable functional groups. By varying the functional monomer composition in copolymers one can tune the properties of the final functionalized polymers. The main advantage for this strategy is the facile tuning of polymer properties for a specific application. One clickable monomer can act as a precursor for a variety of functionalized polymers.
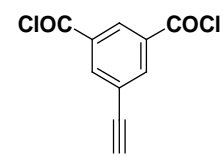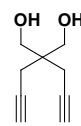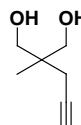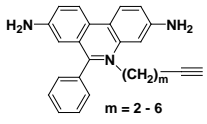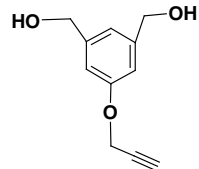
         The clickable monomers that lead to functional polymers *via* ring opening polymerization and step-growth polymerization are summarized in **Table 1.2** and **Table 1.3,** respectively.

Table 1.2 List of monomers containing pendent clickable functional group for ring opening polymerization
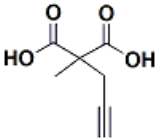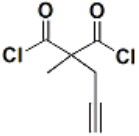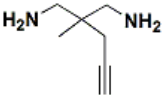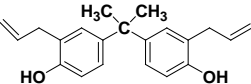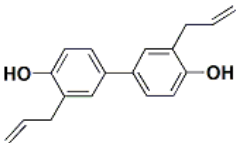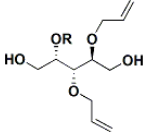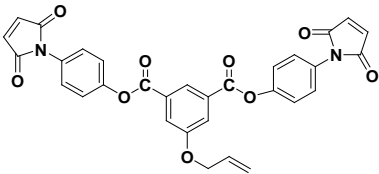
Sr.No.	Monomer	Polymer	Reference
1		Aliphatic Polycarbonate	83
2		Aliphatic Polyester	83
3		Aliphatic Polyester	83
4		Aliphatic Polycarbonate	3
5		Aliphatic Polyester	56, 84
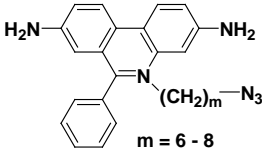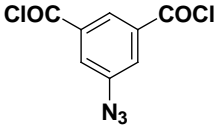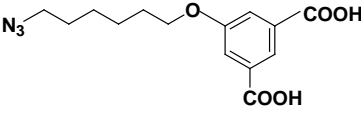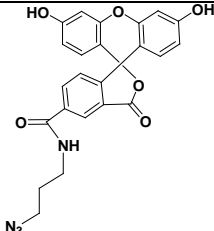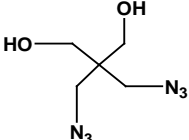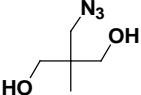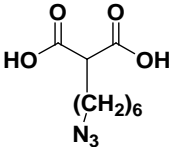
| 6 | | Aliphatic Polycarbonate | 42 |
| 7 | | Aliphatic Polyester | 67 |
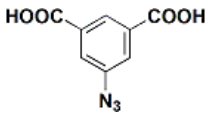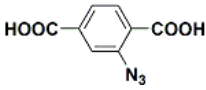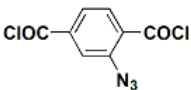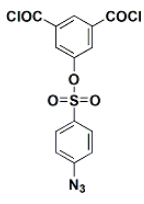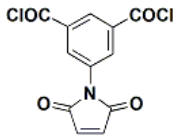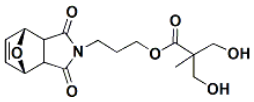
Table 1.3 List of difunctional monomers containing pendent propargyl, allyl, azido or maleimide functional group for step-growth polymerization

Sr. No.	Monomer	polymer	Reference
1		Aromatic Polyester	91
2		Aliphatic Polyester, Polyurethane	58
3		Aliphatic Polyester, Polyurethane	58
4			94
5		Aromatic Polyurethane	58

6		Aliphatic Polyamide	55
7		Aliphatic Polyamide	55
8		Aliphatic Polyamide	55
9			95
10		Aromatic Poly(phthalazinone ether ketone)	61
11		Aliphatic Polyurethane	74
12		Aromatic Bismaleimide	95

13			94
14		Aromatic Polyester	91
15		Modification of poly(4-hydroxystyrene	51
16		PMMA surface modification *via* click reaction	96
17		Polytriazole	97
18		Aliphatic Polyester	59
19		Modification of poly(4-hydroxystyrene	51, 58

20		Aromatic Polyester	98
21		Aromatic Polyester	98
22		Aromatic Polyester	98
23		Aromatic Polyester	98
24		Aromatic Polyester	98
25		Aromatic Polyamide	95
26		Aliphatic polyurethane	92

Introducing functional groups to the polymer and their subsequent functionalization provided an efficient way to tailor the properties of polymers such as, hydrophilicity, elasticity and bioactivity, etc. These properties made them useful materials as anion transport exchange

membranes, membranes with antifouling properties, etc.

1.5 Concluding Remarks

- Functionalized polymers provide many advantages because small changes in structure yield dramatic effects on physical and chemical properties. Post-polymerization functionalization is an attractive approach for the synthesis of functional polymers that overcomes the limited functional group tolerance of a number of polymerization methods.

- The re(discovery) of highly efficient and orthogonal chemistries combined with the development of functional group tolerant living/controlled polymerization techniques and step-growth polymerizations has enormously expanded the scope of post-polymerization modification and resulted in a significant increase in the use of this approach to synthesize functional polymers.

- It is anticipated that click chemistry approach in general and azide-alkyne and thiol-ene click reaction in particular has a potential to expand into all areas of polymer science for creating and functionalizing polymers and surfaces for applications in a wide range of disciplines that involve high performance materials.

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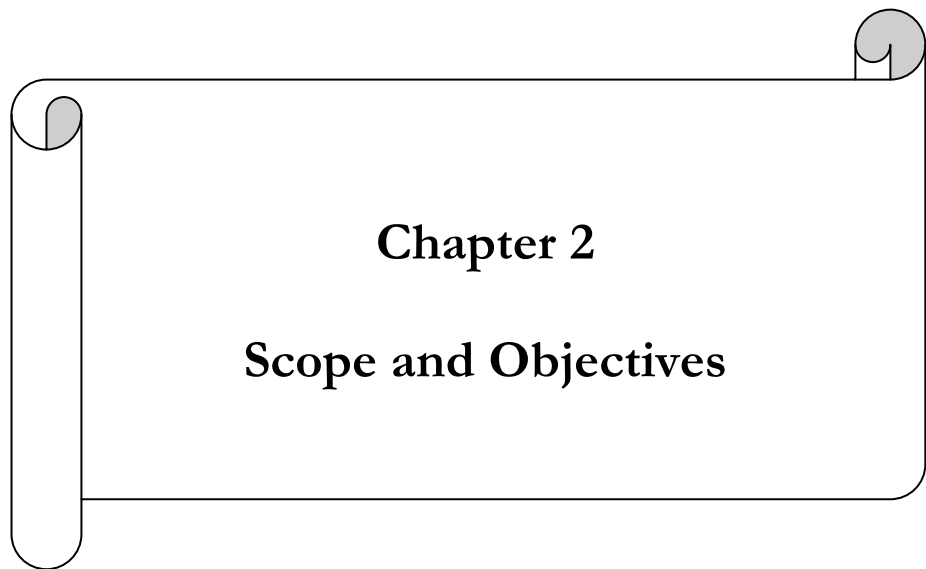
Chapter 2

Scope and Objectives

Scope and Objectives

High performance polymers such as aromatic polyesters and polyamides have received considerable attention due to their notable high impact on industry. These polymers find applications in various industries such as aero-space, automobile, electronics, packaging, coatings, etc, due to their excellent mechanical and thermal properties, good chemical resistance and insulating properties. However, for more specific applications these polymers are limited in scope because of the lack of functionalities on the polymer backbone for further modifications and tailoring.[1-4] In general, to introduce functionalities within the polymer made by step-growth polymerization, two main routes can be considered. The first route involves the use of appropriately functionalized end-capping reagents which lead to polymer chain terminations with the desired functional group at the chain end and to reduce molecular weight. As an alternative, the chain end modification can also be performed after the synthesis of the polymer. The second strategy consists of the direct incorporation of functional groups along the polymer backbone during the step-growth polymerization in a one-pot process. This can be achieved by using functionalized building blocks such as functionalized diols, diacids, diacid chlorides, bisphenols, diamines, etc. Nevertheless, this strategy suffers from a few limitations, among which the synthesis of a specific building block for each application or to consider additional protecting and deprotecting steps, which limits the possibilities of widespread applications.[2-4] Because of these limitations, the focus on the research concerning functionalization of step-growth polymers in general and aliphatic polyesters and polyamides in particular has been moving towards the use of recently discovered click chemistry approach, as introduced by Sharpless and co-workers in 2001.[3, 5-13] This simple approach has won a great deal of attention due to its high selectivity, quantitative yields, mild reaction conditions and absence of by-product(s).[13-15]   It has been reported that combining step-growth polymerization and post-polymerization side chain modification may endow the industrially important polymers with different structures and thus advanced properties. Click chemistry modification has so far been applied mostly to aliphatic step-growth polymers such as polyesters, polyamides, polycarbonates, polyurethanes, [8-12, 16-18, 20-21] and to specific aromatic step-growth polymers *viz*; polyethersulfones and poly(2,6-dimethylphenylene oxide).[19, 21, 22] To the best of our knowledge, chemical modification of high performance polymers such as aromatic polyesters and aromatic polyamides *via* click chemistry approach has not been widely investigated.

Therefore, our approach is focused on a combination of step growth polymerization and click chemistry to obtain functionalized aromatic polyesters and polyamides making use of difunctional clickable monomers for their synthesis followed by post-functionalization *via* click reaction. The first objective of this research was to develop a synthetic scheme that would allow the introduction of clickable functional groups such as pendent propargyloxy, allyloxy or azido groups into the high performance polymers such as aromatic polyesters and polyamides. The

approach involved synthesis of propargyloxy, allyloxy or azido group-substituted bisphenols, isophthalic acids, isophthaloyl chlorides and diisocyanates making use of commercially available starting materials such as 1,1,1-tris(4-hydroxyphenyl)ethane, 5-hydroxyisophthalic acid and 4,4'-bis(4-hydroxyphenyl)pentanoic acid.

The choice of propargyloxy, allyloxy and azido groups was inspired by their ability to undergo click reactions with their complimentary partner.

The propargyloxy functional group is utilized in many organic reactions as a consequence of its versatile reactivity. Propargyloxy groups have been widely studied in a range of coupling reactions (Sonogashira, Glaser and Eglinton)[23-25] and cycloaddition reactions (Diels–Alder with 1,3-dienes, Huisgen 1,3-dipolar)[26, 27]. Propargyloxy group also undergoes reactions such as thiol-yne, hydrogenation, hydroboration and halogenation in which two equivalents of the corresponding reagent can be added to one propargyl group as a result of its double unsaturation.[28] Furthermore, propargyloxy groups are known to act as a crosslinking site upon heating by creation of reticulated alkenes and can participate in a cyclo-trimerization reaction,[29, 30] thus providing an opportunity for converting thermoplastics into thermosettings.

The introduction of azido groups is mainly inspired by its ability to undergo click reaction with a variety of alkynes. Azido groups also provide reactive sites for crosslinking under photochemical conditions. Furthermore, azido group has a unique identity in organic synthesis as it can be readily transformed into versatile functional groups such as amines, nitriles and triazenes, etc.[31]

Allyl groups are known to undergo thiol-ene click reactions with thiols, thus providing an opportunity for post-functionalization *via* click reaction.

The 1,3-disubstitution of the reactive groups *viz*; acids, acid chlorides and isocyanates in the monomer structure was selected for the following reasons: (i) to obtain *meta*-catenation in the polymer backbone. Such catenation is known to increase solubility and reduce the Tg of polymers (ii) the functional groups were located at a sufficient distance from the pendent functional group so that their reaction with comonomers (bisphenols / diamines) would not be sterically hindered.

Another series of monomers *viz*; pentadecyl chain substituted diacid chloride, diazido monomers and an aromatic diamine containing pre-formed amide linkages were designed and synthesized starting from 3-pentadecyl phenol which in turn is obtainable from CNSL- a renewable resource material.[32]

The second objective of this research was to synthesize and characterize aromatic polyesters and polyamides containing pendent propargyloxy, allyloxy, azido groups or pentadecyl chains and to investigate the effect of incorporation of these pendent groups on the solubility and thermal properties of these polymers.

The third objective of the work was to demonstrate the chemical modification reactions of aromatic polyesters and polyamides containing pendent groups *viz;* propargyloxy, azido or allyloxy groups *via* click chemistry approach.
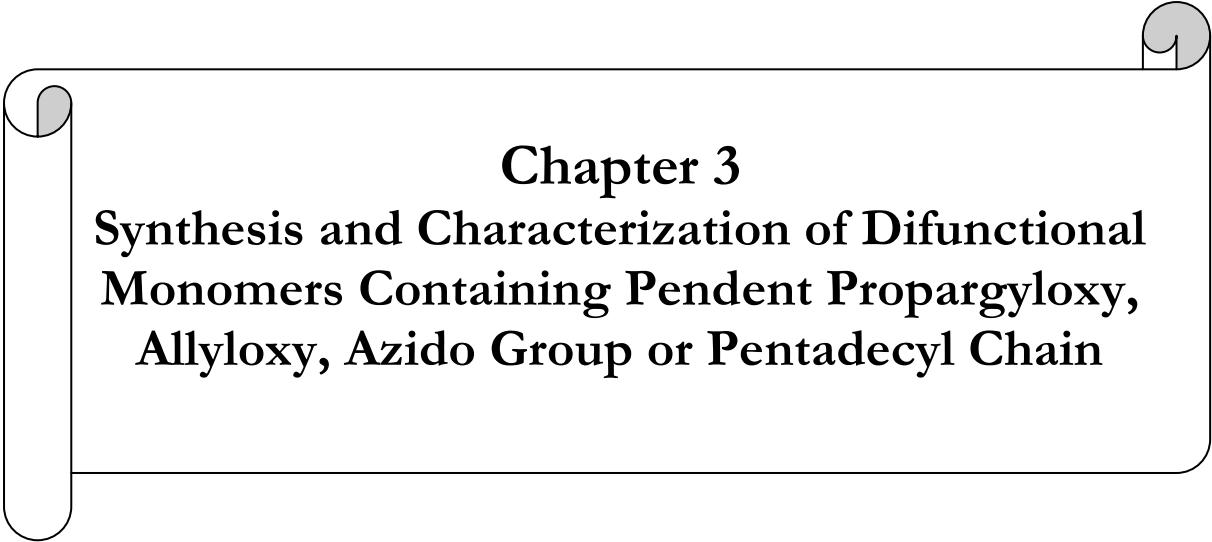
Based on these objectives, the following specific problems were chosen for the present work.

1.   Design and synthesis of pendent propargyloxy or allyloxy group containing diacids, diacid chlorides or diisocyanates starting from commercially available chemical *viz*; 5-hydroxyisophthalic acid.

2.   Design and synthesis of bisphenols containing pendent propargyloxy or azido group starting from 1,1,1-tris(4-hydroxyphenyl)ethane and 4,4'-bis(4-hydroxyphenyl)pentanoic acid, respectively.

3.   Design and synthesis of pendent pentadecyl chain containing difunctional monomers such as diazides, a diacid chloride and a diamine.

4.   Synthesis and characterization of high performance polymers such as aromatic polyesters and polyamides containing pendent propargyloxy, allyloxy, azido groups or pentadecyl chains and study the effect of their incorporation on properties of polymers.

5.   Studies on cure behaviour of selected polyesters and polyamides containing pendent propargyloxy groups in nonisothermal mode using DSC technique.

6.   Post-functionalization of aromatic polyesters and polyamides containing pendent propargyloxy, allyloxy or azido groups by alkyne-azide, thiol-ene or azide-alkyne click reactions using representative azides, thiols or alkyne.

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Chapter 3
Synthesis and Characterization of Difunctional Monomers Containing Pendent Propargyloxy, Allyloxy, Azido Group or Pentadecyl Chain

3.1 Introduction
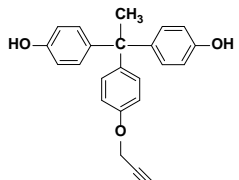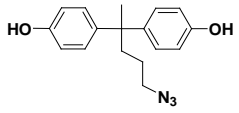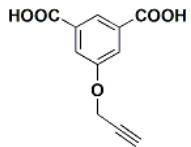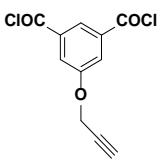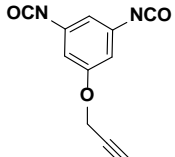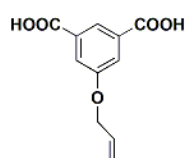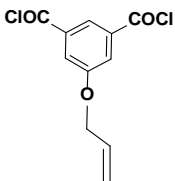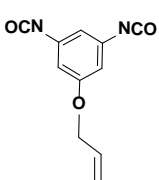
The most important criteria that determine the final properties of a polymer is the structure of monomer and by selecting suitable monomers properties of a polymer can be tailored. [1-3] Therefore, in the synthesis of polymers the first step constitutes the synthesis of desired monomers which can give rise to polymers with expected / targeted functionality and properties.

In modern polymer science, a variety of polymerization methods for the direct synthesis of polymers bearing functional groups are known. However, there are still a large number of functional groups that may either completely prevent polymerization or lead to side reactions. Post-polymerization modification,[1-4] also known as polymer-analogous modification, is an alternative approach to overcome these limitations. It is based on the polymerization of monomers with functional groups that are inert towards the polymerization conditions but allow a quantitative conversion in a subsequent reaction step yielding a broad range of desired functional group(s).
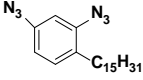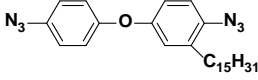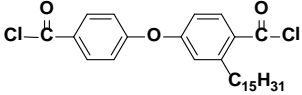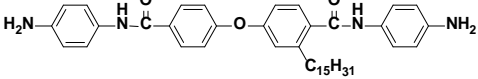
This approach relies on the design of monomers whose functional groups are orthogonal to polymerization reactions. The key criteria of this approach is that the chosen functional group should not interfere in the polymerization reaction, but the functional group could be transformed into a useful moiety in post-polymerization react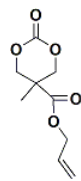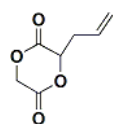ions, and that the conditions of the subsequent reactions should not detrimentally affect the polymer backbone. Monomers containing propargyl, allyl or azido groups are the prominent examples of monomers used for synthesis of clickable polymers. These clickable groups can withstand certain polymerization conditions and can be conveniently transformed afterwards. These groups have the distinct advantage of not requiring a deprotection step after the polymerization reaction.[5, 6] Such monomers are of interest because of the ability of the propargyl, azido and allyl groups to participate in azide-alkyne[7-12] and thiol-ene[8, 13-16] click reactions with their complimentary partner. Furthermore, these functional groups also provide sites for crosslinking reactions.[17-19]

Taking these attractive aspects into consideration, a range of clickable monomers *viz.*, bisphenols, diacids, diacid chlorides and diisocyanates containing propargyloxy, allyloxy or azido group (**Table 3.1**) were designed and synthesized starting from cheap and commercially available chemicals *viz.*1,1,1-tris(4-hydroxyphenyl)ethane, 5-hydroxyisophthalic acid and 4,4'-bis(4-hydroxyphenyl)pentanoic acid. Also, monomers containing pentadecyl chain *viz.*, diazides, a diacid chloride and a diamine containing preformed amide linkages (**Table 3.2**) were synthesized starting from 3-pentadecylphenol which in turn is obtainable from CNSL-a renewable resource material.[28, 20-22]The monomers and intermediates involved in their synthesis were characterized using FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

Table 3.1 List of difunctional monomers containing pendent propargyloxy, allyloxy or azido group

Sr. No.	Monomer structure	Monomer
1		1,1-Bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane
2		4,4'–(5-Azidopentane-2,2-diyl) diphenol
3		5-(Propargyloxy)isophthalic acid
4		5-(Propargyloxy)isophthaloyl chloride
5		5-(Propargyloxy)-1,3-diisocyanatobenzene
6		5-(Allyloxy)isophthalic acid
7		5-(Allyloxy)isophthaloyl chloride
8		5-(Allyloxy)-1,3-diisocyanatobenzene

Table 3.2 List of difunctional monomers containing pendent pentadecyl chain

Sr. No.	Monomer structure	Monomer
9		2,4-Diazido-1-pentadecylbenzene
10		1-Azido-4(4-azidophenoxy)-2-pentadecylbenzene
11		4-(4-(Chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride
12		*N*-(4-Amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

3.2 Experimental

3.2.1 Materials

5-Hydroxyisophthalic acid, 1,1,1-tris(4-hydroxyphenyl)ethane, 4,4'-bis(4-hydroxyphenyl) pentanoic acid and 3-pentadecyl phenol (Aldrich) were used as received. Allyl bromide and propargyl bromide were distilled prior to use. Sulfanilic acid (Loba Chemie) was used as received. *p*-Nitroaniline (Loba Chemie) was recrystallised from a mixture of water: ethanol (1:2, v/v). Pd/C (10 %) (Aldrich), hydrazine hydrate, and sulfuric acid (Loba Chemie) were used as received. Triethylamine, ethylchloroformate, thionyl chloride, *N,N*- dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were of reagent grade and were purified prior to use as per literature procedures.[23] Sodium azide was activa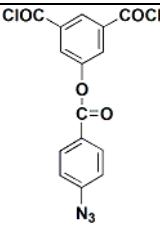ted by trituration with hydrazine hydrate and left overnight. After that it was dissolved in a minimum quantity of water and precipitated into excess acetone, filtered and dried in a vacuum oven at room temperature. Chloroform, acetone, methanol and tetrahydrofuran (THF) (S.D. Fine Chemicals) were used as received. Potassium carbonate, potassium hydroxide and *tert*-butyl alcohol (Loba Chemie) were used as received.

3.2.2 Measurements

Melting points were determined by open capillary method and are uncorrected.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer in chloroform or as KBr pellets.

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 and 50, 100 or 125 MHz for ^{13}C measurements using CDCl$_3$ or DMSO-d$_6$ as a solvent.

3.3 Preparations

3.3.1 Synthesis of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser and an addition funnel were charged 1,1,1-tris(4-hydroxyphenyl)ethane (10 g, 32.7×10^{-3} mol), potassium carbonate (6.08 g, 44×10^{-3} mol) and acetone (100 mL). The solution of propargyl bromide (3.89 g, 32.7×10^{-3} mol) in acetone (15 mL) was added over a period of 30 min to the reaction mixture and stirred at 55 $^{\circ}$C for 3 h. The reaction mixture was filtered while hot. The filtrate was cooled and crude product was isolated by filteration. The crude product was chromatographed on silica gel column with petroleum ether as an eluent to afford pure 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane.

Yield: 3.37g (30 %).

M.P. 150 $^{\circ}$C

FT-IR (KBr, cm^{-1}): 3298 (OH), 2121 (C≡C), 1221 (–C-O-C–).

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 9.26 (s, 2 -OH), 6.93 (d, 2H), 6.86 (d, 2H), 6.80 (d, 4H), 6.65 (d, 4H), 4.75 (d, 2H), 3.55 (t, 1H), 2.01 (s, 3H).

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 155.3, 142.8, 140.0, 129.4, 114.7, 114.1, 79.6, 78.2, 55.5, 50.2, 30.6.

3.3.2 Synthesis of 5-(propargyloxy)isophthaloyl chloride

3.3.2.1 Synthesis of dimethyl-5-hydroxyisophthalate

Into a 250 mL single-necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were placed 5-hydroxyisophthalic acid (25 g, 31.0×10^{-2} mol), methanol (125 mL) and sulfuric acid (1mL). The reaction mixture was refluxed for 8 h. The excess methanol was removed on a rotary evaporator. The residue was dissolved in chloroform (125 mL) and washed with water (2 x 70 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was removed to obtain the crude product which was recrystallized from methanol to afford pure dimethyl-5-hydroxyisophthalate.

Yield: 28.29 g (98 %).

M.P.162 $^{\circ}$C [Lit.[24] M.P. 160 $^{\circ}$C]

FT-IR (CHCl$_3$, cm^{-1}): 3350 (OH), 1760 (C=O).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.24 (s, 1H, Ar-H flanked by carbonyl), 7.77 (d, 2H, Ar-H, *ortho* to ether), 3.94 (s, 6H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 196.5, 157.1, 138.7, 121.3, 120.2, 22.8.

3.3.2.2 Synthesis of dimethyl-5-(propargyloxy)isophthalate

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser and an addition funnel were charged dimethyl-5-hydroxy isophthalate (14.92 g, 71×10^{-3} mol), potassium carbonate (37.28 g, 3.6×10^{-3} mol) and acetone (150 mL). The solution of propargyl bromide (10.2 g, 85×10^{-3} mol) in acetone (15 mL) was added over a period of 30 min to the reaction mixture and stirred at 55 °C for 6 h. The reaction mixture was filtered. The filtrate was cooled and isolated crystals were dried at 40 °C under vacuum. The crude product was recrystallized from ethanol to afford pure dimethyl-5-(propargyloxy)isophthalate.

Yield: 17.18 g (97 %).

M.P. 165 °C

FT-IR (CHCl$_3$, cm^{-1}): 3307 ($\equiv$C-H), 2126 (C$\equiv$C), 1723 (C=O).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.24 (t, 1H, Ar-H flanked by carbonyl), 7.82 (d, 2H, Ar-H, *ortho* to ether), 4.77 (d, 2H, -CH$_2$), 3.93 (s, 6H, -CH$_3$), 2.54 (t, 1H, $\equiv$C-H).

^{13}C-NMR (CDCl$_3$, δ/ppm): 196.5, 138.3, 121.0, 118.6, 83.0, 73.8, 62.0, 22.8.

3.3.2.3 Synthesis of 5-(propargyloxy)isophthalic acid

Into a 250 mL single-necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were charged sodium hydroxide (4.03 g, 0.1 mol), water (50 mL), methanol (50 mL) and dimethyl-5-(propargyloxy)isophthalate (8.4 g, 4×10^{-2} mol) and the reaction mixture was refluxed overnight. The solution was cooled to room temperature and acidified with concentrated HCl. The product was isolated by filtration, washed with water, and dried at 80 °C under vacuum overnight.

Yield: 3.9 g (98 %).

M.P. 262 °C

IR (KBr, cm^{-1}): 3300 ($\equiv$CH), 3248-2400 (OH), 2124 (C$\equiv$C), 1700 (C=O), 1227 (–C-O-C–).

^{1}H-NMR (CDCl$_3$, δ/ppm): 13.37 (s, 2 -OH), 8.11 (t, 1H, Ar-H flanked by carbonyl), 7.72 (d, 2H, Ar-H, *ortho* to ether), 4.96 (d, 2H, -CH$_2$), 3.65 (t, 1H, $\equiv$C-H).

^{13}C-NMR (CDCl$_3$, δ/ppm): 172.0, 161.8, 131.5, 124.0, 120.9, 83.0, 73.8, 62.0.

3.3.2.4 Synthesis of 5-(propargyloxy)isophthaloyl chloride

Into a 250 mL three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were charged 5-(propargyloxy)isophthalic acid (7.56 g, 36×10^{-3} mol) and DMF (2 drops). Thionyl chloride (100 mL) was added dropwise over a period of 30 min and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice. The crude product was purified by distillation under reduced pressure at 160 °C / 10^{-3} mm Hg.

Yield: 7.44 g (80 %).

FT-IR (CHCl$_3$, cm^{-1}): 3307 ($\equiv$C-H), 2127 (C$\equiv$C),1760 (C=O), 1218 (–C-O-C–).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.49 (t, 1H, Ar-H flanked by carbonyl), 7.98 (d, 2H, Ar-H *ortho* to ether), 4.84 (d, 2H, -CH$_2$), 2.60 (t, 1H, ≡C-H)

^{13}C-NMR (CDCl$_3$, δ/ppm): 167.0, 158.0, 135.3, 126.7, 123.2, 77.3, 76.5, 56.5.

3.3.3 Synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene

3.3.3.1 Synthesis of 5-(propargyloxy)isophthaloyl diazide

Into a 100 mL two-necked round bottom flask equipped with an addition funnel, a thermowell and a magnetic stirring bar were placed 5-(propargyloxy)isophthalic acid (1.9 g, 9.04 x 10^{-3} mol) and a mixture of THF and water (3:1, v/v) (7 mL). The reaction mixture was cooled to 0 ^{o}C and the solution of triethylamine (2.73 g, 27 x 10^{-3} mol) in THF (6 mL) was added dropwise over a period of 15 min. To the clear solution formed was added ethylchloroformate (2.92 g, 27 x 10^{-3} mol) drop-wise over a period of 10 min and stirred for 2 h. The solution of activated sodium azide (2.35 g, 36 x 10^{-3} mol) in water (10 mL) was added dropwise over a period of 15 min and the reaction mixture was stirred at 0 ^{o}C for 4 h. Cold water (100 mL) was added gradually to the reaction mixture when the product precipitated out. The precipitate was separated by filtration and washed with cold water (100 mL). The product was dissolved in dichloromethane (25 mL), and the solution was dried over anhydrous sodium sulphate, filtered and dichloromethane was removed under reduced pressure at room temperature to afford 5-(propargyloxy)isophthaloyl diazide.

Yield: 2.04 g (91 %)

M.P. 92 ^{o}C

FT-IR (CHCl$_3$, cm^{-1}): 3301 (≡C-H), 2140 (-N$_3$), 2102 (C≡C),1739 (C=O), 1235 (–C-O-C–).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.27 (t, 1H, Ar-H flanked by carbonyl), 7.85 (d, 2H, Ar-H *ortho* to ether), 4.79 (d, 2H, -CH$_2$), 2.56 (t, 1H, ≡C-H).

^{13}C-NMR (CDCl$_3$, δ/ppm): 173.6, 161.6, 136.8, 122.1, 119.8, 78.7, 76.4, 56.9.

3.3.3.2 Synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet tube and a reflux condenser were placed 5-(propargyloxy)isophthaloyl diazide (1 g, 3.7 x 10^{-3} mol) and dry toluene (20 mL). Nitrogen gas was bubbled gently through the reaction mixture. The reaction mixture was heated at 60 ^{o}C for 24 h. Evaporation of toluene under reduced pressure afforded 5-(propargyloxy)-1,3-diisocyanatobenzene.

Yield: 0.72 g (82 %).

FT-IR (CHCl$_3$, cm^{-1}): 3300 (≡C-H), 2261 (-NCO), 2110 (C≡C), 1219 (–C-O-C–).

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 7.0 (t, 1H, Ar-H flanked by NCO), 6.66 (d, 2H, Ar-H *ortho* to ether), 4.75 (d, 2H, -CH$_2$), 2.56 (t, 1H, ≡C-H).

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 162.0, 135.7, 127.8, 114.7, 108.0, 78.8, 76.0, 56.3.

3.3.4 Synthesis of 5-(allyloxy)isophthaloyl chloride

3.3.4.1 Synthesis of dimethyl -5-(allyloxy)isophthalate

Into a 100 mL round bottom flask equipped with a magnetic stirring bar, a reflux condenser and an addition funnel were charged dimethyl-5-hydroxyisophthalate (4.75 g, 19 x 10^{-3} mol),

potassium carbonate (13.12 g, 95 x 10^{-3} mol) and acetone (40 mL).The solution of allyl bromide (2.66 g, 22 x 10^{-3} mol) in acetone (5 mL) was added over a period of 30 min to the reaction mixture and stirred at 70 °C for 8 h. The reaction mixture was filtered. The filtrate was cooled and isolated crystals were dried at 40 °C under vacuum. The crude product was recrystallized from ethanol to afford pure dimethyl-5-(allyloxy) isophthalate.

Yield: 17.83 g (97 %).

M.P. 70 ^{o}C

FT-IR (CHCl$_3$, cm^{-1}): 3082 (=C-H), 1724 (C=O), 1249 (–C-O-C–).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.25(t, 1H, Ar-H flanked by carbonyl), 7.74 (d, 2H, Ar-H *ortho* to ether), 6.06-5.98 (m, 1H, CH$_2$=C**H**-CH$_2$-O-), 5.46-5.27 (m, 2H, C**H$_2$**=CH-CH$_2$-O-), 4.61 (d, 2H, CH$_2$=CH-C**H$_2$**-O-), 3.92 (s, 6H, -CH$_3$)

^{13}C-NMR (CDCl$_3$, δ/ppm): 197.0, 160.4, 137.6, 133.7, 134.0, 119.9, 118.5, 70.2, 26.6.

3.3.4.2 Synthesis of 5-(allyloxy)isophthalic acid

Into a 250 mL one necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were charged sodium hydroxide (1.76 g, 44 x 10^{-3} mol), water (20 mL), methanol (20 mL), and dimethyl-5-(allyloxy)isophthalate (4.25 g, 17 x 10^{-3} mol) and the mixture was refluxed for 12 h. The solution was cooled to room temperature and acidified with concentrated HCl. The product was filtered, washed with water and dried at 80 °C under vacuum overnight.

Yield: 3.9 g (98 %).

M.P. 234 ^{o}C

FT-IR (KBr, cm^{-1}): 3250 (OH), 3069 (C=C-H) 1700 (C=O), 1245 (–C-O-C–).

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 13.29 (OH), 8.07 (t, 1H, Ar-H flanked by carbonyl), 7.66 (d, 2H, Ar-H *ortho* to ether), 6.11-5.98 (m, 1H, HC=C**H**-CH$_2$-O-), 5.44-5.27 (m, 2H, **H**C=CH-CH-O-), 4.68 (d, 2H, 2H, HC=CH-C**H$_2$**-O-)

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 169.1, 160.04, 134.50, 131.1, 122.9, 119.6, 118.5, 70.02.

3.3.4.3 Synthesis of 5-(allyloxy)isophthaloyl chloride

Into a 250 mL three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were charged 5-(allyloxy)isophthalic acid (8 g, 36 x 10^{-3} mol) and 2 drops of DMF. Thionyl chloride (100 mL) was added dropwise over a period of 30 min and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (15 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice. The crude product was purified by distillation under reduced pressure at 110°C / 10^{-3} mm Hg.

Yield: 7.4 g (80 %).

FT-IR (CHCl$_3$, cm^{-1}): 3069 (C=C-H), 1770 (C=O), 1240 (–C-O-C–).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.43 (t, 1H, Ar-H flanked by carbonyl groups), 7.89 (d, 2H, Ar-H *ortho* to ether), 6.13-5.94 (m, 1H, HC=C**H**-CH$_2$-O-), 5.50-5.35 (m, 2H, **H**C=CH-CH$_2$-O-), 4.68-4.65 (m, 2H, HC=CH-C**H**$_2$-O-).

^{13}C-NMR (CDCl$_3$, δ/ppm): 165.1, 160.0, 134.5, 133.4, 122.7, 119.7, 118.0, 69.0.

3.3.5 Synthesis of 5-(allyloxy)-1,3-diisocyanatobenzene

A similar procedure as the synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene was adapted for the synthesis of 5-(allyloxy)-1,3-diisocyanatobenzene.

Yield: (81 %).

FT-IR (CHCl$_3$, cm^{-1}): 3020 (C=C-H), 2260 (-NCO), 1214 (–C-O-C–).

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 7.0 (t, 1H, Ar-H flanked by NCO), 6.50 (d, 2H, Ar-H *ortho* to ether), 6.05-5.94 (m, 1H, HC=C**H**-CH$_2$-O-), 5.41-5.22 (m, 2H, **H**C=CH-CH$_2$-O-), 4.63 (d, 2H, HC=CH-C**H**$_2$-O-).

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 162.0, 135.7, 133.5, 127.8, 118.2, 114.7, 108.0, 70.0.

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

3.3.6.1 Synthesis of methyl 4,4'–bis(4-hydroxyphenyl)pentanoate

Into a 500 mL two necked round-bottom flask equipped with a reflux condenser were charged, 4, 4'-bis(4-hydroxyphenyl)pentanoic acid (25 g, 87.32 x 10^{-3} mol), and methanol (300 mL). The reaction mixture was stirred for 15 min followed by addition of concentrated sulphuric acid (1.5 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 (150 mL) and dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate:pet ether (50:50, v/v) as eluent to afford methyl 4,4'–bis(4-hydroxyphenyl)pentanoate.

Yield: 23.8 g (91 %)

FT-IR (CHCl$_3$, cm^{-1}): 1730 (C=O)

^{1}H-NMR (DMSO-d$_6$ δ/ppm): 9.24 (s, 2H, phenolic OH), 6.97 (d, 4H, Ar-H *meta* to phenolic OH), 6.69 (d, 4H, *ortho* to phenolic OH), 3.53 (s, 3H, OCH$_3$), 2.31-2.23 (m, 2H, -CH$_2$-), 2.08-2.01 (m, 2H, -CH$_2$-), 1.47 (s, 3H, -CH$_3$).

3.3.6.2 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 aluminium hydride (1.85 g, 48.99 x 10^{-3} mol) and dry THF (80 mL). The solution of methyl 4,4'–bis(4-hydroxyphenyl)pentanoate (5 g, 54 x 10^{-3} mol) in dry THF (30 mL) was added over a period of 30 min. Effervescences were observed during the addition. Reaction mixture was stirred for 8 h, cooled and then moist sodium sulfate was added to deactivate lithium aluminium 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 (60 mL), sodium bicarbonate solution (60 mL), and water (100 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 ethyl acetate:pet ether (40:60, v/v) to obtain 4,4'–(5-hydroxypentane-2, 2-diyl)diphenol as a white powder.

Yield: 3.4 g (75 %)

FT-IR (CHCl$_3$, cm^{-1}): 3150 (OH)

^{1}H-NMR (DMSO-d$_6$ δ/ppm): 8.28 (s, 2H, phenolic OH), 7.05 (d, 4H, Ar-H *meta* to phenolic OH), 6.75 (d, 4H, Ar-H *ortho* to phenolic OH), 3.53 (t, 2H, -CH$_2$OH), 2.10- 2.06 (m, 2H, -CH$_2$), 1.56 (s, 3H, -CH$_3$), 1.39- 1.31 (m, 2H, -CH$_2$)

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

Into a 250 mL two necked round-bottom flask were added 4,4'–(5-hydroxypentane-2,2-diyl)diphenol (5 g, 18.38 x 10^{-3} mol) and dry THF (60 mL) and the solution was cooled to 0°C. To the reaction mixture were added carbon tetrabromide (7.3 g, 22.05 x 10^{-3} mol) and triphenyl phosphine (5.78 g, 22.05 x10^{-3} mol) 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 (100 mL) and extracted into dichloromethane (100 mL). The dichloromethane solution was washed with saturated brine solution (150 mL) and dried over anhydrous sodium sulfate, filtered and dichloromethane was evaporated under reduced pressure. . The crude product was purified by column chromatography using ethyl acetate: pet ether (15:85, v/v) to obtain 4,4'-(5-bromopentane-2,2-diyl)diphenol as a pale yellow oily liquid.

Yield: 5.4 g (87.70 %)

^{1}H-NMR (DMSO-d$_6$ δ/ppm): 6.03 (s, 2H, phenolic OH), 7.05 (d, 4H, Ar-H *meta* to phenolic OH), 6.75 (d, 4H, Ar-H *ortho* to phenolic OH), 3.36 (t, 2H, -CH$_2$Br), 2.17-2.11 (m, 2H, -CH$_2$), 1.58 (s, 3H, -CH$_3$), 1.66-1.59 (m, 2H, -CH$_2$)

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

Into a 250 mL single necked round-bottom flask were added 4,4'-(5-bromopentane-2,2-diyl)diphenol (5g, 14.92 x 10^{-3} mol) and DMF (60 ml). Sodium azide (4.85g, 74.62 x 10^{-3} mol) was added to the solution and the reaction mixture was stirred at room temprature for 24 h. The reaction mixture was washed with water and extracted with ethyl acetate (200 mL). The ethyl acetate solution was washed with saturated brine solution (150 mL) and dried over anhydrous sodium sulfate, filtered and ethyl acetate was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate: pet ether (30:70, v/v) to obtain 4,4'–(5-azidopentane-2, 2-diyl)diphenol as a pale yellow oily liquid.

Yield: 4.2 g (95%)

FT-IR (CHCl$_3$, cm^{-1}): 3270 (OH), 2097 (-N$_3$),

^{1}H-NMR (CDCl$_3$δ/ppm): 6.38 (s, 2H, phenolic OH), 7.02 (d, 4H, Ar-H *meta* to phenolic OH), 6.74 (d, 4H, Ar-H *ortho* to phenolic OH), 3.21 (t, 2H, -CH$_2$N$_3$), 2.08 (s, 3H, -CH$_3$),   1.39 (t, 2H, -CH$_2$), 1.30-1.23 (m, 2H, -CH$_2$)

^{13}C-NMR (CDCl$_3$, δ/ppm): 153.2, 141.5, 128.2, 114.8, 51.9, 44.5, 38.8, 27.7, 24.3.

3.3.7 Synthesis of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

3.3.7.1 Synthesis of 4-amino-3-pentadecylphenol

Into a 500 mL three-necked round bottom flask equipped with a reflux condenser, a thermowell, and a magnetic stirrer were placed 3-pentadecyl phenol (30.4 g, 0.1 mol), potassium hydroxide (28.0 g, 0.50 mol), and ethyl alcohol (200 mL). The reaction mixture was stirred and to the reaction mixture was added diazonium chloride prepared from sulphanilic acid dihydrate (21 g, 0.10 mol) at –5 ^{o}C. The resulting red dye solution was stirred for 2 h and then heated at 75 °C on a water bath. At that temperature, a saturated solution of sodium dithionite (53 g, 0.30mol) was added to the dye solution over a period of 10 min and the reaction mixture was stirred for 30 min (color of reaction mixture changed from dark red to orange). To the reaction mixture was then added acetic acid (18.0 g, 0.30 mol) dissolved in water (20 mL) and was refluxed for 1 h (color changed to pale tan). The reaction mixture was poured into water (200 mL). The product was filtered, dried and recrystallized from toluene.

Yield: 25.0 g (79 %).

M.P. 105 ^{o}C [Lit.[25] M.P. 105-106 ^{o}C].

FT-IR (CHCl$_3$, cm^{-1}): 3400 and 3350 (-NH$_2$).

^{1}H-NMR (CDCl$_3$, δ/ppm): 6.62-6.51 (m, 3H, Ar-H), 3.65 (s, 2H, -NH$_2$), 2.43 (t, 2H, benzylic -CH$_2$), 1.57 (t, 2H, -CH$_2$ β to aromatic ring), 1.26-1.22 (m, 24H, methylene, -CH$_2$), 0.87 (t, 3H, -CH$_3$)

^{13}C-NMR (CDCl$_3$, δ/ppm): 147.1, 139.1, 127.4, 116.3, 113.7, 32.4, 30.3, 27.0, 23.1, 14.0.

3.3.7.2 Synthesis of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine

Into a 500 mL three-necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were placed 4-amino-3-pentadecyl phenol (22 g, 62 x 10^{-3} mol), 1-chloro-4-nitrobenzene (9.87 g, 62 x 10^{-3} mol), potassium carbonate (9.53 g, 68 x 10^{-3} mol) and DMF (100 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. After completion of the reaction time, reaction mixture was cooled to room temperature and poured into water (1000 mL). The precipitated product was filtered, dried and recrystallized from ethanol.

Yield: 18.9 g (90 %).

M.P. 67 ^{o}C [Lit.[25] M.P. 67 ^{o}C].

FT-IR (CHCl$_3$, cm^{-1}): 1534 (-NO$_2$, asymmetric stretching), 1340 (-NO$_2$, symmetric stretching), 1250 (C-O-C)

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.15 (d, 2H, Ar-H *ortho* to –NO$_2$), 6.93 (d, 2H, Ar-H *meta* to –NO$_2$), 6.81-6.66 (m, 3H, Ar-H *ortho* –NH$_2$), 2.45 (t, 2H, benzylic –CH$_2$), 1.60 (t, 2H, -CH$_2$ β to aromatic ring), 1.26-1.24 (m, 24H, -CH$_2$-CH$_2$-), 0.86 (t, 3H, - CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 1.64.6, 148.3, 142.0, 128.8, 125.8, 121.6, 119.0, 116.4, 116.1, 77.6, 77.0, 31.8, 31.2, 29.6, 28.3, 26.6, 14.0.

3.3.7.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

Into a 250 mL three-necked round bottom flask equipped with a dropping funnel and a reflux condenser were placed 4-(4'-nitrophenoxy)-2-pentadcylbenzenamine (10 g, 22 x 10^{-3} mol), and ethanol (100 mL). Pd/C (0.3 g) was added in portions to the reaction mixture. Hydrazine hydrate (34.13 g, 0.68 mol) was added drop wise over a period of 15 min. After the addition was complete, the reaction mixture was refluxed for 3 h. The reaction mixture was filtered to remove Pd/C. The product precipitated on cooling, was isolated by filtration and was recrystallized twice from ethanol.

Yield: 8.38 g (90 %).

M.P. 81 $^{\circ}$C [Lit.[25] M.P. 81 $^{\circ}$C].

FT-IR (CHCl$_3$, cm^{-1}): 3400-3300 (-N-H stretching).

^{1}H-NMR (CDCl$_3$, δ/ppm): 6.82-6.66 (m, 7H, Ar-H), 3.12 (s, -NH$_2$), 2.43 (t, 2H, benzylic –CH$_2$), 1.57 (t, 2H, -CH$_2$ β to aromatic ring), 1.27-1.23 (m, 24H, methylene –CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 150.7, 150.4, 141.4, 139.3, 128.5, 119.7, 119.3, 116.8, 116.3, 116.1, 77.6, 77.0, 31.8, 31.3, 29.8. 29.3, 28.6, 22.6, 14.0.

3.3.7.4 Synthesis of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

Into a 100 mL two-necked round bottom flask equipped with an addition funnel, a magnetic stirring bar and a reflux condenser were placed sodium azide (0.55 g, 8.46 x 10^{-3} mol), water (3 mL), *tert*-butyl alcohol (5 mL), 4-(4'-aminophenoxy)-2-pentadecylbenzenamine (0.5 g, 1.13 x 10^{-3} mol) and *tert*-butyl nitrite (6 mL, 0.036 mol). The reaction mixture was heated at 80 $^{\circ}$C for 2 h. The reaction mixture was extracted with ethyl acetate (2 x 250 mL). The ethyl acetate solution was successively washed with water (2 x 100 mL), brine (2 x 100 mL) and water (2 x 100 mL). The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The removal of solvent on rotary evaporator afforded a crude product which was chromatographed on silica gel column with petroleum ether as an eluent to obtain 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene as a viscous liquid.

Yield: 0.51 g (92 %).

FT-IR (CHCl$_3$, cm^{-1}): 2121 (-N$_3$), 1213 (–C-O-C–).

^{1}H NMR (CDCl$_3$, δ/ppm): 7.04-6.81 (m, 7H, Ar-H), 2.50 (t, 2H, benzylic –CH$_2$,), 1.65-1.40 (m, 2H, -CH$_2$ β to aromatic ring), 1.35-1.15 (m, 24H, methylene -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 154.5, 153.8, 136.2, 134.8, 133.1, 120.7, 120.2, 119.8, 119.2, 117.3, 31.9, 31.2, 29.6, 29.3, 22.6, 14.1.

3.3.8 Synthesis of 2,4-diazido-1-pentadecylbenzene

3.3.8.1 Synthesis of 1-methylsulfonyloxy-3-pentadecylbenzene

Into a 250 mL two necked round bottom flask equipped with an addition funnel and an air condenser were added 3-pentadecylphenol (5 g, 16.4 x 10^{-3} mol), triethyl amine (1.8 g, 18 mol) and dichloromethane (50 mL). To the reaction mixture, methanesulfonyl chloride (2.06 g, 18 mol) was added dropwise at 0 $^{\circ}$C. After completion of addition, the reaction mixture was stirred for 2

days. The reaction mixture was extracted with dichloromethane (2 x 100 mL). The dichloromethane solution was washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The evaporation of solvent on a rotary evaporator afforded 1-methanesulfonyloxy-3-pentadecyl benzene, which was purified by recrystallization from methanol.

Yield: 4 g (95 %).

M.P. 58 ^{o}C [Lit.[25] M.P. 58 ^{o}C]

FT-IR (CHCl$_3$, cm^{-1}): 1371 (-SO$_2$ asymmetric stretching), 1127 (-SO$_2$ symmetric stretching).

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.34 (t, 1H, Ar-H *meta* to mesyl), 7.05-7.16 (m, 3H, *ortho* and *para* to mesyl), 3.12 (s, 3H, methyl protons of mesyl ester), 2.62 (t, 2H, benzylic -CH$_2$), 1.60 (t, 2H, -CH$_2$ β to aromatic ring), 1.38–1.24 (m, 24H, -CH$_2$-), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 149.3, 145.5, 129.6, 127.4, 121.8, 119.0, 37.2, 35.6, 31.9, 29.68, 29.5, 29.3, 29.2, 22.7, 14.1.

3.3.8.2 Synthesis of pentadecyl benzene

Into a 250 mL two necked round bottom flask were taken 1-methane sulfonyloxy-3-pentadecyl benzene (5 g, 13.6 x 10^{-3} mol), Pd/C (0.5 g), magnesium metal (0.39 g, 16.3 x 10^{-3} mol), ammonium acetate (14.7 g, 191 x 10^{-3} mol) and methanol (50 mL) and the reaction mixture was degassed by three vaccum / N$_2$ cycles. The reaction mixture was stirred under nitrogen atmosphere at room temperature. After completion of the reaction, the reaction mixture was filtered and the filtrate was extracted with dichloromethane (500 mL). The dichloromethane solution was washed with saturated aqueous sodium chloride solution (2 x 100 mL), followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The removal of solvent afforded pentadecyl benzene as a yellow liquid. The purification was done by column chromatography (eluent: pet ether).

Yield: 2.3 g (62 %)

FT-IR (CHCl$_3$, cm^{-1}): 2923 and 2850 (aliphatic C-H stretching), 1600 (aromatic C=C stretching).

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.33-7.13 (m, 5H, Ar-H), 2.60 (t, 2H, benzylic -CH$_2$), 1.61 (t, 2H, -CH$_2$ β to aromatic ring), 1.38–1.24 (m, 24H, methylene -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 142.9, 128.4, 128.2, 125.5, 36.0, 31.9, 31.5, 29.7, 29.4, 22.7, 14.1.

3.3.8.3. Synthesis of 2,4-dinitro-1-pentadecylbenzene

Into a 100 mL two-necked round bottom flask equipped with a dropping funnel and a magnetic stirring bar were placed fuming nitric acid (1.5 mL, 35 x 10^{-3} mol) and zeolite H-β (1 g). The reaction mixture was cooled to 0 °C and acetic anhydride (4.5 mL, 48 x 10^{-3} mol) was added dropwise over a period of 10 min and stirred. Pentadecylbenzene (10 g, 35 x 10^{-3} mol) was added dropwise to the reaction mixture over a period of 45 min and stirred for additional 30 min. Next, fuming nitric acid (1.5 mL, 35 x10^{-3} mmol) and trifluoroacetic anhydride (6.8 mL, 48 x 10^{-3} mol) were added and the reaction mixture was stirred for 2 h. The reaction mixture was filtered to remove zeolite H-β catalyst and the catalyst was washed with copious amount of acetone and

filtered. The solvent was removed on a rotary evaporator to obtain crude product which was chromatographed on silica gel column with petroleum ether as an eluent to obtain pure 2,4-dinitro-1-pentadecylbenzene.

Yield: 10.5 g (80 %).

M.P. 51 °C [Lit[26] M.P 51 °C]

FT-IR (CHCl$_3$, cm^{-1}): 1592 (aromatic C=C stretching), 1530 (-NO$_2$ asymmetric stretching), 1345 (-NO$_2$ symmetric stretching).

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.72 (d, 1H, Ar-H flanked by nitro groups), 8.33 (dd, 1H, Ar-H *ortho* and *para* to the nitro group), 7.54 (d, 1H, Ar-H *ortho* to the pentadecyl chain), 2.97 (t, 2H, benzylic -CH$_2$), 1.38–1.25 (m, 26H, -CH$_2$-), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 14.1, 22.7, 29.2, 29.3, 29.7, 30.5, 31.9, 33.1, 120.2, 126.7, 133.1, 144.8, 146.2, 149.2.

3.3.8.4 Synthesis of 4-pentadecylbenzene-1,3-diamine

Into a 250 mL three-necked round bottom flask equipped with a dropping funnel and a reflux condenser were placed 2,4-dinitro-1-pentadecylbenzene (10 g, 0.026 mol), Pd/C (0.3 g, 3 wt % based on dinitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 °C and hydrazine hydrate (39.7 mL, 0.79 mol) was added dropwise over a period of 15 min and refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was removed on a rotary evaporator to obtain crude diamine. The diamine was chromatographed over neutral alumina with dichloromethane as an eluent to obtain pure 4-pentadecylbenzene-1,3-diamine.

Yield: 6.0 g (71 %).

M.P. 75 °C [Lit[26] M.P 75 °C]

FT-IR (CHCl$_3$, cm^{-1}): 3405, 3319 and 3209 (-N-H stretching)

^{1}H-NMR (CDCl$_3$, δ/ppm): 6.79 (d, 1H, Ar-H *meta* to amino group and *ortho* to alkyl chain), 6.12 (dd, 1H, Ar-H *ortho* to amino group), 6.06 (d, 1H, Ar-H *ortho* to amino group), 3.30 (s, 4H, -NH$_2$), 2.38 (t, 2H, benzylic -CH$_2$), 1.38-1.25 (m, 26H, -CH$_2$-), 0.88 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 145.36, 144.84, 130.27, 117.79, 106.15, 102.62, 31.94, 30.62, 29.71, 29.38, 29.30, 22.71, 14.13.

3.3.8.5 Synthesis of 2,4-diazido-1-pentadecylbenzene

Into a 100 mL two-necked round bottom flask equipped with an addition funnel, a magnetic stirring bar and a reflux condenser were placed sodium azide (1.42 g, 22 x 10^{-3} mol), water (8 mL) *t*-BuOH (7 mL), 4-pentadecylbenzene-1,3-diamine (1 g, 3.14 x 10^{-3} mol) and *tert*-butylnitrite (*t*-BuONO) (10.4 mL, 94 x 10^{-3} mol). The reaction mixture was stirred at 80 °C for 3 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (2 x 250 mL). The ethyl acetate solution was washed with water (2 x 100 mL), brine (2 x100 mL) and water (2 x 100 mL). The organic layer was separated, dried over anhydrous sodium sulfate and filtered. Removal of solvent on rotary evaporator afforded a crude product which was chromatographed on silica gel column with petroleum ether as an eluent to obtain 2,4-diazido-1-pentadecylbenzene.

Yield: 1.12 g (81 %).

M.P. 30 °C

FT-IR (CHCl$_3$, cm^{-1}): 2121 (-N$_3$)

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.11 (dd, 1H, Ar-H *ortho* to –N$_3$ and *para* to alkyl chain), 6.77-6.72 (m, 2H, Ar-H), 2.50 (t, 2H, benzylic -CH$_2$), 1.51-1.45 (m, 2H, -CH$_2$ β to aromatic ring), 1.44-1.20 (m, 24H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 139.0, 138.8, 131.4, 131.2, 31.9, 30.7, 30.3, 29.6, 29.3, 14.1.

3.3.9 Synthesis of N-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

3.3.9.1 Synthesis of 1-pentadecyl-3-phenoxybenzene

Into a 1000 mL two-necked round bottom flask fitted with a Dean and Stark assembly with a reflux condenser were placed 3-pentadecyl phenol (100 g, 0.33 mol), potassium hydroxide (22 g, 0.39 mol), *N,N*-dimethylacetamide (300 mL) and toluene (150 mL). The reaction mixture was refluxed for 7 h and the water formed was removed from the reaction mixture azeotropically. After completion of the reaction, the solvent was distilled off and the dark sticky product was dried under reduced pressure. The compound obtained was potassium salt of 3-pentadecyl phenol. Into a 1000 mL round bottom flask containing potassium salt of 3-pentadecyl phenol (111 g, 0.32 mol) was added bromobenzene (50.88 g, 0.32 mol), followed by addition of Cu powder (2.22 g, 2 wt %) and N,N-dimethylacetamide (150 mL). The reaction mixture was heated at 150 °C for 6 h. After completion of the reaction, the obtained dark colored reaction mixture was poured into water (500 mL); the Cu salts were removed by filtration; The filtrate was extracted with ethyl acetate (2 x 300 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 1-pentadecyl-3-phenoxy benzene. Pure 1-pentadecyl-3-phenoxy benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 70 g (57 %).

M.P. 32 °C [Lit[25] M.P 32 °C]

FT-IR (CHCl$_3$, cm^{-1}): 1267(–C-O-C– stretching)

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.36-6.80 (m, 7H, Ar-H), 2.57(t, 2H, benzylic -CH$_2$), 1.55 (t, 2H, -CH$_2$-), 1.27-1.22 (m, 24 H, -CH$_2$-), 0.88 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 157.4, 157.0, 145.0, 129.6, 123.4, 122.9, 119.0, 118.6, 116.0, 77.6, 77.0, 76.3, 35.84, 31.9, 31.3, 29.78, 29.5, 29.2, 22.7, 14.1.

3.3.9.2 Synthesis of 1-bromo-4-(4-bromophenoxy)-2-pentadecylbenzene

Into a 500 mL three necked round bottom flask equipped with a stirrer, a condenser, and a dropping funnel were placed 1-pentadecyl-3-phenoxy benzene (25 g, 66 x10^{-3} mol) and dichloromethane (150 mL). To the reaction mixture bromine (22 g, 0.14 mol) was added dropwise protecting from light. The top of the condenser was equipped with a trap to absorb the HBr released during the reaction. Bromine was added at a temperature between -5 to 0 °C over a period

of 15 min. After completion of the addition, the reaction mixture was stirred at the same temperature for 1 h and then refluxed overnight. After completion of reaction, excess bromine and HBr were neutralized with aqueous 10 % NH_3 (100 mL). Two phases formed in the reaction mixture were separated, and the organic layer was washed with water (2 x 300 mL). After drying of dichloromethane solution over sodium sulfate and distillation, crude 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained. Pure 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 30 g. (84 %).

M.P.: 43 ^{o}C [Lit[25] M.P 43 ^{o}C]

FT-IR (CHCl$_3$, cm^{-1}): 796 (C-Br stretching).

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.49-7.38 (m, 3H, Ar-H), 6.90-6.85 (m, 2H *ortho* to ether, 1H, *ortho* to pentadecyl chain), 6.69 (dd, *meta* to bromine atom), 2.66 (t, 2H, benzylic -CH$_2$), 1.58 (t, 2H, -CH$_2$- β to aromatic ring), 1.27-1.23 (m, 24H, -CH$_2$-), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 156.2, 155.9, 143.9, 133.6, 132.7, 120.6, 120.3, 118.3, 117.8, 115.8, 77.2, 77.0, 76.7, 36.2, 31.9, 29.7, 29.3, 22.3, 22.7, 14.1.

3.3.9.3 Synthesis of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile

Into a 250 mL three-necked round bottom flask containing 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene (10 g, 18 x10^{-3} mol) was added copper cyanide (6.65 g, 74 x10^{-3} mol) followed by CuSO$_4$ (0.10 g) and DMF (50 mL). The reaction mixture was refluxed overnight. After completion of the reaction, the obtained brown colored solution was poured into concentrated hydrochloric acid (50 mL); and the solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile. Pure 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 6.7 g (83 %).

M.P. 64°C [Lit[20] M.P 64 ^{o}C]

FT-IR (CHCl$_3$, cm^{-1}): 2225 (-CN)

^{1}H-NMR (CDCl$_3$, δ/ppm): 7.71-7.57 (m, 3H, Ar-H, *ortho* to -CN), 7.07 (d, 2H, *meta* to -CN), 6.98-6.86 (m, 2H, *meta* to –CN), 2.80 (t, 2H, benzylic –CH$_2$), 1.64 (t, 2H, , -CH$_2$- β to aromatic ring), 1.26-1.22 (m, 24H, -CH$_2$-), 0.86 (t, 3H, -CH$_3$).

^{13}C-NMR (CDCl$_3$, δ/ppm): 159.4, 158.8, 149.9, 134.8, 134.3, 119.9, 119.3, 118.2, 117.5, 117.0, 108.1, 107.8, 77.6, 77.0, 76.9, 34.5, 31.8, 30.6, 29.6, 29.2, 22.6, 14.0.

3.3.9.4 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

Into a 250 mL single necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile (5g, 11 x10^{-3} mol), potassium hydroxide (7.81 g, 140 x10^{-3} mol), triethylene glycol (75 mL) and water (10 mL). The

reaction mixture was refluxed for 72 h. Next, the temperature of the reaction mixture was maintained at 120 $^{\circ}$C and water (50 mL) was added and the reaction mixture was heated at 100 $^{\circ}$C for additional 48 h. After completion of the reaction time, the reaction mixture was diluted with water (50 mL) and poured into excess concentrated hydrochloric acid. Crude 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid precipitated as a grey solid which was filtered and thoroughly washed with water. The obtained solid was dissolved in aqueous potassium hydroxide solution and was precipitated by addition of concentrated hydrochloric acid (pH 2). The product was filtered and washed repeatedly with water and dried. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid was purified by column chromatography (eluent: pet ether: ethyl acetate 80:20, v/v).

Yield: 3.7 g (68 %).

M.P. 130 $^{\circ}$C [Lit[25] M.P 130 $^{\circ}$C]

FT-IR (CHCl$_3$, cm^{-1}): 3242-3000 (-OH), 1689 (C=O), 1244 (–C-O-C– stretching)

^{1}H-NMR (DMSO-d$_6$, δ/ppm): 12.82 (s,-OH), 7.97 (d, 2H, Ar-H *ortho* to –COOH), 7.87 (d, 1H, Ar-H *ortho* to –COOH), 7.13-6.89 (m, 4H, Ar-H), 2.90 (t, 2H, benzylic –CH$_2$), 1.50 (t, 2H, -CH$_2$-β to aromatic ring), 1.22-1.88 (m, 24H, , -CH$_2$-), 0.83 (t, 3H, -CH$_3$).

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 168.16, 166.87, 159.97, 158.13, 147.24, 133.26, 131.93, 126.30, 126.11, 121.11, 116.44, 116.34, 39.70, 33.79, 31.53, 29.27, 22.33, 14.14.

3.3.9.5 Synthesis of 4-(4-chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride

Into a 250 mL two-necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid (14 g, 29.9 x10$^-$^{3} mol) and DMF (0.25 ml). Thionyl chloride (100 mL) was added dropwise over a period of 30 min and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice to get 4-[4'-(chlorocarbonyl) phenoxy]-2-pentadecylbenzoyl chloride as a viscous liquid.

Yield: 12.50 g (92 %).

FT-IR (CHCl$_3$, cm^{-1}): 1740 (C=O), 1244 (–C-O-C– stretching)

^{1}H- NMR (DMSO-d$_6$, δ/ppm): 8.50 (d, 2H, Ar-H *ortho* to –COCl), 8.35 (d, 1H, Ar-H *ortho* to –COCl), 7.23-7.0 (m, 4H, Ar-H), 3.0 (t, 2H, benzylic –CH$_2$), 1.55 (t, 2H, -CH$_2$ β to aromatic ring),1.23-1.89 (m, 24H, , -CH$_2$-), 0.83 (t, 3H, -CH$_3$).

^{13}C-NMR (DMSO-d$_6$, δ/ppm): 163.0, 141.8, 130.9, 128.3, 117.6, 114.6, 32.4, 30.3, 29.9, 28.5, 23.1, 14.0.

3.3.9.6 Synthesis of N-(4-amino-3-pentadecyl)-4-(4-((4-nitrophenyl)carbamoyl)phenoxy)benzamide

Into a 250 mL three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were placed 4-(4-chlorocarbonyl)phenoxy)-2-

pentadecylbenzoyl chloride (2.158 g, 4.2 x10⁻³ mmol) and DMAc (40 mL). The solution of *para*-nitro aniline (1.36 g, 9.8 x10⁻³ mmol) in DMAc (20 mL) and a solution of triethylamine (0.994 g, 9.8 x10⁻³ mol) in DMAc (5 mL) were added dropwise simultaneously to the reaction mixture. The reaction mixture was stirred for 24 h. After completion of the reaction, DMAc was removed under reduced pressure and the residue was poured into a mixture of methanol and water (1:1,v/v, 150 mL). The precipitated crude solid was filtered at suction, washed with water and dried. The crude product thus obtained was purified by recrystallization from ethanol to get pure *N*-(4-amino-3-pentadecyl)-4-(4-((4-nitrophenyl)carbamoyl)phenoxy)benzamide

Yield: 2.9 g (96 %).

FT-IR (CHCl₃, cm⁻¹): 3378 (-NH), 1682 (-C=O), 1534 (-NO₂ asymmetric stretching), 1340 (-NO₂, symmetric stretching).

¹H-NMR (DMSO-d₆, δ/ppm): 11.01(s, 1H, -NH-), 10.81(s, 1H, -NH-CO), 8.29-8.24 (d, 4H, Ar-H *ortho* to nitro), 8.09-7.96 (m, 6H, Ar-H *ortho* to amide and *ortho* to C=O), 7.62-7.58 (d, 1H, Ar-H *ortho* to C=O and *meta* to pentadecyl chain), 7.20 (d, 4H, Ar-H *meta* to amide), 7.06 (d, 1H, Ar-H *ortho* to amide and *meta* to pentadecyl chain), 2.72 (t, 2H, benzylic –CH₂), 1.52 (t, 2H, methylene protons β to aromatic ring), 1.26-1.23 (m, 24H, -CH₂-), 0.83 (t, 3H, -CH₃).

¹³C-NMR (DMSO-d₆, δ/ppm): 165.2, 159.3, 144.3, 144.0, 127.0, 123.8, 121.3, 117.2, 114.6, 32.5, 30.3, 28.9, 23.1, 14.0.

3.3.9.7 Synthesis of N-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, an addition funnel and a reflux condenser were placed N-(4-amino-3-pentadecyl)-4-(4-((4-nitrophenyl)carbamoyl)phenoxy)benzamide (2.25 g, 3.17 x10⁻³ mol) and Pd/C (0.067 g, 3 wt % based on dinitro compound). Hydrazine hydrate (4.92 g, 98 x 10⁻³ mol) was added dropwise over a period of 15 min and reaction mixture was cooled and filtered to remove Pd/C. Ethanol was removed under reduced pressure .The crude product thus obtained was purified by recrystallization from methanol to get a white crystalline pure *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Yield: 4.5 g (76 %).

M.P. 185 °C

FT-IR (KBr, cm⁻¹): 3409, 3293 (-NH₂), 1642 (C=O) 1235 (–C-O-C–).

¹H-NMR (DMSO-d₆, δ/ppm): 9.91 (s ,1H, -NH-CO), 9.85 (s ,1H, -NH-CO), 7.98 (d, 2H, Ar-H *ortho* to amide), 7.44 (d, 1H, Ar-H *ortho* to amide and *meta* to ether), 7.34 (dd, 4H, Ar-H *ortho* to amide), 7.09 (d, 3H, Ar-H *ortho* to ether and *meta* to amide), 6.98-6.92(m, 1H, Ar-H *ortho* to ether), 6.55-6.51 (m, 4H, Ar-H *ortho* to amine), 4.95 (s, 4H, -NH₂), 2.72 (t, 2H, benzylic –CH₂), 1.52 (t, 2H, methylene proton β to aromatic ring), 1.27-1.23 (m, 24H, -CH₂-),), 0.83 (t, 3H, -CH₃)

¹³C-NMR (DMSO-d₆, δ/ppm): 166.7, 164.0, 159.1, 156.5, 145.4, 145.2, 143.4, 133.7, 130.5, 129.9, 128.7, 128.3, 122.5, 121.6, 120.3, 117.9, 116.1, 32.8, 31.5, 31.0, 29.3, 22.3, 14.1.

3.4 Results and discussion

3.4.1 Synthesis of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

Scheme 3.1 depicts route for the synthesis of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane.

Scheme 3.1: Synthesis of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

The synthesis of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane was carried out starting from commercially available 1,1,1-tris(4-hydoxyphenyl)ethane in a single step reaction using one equivalent of propargyl bromide in the presence of K_2CO_3 in acetone. 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, 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane was isolated by silica gel column chromatography with pet ether : ethyl acetate as an eluent and was characterized by FT-IR, ^{1}H-and ^{13}C-NMR spectroscopy.

FT-IR spectrum (**Figure 3.1**) of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane exhibited characteristics bands for propargyl and OH group at 2121 cm^{-1}(C≡C) and 3298 cm^{-1}, respectively. The –C-O-C-stretching was observed at 1221 cm^{-1}.
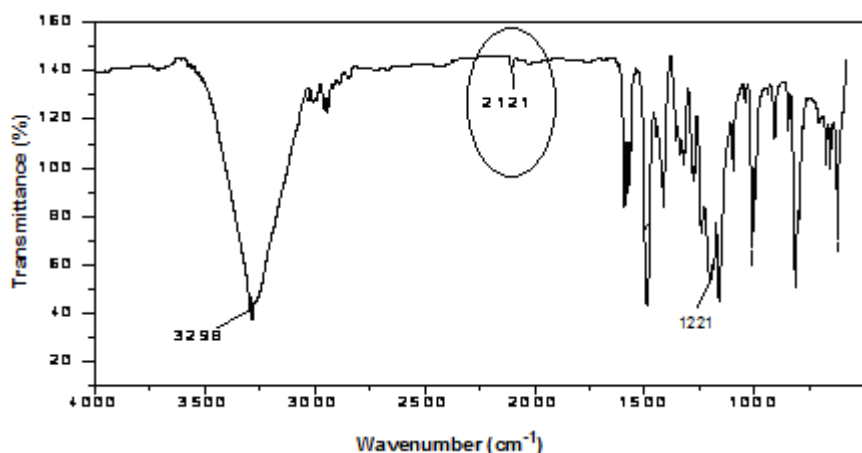
Figure 3.1: FT-IR spectrum of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

^{1}H-NMR spectrum of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane along with assignments is presented in **Figure 3.2**. The singlet appeared at 9.26 δ ppm is due to the hydroxyl group. The doublets displayed at 6.93, 6.86, 6.80 and 6.65 δ ppm are due to protons "d", "c", "f" and "e", respectively. The methylene protons "b" appeared as a doublet at 4.75 δ ppm. The proton "a" of propargyl group exhibited a triplet at 3.55 δ ppm. The methyl protons "h" appeared as a singlet at 2.01 δ ppm.
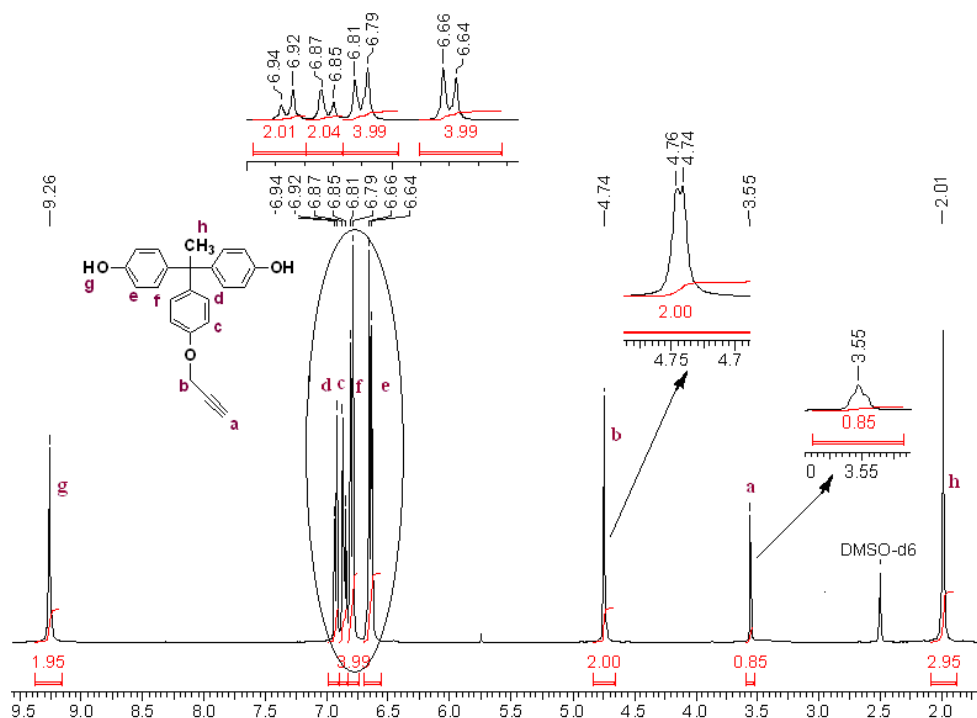
Figure 3.2 ^{1}H-NMR spectrum (DMSO-d$_6$) of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane

^{13}C-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-1-(4'-propargyloxyphenyl)ethane along with the assignments of carbon atoms is depicted in **Figure 3.3.**
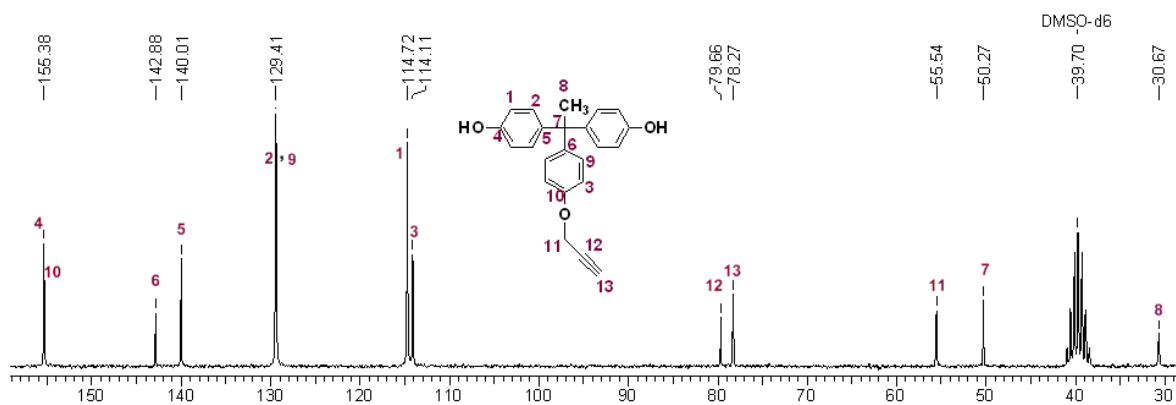
Figure 3.3 ^{13}C-NMR spectrum (DMSO-d$_6$) of 1,1-bis(4'-hydoxyphenyl)-1-(4-propargyloxyphenyl)ethane

3.4.2 Synthesis of 5-(propargyloxy)isophthaloyl chloride

Scheme 3.2 outlines route for the synthesis of 5-(propargyloxy)isophthaloyl chloride.
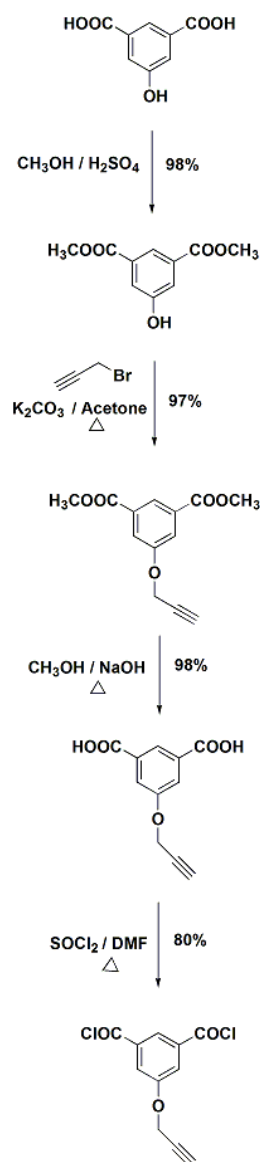
Scheme 3.2 Synthesis of 5-(propargyloxy)isophthaloyl chloride

In the first step, dimethyl-5-hydroxyisophthalate was subjected to propargylation reaction using propargyl bromide in the presence of K_2CO_3 in acetone to obtain dimethyl-5-(propargyloxy)isophthalate. The alkaline hydrolysis of dimethyl-5-(propargyloxy)isophthalate yielded the corresponding diacid, *viz.,* 5-(propargyloxy)isophthalic acid. 5-(Propargyloxy)isophthalic acid on treatment with excess thionyl chloride in the presence of DMF as a catalyst yielded 5-(propargyloxy)isophthaloyl chloride.[27] The diacid chloride was obtained in the pure form by distillation under reduced pressure and was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 5-(propargyloxy)isophthaloyl chloride (**Figure 3.4)** exhibited characteristic absorption band of carbonyl at 1760 cm^{-1}. The absorption bands corresponding to propargyl group were observed at 2127 cm^{-1} (C≡C) and 3307 cm^{-1} (≡C-H). The C-O-C stretching band was observed at 1218 cm^{-1}.
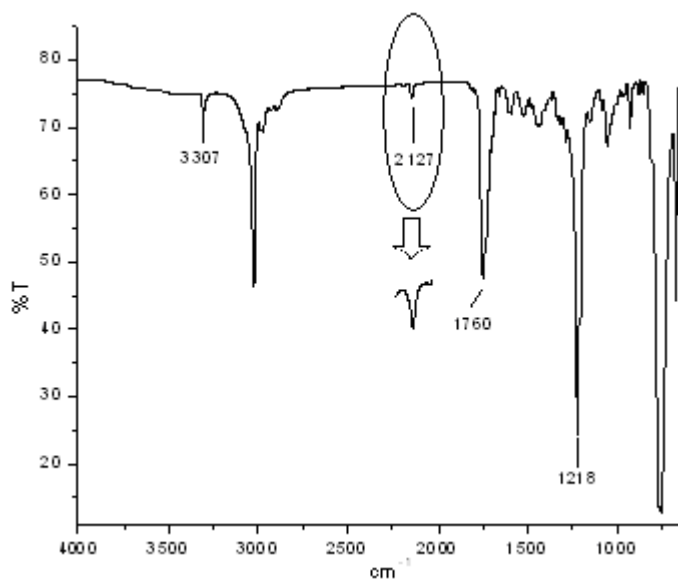
Figure 3.4 FT-IR spectrum of 5-(propargyloxy)isophthaloyl chloride

^{1}H-NMR spectrum of 5-(propargyloxy)isophthaloyl chloride is presented in **Figure 3.5**. The proton 'a' flanked by acid chloride groups appeared as a triplet at 8.49 δ ppm. The protons "b" appeared as a doublet at 7.98 δ ppm. The methylene protons "c" of popargyl group exhibited a doublet at 4.84 δ ppm. The triplet at 2.60 δ ppm corresponds to proton "d" of propargyl group.
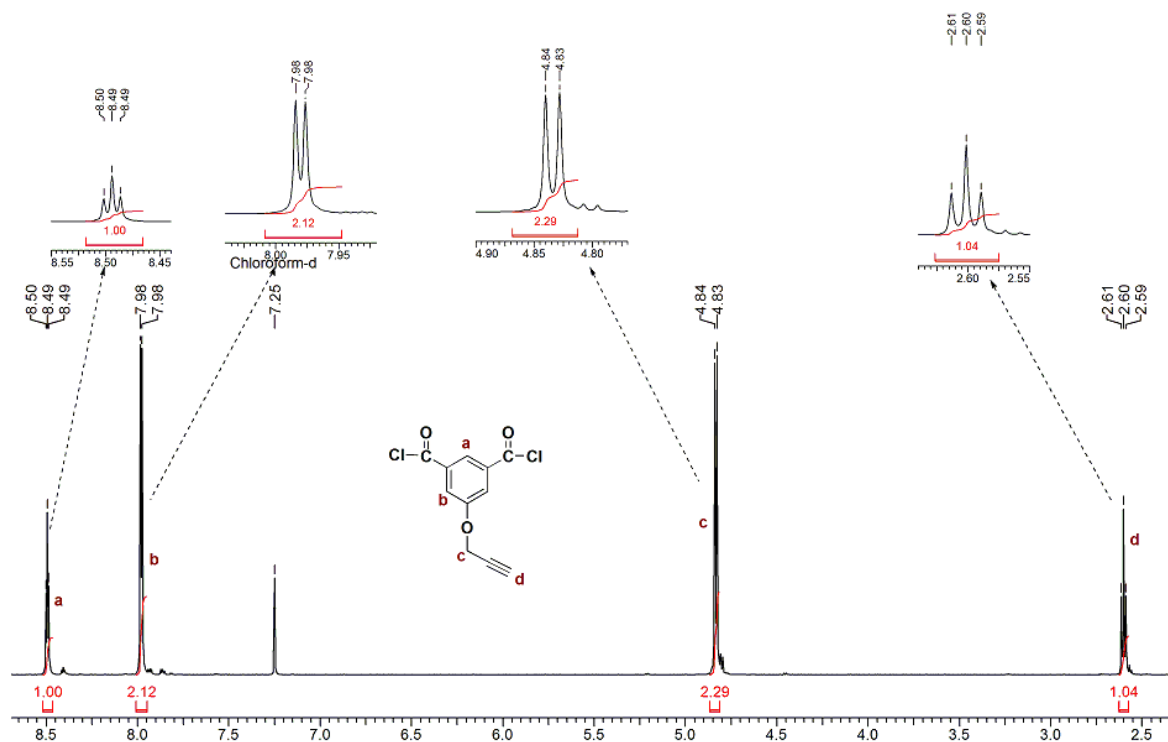
Figure 3.5 ^{1}H-NMR spectrum (CDCl₃) of 5-(propargyloxy)isophthaloyl chloride

^{13}C-NMR spectrum of 5-(propargyloxy)isophthaloyl chloride along with the assignments of carbon atoms is depicted in **Figure 3.6.**
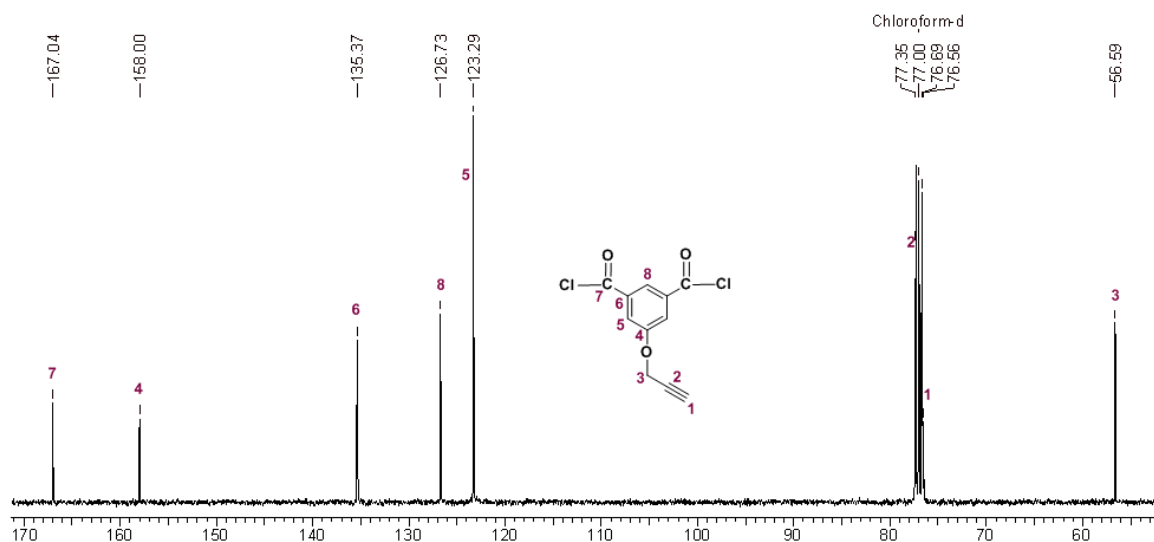
Figure 3.6 ^{13}**C-NMR spectrum (CDCl$_3$) of 5-(propargyloxy)isophthaloyl chloride**

3.4.3: Synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene

Scheme 3.3 illustrates route followed for the synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene.
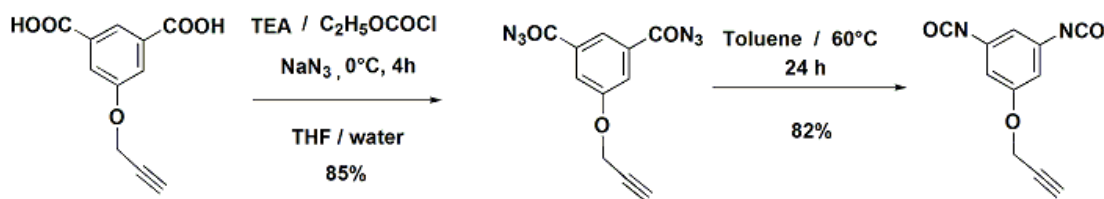
Scheme 3.3 Synthesis of 5-(propargyloxy)-1,3-diisocyanatobenzene

A new *meta*-oriented pendent propargyloxy group containing diisocyanate was synthesized by the non-hazardous, non-phosgenation Curtius rearrangement reaction of 5-(propargyloxy) isophthaloyl diazide. Acyl azides are usually prepared from acid derivatives such as acid halides or acid hydrazides.[28, 29] The direct conversion of carboxylic acids to acyl azides can be brought about by employing acid activators such as ethyl chloroformate,[30] phenyldichlorophosphate,[31] SOCl$_2$-DMF,[32] NCS- triphenylphosphine,[33] triphosgene,[34] 3,4,5-trifluorobenzeneboronic acid,[35] or cyanuric chloride,[36] followed by the reaction with sodium azide.. In the present work, the diacylazide was prepared from 5-(propargyloxy) isophthalic acid by the elegant 'one-pot' Weinstock modification of the Curtius reaction.[37] 5-(Propargyloxy)isophthalic acid was treated successively with triethylamine, ethylchloroformate and sodium azide. The reaction of a diacid with triethylamine produces a salt which on treatment with ethylchloroformate results in the formation of a mixed carboxylic-carbonic anhydride. In the reaction of mixed carboxylic-carbonic anhydride, the azide ion attacks the more electrophilic carbonyl group resulting in the formation of the diacylazide. The reaction conditions employed are mild and there are apparently no side products formed in this 'one-pot' reaction. 5-(Propargyloxy)isophthaloyl diazide was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy. FT-IR spectrum of 5-(propargyloxy)isophthaloyl diazide is presented in **Figure 3.7**.
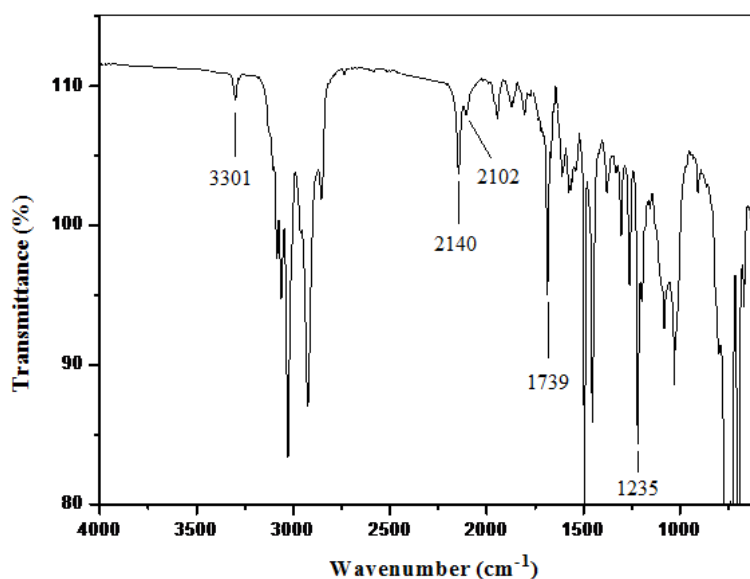
Figure 3.7 FT-IR spectrum of 5-(propargyloxy)isophthaloyl diazide

A strong absorption band was observed at 2140 cm^{-1} which is due to asymmetric stretching vibration of -N$_3$ group. The characteristic bands of propargyl group were observed at 3301 cm^{-1} ($\equiv$C-H) and 2102 cm^{-1} (C$\equiv$C). The characteristic band of carbonyl group appeared at 1739 cm^{-1}. The C-O-C stretching band was observed at 1235 cm^{-1}.

^{1}H-NMR spectrum of 5-(propargyloxy)isophthaloyl diazide is presented in **Figure 3.8.**
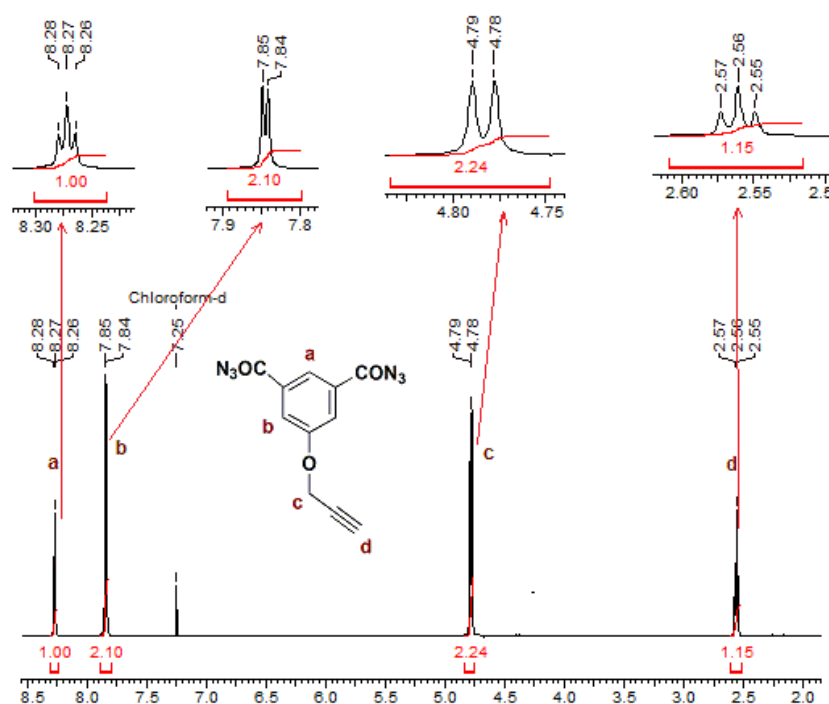
Figure 3.8 ^{1}H-NMR spectrum (CDCl$_3$) of 5-(propargyloxy)isophthaloyl diazide

In ^{1}H-NMR spectrum of 5-(propargyloxy)isophthaloyl diazide, proton "a" flanked by acyl azide groups appeared as a triplet at 8.27 δ ppm. The proton "b" appeared as a doublet at 7.85 δ ppm. The doublet at 4.79 δ ppm is due to methylene protons "c". The proton "d" of propargyl group appeared as a triplet at 2.56 δ ppm.

The thermal Curtius rearrangement[37] of 5-(propargyloxy)isophthaloyl diazide in dry toluene was carried out to afford the desired diisocyanate.

FT-IR spectrum of 5-(propargyloxy)-1,3-diisocyanatobenzene is presented in **Figure 3.9.** The characteristic bands of propargyl group appeared at 3300 cm^{-1} ($\equiv$C-H) and 2110 cm^{-1} (C$\equiv$C). The absorption bands at 2261 cm^{-1} and 1219 cm^{-1} are the characteristic bands of the asymmetric stretching vibration of isocyanate group and ether group, respectively.
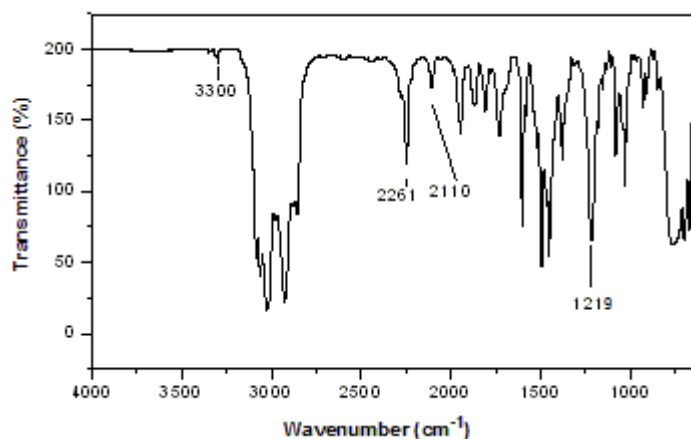
Figure 3.9 FT-IR spectrum of 5-(propargyloxy)-1,3-diisocyanatobenzene

^{1}H-NMR spectrum of 5-(propargyloxy)-1,3-diisocyanatobenzene is presented in **Figure 3.10**. The proton 'a' flanked by isocyanate groups exhibited a triplet at 7.0 δ ppm. The proton 'b' appeared as a doublet at 6.66 δ ppm. The doublet appeared at 4.75 δ ppm is due to methylene protons "c". The proton "d" of propargyl group appeared as a triplet 2.56 δ ppm. The up field chemical shift of the aromatic protons in the diisocyanate is likely to be due to a combination of electron donating effect of ether oxygen and shielding due to neighboring group anisotropy of the isocyanate group. The dominating effect appears to be the electron donating effect of the ether oxygen. The aromatic protons in the corresponding diacyl azide (**Figure 3.8)** appeared downfield in comparison to the aromatic protons of the diisocyanate (**Figure 3.10**). In the case of diacyl azide, the electron donating effect of the ether oxygen and the neighbouring group anisotropy of the carbonyl of acyl azide group would be operative. The downfield chemical shift indicates that the latter dominates over the former.
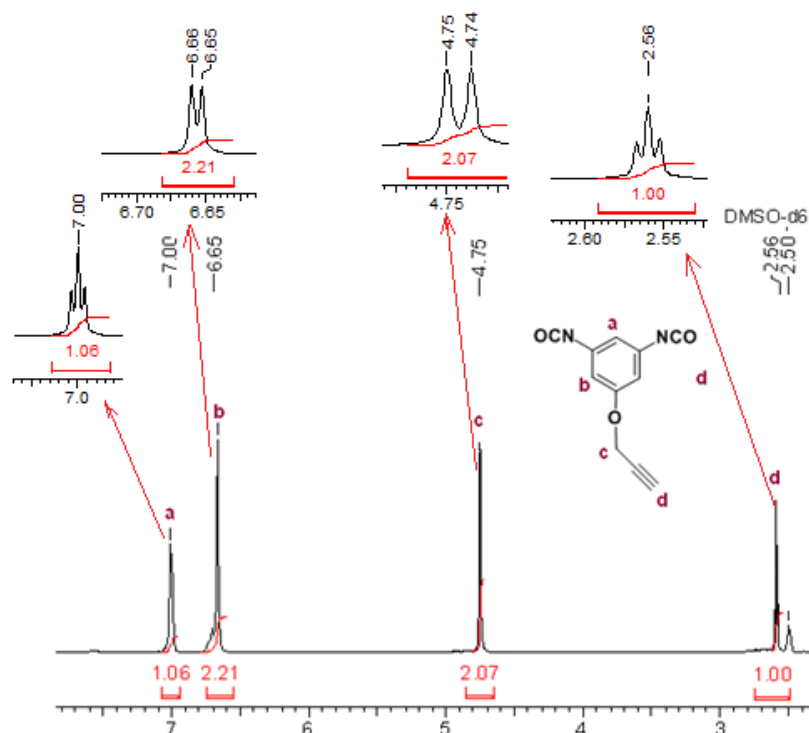
Figure 3.10 ^{1}H-NMR spectrum (DMSO-d$_6$) of 5-(propargyloxy)-1,3-diisocyanatobenzene

^{13}C-NMR spectrum of 5-(propargyloxy)-1,3-diisocyanatobenzene along with the assignments of carbon atoms is shown in **Figure 3.11.**
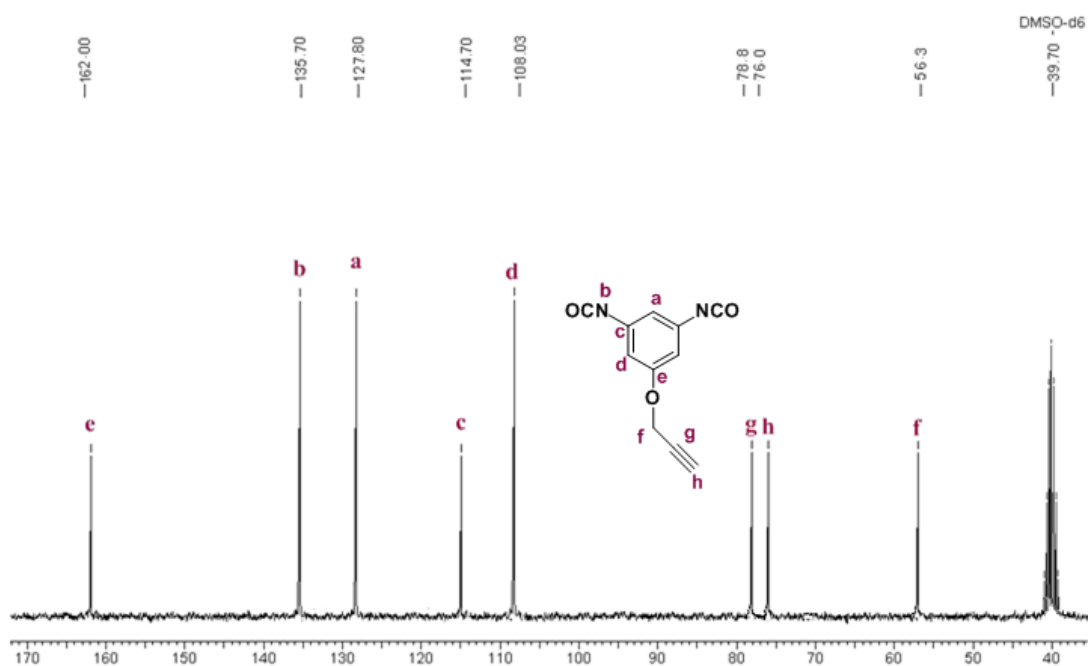
Figure 3.11 ^{13}C-NMR spectrum (DMSO-d$_6$) of 5-(propargyloxy)-1,3-diisocyanatobenzene

3.4.4 *Synthesis of 5-(allyloxy)isophthaloyl chloride*

Scheme 3.4 depicts route for the synthesis of of 5-(allyloxy)isophthaloyl chloride.
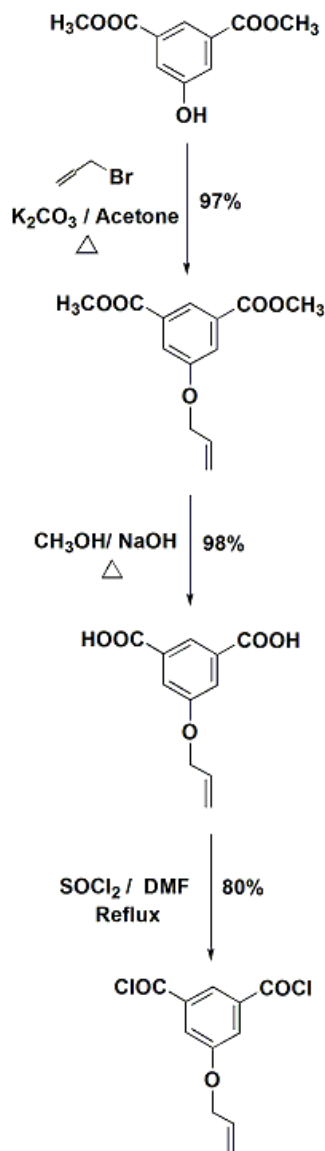
Scheme 3.4 Synthesis of 5-(allyloxy)isophthaloyl chloride

In the first step, 5-hydroxyisophthalic acid dimethyl ester was subjected to allylation reaction using allyl bromide in the presence of K_2CO_3 in acetone to obtain dimethyl-5-(allyloxy) isophthalate. The alkaline hydrolysis of dimethyl 5-(allyloxy)isophthalate yielded 5-(allyloxy) isophthalic acid which on treatment with excess thionyl chloride in the presence of catalytic amount of DMF yielded 5-(allyloxy)isophthaloyl chloride.[27] The diacid chloride was obtained in the pure form by distillation under reduced pressure and was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

In FT-IR spectrum of 5-(allyloxy)isophthaloyl dichloride (**Figure 3.12)** the characteristic band of carbonyl group appeared at 1770 cm^{-1}. The characteristic bands of allyl group and C-O-C linkage were observed at 3069 cm^{-1} and 1240 cm^{-1}, respectively.
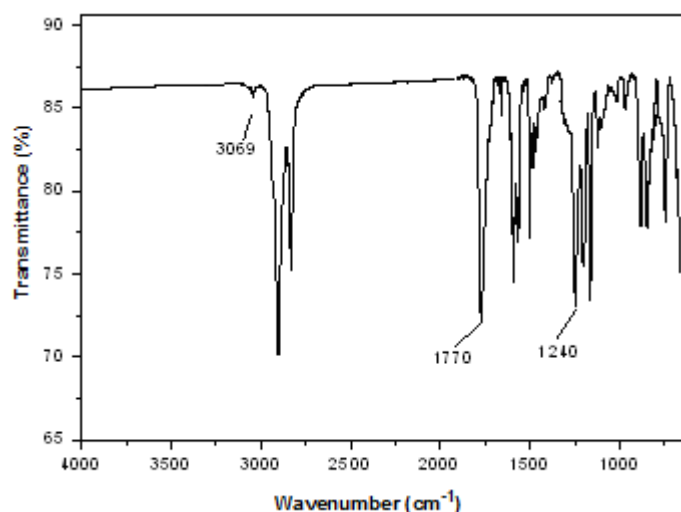
Figure 3.12 FT-IR spectrum of 5-(allyloxy)isophthaloyl chloride

^{1}H-NMR spectrum of 5-(allyloxy)isophthaloyl chloride along with assignments is depicted in **Figure 3.13** The proton "a" flanked by acid chloride groups exhibited a triplet at 8.43 δ ppm while the other two aromatic protons "b" appeared as a doublet at 7.90 δ ppm. The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range 6.13-5.94 δ ppm, and 5.50-5.35 δ ppm which correspond to protons "d" and "e", respectively. The peaks appeared the range 4.68-4.65 δ ppm are due to methylene protons "c".
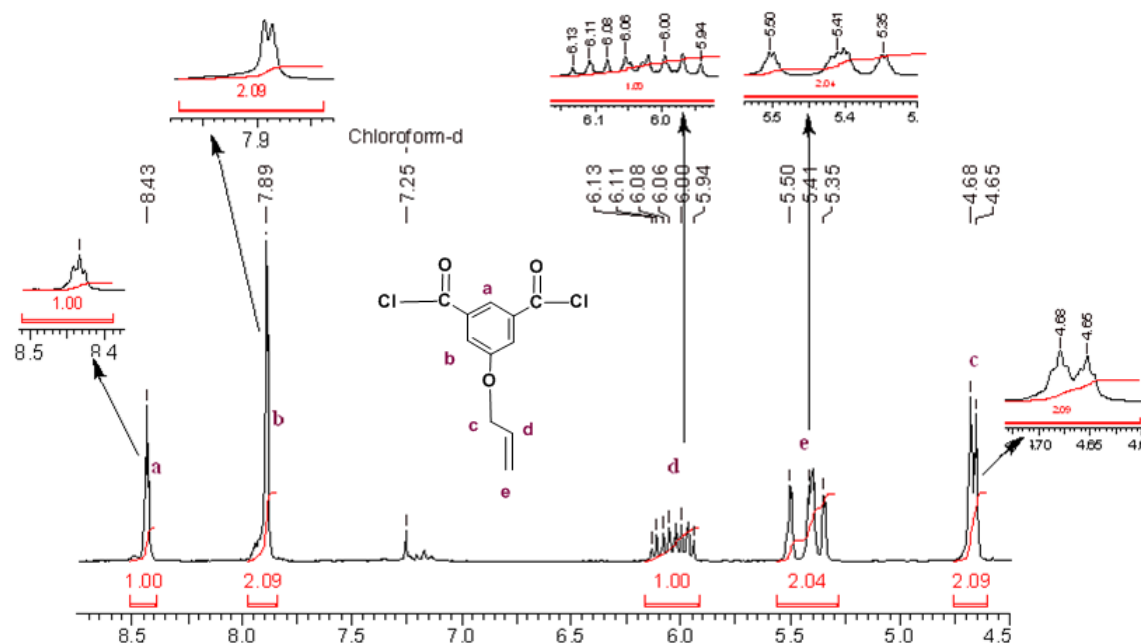
Figure 3.13 ^{1}H-NMR spectrum (CDCl$_3$) of 5-(allyloxy)isophthaloyl chloride

In ^{13}C-NMR spectrum of 5-(allyloxy)isophthaloyl chloride (**Figure 3.14**) the peaks corresponding to allyl group appeared at 134.50 and 118.04 δ ppm. The spectral data corresponding to other carbon atoms was in good agreement with the structure.
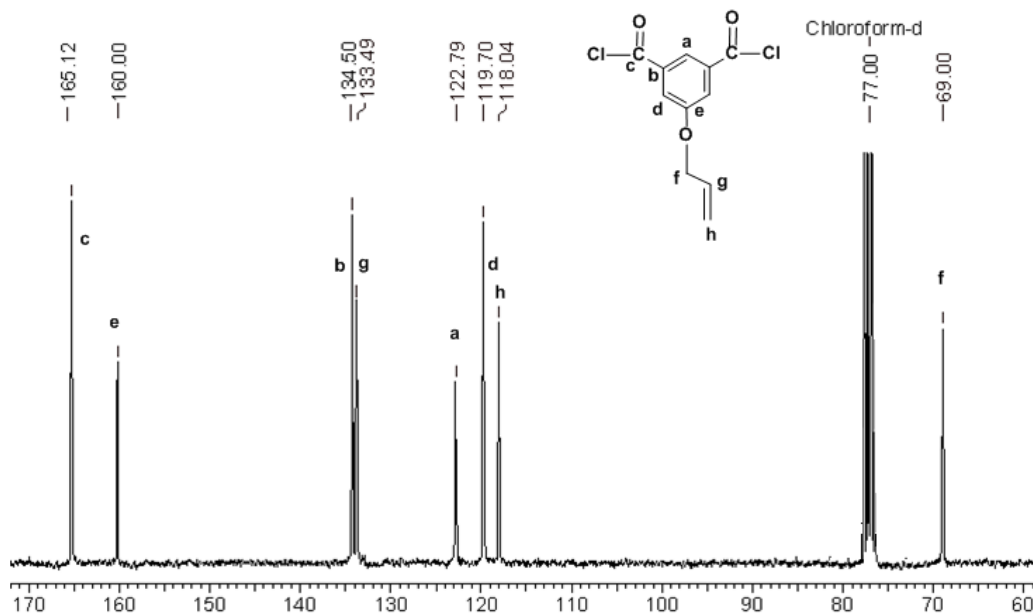
Figure 3.14 ^{13}C-NMR spectrum (CDCl$_3$) of 5-(allyloxy)isophthaloyl chloride

3.4.5 Synthesis of 5-(allyloxy)-1,3-diisocyanatobenzene

Scheme 3.5 outlines route for synthesis of 5-(allyloxy)-1,3-diisocyanatobenzene
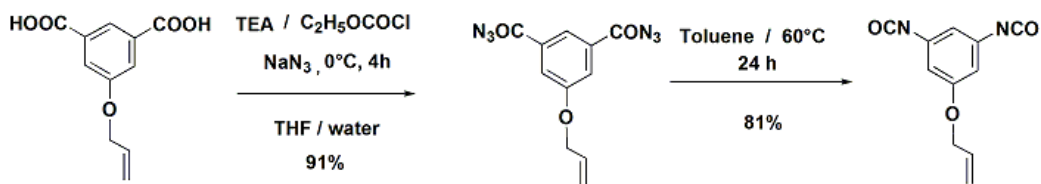
Scheme 3.5: Synthesis of 5-(allyloxy)-1,3-diisocyanatobenzene

5-(Allyloxy)isophthalic acid was treated successively with triethylamine, ethylchloroformate and sodium azide to yield 5-(allyloxy)isophthaloyl diazide which on thermal Curtius rearrangement afforded 5-(allyloxy)-1,3-diisocyanatobenzene.

In FT-IR spectrum of 5-(allyloxy)-1,3-diisocyanatobenzene **(Figure 3.15)** the characteristic bands of allyl and C-O-C linkage were observed at 3020 cm^{-1} and 1214 cm^{-1}, respectively. Strong absorption band at 2260 cm^{-1} was observed due to isocyanate group.
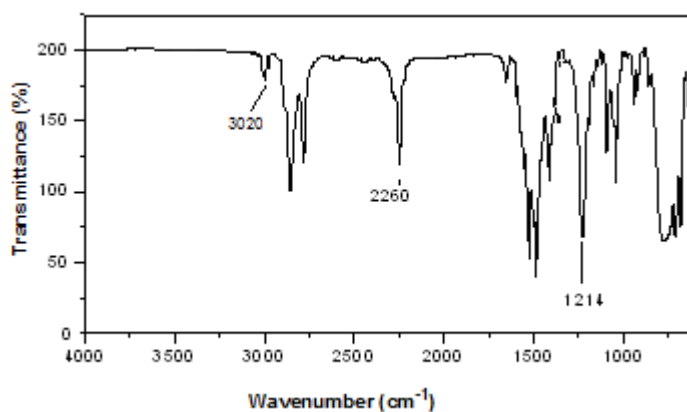
Figure 3.15 FT-IR spectrum of 5-(allyloxy)-1,3-diisocyanatobenzene

Figure 3.16 represents ^{1}H-NMR spectrum of 5-(allyloxy)-1,3-diisocyanatobenzene along with the assignments. The proton "a" flanked by isocyanate groups exhibited a triplet at 7.0 δ, ppm. The protons "b' appeared as a doublet at 6.51 δ ppm. The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range 6.05-5.94 δ ppm, and 5.41-5.22 δ, ppm which correspond to proton "d" and protons "e" respectively. The peaks appeared in the range 4.63 – 4.7 δ ppm are due to protons "c".
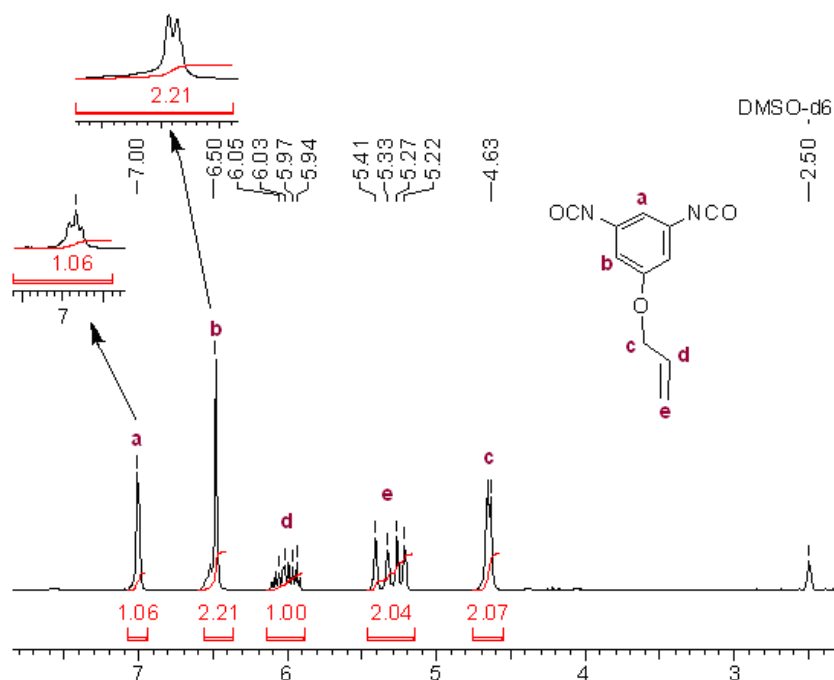
Figure 3.16 ^{1}H-NMR spectrum (DMSO-d$_6$) of 5-(allyloxy)-1,3-diisocyanatobenzene

In ^{13}C-NMR spectrum of 5-(allyloxy)-1,3-diisocyanatobenzene (**Figure 3.17**) the peaks corresponding to allyl group appeared at 133.50 and 118.20 δ, ppm.
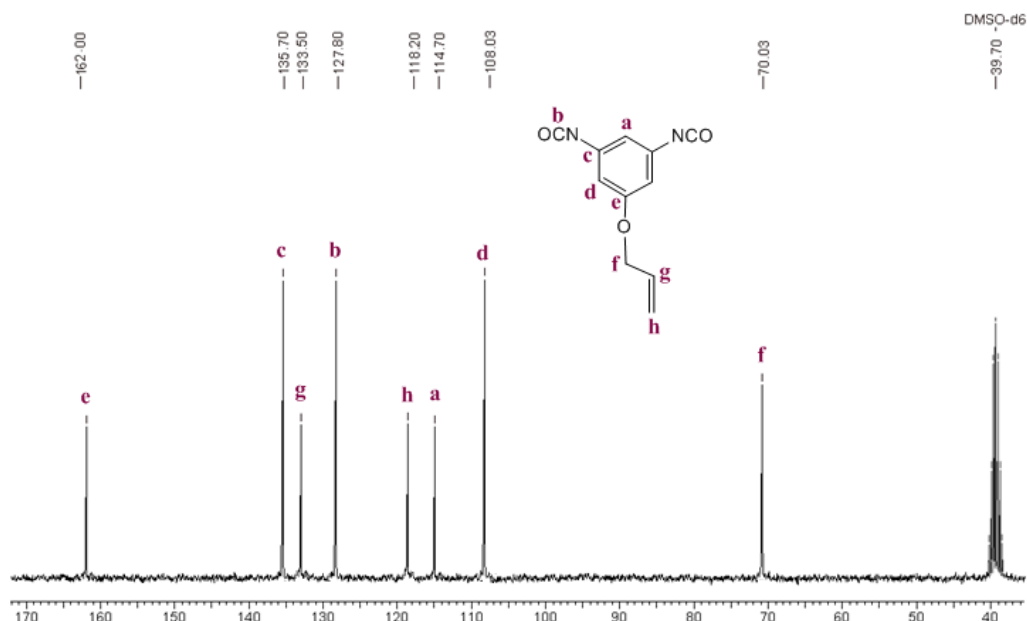
Figure 3.17 ^{13}C-NMR spectrum (DMSO-d$_6$) of 5-(allyloxy)-1,3-diisocyanatobenzene

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

Synthesis of 4, 4'–(5-azidopentane-2, 2-diyl)diphenol is illustrated in **Scheme 3.6.**
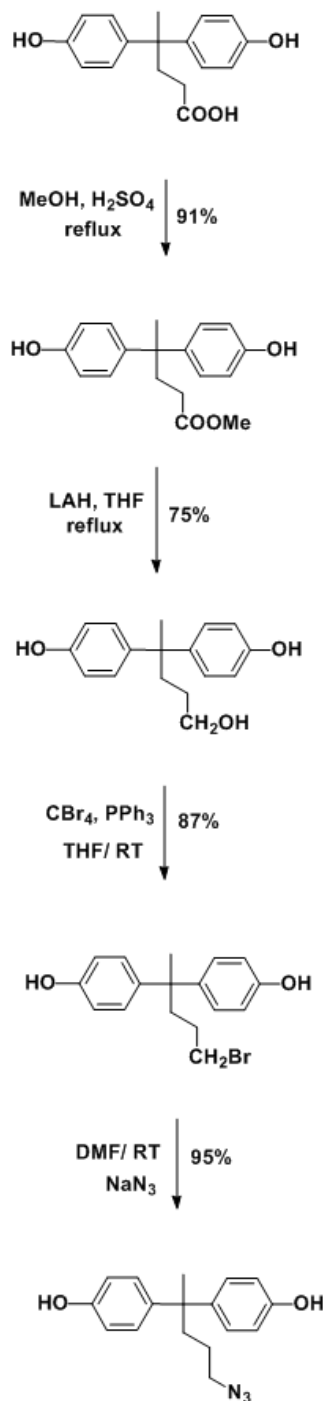
Scheme 3.6 Synthesis of 4, 4'–(5-azidopentane-2, 2-diyl)diphenol

Commercially available 4,4'-bis(4-hydroxyphenyl)pentanoic acid, which in turn is derived from levulenic acid –a platform chemical obtained from biomass, was utilized for synthesis of 4,4'–(5-azidopentane-2,2-diyl)diphenol**.** In the first step, 4,4'-bis (4-hydroxyphenyl) pentanoic acid was esterified using methanol in the presence of a catalytic amount of concentrated sulphuric acid to yield methyl ester of 4,4'-bis(4-hydroxyphenyl) pentanoic acid which on reduction in the presence of lithium aluminium hydride (LAH) afforded 4,4'–(5-hydroxypentane-2,2-diyl)diphenol. The conversion of 4,4'-(5-hydroxypenentane-2,2-diyl)diphenol to 4,4'-(5-

bromopentane-2,2-diyl)diphenol was achieved by bromination of 4,4'-(5-hydroxypenentane-2,2-diyl)diphenol using carbon tetrabromide as a brominating agent in the presence of triphenyl phosphine in THF. The conversion of 4,4'-(5-bromopentane-2,2-diyl)diphenol to 4,4'–(5-azidopentane-2,2-diyl)diphenol was accomplished using sodium azide in the presence of DMF as a solvent. 4,4'-(5-Azidopentane-2,2-diyl)diphenol was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy. Low molecular weight azides are generally explosive-especially under acidic conditions[38] However, the monomer was safe to handle at room temperature. No decomposition or explosion was observed when it was vacuum dried at room temperature for one day, although like all azido compounds, this monomer should always be handled with precaution.

In FT-IR spectrum of 4,4'-(5-azidopentane-2,2-diyl)diphenol (**Figure 3.18**), the characteristics bands of azido and hydroxyl groups appeared at 2097 and 3270 cm^{-1}, respectively.
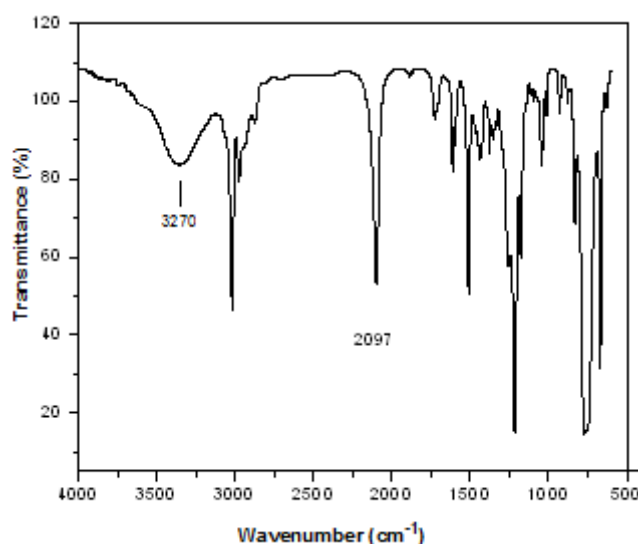
Figure 3.18 FT-IR spectrum of 4,4'-(5-azidopentane-2,2-diyl)diphenol

Figure 3.19 represents ^{1}H-NMR spectrum of 4,4'-(5-azidopentane-2,2-diyl)diphenol along with the assignments.
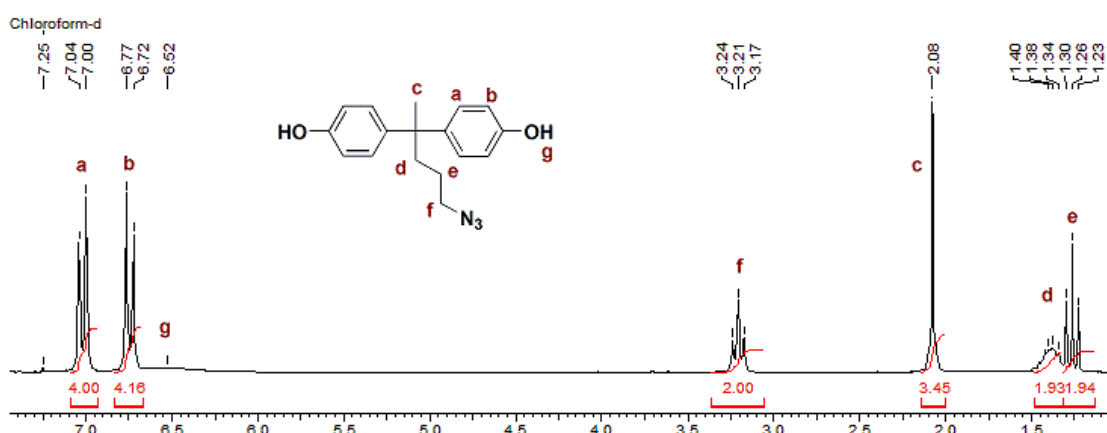
Figure 3.19 ^{1}H-NMR spectrum (CDCl$_3$) of 4,4'-(5-azidopentane-2,2-diyl)diphenol

The protons "a" *meta* to phenolic –OH groups appeared as a doublet at 7.02 δ ppm. The protons "b" *ortho* to phenolic –OH groups appeared as a doublet at 6.74 δ ppm. The phenolic OH

appeared as a broad peak at 6.38 δ ppm. The methylene proton "f" appeared as a triplet at 3.21 δ ppm. The methyl protons "c" appeared a singlet at 2.08 δ ppm. The triplet appeared at 1.39 δ ppm is due methylene protons "d". The methylene protons "e" appeared as a multiplet in the range 1.30-1.23 δ ppm.

^{13}C-NMR spectrum of 4,4'-(5-azidopentane-2,2-diyl)diphenol along with the assignments of carbon atoms is presented in **Figure 3.20.**
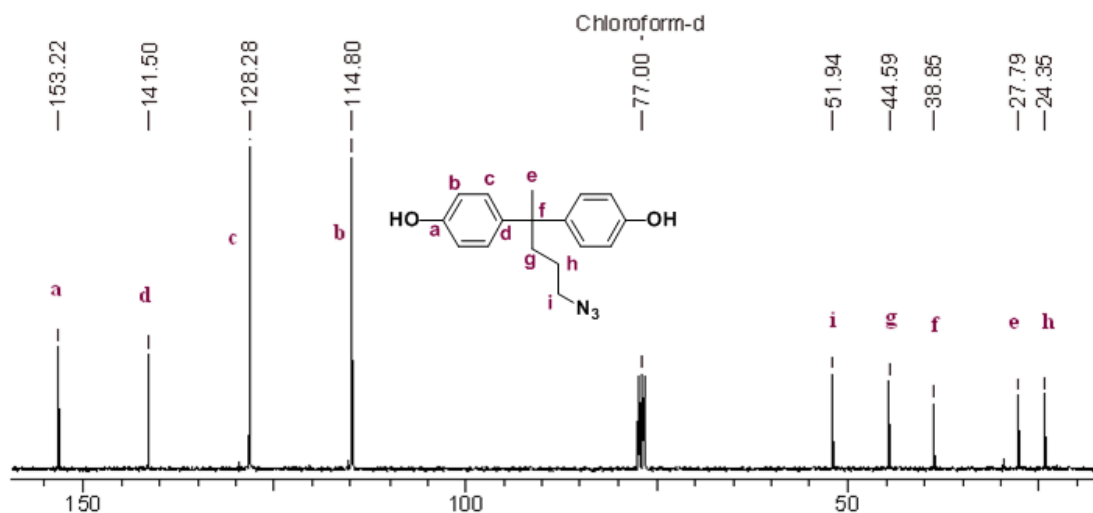
Figure 3.20 ^{13}C-NMR spectrum (CDCl$_3$) of 4,4'-(5-azidopentane-2,2-diyl)diphenol

3.4.7 Synthesis of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

Diazides constitute a highly important class of monomers for the synthesis of polymers having a triazole ring along the polymer backbone. The most straightforward route for the preparation of aryl azides involves diazotization of amines with nitrous acid followed by reaction with sodium azide at low temperature.[39, 40] Alternatively, aryl amines have been transformed into aryl azides by treating the former with *para*-toluenesulfonyl azide in the presence of a Grignard reagent or a strong base.[41, 42] Aryl azides have also been prepared from arylmagnesium halides or aryl lithium reagents, generated from aryl halides,[43] and *para*-toluenesulfonyl azide.[44] The above conversion has also been accomplished under mild condition using a combination of triflyl azide, CuSO4, and triethylamine.[45] Very recently, the coupling of aromatic and vinyl halides with sodium azide under catalysis with Cu(I)–L-proline was reported to produce aryl/vinyl azides in good to excellent yields.[46] However, all these transformations require either acidic or basic conditions, which are not compatible with many functional groups present in a substrate. The preparation of aryl azides from aryl amines can be achieved under neutral conditions. In the presence of a strong nucleophile such as azide, a deamination reaction could be diverted to azide formation, since aryl amines do undergo diazotization with alkyl nitrite.[47, 48]

Scheme 3.7 depicts route for synthesis of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene.
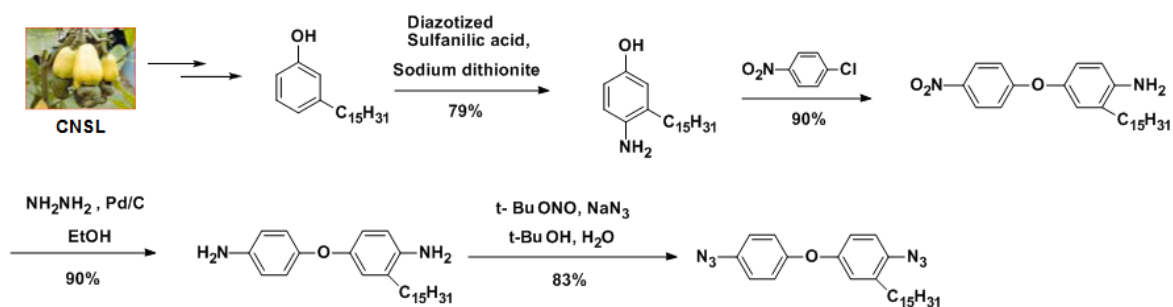
Scheme 3.7 Synthesis of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

A new unsymmetrical aromatic diazide *viz*; 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene was synthesized in four steps starting from 3-pentadecylphenol (3-PDP) which in turn is obtainable from CNSL- a renewable resource material.[49, 50] In the first step, 3-PDP was converted to 4-amino-3-pentadecyl phenol by reaction with diazotized sulfanilic acid and sodium dithionite. 4-Amino-3-pentadecyl phenol was condensed with 1-chloro-4-nitrobenzene in the presence of potassium carbonate to yield 4-(4'-nitrophenoxy)-2-pentadecylbenzamine which on reduction[51] in the presence of hydrazine hydrate and catalytic amount of Pd/C afforded 4-(4'-aminophenoxy)-2-pentadecylbenzenamine. Finally, conversion of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine to 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene was carried out in *tert*-butyl alcohol and water as a solvent in the presence of excess *tert*-butyl nitrite (*t*-BuONO) and NaN$_3$.[48] 1-Azido-4-(4-azidophenoxy)-2-pentadecylbenzene was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

In FT-IR spectrum of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene (**Figure 3.21)** the characteristic bands of azido and ether group were observed at 2121 cm^{-1} and 1213 cm^{-1}, respectively.
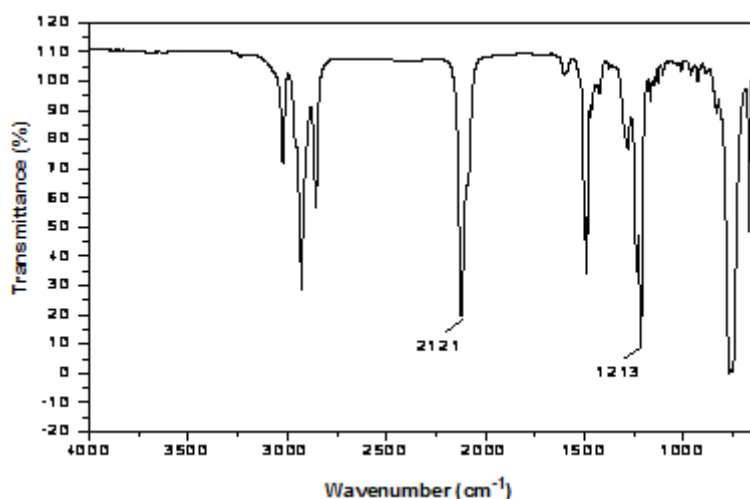
Figure 3.21 FT-IR spectrum of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

In ^{1}H-NMR spectrum of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene (**Figure 3.22)** the peaks appeared in the range 7.04-6.81 δ, ppm correspond to aromatic protons a, b, c, d, and e. The triplet at 2.50 δ ppm corresponds to benzylic –CH$_2$. The methylene protons β to aromatic ring exhibited a multiplet in the range 1.65 – 1.40 δ ppm. The peaks in the range 1.35-1.15 δ ppm could

be assigned to the methylene protons of the pentadecyl chain. The methyl protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.
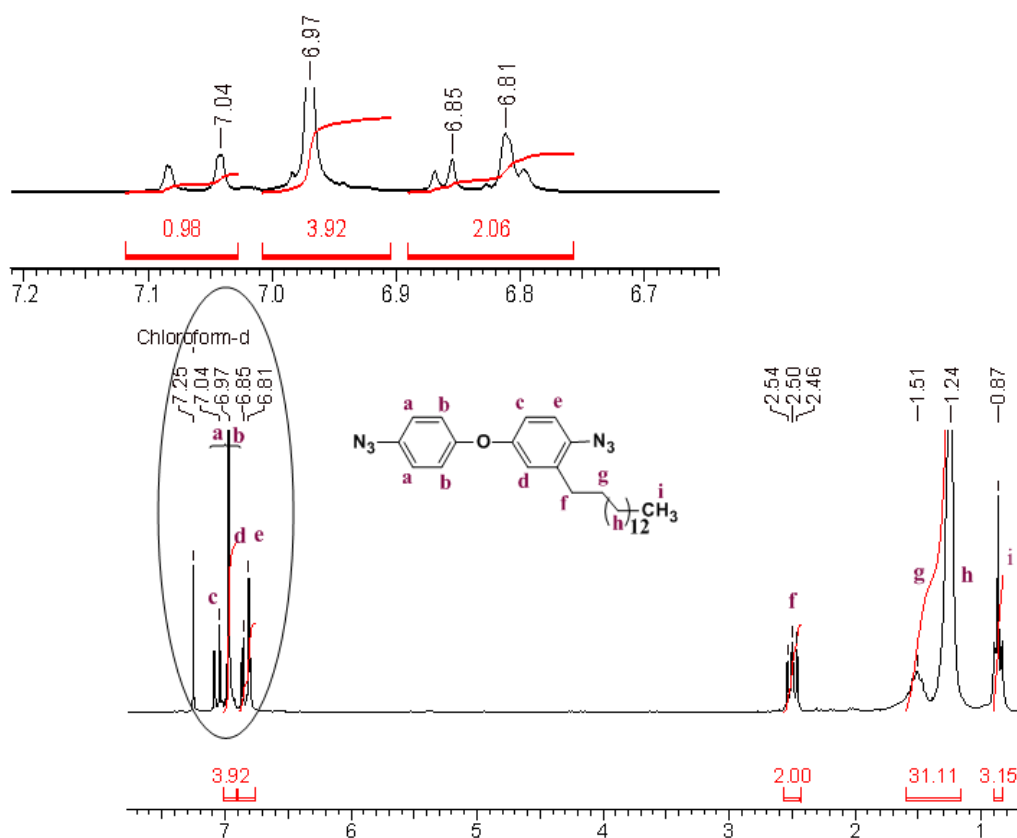
Figure 3.22 ^{1}H- NMR spectrum (CDCl$_3$) of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene.

^{13}C-NMR spectrum of 1-azido-4-(4azidophenoxy)-2-pentadecylbenzene along with the assignments of carbon atoms is shown in **Figure 3.23.**
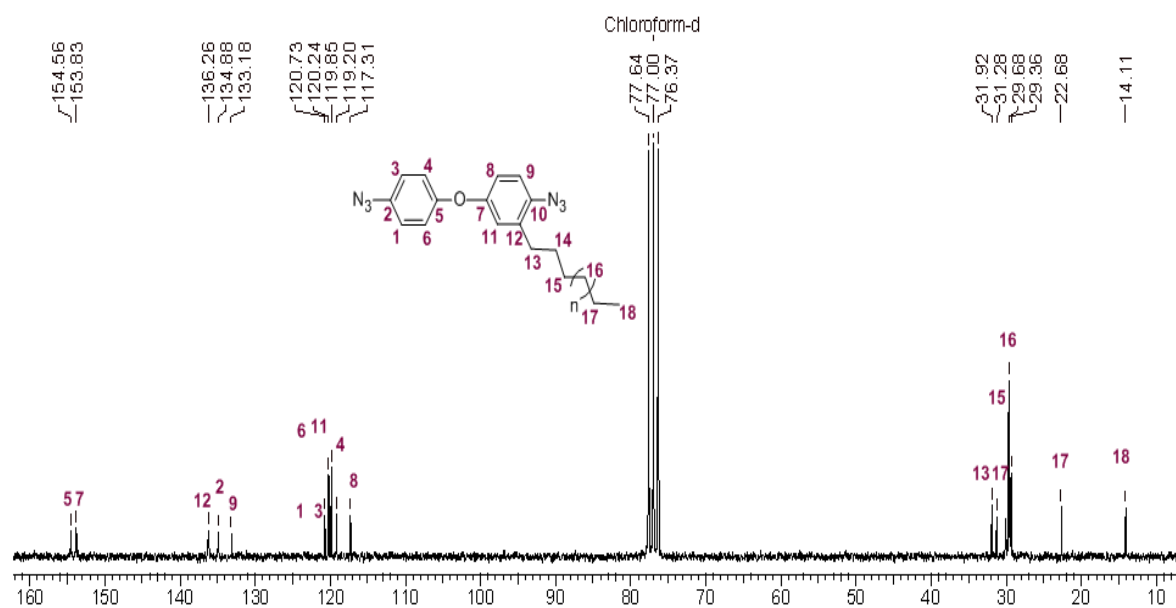
Figure 3.23 ^{13}C-NMR spectrum (CDCl$_3$) of 1-azido-4-(4-azidophenoxy)-2-pentadecylbenzene

3.4.8 Synthesis of 2,4-diazido-1-pentadecylbenzene

      Scheme 3.8 depicts route for synthesis of 2,4-diazido-1-pentadecylbenzene.
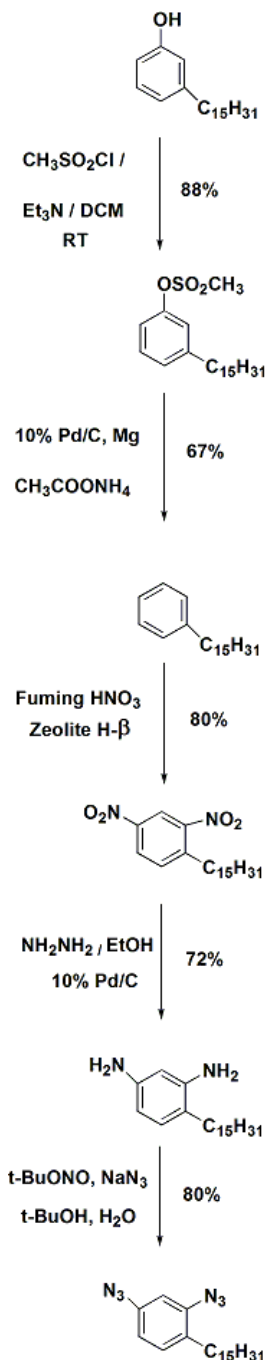
Scheme 3.8 Synthesis of 2,4-diazido-1-pentadecylbenzene

      In the first step, 1-methylsulfonyloxy-3-pentadecylbenzene was obtained by reaction of 3-pentadecyl phenol with methanesulfonyl chloride in the presence of triethylamine in dichloromethane which on treatment with Pd/C catalyst,[51] magnesium metal and ammonium acetate in the presence of methanol yielded pentadecylbenzene. In the next step, conversion of pentadecylbenzene to 2,4-dinitro-1-pentadecylbenzene was accomplished using zeolite H-β as a catalyst[52] and fuming nitric acid, acetic anhydride as a nitrating reagent. Next, 4-pentadecylbenzene-1,3-diamine was synthesized by reduction of 2,4-dinitro-1-pentadecylbenzene using catalytic amount of Pd/C and hydrazine hydrate.[51] Conversion of 4-pentadecylbenzene-1,3-diamine to 2,4-

diazido-1-pentadecylbenzene was accomplished using *tert*-butyl nitrite (*t*-BuONO) and sodium azide in a mixture of *tert*-butyl alcohol and water. 2,4-Diazido-1-pentadecylbenzene was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

In FT-IR spectrum of 2,4-diazido-1-pentadecylbenzene (**Figure 3.24**) a strong characteristic absorption band at 2121 cm^{-1} appeared due to asymmetric stretching vibration of $-N_3$ group.
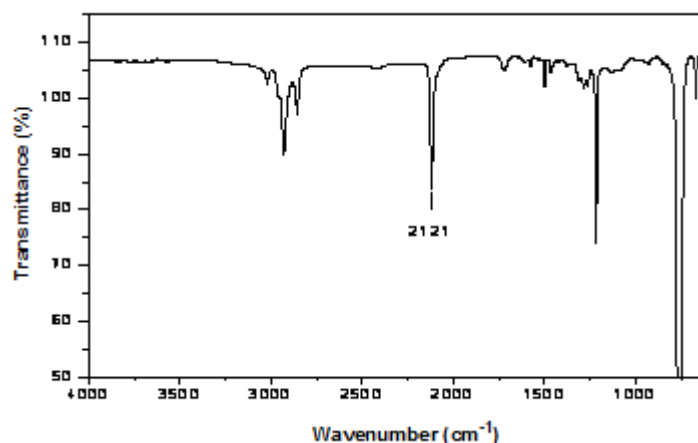
Figure 3.24 FT- IR spectrum of 2,4-diazido-1-pentadecylbenzene

Figure 3.25 represents ^{1}H-NMR spectrum of 2,4-diazido-1-pentadecylbenzene along with the assignments. The doublet of doublet at 7.11 δ ppm corresponds to aromatic proton "b". The peaks appeared in the range 6.77-6.72 δ ppm are due to protons "a" and "c". The triplet at 2.50 δ, ppm corresponds to benzylic $-CH_2$ of pentadecyl group. The methylene protons "e" β to aromatic ring exhibited multiplet in the range 1.6-1.4 δ, ppm. The peaks in the range 1.44-1.20 δ, ppm could be assigned to the remaining methylene protons in the pentadecyl chain. The methyl protons "g" of pentadecyl chain appeared as a triplet at 0.87 δ ppm.
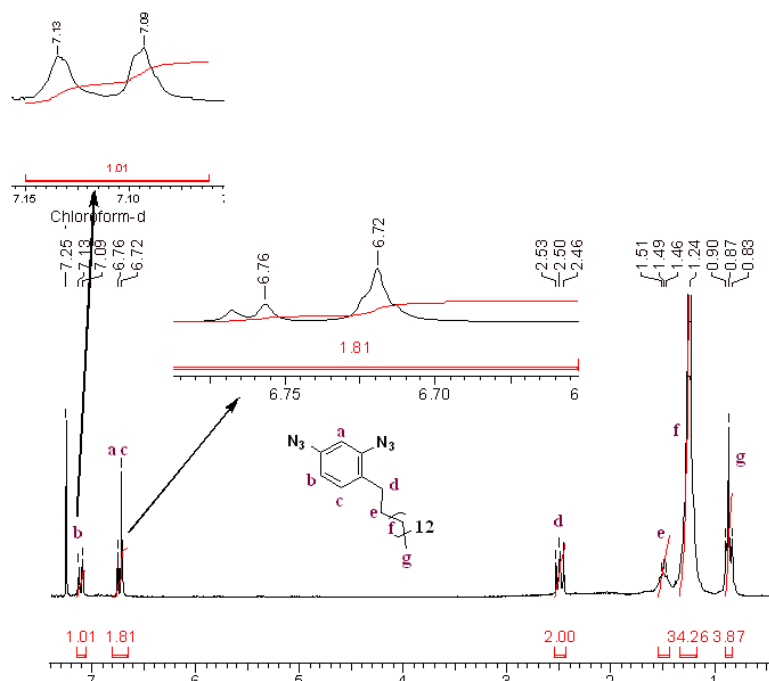
Figure 3.25 ^{1}H-NMR spectrum (CDCl$_3$) of 2,4-diazido-1-pentadecylbenzene

3.4.9 Synthesis of N-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Scheme 3.9 outlines route for synthesis of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide.
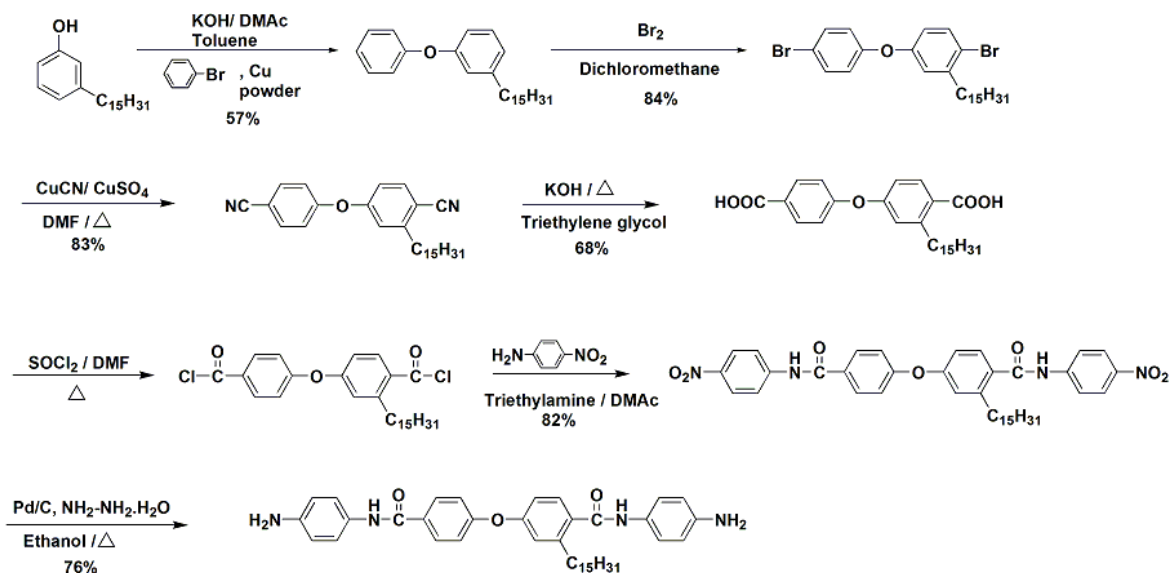
Scheme 3.9 Synthesis of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

1-Pentadecyl-3-phenoxy benzene was prepared by reaction of 3-pentadecyl phenol with bromobenzene in the presence of potassium hydroxide and Cu as a catalyst under classical Ullmann etherification reaction conditions[53, 54] and was subsequently selectively brominated at *para* positions to obtain 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene. In the next step, 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was treated with copper cyanide in the presence of copper sulfate in DMF as a solvent to obtain 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile which was hydrolyzed under alkaline conditions to yield 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid. Next, 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid on treatment with thionyl chloride in the presence of DMF yielded 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecylbenzoyl chloride.[27] 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride was treated with *para*-nitroaniline in the presence of triethylamine in DMAc at room temperature to yield *N*-(4-amino-3-pentadecyl)-4-(4-((4-nitrophenyl)carbamoyl)phenoxy)benzamide which on reduction[51] in the presence catalytic amount of hydrazine hydrate/ Pd/C yielded *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

The synthesized diamine was characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

In FT-IR spectrum of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide **(Figure 3.26)**, absorption bands at 3409 cm^{-1} and 3293 cm^{-1} were attributed to –NH$_2$ group and –NH of the amide group, respectively. The absorption bands at 1642 cm^{-1} and 1235 cm^{-1} correspond to the carbonyl of the amide group and C-O-C linkage, respectively. The characteristics absorption bands of the nitro group were not

observed indicating complete reduction of the nitro compound to the amine.
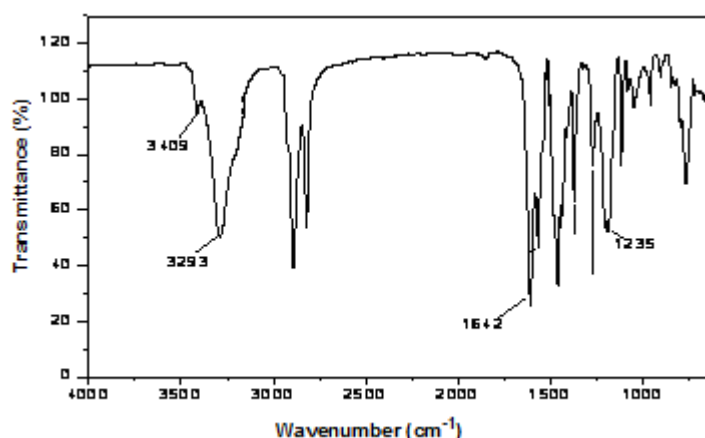
Figure 3.26 FT-IR spectrum of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Figure 3.27 represents ^{1}H-NMR spectrum of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide along with the assignments.
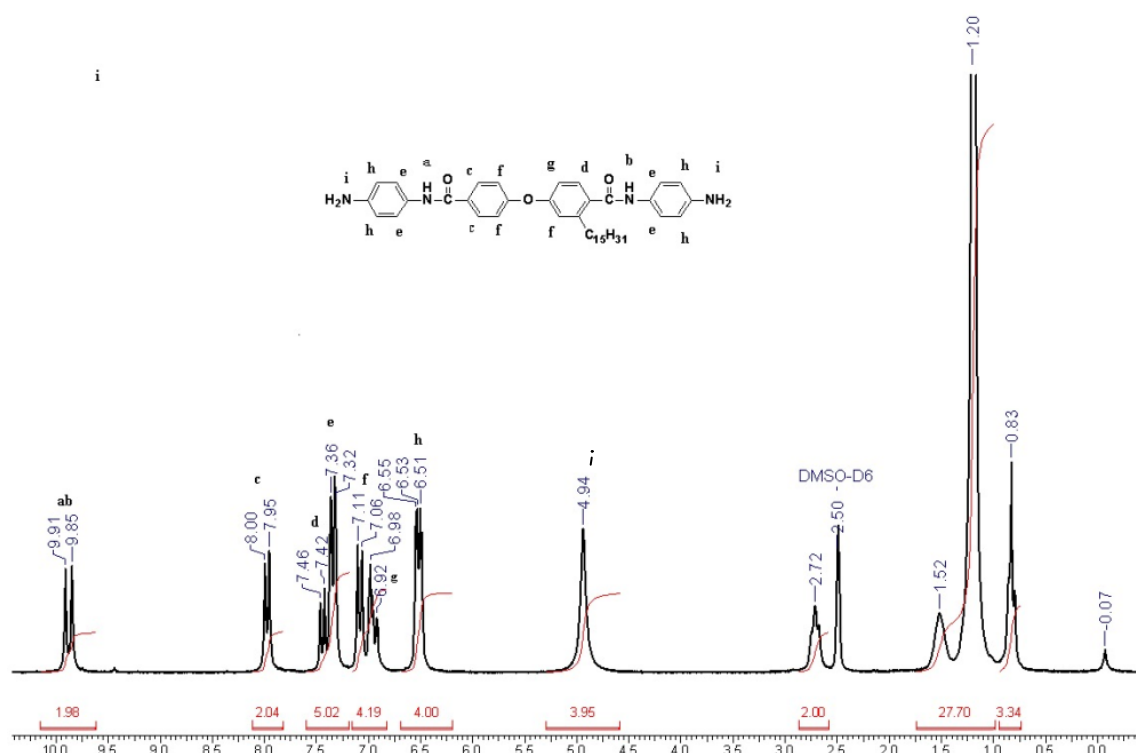
Figure 3.27 ^{1}H-NMR spectrum (DMSO-d$_6$) of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

The protons "a" and "b" appeared as singlets at 9.91 and 9.85 δ ppm, respectively. Aromatic proton "c" exhibited a doublet at 7.98 while the aromatic proton "d" appeared as a doublet at 7.44 δ ppm. The proton "e" appeared as a doublet at 7.34 δ ppm. The doublet at 7.09 δ ppm is due to proton "f". The peaks appeared in the range 6.98-6.92 δ ppm are due to protons "g". The peaks appeared in the range 6.55-6.51 δ ppm are due to protons "h". The protons "i" appeared as a singlet at 4.94 δ ppm. The triplet at 2.72 δ, ppm corresponds to benzylic –CH$_2$ proton of

pentadecyl group. The methylene protons β to aromatic ring exhibited a triplet 1.52 δ, ppm. The peaks appeared in the range 1.27-1.23 δ, ppm could be assigned to the remaining methylene protons of the pentadecyl chain. The methyl protons of pentadecyl chain appeared as a triplet at 0.83 δ ppm.

^{13}C-NMR spectrum of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide along with the assignments of carbon atoms is shown in **Figure 3.28**.
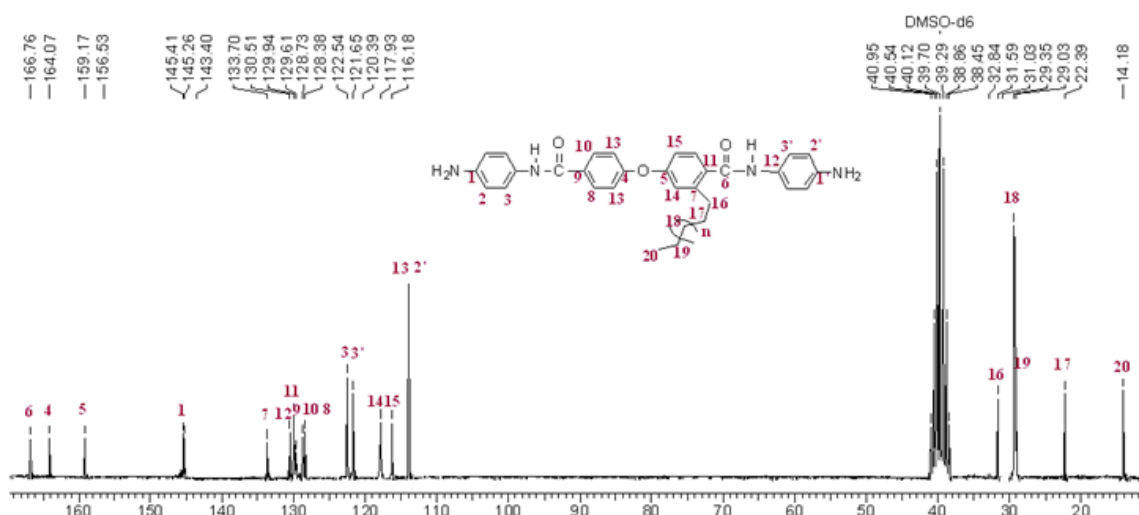
Figure 3.28 ^{13}C-NMR spectrum (DMSO-d$_6$) of *N*-(4-amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

3.5 Conclusions
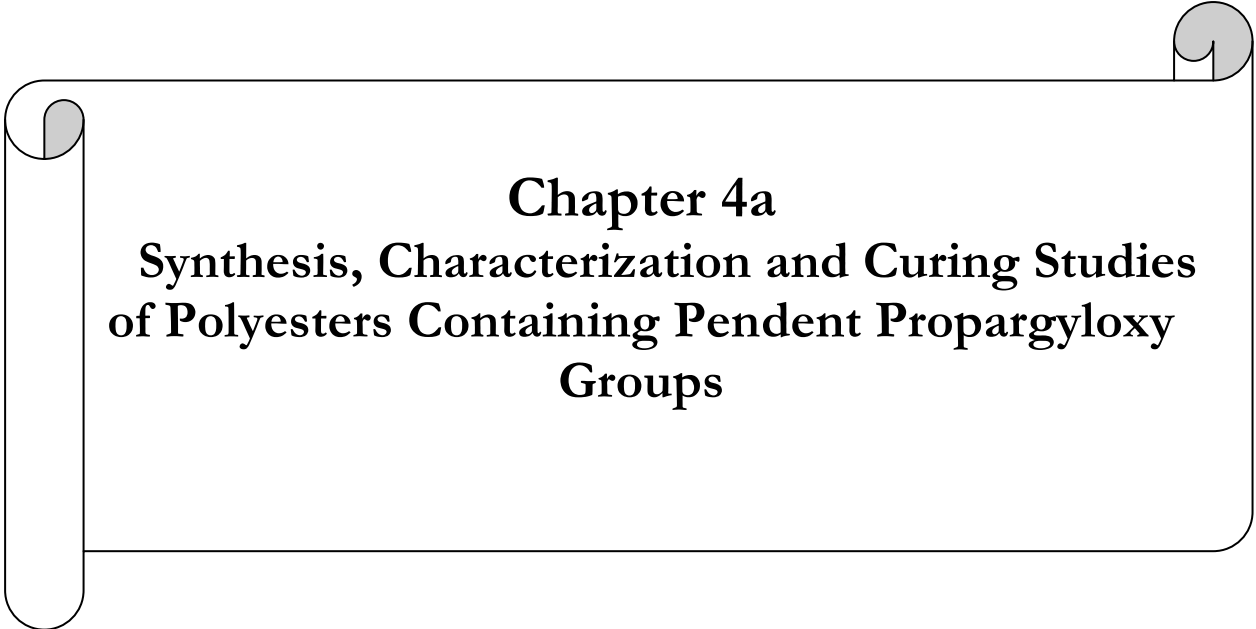
1. A new bisphenol containing pendent propargyloxy group *viz*; 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane was synthesized starting from commercially available 1,1,1-tris (4-hydoxyphenyl)ethane.

2. Diacids, diacid chlorides and diisocyanates containing pendent propargyloxy and allyloxy group were synthesized starting from 5-hydroxyisophthalic acid.

3. A new bisphenol containing pendent azido group was synthesized starting from 4, 4'-bis (4-hydroxyphenyl)pentanoic acid

4. Starting from a renewable resource material- cashew nut shell liquid (CNSL), two new diazido monomers and a new aromatic diamine containing pre-formed amide linkage and possessing pendent pentadecyl chain were synthesized.

5. Difunctional monomers are potentially useful for the synthesis of a host of step-growth polymers.

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Chapter 4a
Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy Groups

4a.1 Introduction

Aromatic polyesters exhibit good thermal stability, solvent resistance, and mechanical properties and are, therefore, applied widely in the aviation, automobile and electronic industries.[1-3] It is expected that functionalized polyester may lead to applications that are beyond that of conventional polyesters.[4, 5] The combination of step-growth polymerization and click chemistry has been exploited as a convenient and facile route for synthesis of functionalized aliphatic polyesters.[6-10] However, for the synthesis of aromatic polyesters containing pendent clickable groups has not been widely investigated except for the mention of aromatic polyesters containing pendent azido groups in the patent literature.[11]

In this study, a series of new aromatic (co)polyesters containing pendent propargyloxy groups was synthesized by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A. Homopolyester was also synthesized by polycondensation of 5-(propargyloxy)isophthaloyl chloride with bisphenol A. Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Curing behaviour of polyesters was studied by DSC in nonisothermal mode.

4a.2 Experimental

4a.2.1 Materials

5-(Propargyloxy)isophthaloyl chloride (P-IPC) was synthesized as described in **Chapter 3** and was purified by distillation under reduced pressure prior to use in polymerization reactions. Bisphenol A (BPA) (Aldrich) was sublimed under reduced pressure prior to use. Benzyltriethyl ammonium chloride (BTEAC) (Aldrich) was used as received. Isophthaloyl chloride (IPC) was synthesized from isophthalic acid (Aldrich) using excess thionyl chloride in the presence of *N,N*-dimethylformamide (DMF) as a catalyst and was purified by distillation under reduced pressure.[12] Dichloromethane (S.D. Fine Chemicals) was dried over calcium hydride and distilled. Other solvents were purified according to standard procedures.[13]

4a.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured with 0.5 % (w/v) solution of polyester in chloroform at 30 ± 0.1 ^{o}C using an Ubbelohde suspended level viscometer.

Solubility of polyesters was determined at 3 % (w/v) concentration in different solvents at room temperature.

Molecular weight of polyesters was measured on ThermoFinnigan make gel permeation chromatograph (GPC) using the following conditions: column – polystyrene - divinylbenzene (10^5

Å to 50 Å), Detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in chloroform (5 mL) and filtered through 0.45 μ filter.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent

X-Ray diffractograms of polyesters were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2°/minute. Dried polymer films were used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 10 °C / minute in nitrogen atmosphere.

Differential scanning calorimetry (DSC) analysis was carried out on TA instrument DSC Q10 at a heating rate of 10 °C / minute in nitrogen atmosphere.

4a.3 Synthesis of aromatic polyesters containing pendent propargyloxy groups
4a.3.1 Synthesis of homopolyester containing pendent propargyloxy groups

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed bisphenol A (1.40 g, 6.14×10^{-3} mol) dissolved in 1M NaOH (12.3 mL). The reaction mixture was stirred at 10 ℃ for 1h. Thereafter, BTEAC (0.17 g) was added to the reaction mixture. The solution of 5-(propargyloxy)isophthaloyl chloride (1.57 g, 6.14×10^{-3} mol) dissolved in dichloromethane (40 mL) was added in one lot to the reaction mixture and the reaction mixture was stirred vigorously at 2000 rpm at 10 °C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and precipitated into methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 °C under reduced pressure for two days.

4a.3.2 Synthesis of copolyesters containing pendent propargyloxy groups

A representative procedure for synthesis of copolyesters is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel, were placed bisphenol A (1.40 g, 6.14×10^{-3} mol) dissolved in 1M NaOH (12.3 mL). The reaction mixture was stirred at 10 ℃ for 1h. Thereafter, BTEAC (0.17 g) was added to the reaction mixture. The solution of 5-(propargyloxy)isophthaloyl chloride (0.79 g, 3.07×10^{-3} mol) and isophthaloyl chloride (0.62 g, 3.07×10^{-3} mol) dissolved in dichloromethane (40 mL) was added in one lot to the reaction mixture and the reaction mixture was stirred vigorously at 2000 rpm at 10 °C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and precipitated into methanol:water (1:1, v/v), (1000 mL) mixture.

Polymer was filtered, washed with methanol and dried at 50 ^{o}C under reduced pressure for two days.

4a.4 Curing studies of polyesters
4a.4.1 DSC analysis

DSC measurements were performed on TA instrument (Q10) supported by TA Universal Analysis software for data acquisition. Samples (5 mg) were sealed in hermetic aluminium pans and experiments were performed under a nitrogen flow of 50 mL / min. In nonisothermal studies, polyesters were subjected to a dynamic DSC scan at the heating rate of 10 °C/min. The total enthalpy of curing ($\Delta H)$ was determined from the area under the exothermic curve. The cure onset temperature (T_o) was considered as the intercept of slope of baseline and tangent of curve leading to peak of transition (**Figure 4a.1**).

(A)   (B)
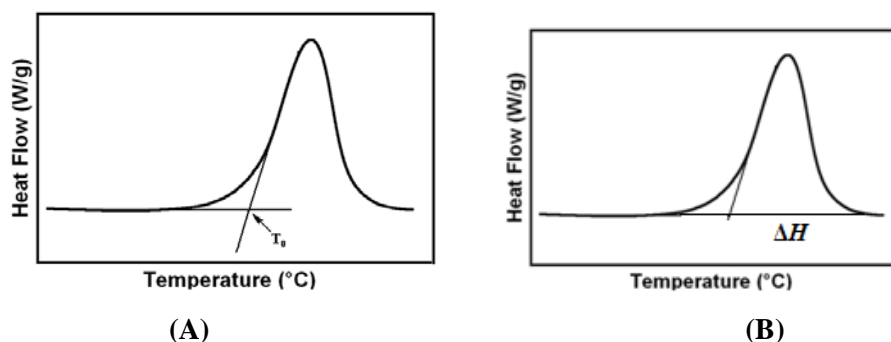
Figure 4a.1 Theoretical DSC curve illustrating (A) cure onset temperature (B) total enthalpy of curing (ΔH)

4a.5 Results and discussion
4a.5.1 Synthesis of aromatic polyesters containing pendent propargyloxy groups

In the present study, polyester containing pendent propargyloxy groups was synthesized by phase transfer-catalyzed interfacial polycondensation of 5-(propargyloxy)isophthaloyl chloride with bisphenol A (**Scheme 4a.1**). Random copolyesters containing pendent propargyloxy groups were synthesized from a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A under the same conditions. (**Scheme 4a.2**). The synthesis of polyesters with varying mol percent of propargyloxy functionalities was achieved by varying the molar ratio of 5-(propargyloxy)isophthaloyl chloride in the feed during copolymerization (**Table 4a.1**).
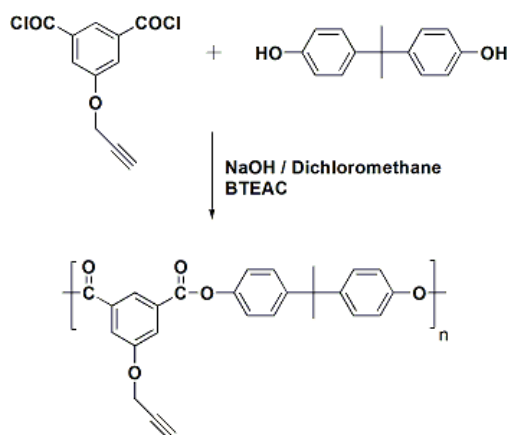
Scheme 4a.1 Synthesis of polyester from 5-(propargyloxy)isophthaloyl chloride and BPA

Where, m = mol of P-IPC
n = mol of IPC
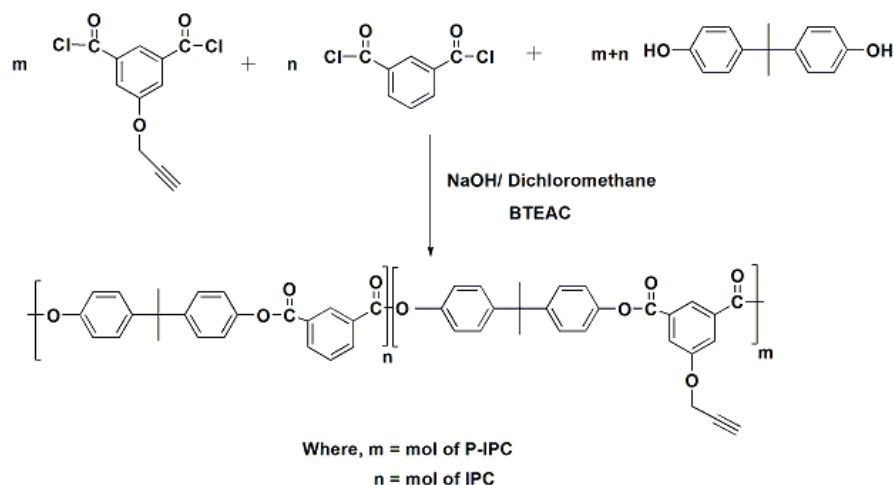
Scheme 4a.2 Synthesis of copolyesters from a mixture of 5-(propargyloxy)isophthaloyl chloride and IPC with BPA

Table 4a.1 Synthesis of aromatic (co)polyesters containing pendent propargyloxy groups

Polyester	Bisphenol A (mol %)	Diacid Chloride (mol %)		η_{inh} [a] (dL/g)	Molecular weight [b]		Mw/ Mn
		IPC	P-IPC		Mn	Mw	
PES-1	100	75	25	1.0	58,000	1,21,800	2.1
PES-2	100	50	50	0.77	43,600	88,000	2.0
PES-3	100	25	75	1.33	1,18,000	2,36,000	2.0
PES-4	100	0	100	0.90	68,000	1,30,000	2.0

a: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in chloroform at $30 \pm 0.1^{\circ}C$.
b: Measured by GPC in chloroform; polystyrene was used as the calibration standard.

Inherent viscosities of polyesters were in the range 0.90-1.33 dL/g **(Table 4.1)** indicating formation of medium to reasonably high molecular weight polymers. This was further supported by GPC measurements which gave Mn and polydispersities (Mw/Mn) in the range 68,000 – 1,18,000 and 2.0-2.1, respectively. However, molecular weights measured by GPC should not be taken as absolute as the measurements were carried out using polystyrene standards. Tough, transparent, and flexible films of polyesters could be cast from their chloroform solutions.

4a.5.2 Structural characterization

The structural characterization of polyesters was done using FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

A representative FT-IR spectrum of polyester based on 5-(propargyloxy)isophthaloyl chloride and BPA is shown in **Figure 4a.2**.
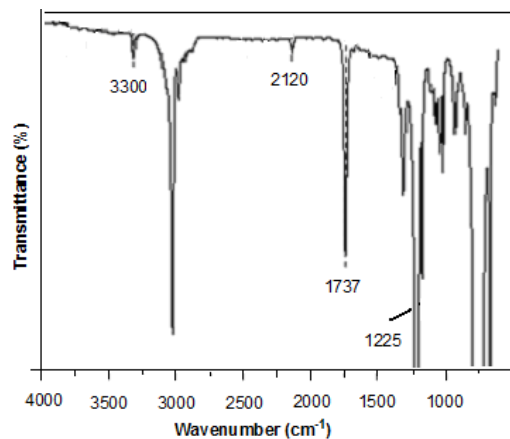
Figure 4a.2: FT-IR spectrum of polyester from 5-(propargyloxy)isophthaloyl chloride and BPA (PES-4)

The incorporation of propargyloxy groups was evidenced by the presence of characteristic bands of ≡C-H and C≡C which appeared at 3300 and 2120 cm^{-1}, respectively. Ester carbonyl band of polyester was observed at 1737 cm^{-1}. Absorption band corresponding to C-O-C stretching was observed at 1225 cm^{-1}.

^{1}H-NMR spectrum of polyester derived from 5-(propargyloxy)isophthaloyl chloride and BPA is reproduced in **Figure 4a.3.**
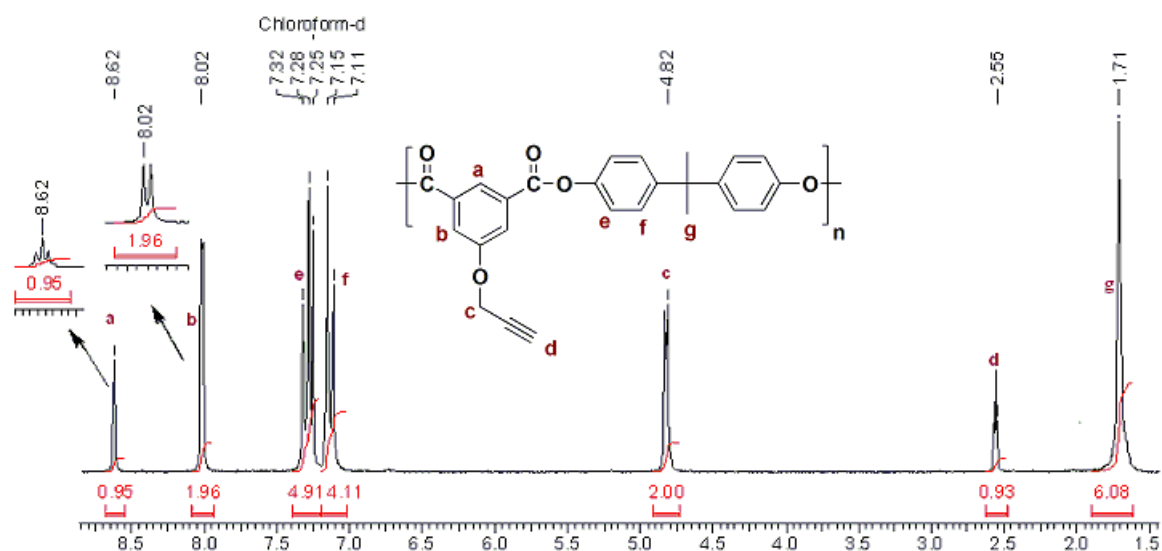
Figure 4a.3 ^{1}H-NMR spectrum (CDCl$_3$) of polyester from 5-(propargyloxy)isophthaloyl chloride and BPA (PES-4)

The proton "a" flanked by ester carbonyl groups appeared as a triplet at 8.62 δ ppm. The protons "b" exhibited a doublet at 8.0 δ ppm. The doublets at 7.30 and 7.13 δ ppm are due to

aromatic protons "e" and "f", respectively. The peak displayed at 4.82 δ ppm corresponds to the methylene protons "c" of propargyl group. The peak appeared at 2.55 δ ppm is due to proton "d" of propargyl group. The methyl group protons "g" attached to bridge carbon exhibited a singlet at 1.71 δ ppm.

The evidence to support the random copolyester formation was given by ^{1}H-NMR spectroscopy **(Figure 4a.4)**, which showed two distinct triplets at 8.98 and 8.62 δ ppm for protons "d" and "g" flanked by ester carbonyl groups.
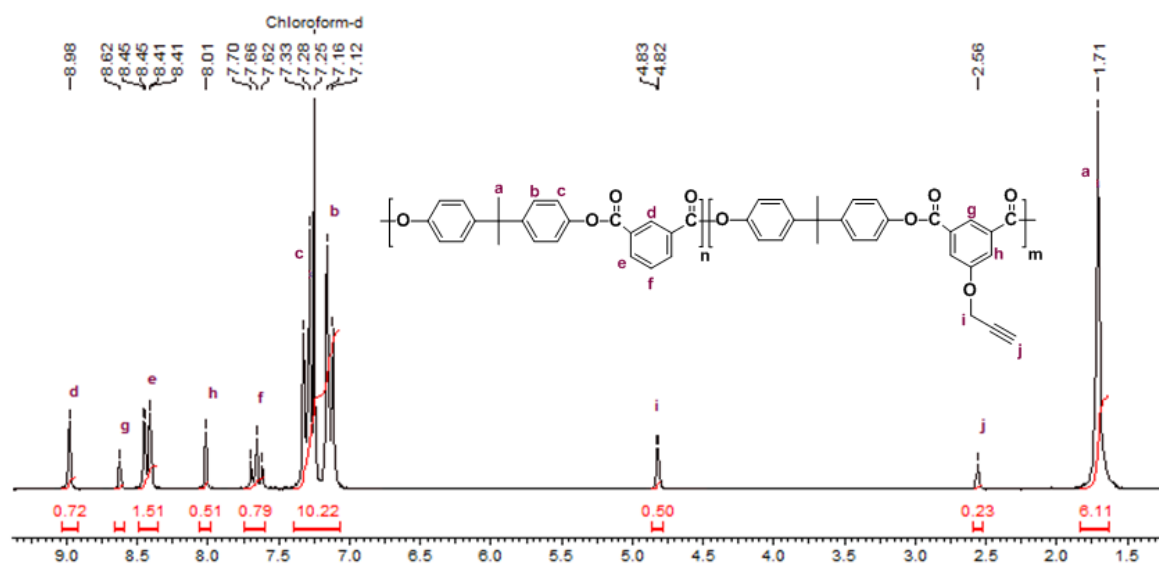
Figure 4a.4 ^{1}H-NMR spectrum (CDCl₃) of copolyester from a mixture of 5-(propargyloxy)isophthaloyl chloride and IPC with BPA (PES-1)

The protons "e" appeared as a doublet 8.43δ ppm. The peak displayed at 8.01 δ ppm is due to protons "h". The triplet at 7.66 δ ppm is due to proton "f". The doublets at 7.30 and 7.14 δ ppm are due to aromatic protons "c" and "b", respectively. The methylene protons "i" exhibited a doublet at 4.83 δ ppm. The peak appeared at 2.56 δ ppm is due to proton "j" of propargyl group, which confirmed the presence of propargyl functionality in the polymer. The protons of methyl groups attached to bridge carbon exhibited a singlet at 1.71 δ ppm.

The compositions of copolyesters were determined by ^{1}H NMR spectroscopy. The integration of the signal ''g'' at 8.62 δ ppm from P-IPC was compared with the integration of signal "d" at 8.98 δ ppm from IPC. As presented in **Table 4a.2**, polymer composition calculated from ^{1}H-NMR spectra was in good agreement with the feed ratios.

Table 4a.2 Copolyester composition determined from ^{1}H-NMR spectra

Copolyester	Feed P-IPC, mol %	Observed P-IPC, mol %
PES-1	25	26
PES-2	50	50
PES-3	75	76

^{13}C-NMR spectrum of polyester obtained from 5-(propargyloxy)isophthaloyl chloride and BPA along with assignments of carbon atoms is reproduced in **Figure 4a.5**.
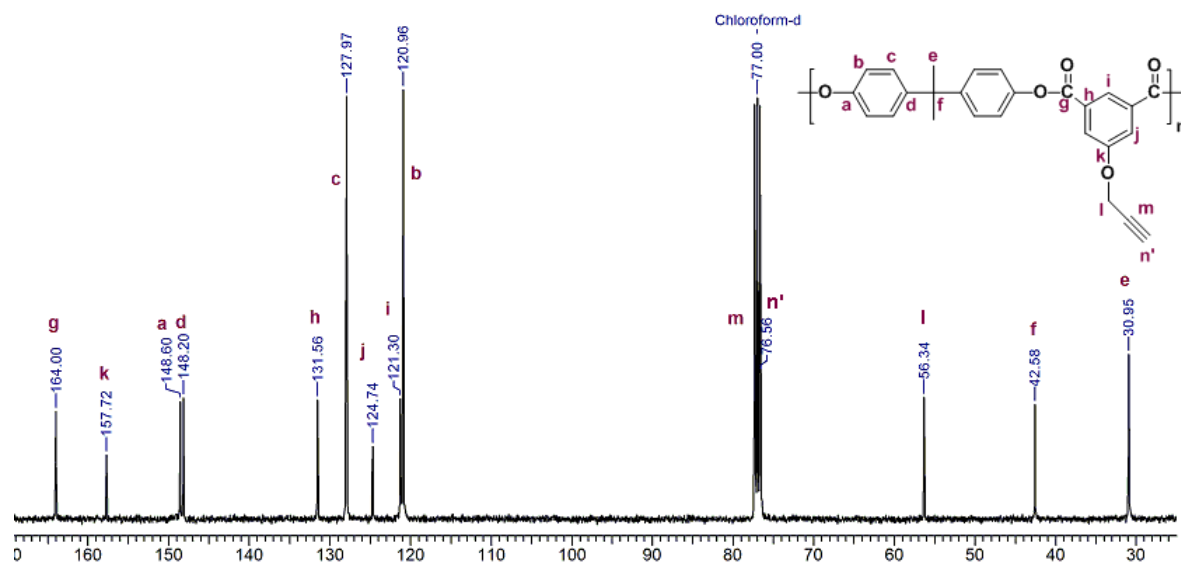
Figure 4a.5 ^{13}C-NMR spectrum (CDCl$_3$) of polyester obtained from 5-(propargyloxy) isophthaloyl chloride and BPA (PES-4)

Thus, FT-IR, ^{1}H and ^{13}C-NMR spectra confirmed the formation of polyesters with the chemical structures shown in **Scheme 4a.1** and **Scheme 4a.2,** that is, formation of polyesters with pendent propargyloxy groups.

4a.5.3 Solubility of polyesters

Solubility data of polyesters containing pendent propargyloxy groups in different organic solvents at 3 wt % (w/v) concentration is listed in **Table 4a.3.**

Polyesters were soluble in common organic solvents such as dichloromethane, chloroform and tetrahydrofuran and aprotic polar solvents such as NMP, DMAc, etc. In contrast to these results, reference polyester derived from BPA and IPC (**PES-Ref**)[14, 15] is reported to be not soluble in these organic solvents. These results indicated that the incorporation of pendent propargyloxy groups into polyester interrupted the chain packing, thus leading to improved solubility.

Table 4a.3 Solubility data of aromatic polyesters containing pendent propargyloxy groups

Polyester	CHCl$_3$	DCM	THF	m-cresol	Pyridine	DMF	NMP	DMAc
PES-1	+ +	+ +	+ +	+ +	+ +	++	+ +	+ +
PES-2	+ +	+ +	+ +	+ +	+ +	++	+ +	+ +
PES-3	+ +	+ +	+ +	+ +	+ +	++	+ +	+ +
PES-4	+ +	+ +	+ +	+ +	+ +	++	+ +	+ +
*PES-Ref	--	--	--	--	--	--	--	--

+ +: soluble, -- : insoluble

*PES-Ref : [polyester derived from BPA with IPC, Solubility data are taken from reference 14, 15]

4a.5.4 X-Ray diffraction studies

Wide-angle X-ray diffraction (WAXD) patterns of polyesters are shown in **Figure 4a.6**. Polyesters showed broad halo over the range 2θ ≈ 12–35º, suggesting their amorphous nature. It is reported that polyester derived from BPA and IPC (**PES-Ref**) is partially crystalline in nature.[14, 16] Apparently, the introduction of pendent propargyloxy groups in polyesters interfere with the dense chain packing, thus resulting in their amorphous nature, which is also reflected in their improved solubility.
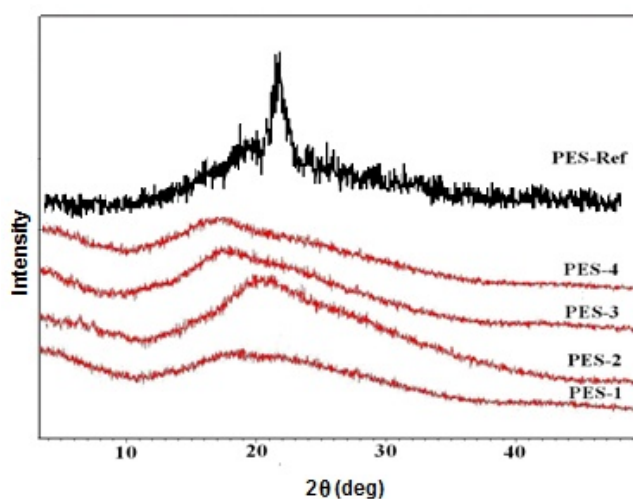
Figure 4a.6   X-Ray diffractograms of aromatic polyesters containing pendent propargyloxy groups along with that of reference polyester PES-Ref (X-Ray diffractogram of PES-Ref was taken from reference 14)

4a.5.5 Thermal properties

Thermal stability of polyesters was determined by thermogravimetric analysis at a heating rate of 10 °C/min in nitrogen atmosphere. TG curves of polyesters are shown in **Fig. 4a.7** and the temperature at 10% weight loss (T_{10}) values obtained from TG curves of polyesters are tabulated in **Table 4a.4.** T_{10} values of polyesters were in the range 390- 420 °C indicating their good thermal stability.
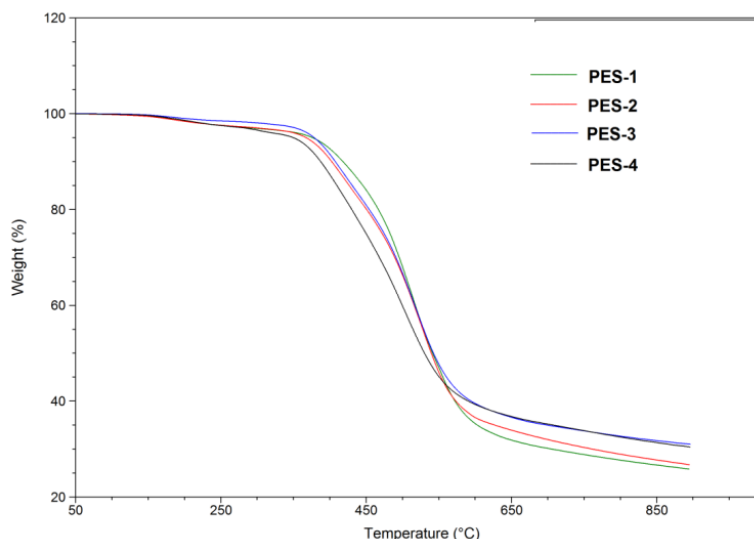
Figure 4a.7: TG curves of polyesters containing pendent propargyloxy groups

Table 4a.4 Thermal properties of aromatic polyesters containing pendent propargyloxy groups

Polyester	Tg (°C)[a]	T_{10} (°C)[b]
PES-1	170	420
PES-2	156	410
PES-3	150	405
PES-4	146	390
PES-Ref	181[c]	490[c]

PES-Ref[15] : Polyester derived from BPA and IPC, a : Measured on DSC at a heating rate of 10 °C/min. in nitrogen, b : Measured by TGA at a heating rate of 10 °C/min in nitrogen.
c : Tg and T_{10} values are taken from reference 15.

Glass transition temperature (Tg) of polyesters was measured by differential scanning calorimetry (DSC) from second heating scan at a heating rate of 10 °C / minute (**Figure 4a.8).** It is reported that propargyloxy groups present in the polymers undergo crosslinking reaction in the temperature range 220-350 °C.[17, 18] Therefore, polyesters sontaining pendent propargyloxy groups were heated only upto 200 °C in DSC measurements. Tg values are collected in **Table 4a.4.**

Polyester based on P-IPC with BPA showed Tg at 146 ℃ which is lower than Tg value (181 ℃) of reference polyester based on IPC and BPA.[15] This clearly results from the presence of the pendent propargyloxy groups which are responsible for the decrease in the intermolecular interaction which in turn results in decrease in Tg. Copolyesters containing varying mole percent incorporation of P-IPC showed Tg values in the range 150 ℃ -170 ℃ and the values tend to decrease with increase in mol % incorporation of P-IPC.
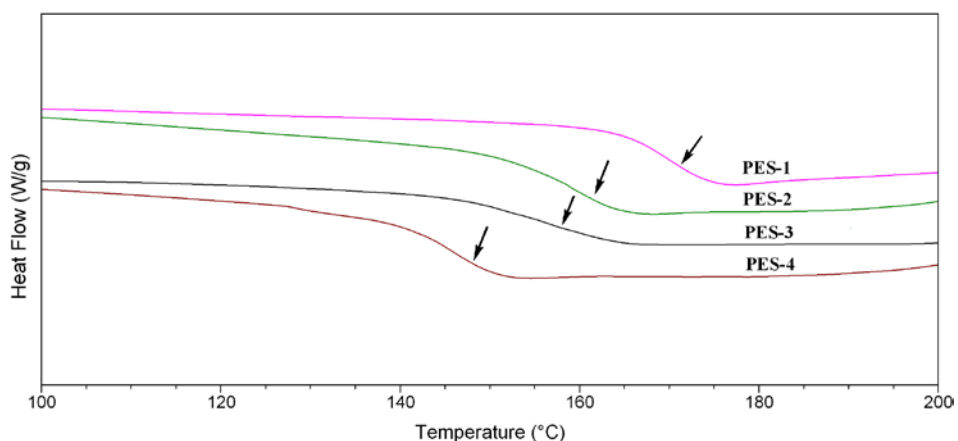
Figure 4a.8: DSC curves of polyesters containing pendent propargyloxy groups.

4a.6 Non-isothermal curing studies of polyesters

It has been reported that the uncatalyzed crosslinking of resins with propargyloxy groups in the side chain takes place *via* sigmatropic thermal rearrangement to form 2H-1-benzopyran (2H-chromenes) rings which then undergo polymerization (**Scheme 4a.3**) to yield network structure,[17, 19-25] thus providing an opportunity for converting thermoplastics to thermosettings. Polymers containing crosslinkable moiety such as propargyloxy groups undergo crosslinking reaction without the evolution of small volatile compounds and provide void free clear films and coatings.[26]

$R = C(CH_3)_2, O, S, C=O, SO_2, $ etc.

General structure of bispropargyl ether
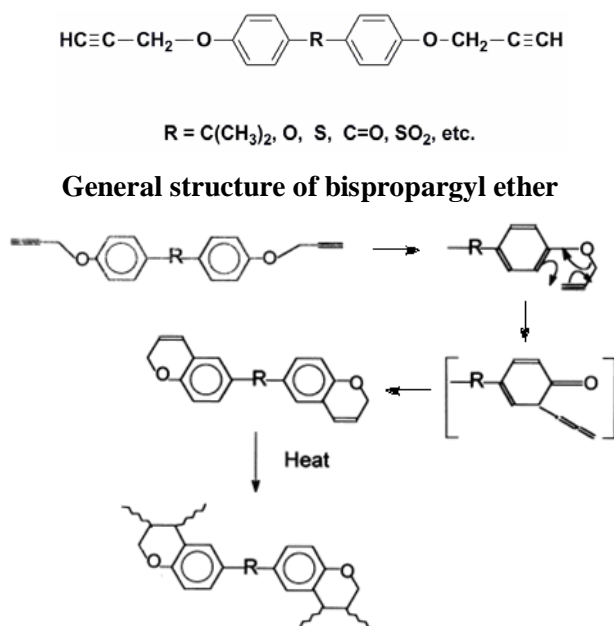
Scheme 4a.3 Curing reaction of bispropargyl ether[17]

Thermoplastic polymer	Thermal curing →	Thermoset
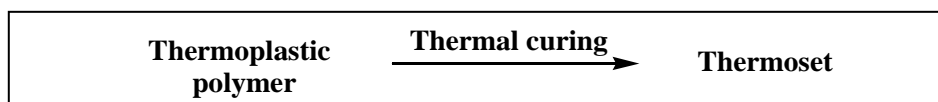
In order to investigate cure characteristics of these polyesters such as cure onset temperature (T_0), maximum cure temperature (T_p), final cure temperature (T_f) and enthalpy of cure reaction (ΔH), curing studies were performed. DSC in nonisothermal mode was applied to evaluate the cure behaviour of polyesters containing pendent propargyloxy groups. A representative DSC profile of polyester PES-4 is reproduced in **Figure 4a.9.** It exhibited an intense exothermic peak maximum at 285 °C during the first DSC heating scan in which the exotherm starts at 220 °C and finishes at around 330 °C. The exotherm corresponds to the curing reaction of the propargyloxy groups that results in a network structure with a release of heat (413 J/g). In the second scan of DSC experiment, no trace of exothermic peak was observed indicating the curing (cross-linking) had been completed during the first scan.
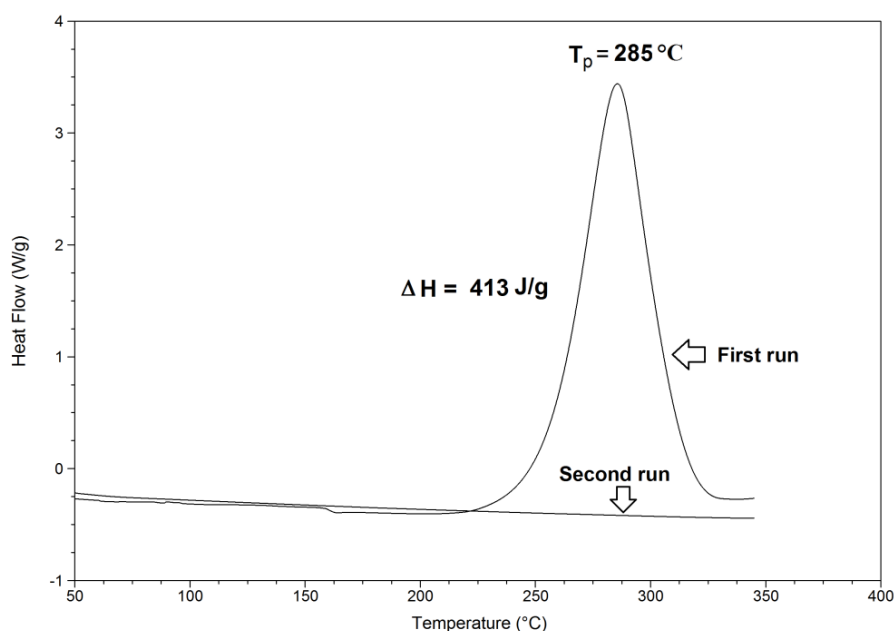
Figure 4a.9 DSC curves of polyester (PES-4) containing pendent propargyloxy groups.
[scanned from 50 – 350 °C @ 10 °C/min (first run), rescanned from 50 – 350 °C @ 10 °C/min (second run)]

DSC curves of PES-1, PES-2, PES-3 and PES-4 are given in **Figure 4a.10.** Cure characteristics of polyesters such as cure onset temperature (T_0), maximum cure temperature (T_p), final cure temperature (T_f) and enthalpy of cure reaction (ΔH) are summarized in **Table 4a.5.**
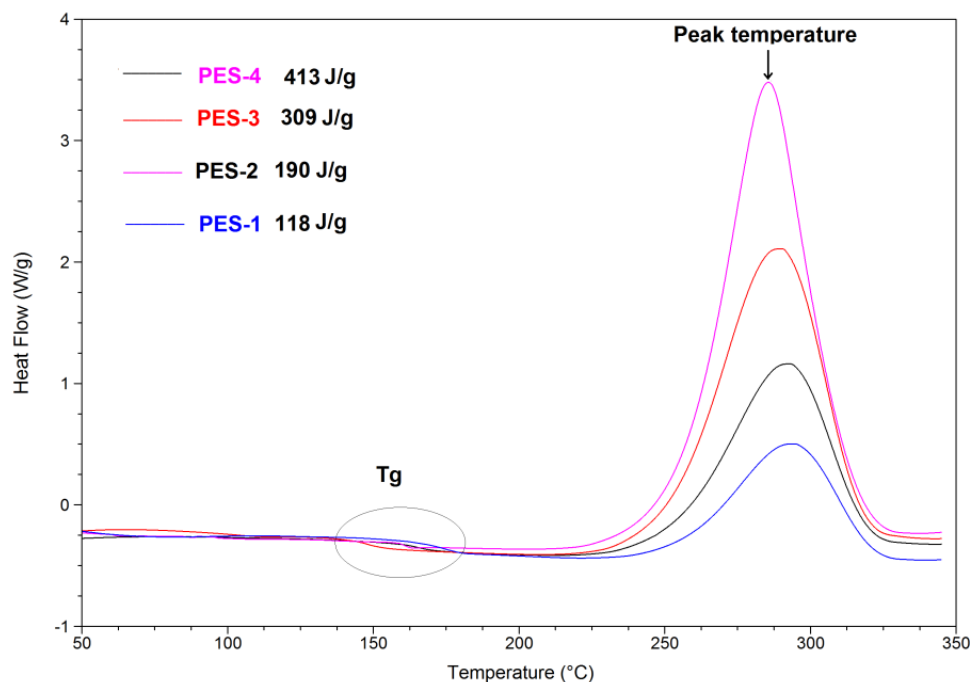
Figure 4a.10 DSC curves of polyesters containing pendent propargyloxy groups

All the thermograms showed a single exotherm. The exotherms were attributed to the curing reactions of the polyesters. The cure temperatures were in the range 220-330 °C. It is noteworthy that PES-1, PES-2, PES-3 and PES-4 exhibited T_p in the range of 285-295 °C which indicated the similar cure behavior of these polyesters. The peak cure temperature do not seem to depend on the degree of functionalization (**Table 4a.5**) and the cure temperatures were similar to those reported in the literature (220-350 ºC) for bispropargyl ether resins.[21] ΔH values were in the range 118-413 J/g and the values increased as the composition of P-IPC content was increased. These results could be attributed to the increase in crosslinked density with increase in the propargyloxy content.

Table 4a.5 Cure characteristics of polyesters containing pendent propargyloxy groups

Polyester	Bisphenol A (mol %)	IPC (mol %)	P-IPC (mol %)	T_0 (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
PES-1	100	75	25	225	295	330	118
PES-2	100	50	50	225	290	327	190
PES-3	100	25	75	225	290	328	309
PES-4	100	0	100	220	285	330	413

T_o – Cure onset (initiation) temperature, T_p – Maximum cure (peak) temperature
T_f – Final cure temperature, ΔH – Enthalpy of curing

By virtue of their easier thermally crosslinking process and no formation of by products, polyesters containing pendent propargyloxy groups are potentially useful as the base materials for high temperature adhesives, enamel coatings and matrices of composites.
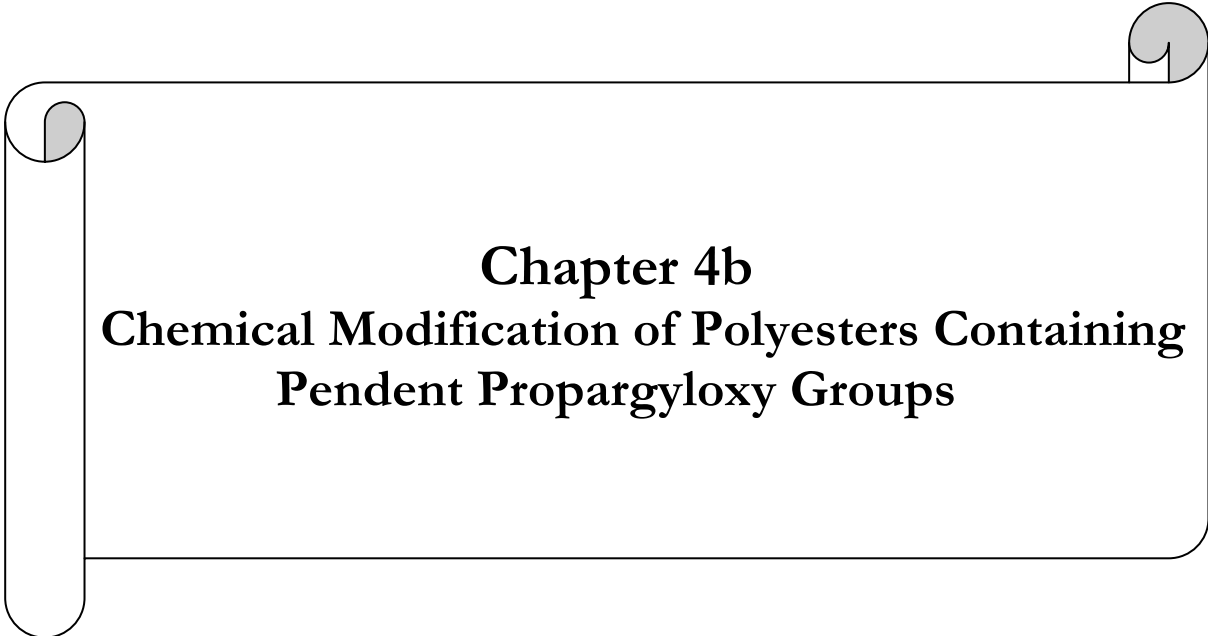
4a.7 Conclusions

1. Medium to reasonably high molecular weight aromatic polyesters containing pendent propargyloxy groups were successfully synthesized from 5-(propargyloxy)isophthaloyl chloride, isophthaloyl chloride and bisphenol A by phase-transfer catalyzed interfacial polycondensation method.

2. The presence of pendent propargyloxy groups in the polyesters resulted in their improved solubility in common organic solvents such as dichloromethane, chloroform and tetrahydofuran. Tough, transparent and flexible films could be cast from solutions of polyesters in chloroform.

3. T_{10} values of the polyesters were in the range 390- 420 $^{\circ}$C indicating their good thermal stability.

4. The curing of polyesters occurred in the temperature range 220–330 °C. The percentage incorporation of propargyloxy functionalities into the polyesters did not influence the cure onset and the cure peak temperature during the thermal curing process.

5. The heat of cure reaction of polyesters studied in uncatalyzed nonisothermal mode using DSC was in the range of 118–413 J/g. Increase in ΔH was observed with increase in the content of propargyloxy functional groups in the polyesters.

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Chapter 4b
Chemical Modification of Polyesters Containing Pendent Propargyloxy Groups

4b.1 Introduction

Introduction of functional groups into polymers and subsequent functionalization provides an efficient methodology to tailor the properties of polymers such as thermal stability, crystallinity, hydrophilicity, photophysical properties, etc.[1-5] Such functionalized polymers widen the application areas compared to their non-functional counterparts.[6, 7] Despite significant advances in the field of polyesters, synthesis of functionalized aromatic polyesters is still a challenge.[8]

Click chemistry is a powerful methodology for post-functionalization of polymers.[9-12] Because of its high selectivity, reliability, and tolerance to a broad range of functional groups and simple reaction conditions, click chemistry, specifically the copper(I)-mediated 1,3-dipolar cycloaddition of azides and alkynes, is a powerful strategy for elaborating polymer architectures.[13] Because of the cycloaddition reactions, high functional groups tolerance,[2, 14-17] and excellent yields, this particular click reaction is gaining widespread use for the synthesis and modification of polymers.[18, 19] Several reports are available on the post-functionalization of aliphatic polyesters containing pendent clickable groups such as alkynes, azides and alkenes. However, click chemistry modification of aromatic polyesters has not been exploited.

We present herein post-functionalization of aromatic polyester containing pendent propargyloxy groups (PES-2), synthesized in **chapter 4a**) by alkyne-azide click reaction using azides *viz*; 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene, azido-terminated polystyrene (PS-N_3) and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, PEG_{550}-N_3, PEG_{1000}-N_3)

The efficiency of post-functionalization of the polyester by click reaction was confirmed by FT-IR, ^{1}H-NMR spectroscopy and GPC. Polymers modified by1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene were further characterized by, UV-Vis, and fluorescence spectroscopy techniques while polyesters obtained by grafting PS-N_3 and azido-terminated polyethylene glycol monomethyl ether were characterized by water contact angle measurements.

4b.2 Experimental

4b.2.1 Materials

Polyester containing pendent propargyloxy groups (PES-2) was synthesized as described in **Chapter 4 a.** Polyethylene glycol monomethylether, Mn = 550 and 1000 g/mol (PEG_{550}, PEG_{1000}), were procured from Aldrich, and were purified by azeotropic distillation method before use. 1-Pyrenebutanol, 9-(chloromethyl)anthracene, methane sulfonyl chloride, triethyl amine, 2-chloroethanol, *N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) and copper bromide (CuBr) were purchased from Aldrich and were used as received. Styrene procured from Aldrich was dried over calcium hydride for 3 days and distilled under reduced pressure before use. Copper sulphate and sodium ascorbate (Loba Chemie) were used as received. Tetrahydrofuran (S.D. Fine

Chemicals) was stirred over calcium hydride for 12 h, filtered and distilled. Further it was refluxed over sodium-benzophenone complex for 2 days and distilled. *N, N*-Dimethylformamide (DMF) was of reagent grade and was distilled prior to use as per literature procedure.[20] Sodium azide was 'activated' by trituration with hydrazine hydrate and left overnight. It was dissolved in a minimum quantity of water and precipitated into acetone, filtered and dried at room temperature under vacuum. Other solvents were purified according to standard procedures.[20]

4b.2.2 Measurements

Molecular weights of polyesters were measured on ThermoFinnigan make gel permeation chromatography (GPC), using the following conditions: column – polystyrene - divinylbenzene (10^5 Å to 50 Å), detector-RI, room temperature. Polystyrene was used as the calibration standard. The polyester sample (5 mg) was dissolved in chloroform (5mL) and filtered through 0.45 µ filter.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz using $CDCl_3$ as a solvent.

Ultraviolet–Visible (UV–Vis) spectra of polyester solutions in chloroform were recorded on Perkin-Elmer Lambda 950 UV/Vis Spectrometer.

Fluorescence measurements of polyester solutions in chloroform were carried out using a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Contact angle measurements were carried out on GBX Contact angle meter by sessile drop method. A 5 wt. % solution of the respective polymers were drop-cast on a glass slit. Water was used as the wetting liquid.

4b.3 Preparation of azides
4b.3.1 Preparation of 1-(4-azidobutyl)pyrene (PY-N₃)
4b.3.1.1 Preparation of 4-(pyrene-1-yl)butyl methanesulfonate

Into a 100 mL three necked round bottom flask equipped with a dropping funnel were placed 1-pyrenebutanol (1.6 g, 5.8 x 10^{-3} mol) and dry dichloromethane (12 mL). The reaction mixture was cooled to 0 °C. Triethylamine (2.44 mL, 17.48 x 10^{-3} mol) was added dropwise under constant stirring at 0 °C followed by dropwise addition of methane sulphonyl chloride (1.3 mL, 11.6 x 10^{-3} mol). The reaction mixture was stirred at 0 °C for 4 h. After completion of the reaction, the reaction mixture was extracted with dichloromethane (200 mL). The dichloromethane solution was dried over anhydrous sodium sulphate, filtered and dichloromethane was evaporated under reduced pressure. The removal of solvent yielded 4-(pyrene-1-yl)butyl methanesulfonate as a viscous liquid.

Yield 2 g (99 %)

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.27-7.82 (m, Ar-H), 3.50 (t, 2H), 2.90 (s, 3H), 2.1 (t, 2H), 1.81 (t, 2H)

4b.3.1.2 Preparation of 1-(4-azidobutyl)pyrene (PY-N$_3$)

Into a 100 mL two necked round bottom flask were charged 4-(pyrene-1-yl)butyl methanesulfonate (1g, 2.81 x 10^{-3} mol), sodium azide (0.90 g, 15.9 x 10^{-3} mol) and DMF (10 mL). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, DMF was evaporated under reduced pressure and the product was precipitated into methanol, washed repeatedly with a mixture of methanol and water (1:1, v / v); (100 mL) and dried under vacuum at room temperature to obtain 1-(4-azidobutyl)pyrene.

Yield: 1 g (90 %).

FT-IR (CHCl$_3$, cm^{-1}): 2120 (N$_3$)

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.27-7.83 (m, Ar-H), 3.40-3.29 (m, 4H), 2.01 (t, 2H), 1.81 (t, 2H)

4b.3.2 Preparation of 9-(azidomethyl)anthracene (An-N$_3$)

Into a 100 mL two necked round bottom flask were charged 9-(chloromethyl)anthracene (1 g, 4.41 x 10^{-3} mol), sodium azide (2.86 g, 44.10 x 10^{-3} mol) and DMF (15 mL). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, DMF was removed under reduced pressure and the product was precipitated into methanol, washed repeatedly with a mixture of methanol and water (1:1, v / v); (100 mL) and dried under vacuum at room temperature to obtain 9-(azidomethyl)anthracene.

Yield 1 g (99 %).

FT-IR (CHCl$_3$, cm^{-1}): 2120 (N$_3$)

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.10- 7.50 (m, 9H, Ar-H), 3.10 (s, 2H)

4b.3.3 Preparation of azido-terminated polyethylene glycol monomethyl ether (PEG-N$_3$)

Into a 500 mL three-necked flask, polyethylene glycol monomethyl ether (Mn = 1000, 17 g, 17 x 10^{-3} mol) was dissolved in toluene (250 mL). Traces of water were removed by azeotropic distillation and 250 mL of toluene was removed under reduced pressure. The reaction mixture was cooled to 0 °C. Dichloromethane (75 mL) and triethyl amine (7.1 mL, 5.1 x 10^{-3} mol) were added to the reaction mixture. Methane sulfonyl chloride (3.85 g, 3.4 x 10^{-3} mol) was added drop wise by syringe over a period of 45 minutes. The reaction mixture was stirred at the same temperature for additional 15 min then stirring continued at room temperature for additional 3.5 h. The reaction mixture was passed through a plug of short silica column. The solvent was evaporated and the oily residue was precipitated in diethyl ether and dried under vacuum to yield mesyl-terminated PEG.

In the next step, into a 200 mL three-necked flask were placed mesylate-terminated PEG (5 g, 1.1 mol), DMF (15 mL) and sodium azide (0.6 g, 10.1 mol). The reaction mixture was stirred magnetically at room temperature for 24 h. After completion of the reaction, DMF was removed under reduced pressure and the reaction mixture was extracted with dichloromethane,

(150 mL). The resulting azido-terminated polyethylene glycol monomethyl ether ($PEG_{1000}-N_3$) was isolated by precipitation into diethyl ether and dried under vacuum at 25 °C for 24 h.

Yield: (95 %).

^{1}H-NMR (CDCl$_3$, δ/ppm): 3.63 (s, -O-**CH**$_2$-**CH**$_2$), 1.47 (s, –**CH**$_2$-N$_3$)

4b.3.4 Preparation of 2-azidoethyl-2-bromo-2-methylpropanoate

4b.3.4.1 Preparation of 2-azidoethanol

Into a 1000 mL two necked round-bottom flask equipped with a dropping funnel were charged 2-chloroethanol (15 g, 0.187 mol) and water (62 mL). The reaction mixture was stirred for 20 minutes. The solution of sodium azide (73 g, 1.12 mol) in water (300 mL) was added dropwise over a period of 30 min. The reaction mixture was refluxed for 8 h, allowed to attain room temperature and then extracted with ethyl acetate (120 mL). The organic layer was dried over anhydrous sodium sulphate, filtered and ethyl acetate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate: pet ether (25:75, v/v) as an eluent.

Yield: 13.5 g (89 %)

FT-IR (CHCl$_3$, cm^{-1}): 3200 (OH), 2108 (N$_3$)

^{1}H-NMR (CDCl$_3$, δ/ppm): 3.73 (t, 2H), 3.39 (t, 2H), 2.87 (s, 1H).

4b.3.4.2 Preparation of 2-azidoethyl-2-bromo-2-methylpropanoate

Into a 250 mL two necked round-bottom flask equipped with a dropping funnel were charged 2-azidoethanol (10 g, 0.11 mol), triethylamine (17.40 g, 0.17 mol), and dry chloroform (25 mL). The reaction mixture was cooled to 0 °C. The solution of 2-bromoisobutyryl bromide (39.64 g, 0.17 mol) in dry dichloromethane (24 mL) was added dropwise into the reaction mixture under stirring at 0 °C over a period of 30 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to attain room temperature and then stirred overnight. The reaction mixture was washed with 5% aqueous NaHCO$_3$ solution (3 x 50 mL) and water (3 x 50 mL). The organic layer was dried over anhydrous sodium sulphate, filtered and ethyl acetate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate: pet ether (25:75, v/v) as an eluent.

Yield: 24.4 g (90 %)

FT-IR (CHCl$_3$, cm^{-1}): 2110, (N$_3$) 1730 (C=O)

^{1}H-NMR (CDCl$_3$, δ/ppm): 4.21 (t, 2H, -OCH$_2$), 3.39 (t, 2H, -CH$_2$), 1.92 (s, 6H, 2 -CH$_3$)

4b.3.5 Synthesis of azido-terminated polystyrene (PS-N$_3$)

In a typical experiment, Schlenk tube equipped with a magnetic stir bar was charged with CuBr (0.137 g, 0.96 x 10^{-3} mol) and the tube was thoroughly flushed with argon. 2-Azidoethyl 2-bromo-2- methylpropanoate (0.227 mg, 0.96 x 10^{-3} mol) was dissolved in styrene (5 g, 48 x 10^{-3} mol) in a separate sample vial, degassed and the solution was transferred *via* argon-purged syringe into the Schlenk tube under argon atmosphere. The reaction mixture was degassed

three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was opened and *N, N, N', N', N"*-pentamethyldiethylenetriamine (200 µL, 9.6 x 10^{-4} mol) was added rapidly. The Schlenk tube was sealed with a stopper and the reaction mixture was stirred at 110 °C for 3 h. The reaction was quenched by cooling the reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into excess methanol (500 mL) to precipitate the polymer. The polymer was dried under reduced pressure for 24 h.

FT-IR (CHCl$_3$, cm^{-1}): 2139 (N$_3$) 1726 (C=O)

^{1}H-NMR (CDCl$_3$ δ/ppm): 7.08-6.48 (m, Ar-H from polystyrene), 4.45-3.58 (m, -CH$_2$ from initiator fragment), 2.20-0.91 (m, -CH from polystyrene + protons from initiator fragment)

Mn: 6800 (determined by GPC, polystyrene standard)

4b.4 *Functionalization of copolyester containing pendent propargyloxy groups with azido compounds*

A representative procedure for click reaction between copolyester (PES-2) and PY-N$_3$ is described below.

To a Schlenk tube equipped with a magnetic stirring bar were added PES-2 (1 eq), PY-N$_3$ (3 eq), copper sulphate (0.05 eq), sodium ascorbate (0.1 eq) and a mixture of THF and DMF (1:1, v/v, 20 mL). The reaction mixture was degassed by three times freeze-pump-thaw cycles and then sealed under vacuum. The reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was diluted with THF (150 mL) and then passed through a column of neutral alumina to remove metal salt. The reaction mixture was concentrated and precipitated into methanol to remove the catalyst residue and excess of the azide, and dried in vacuum at room temperature for 8 h.

FT-IR (CDCl$_3$, cm^{-1}): 1745 (C=O)

^{1}H-NMR (CDCl$_3$, δ/ppm): 8.9-6.8 (m Ar-H, 9H)

4b.5 *Results and discussion*

4b.5.1 *Functionalization of copolyester containing pendent propargyloxy groups with azides*

In the present study, post-functionalization of polyester containing pendent propargyloxy groups (synthesized in **Chapter 4a, entry 1, PES-2**) was carried out by click reaction with five different azides (**Scheme 4b.2).** Two azido containing molecules *viz*; 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene as well as three types of azido containing polymeric chains, including azido-terminated polystyrene (PS-N$_3$) and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, PEG$_{550}$-N$_3$, PEG$_{1000}$-N$_3$) were chosen to react with polyester containing pendent propargyloxy groups. 1-(4-Azidobutyl)pyrene and

9-(azidomethyl)anthracene were selected as the azide precursors for chemical modification to introduce photophysical properties[15, 19, 21, 22] to the polyester where as azido–terminared polystyrene and azido-terminated polyethylene glycol monomethyl ether was chosen as the azide precursors to tune the specific surface properties of the polyester.[23, 24] PEG contributes some distinct behaviour to the polymer because of its physical properties such as non-toxicity and high water solubility.[23, 24]

Azides were prepared independently as a click component. PS-N$_3$ was synthesized according to literature procedure. Atom transfer radical polymerization (ATRP) of styrene in bulk was carried out using 2-azidoethyl-2-bromo-2-methylpropanoate as an initiator and CuBr/PMDETA as a catalyst system. **Scheme 4b.1** illustrates synthesis of polystyrene by ATRP.
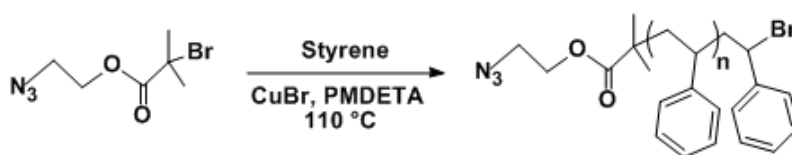
Scheme 4b.1 Synthesis of azido-terminated polystyrene

The conditions and results of synthesis of azido-terminated polystyrene are summarized in **Table 4b.1.**

Table 4b.1 Reaction conditions and results for synthesis of azido-terminated polystyrene

Sr. No.	[a] [M]$_0$: [I] : [Cu]: [L]	Time (h)	[b] Mn$_{,theo}$	[c]Mn$_{,GPC}$	Mw/Mn
1	50:1:1:1	3	5200	6800	1.10

a- [M]$_0$:[I]$_0$:[L] = [Monomer]:[Initiator]:[CuBr]:[PMDETA]

b-Mn $_{theo}$= $\underline{[M]_O}$ x (% conv.) x mol. wt. of monomer] + mol. wt. initiator (614)
            [I]$_O$

c- Mn,$_{GPC}$- Determined from GPC; Polystyrene standard; CHCl$_3$ eluent

The appearance of the peaks in the range 7.25-6.48 δ ppm corresponds to phenyl ring protons of polystyrene chain (**Figure 4b.1**).
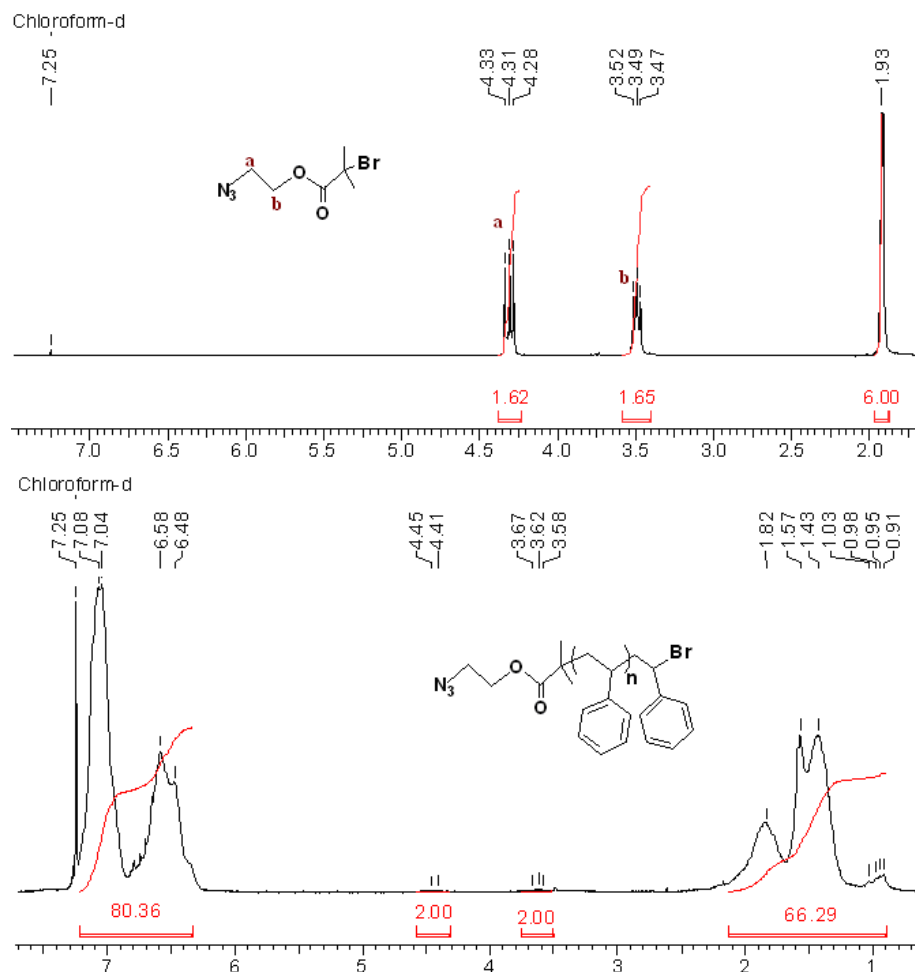
Figure 4b.1 ^{1}H-NMR spectra (CDCl$_3$) of (top) 2-azidoethyl-2-bromo-2-methylpropanoate and (bottom) azido-terminated polystyrene

PEG-N$_3$ was synthesized according to the literature procedure[25]. Monomethyl ether of PEG was first converted to mesyl-terminated PEG (PEG-OSO$_2$CH$_3$) by reaction with methanesulfonyl chloride. Mesyl-terminated PEG on substitution reaction with NaN$_3$ afforded the corresponding azido substituted monomethyl ether of PEG.

1-(4-Azidobutyl)pyrene (PY-N$_3$) was synthesized from 1-pyrene butanol by its reaction with methanesulfonyl chloride followed by the reaction of corresponding mesyl derivative with NaN$_3$. 9-(Azidomethyl)anthracene was synthesized from 9-(chloromethyl)anthracene by nucleophilic substitution reaction with NaN$_3$.
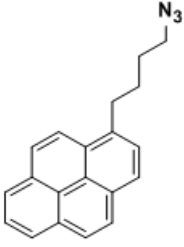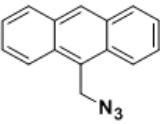
Propargyl functionalized polyester was post-functionalized with the above synthesized azides *via* copper-catalyzed (CuSO$_4$/Na$_{asc}$) azide-alkyne click reactions in THF: DMF (1:1, v/v) solvent system at 60 °C for 24 h. After passing through neutral alumina to remove metal salt and precipitating in methanol, the obtained functionalized polyesters were characterized.

The general reaction sequence employed for post-functionalization of the polyester containing pendent propargyloxy groups (PES-2) is shown in **Scheme 4b.2** and the results of click reaction are compiled in **Table 4b.2.**
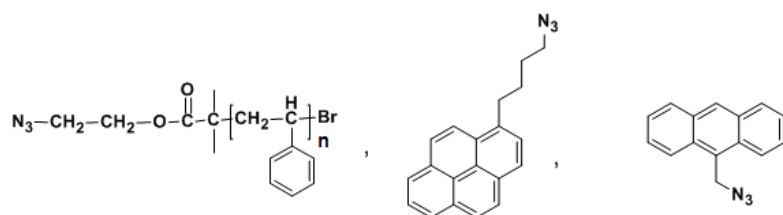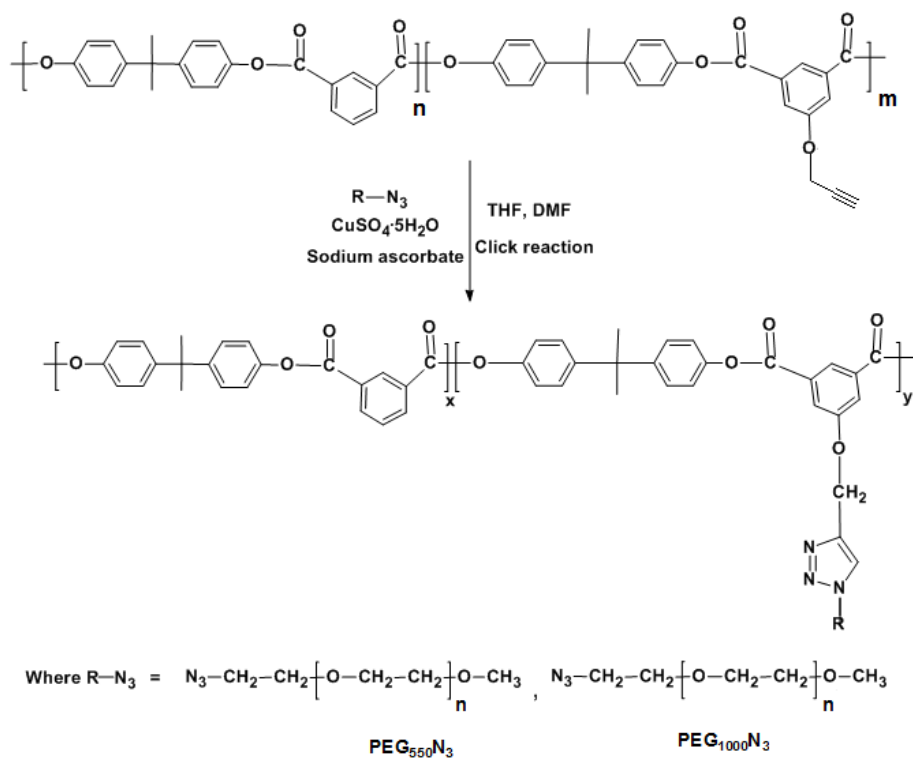
Scheme 4b.2 The general scheme of copper-catalyzed azide-alkyne click reaction between polyester containing pendent propargyloxy groups and azides

Table 4b.2 Results of the click reactions between propargyl containing copolyester (PES-2) and azides

Entry	Functionalized Polyester	Azides used for click reaction	Molecular weight[a] Mn
1	PES-PEG$_{550}$	$N_3-CH_2-CH_2[O-CH_2-CH_2]_n O-CH_3$ PEG$_{550}$-N$_3$	50,600
2	PES-PEG$_{1000}$	$N_3-CH_2-CH_2[O-CH_2-CH_2]_n O-CH_3$ PEG$_{1000}$-N$_3$	*
3	PES-PS	$N_3-CH_2-CH_2-O-\overset{O}{\underset{}{C}}-C[CH_2-\overset{H}{\underset{}{C}}]_n Br$	59,000
4	PES-PY	(pyrene structure with N$_3$)	52,000
5	PES-An	(anthracene structure with N$_3$)	50,200

Starting polymer: PES-2, Mn = 43,600, Reaction conditions: PES-2 (1eq), azide (3 eq), Catalyst = CuSO$_4$/Na$_{asc}$: 0.05 and 0.1 eq, a: Determined by GPC using chloroform as a solvent, calibrated with polystyrene standard, *: Molecular weight not determined.

4b.5.1.1 Chemical modification of polyester containing pendent propargyloxy groups with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene via click reaction

4b.5.1.1.1 Structural characterization

Polyester functionalized with PY-N$_3$ was characterized by FT-IR spectroscopy (**Figure 4b.2**).
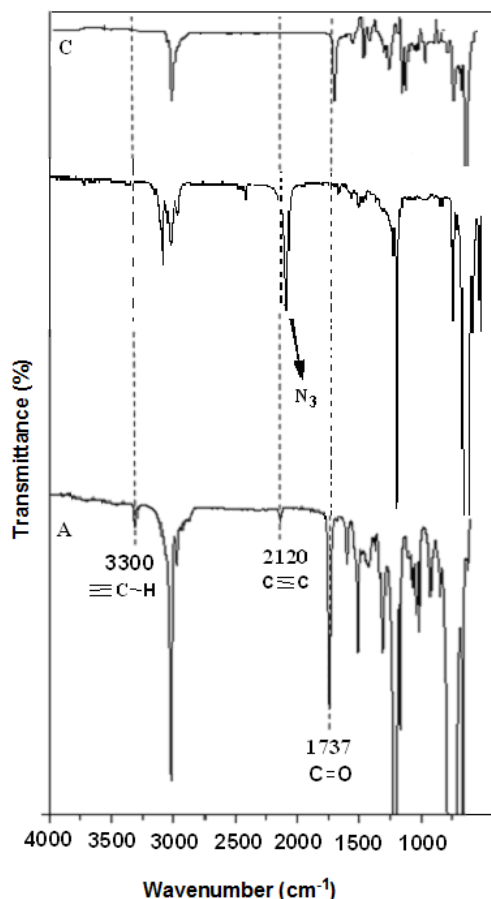
Figure 4b.2 FT-IR spectra of (A) PES-2 (B) PY–N$_3$ (C) PES-2 functionalized with PY–N$_3$ *via* alkyne-azide click reaction

The absorption peak at 3300 ($\equiv$CH) and 2120 cm^{-1} (C$\equiv$C) ascribed to propargyl group completely disappeared after click reaction with PY–N$_3$ indicating quantitative click reaction, which was further supported by ^{1}H-NMR spectra.

^{1}H-NMR spectra of the functionalized polyester (PES-PY) along with the parent polyester (PES-2) are shown in the **Figure 4b.3.**
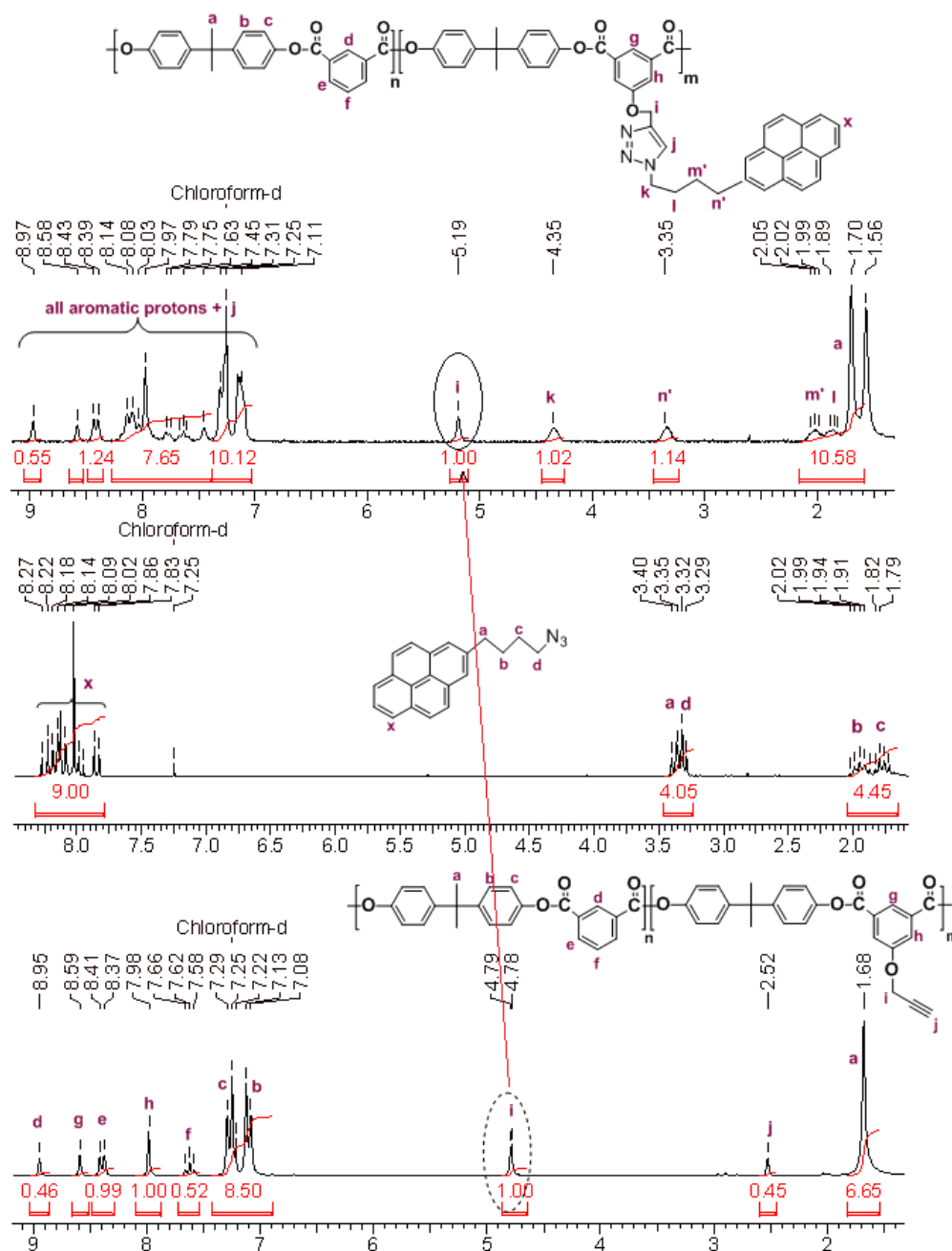
Figure 4b.3 ^{1}**H-NMR spectrum (CDCl$_3$) of the (lower spectrum) starting polyester (PES-2), (middle spectrum) PY-N$_3$ and (top spectrum) PES-PY**

In ^{1}H-NMR spectra, (**Figure 4b.3**, lower spectrum) the shifting of methylene protons "i" from 4.78 to 5.19 δ ppm after click reaction indicated the quantitative functionalization.

Similar observations were drawn from the click reaction between polyester containing pendent propargyloxy groups (PES-2) and An-N$_3$. The complete disappearance of FT-IR absorption peak at 2120 cm^{-1} (C≡C) and 3300 (≡CH) ascribed to propargyl group confirmed the successful click reaction (spectrum not shown).

The representative GPC traces of polyester functionalized with PY-N$_3$ (**Figure 4b.4**) showed that after the click reaction the functionalized polyester had a higher number average

molecular weight than the starting polyester which confirmed the success of the click reaction and also suggested that the backbone of the polyester did not degrade under click reaction protocol.[22]
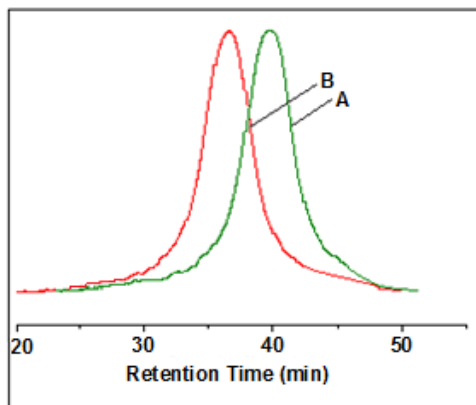
Figure 4b.4 GPC traces of (A) parent polyester (PES-2) and (B) PES- PY

4b.5.1.1.2 Photophysical properties of the polyesters functionalized with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene

Polyesters functionalized with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene were further characterized by the UV-Vis absorption (**Figure 4b.5)** and fluorescence spectroscopy. UV-Vis absorption peaks at 315, 330, 345 nm are typical peaks of pyrene chromophore [**Figure 4b.5 (a**)] whereas polyester clicked with anthracene showed the maximum absorption peak at 275 nm [**Figure 4b.5 (b)**].

| (a) | (b) |
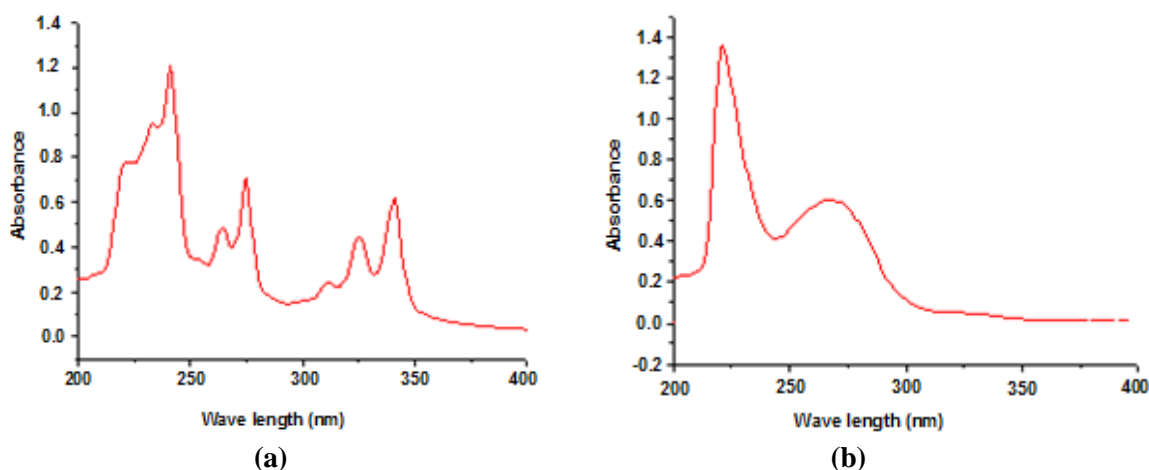
Figure 4b.5 UV-Vis absorbance profiles of (a) PES-PY (b) PES-An (0.00001 wt % (w/v) concentration in chloroform)

Additional evidence for the functionalization was obtained from fluorescence spectroscopy. The spectral emission of polyesters functionalized with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene was observed at 485 and 440 nm, respectively (**Figure 4b.6)**. These emissions of the pyrene and anthracene fluorophores[26-28] provide proof for successful functionalization of polyester by pyrene and anthracene derivatives *via* click reaction.

(a)   (b)
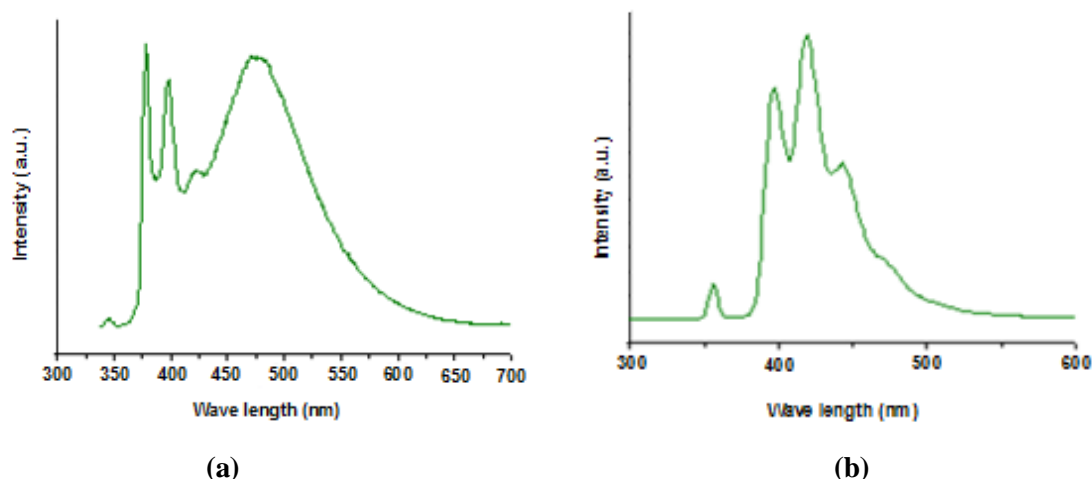
Figure 4b.6 Solution fluorescence emission spectra of (a) PES-PY (0.00001 wt % (w/v)
            concentration in chloroform) and (b) PES-An ((0.0001 wt % (w/v)
            concentration in chloroform)

4b.5.1.2   Chemical modification of polyester with PS-N$_3$ and PEG-N$_3$ via click reaction

4b.5.1.2.1 Structural characterization

Polyester functionalized with PS-N$_3$ and PEG-N$_3$ was characterized by FT-IR, ^{1}H-NMR spectroscopy, GPC and contact angle measurements.

In FT-IR spectra (**Figure 4b.7**), the complete disappearance of the characteristics absorption peaks at 3300 cm^{-1}(≡CH) and 2120 cm^{-1} (C≡C) of propargyl group confirmed the quantitative functionalization of the polyester.
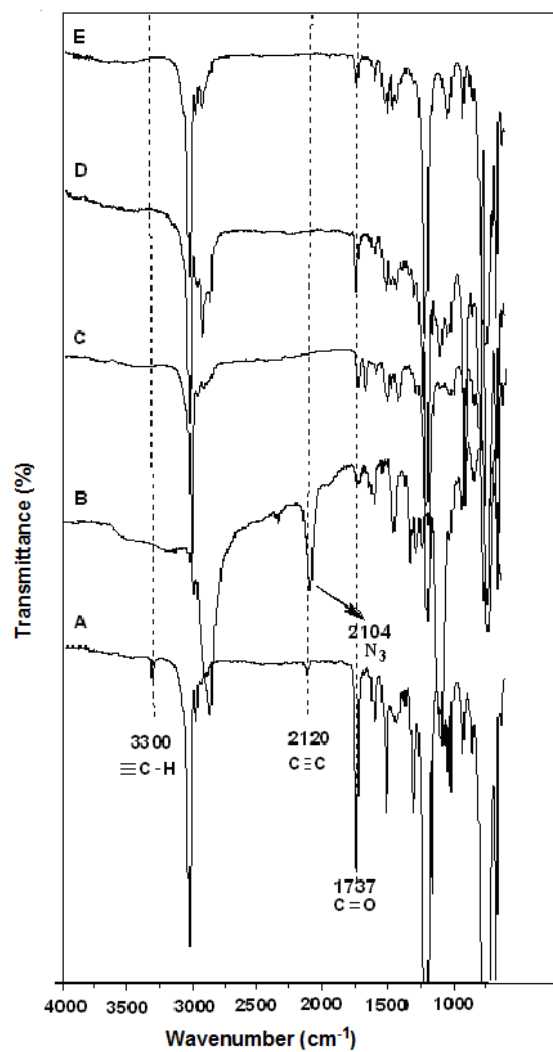
Figure 4b.7 FT-IR spectra of (A) Polyester, PES-2 (B) PEG$_{550}$ −N$_3$,(C) PES-PEG$_{550}$,(D) PES-PEG$_{1000}$ and (E) PES-PS

The click reaction between (i) PES-2 and $PEG_{550}-N_3$ and (ii) PES-2 and $PS-N_3$, was further supported by ^{1}H-NMR spectroscopy (**Figure 4b.8**).
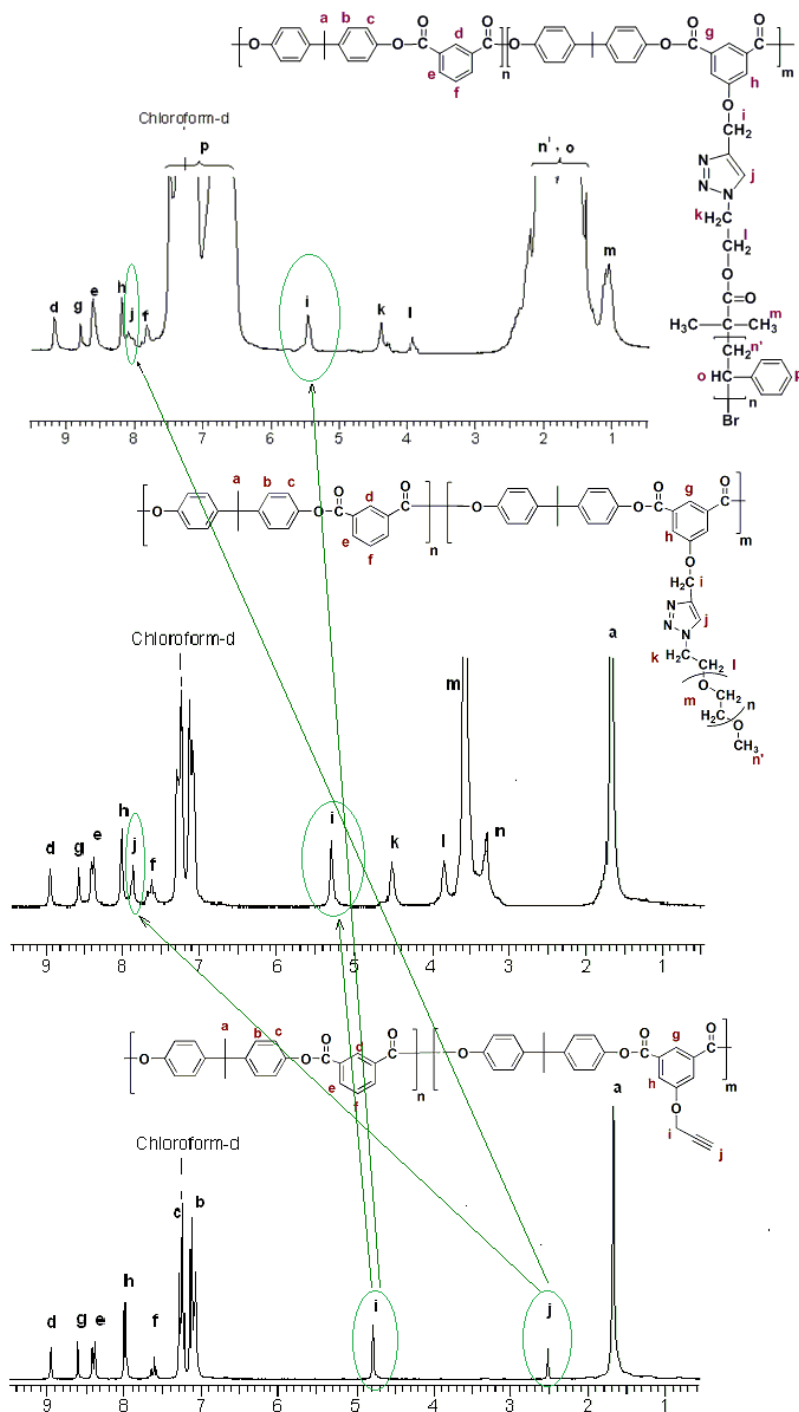
Figure 4b.8 ^{1}H-NMR spectra ($CDCl_3$) of (bottom) PES-2, (middle) PES-PEG and (top) PES-PS

The success of the click reaction between polyester (PES-2) and $PEG-N_3$ and $PS-N_3$ was confirmed by the disappearance of the signal "j" of propargyl group at 2.50 δ ppm and the appearance of a new proton signal originating from the formed triazole ring at 7.75 and 8.0 δ ppm, respectively (**Figure 4b.8**, **middle** and **top** spectra). The shifting of methylene protons "i" of

propargyl group from 4.78 to 5.3 δ ppm also confirmed the click reaction. Further, new peaks ascribed to PEG appeared at 4.50 δ ppm and 3.35-3.90 δ ppm. Additionally, appearance of new peaks corresponding to PS chain in the range 7.52-6.33 δ ppm and 2.58-0.98 δ ppm confirmed the polyester was quantitatively modified *via* click reaction.

4b.5.1.2.2 Contact angle measurement

Water contact angle measurements were performed on drop-cast films of functionalized polyesters, PES-PEG and PES-PS to evaluate the surface properties of the polyester before and after modification**.** Contact angle (CA) was calculated as the average between the values obtained from ten drops having the same volume (about 1 μL), spotted on different points of the chip. Contact angle images of PES-PEG and PES-PS are shown in **Figure 4b.9**, which showed change in contact angle after the click reactions. The contact angle of PEG grafted polyester (37°) was lower than that of parent polyester (88°). The lowering of CA could be possibly due to better spatial arrangement of the hydrophilic PEG moiety to the polyester surface. In case of PS grafting, the contact angle increased from 88º to 97º which could be attributed to the grafting of the hydrophobic PS moiety onto the polyester.

88º   **37º**   **97º**
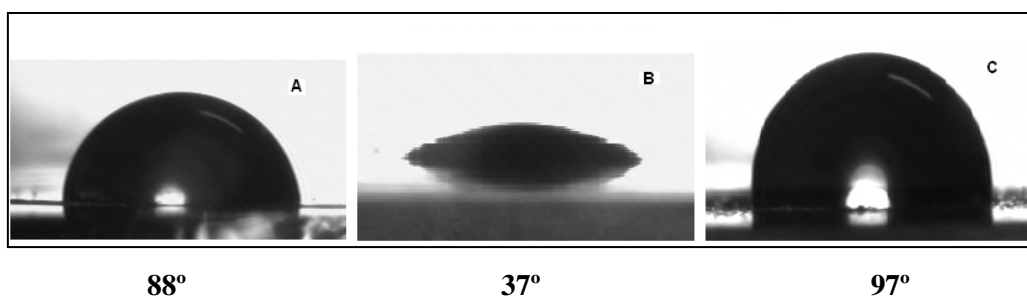
Figure 4b.9 Water droplet on (left) PES-2 (middle) PES-PEG and (right) PES-PS
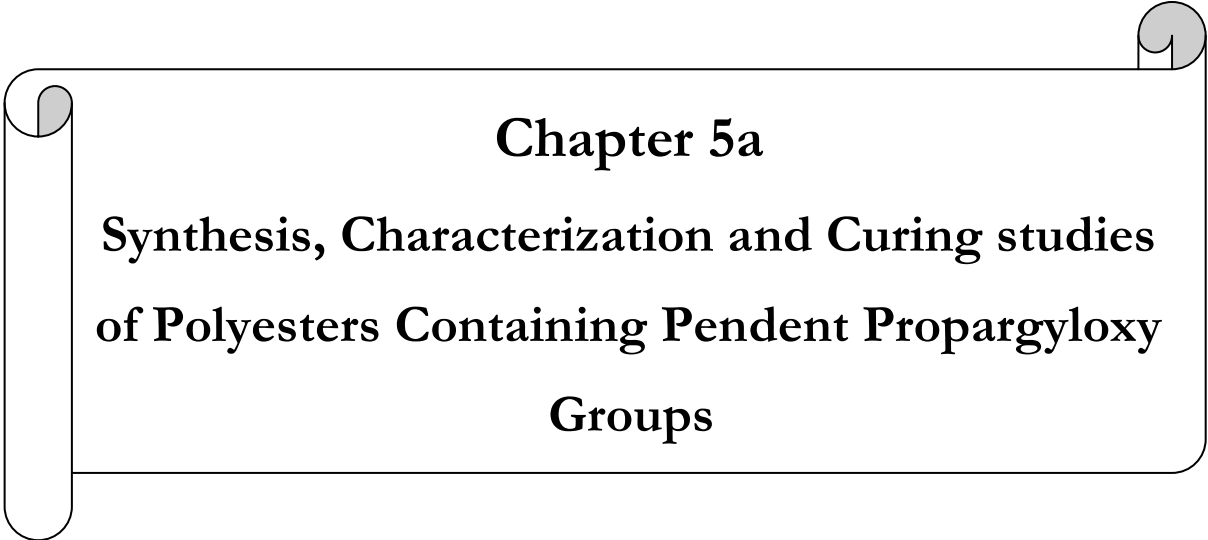
4b.6 Conclusions

1.   The click reaction turned out to be a very efficient approach to functionalize aromatic polyester containing pendent propargyloxy groups with interesting hydrophilic, hydrophobic and fluorescent compounds under mild conditions. This approach opens up new opportunities for introduction of desired functional groups into aromatic polyester so as to exhibit targeted properties by appropriate choice of azido compounds.

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Chapter 5a

Synthesis, Characterization and Curing studies of Polyesters Containing Pendent Propargyloxy Groups

5a.1 Introduction

The modification of structure of aromatic polyester is possible by the choice of appropriate combination of bisphenol and aromatic diacid or diacid chloride. Thus, the desired functional groups could be introduced into aromatic polyester *via* either functional group containing bisphenol or diacid chloride.[1-4] In chapter 4a, we presented synthesis of aromatic polyesters containing pendent propargyloxy groups based on 5-(propargyloxy)isophthaloyl chloride.

This chapter describes synthesis of a series of new aromatic polyesters containing pendent propargyloxy groups by polycondensation of a bisphenol containing propargyloxy group *viz*; 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane with isophthaloyl chloride or terephthaloyl chloride or a mixture of isophthaloyl chloride and terephthaloyl chloride (50:50 mol %). Copolyesters were also synthesized by polycondensation of a mixture of 1,1-bis (4-hydoxyphenyl)-1-(4-propargyloxyphenyl) ethane and bisphenol A with isophthaloyl chloride.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Cure behavior of polyesters was studied in nonisothermal mode using DSC technique.

5a.2 Experimental

5a.2.1 Materials

1,1-Bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane (Pro-BPA) was synthesized as described in **Chapter 3.** Bisphenol-A (BPA) (Aldrich) was sublimed under reduced pressure before use. Benzyltriethyl ammonium chloride (BTEAC) (Aldrich) was used as received. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were synthesized from terephthalic acid and isophthalic acid, (Aldrich), respectively using excess thionyl chloride in the presence of *N,N*-dimethylformamide (DMF) as a catalyst and were purified by distillation under reduced pressure.[5] Dichloromethane (S.D.Fine Chemicals) was dried over calcium hydride and distilled. Other solvents were purified according to standard procedures.[6]

5a.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured with 0.5 % (w/v) solution of polyester in chloroform at 30 ± 0.1^{o}C using an Ubbelohde suspended level viscometer.

Solubility of aromatic polyesters was determined at 3 % (w/v) concentration in different organic solvents at room temperature.

Molecular weight of polyesters was measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: column – polystyrene - divinylbenzene (10^{5} Å to 50 Å), detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in chloroform (5 mL) and filtered through 0.45 μ filter.

FT-IR spectra were recorded using polyester films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using CDCl$_3$ as a solvent

X-Ray diffractograms of polyesters were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2°/min. Dried polymer film or powder was used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 10 $^\circ$C/min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) analysis was carried out on TA instrument DSC Q10 at a heating rate of 10 $^\circ$C/min in nitrogen atmosphere.

5a.3 Synthesis of aromatic polyesters containing pendent propargyloxy groups

5a.3.1 Synthesis of homopolyesters containing pendent propargyloxy groups

A representative procedure for synthesis of homopolyester is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane (1 g, 2.9 x 10^{-3} mol) dissolved in 1M NaOH (12 mL). The reaction mixture was stirred at 10 $^\circ$C for 1h. Thereafter, BTEAC (0.08 g) was added to the reaction mixture. The solution of terephthaloyl chloride (0.58 g, 2.9 x 10^{-3} mol) dissolved in dichloromethane (35 mL) was added in one lot to the reaction mixture and the mixture was stirred vigorously at 2000 rpm at 10 $^\circ$C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (25 mL) and precipitated into methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 $^\circ$C under reduced pressure for two days.

5a.3.2 Synthesis of aromatic copolyesters containing pendent propargyloxy groups

A representative procedure for synthesis of copolyester is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed 1,1-bis (4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane (1 g, 2.9 x 10^{-3} mol) and BPA (0.66 g, 2.9 x 10^{-3} mol) dissolved in 1M NaOH (24 mL). The reaction mixture was stirred at 10°C for 1 h. Thereafter, BTEAC (320 mg) was added to the reaction mixture. The solution of isophthaloyl chloride (1.21 g, 5.8 x 10^{-3} mol) dissolved in dichloromethane (30 mL) was added in one lot to the reaction mixture and the mixture was stirred vigorously at 2000 rpm at 10 $^\circ$C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (25 mL) and precipitated into methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 $^\circ$C under reduced pressure for two days.

5a.4 Curing studies of polyesters containing pendent propargyloxy groups

5a.4.1 DSC analysis

DSC measurements were performed on TA Instrument (Q10) supported by TA Universal Analysis software for data acquisition. Samples (5 mg) were sealed in hermetic aluminium pans and experiments were performed under a nitrogen flow of 50 mL / min. In nonisothermal studies, polyesters containing pendent propargyloxy groups were subjected to a dynamic DSC scan at the heating rate of 10 °C/min. The total enthalpy of curing (ΔH) was determined from the area under the exothermic curve. The cure onset temperature (T_o) was considered as the intercept of slope of baseline and tangent of curve leading to peak of transition (**Figure 5a.1**).

| (A) | (B) |
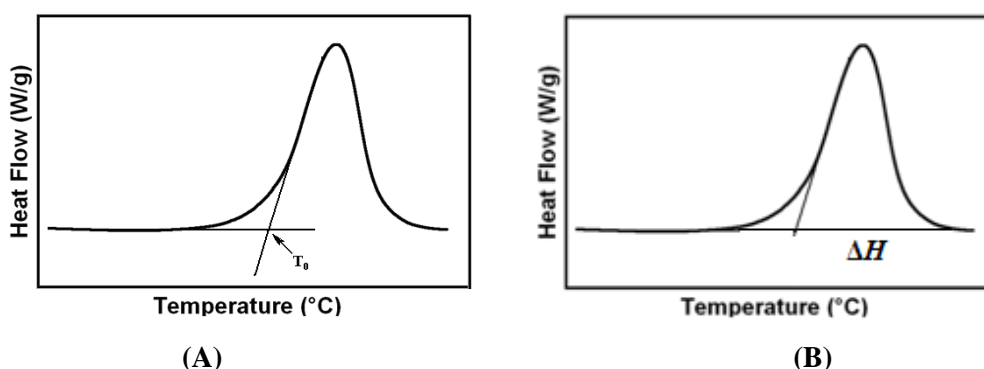
Figure 5a.1 Theoretical DSC curve illustrating (A) cure onset temperature (B) total enthalpy of curing (ΔH)

5a.5 Results and discussion

5a.5.1 Synthesis of aromatic polyesters containing pendent propargyloxy groups.

Clickable polyesters containing pendent propargyloxy groups were synthesized by interfacial polycondensation of 1,1-bis (4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane with IPC or TPC or IPC+TPC (50:50, mol %) in dichloromethane-aqueous sodium hydroxide system using BTEAC as a phase transfer catalyst. Copolyesters were also synthesized by polycondensation of a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA with IPC. Copolyesters with varying content of propargyloxy functionalities were synthesized by varying the molar ratio of 1,1-bis (4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA in the feed during copolymerization.

Scheme 5a.1 illustrates synthesis of polyesters from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and aromatic diacid chlorides.
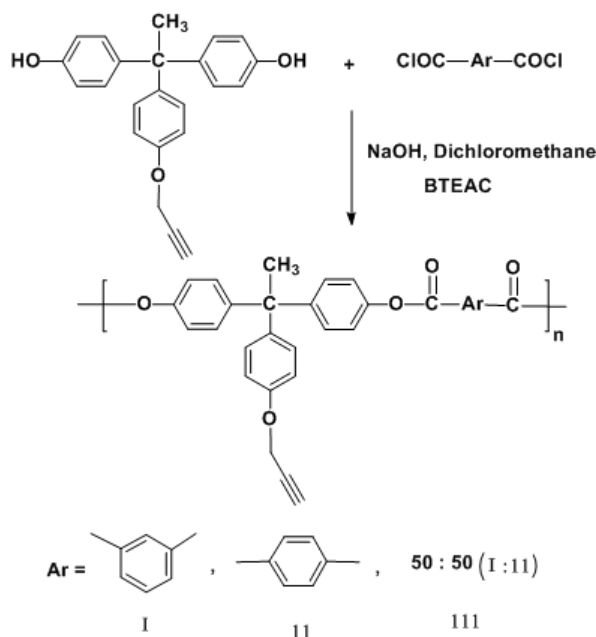
Scheme 5a.1 Synthesis of aromatic polyesters from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and aromatic diacid chlorides

Scheme 5a.2 illustrates synthesis of copolyesters from a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA with IPC.
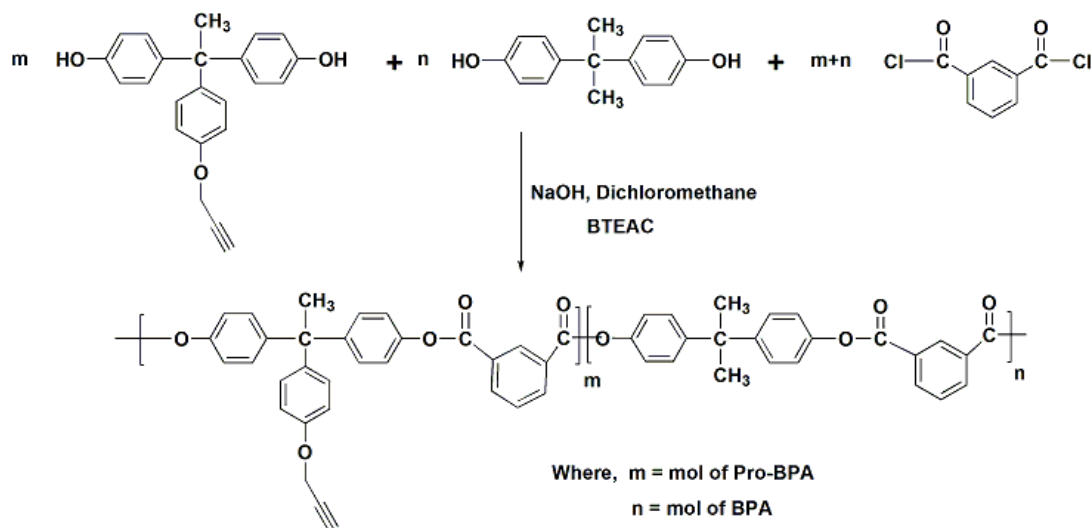
Scheme 5a.2 Synthesis of aromatic copolyesters from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA with IPC

Polyesters were isolated as white fibrous materials with inherent viscosities in the range 0.50–0.75 dL/g. Number average molecular weights (Mn) of polyesters were in the range 13,200-34,000 with polydispersity index in the range 2.0-2.3 (**Table 5a.1**). Tough, transparent and flexible films of polyesters containing pendent propargyloxy group could be cast from their solutions in chloroform.

Table 5a.1 Synthesis of aromatic (co)polyesters containing pendent propargyloxy groups

Polyester	Composition of Bisphenol (mol%)		Diacid Chloride (mol%)		η_{inh},[a] dL/g	Molecular weight [b]		Polydispersity Index (Mw/Mn)
	BPA	Pro-BPA	IPC	TPC		Mn	Mw	
PPES-1	0	100	100	0	0.70	30,300	69,700	2.3
PPES-2	0	100	0.0	100	0.51	16,000	32,000	2.0
PPES-3	0	100	50	50	0.50	13,200	29,000	2.2
PPES-4	50	50	100	0	0.50	15,500	32,600	2.1
PPES-5	75	25	100	0	0.75	34,000	71,400	2.1

a: η_{inh} of polyester was measured with 0.5% (w/v) solution in chloroform at $30 \pm 0.1\ ^{o}C$.
b: Measured on GPC in chloroform; polystyrene was used as the calibration standard.

5a.5.2 Structural characterization

Polyesters were characterized by FT-IR and ^{1}H-NMR spectroscopy.

FT-IR spectrum of polyester derived from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and TPC is shown in **Figure 5a.2.**
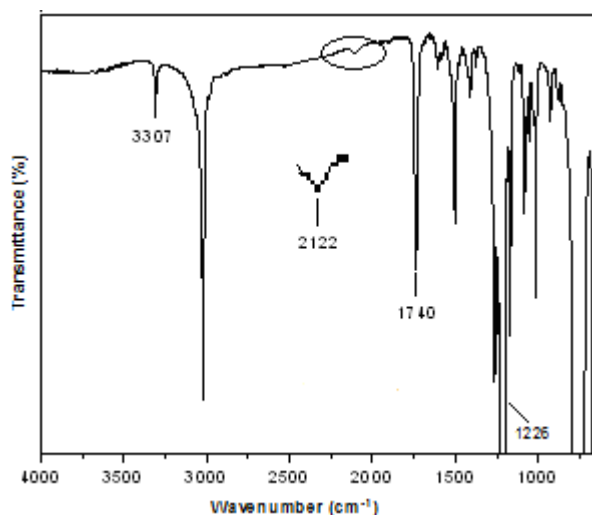
Figure 5a.2 FT-IR spectrum of polyester derived from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and TPC

In FT-IR spectrum, the absorption bands at 3307 cm^{-1} ($\equiv$C-H) and 2122 cm^{-1} (C$\equiv$C), confirmed the incorporation of propargyloxy functionality in the polyester. Ester carbonyl band of polyester appeared at 1740 cm^{-1}. The absorption band corresponding to -C-O-C- stretching vibration was observed at 1226 cm^{-1}.

^{1}H-NMR spectrum of polyester derived from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and TPC is reproduced in **Figure 5a.3.**
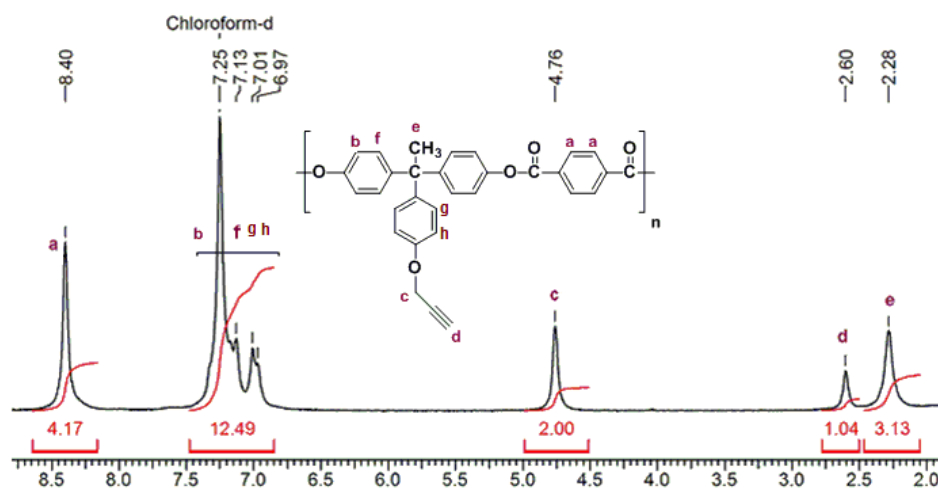
Figure 5a.3 ¹**H-NMR spectrum (CDCl₃) of polyester from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and TPC (PPES-1)**

The peak appeared at 8.40 δ ppm is due to aromatic protons "a". The peaks in the range 7.25-6.97 δ ppm are due to protons "b", "f", "g" and "h". The peak displayed at 4.76 δ ppm is due to methylene protons "c". The peak appeared at 2.60 δ ppm is due to proton "d" of propargyl group, which confirmed the incorporation of propargyl group into the polymer. The methyl group protons "e" exhibited a singlet at 2.28 δ ppm.

¹H-NMR spectrum of copolyester derived from a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA with IPC along with assignments is shown in **Figure 5a.4**.
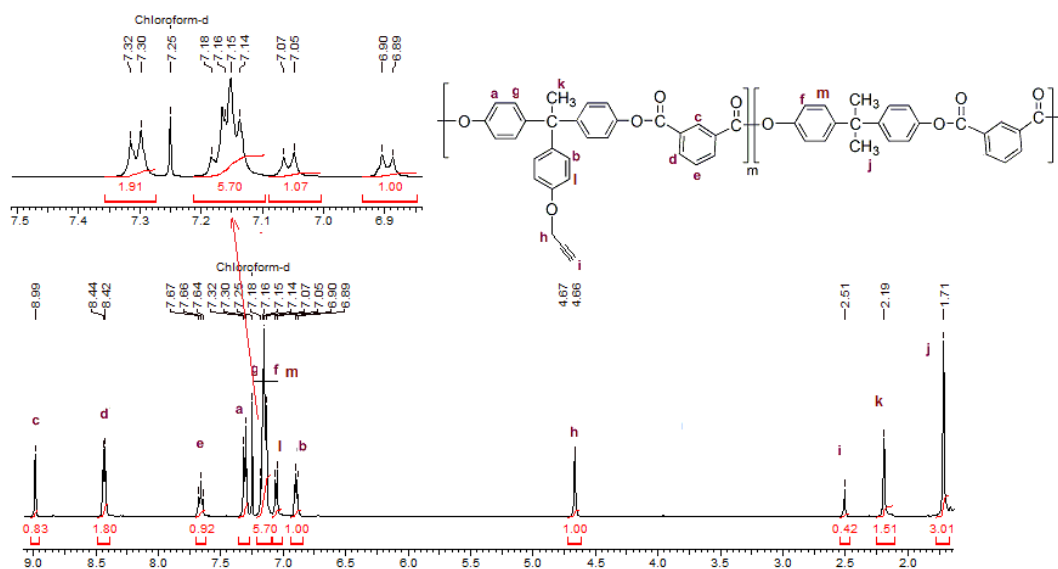
Figure 5a.4 ¹**H NMR spectrum (CDCl₃) of copolyester from a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and BPA with IPC (PPES-4)**

The proton "c" flanked by ester carbonyl groups appeared as a singlet at 8.99 δ ppm. The doublet at 8.43 δ ppm is due to proton "b". The triplet at 7.66 δ ppm is due to proton "e". The proton "a" appeared as a doublet at 7.31 δ ppm. The peaks appeared in the range 7.18-7.14 δ ppm are due to protons "g", "f" and "m". The protons "l" and "b" appeared as doublets at 7.06 and 6.89

δ ppm, respectively. The proton "h" appeared as doublet at 4.66 δ ppm. The peak appeared at 2.51 δ ppm is due to proton "i". The methyl group protons "k" and "j" appeared as singlets at 2.19 and 1.71 δ ppm, respectively.

The monomer composition in copolyesters determined by ^{1}H-NMR spectroscopy from the relative integrated intensity ratio of CH_3 (signal "k" at 2.19 δ ppm) from Pro-BPA with -CH_3 (signal "j" at 1.71 δ ppm) from BPA correlated well with the feed ratios (**Table 5a.2).**

Table 5a.2 Composition of copolyesters determined from ^{1}H-NMR spectra

Copolyester	Feed Pro-BPA, (mol %)	Observed Pro-BPA, (mol %)
PPES-4	50	48
PPES-5	25	25

5a.5.3 Solubility of polyesters

Solubility data of polyesters containing pendent propargyloxy groups in different organic solvents at 3 wt % (w/v) concentration is shown in **Table 5a.3.**

Table 5a.3 Solubility of aromatic polyesters containing pendent propargyloxy groups.

Polyester	CHCl$_3$	DCM	THF	Pyridine	NMP	DMF
PPES-1	++	++	++	++	++	++
PPES-2	++	++	++	++	++	++
PPES-3	++	++	++	++	++	++
PPES-4	++	++	++	++	++	++
PPES-5	++	++	++	++	++	++
*HPES-Ref	++	++	++	++	++	++

++ : Soluble, *HPES-Ref: polyester derived from 1,1-bis(4-hydroxyphenyl)-1-phenylethane and IPC. Solubility data for HPES-Ref is taken from reference 7.

Polyesters were soluble in solvents such as dichloromethane, chloroform, THF, DMF, pyridine and NMP. Polyesters derived from BPA with IPC and BPA with TPC have been reported to be insoluble in the above mentioned solvents[8] while polyester derived from 1,1-bis(4-hydroxyphenyl)-1-phenylethane and IPC (HPES-Ref) is soluble in the above mentioned solvents.[7] The good solubility of 1,1-bis(4-hydoxyphenyl)-1-(4'- propargyloxyphenyl)ethane –based polyesters could be attributed to the effect of weakening of the intermolecular interactions due to the presence of pendent phenyl rings containing propargyloxy group.

5a.5.4 X-Ray diffraction studies

X-Ray diffractograms of polyesters containing pendent propargyloxy groups are shown in **Figure 5a.5 (a)**. Polyesters showed broad halo over the range 2θ ≈ 15–25º in the wide angle region

indicating that the polymers were amorphous in nature. It is reported that polyesters derived from BPA with TPC (PPES-Ref 1) and BPA with IPC (PPES-Ref 2) **[Figure 5a.5 (b)]** are partially crystalline in nature.[8] The amorphous nature of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane –based polyesters could be explained in terms of the presence of pendent phenyl ring containing propargyloxy groups in the polymer backbone which hinders packing of the polymer chains and decreases the intermolecular forces.

(a)   (b)
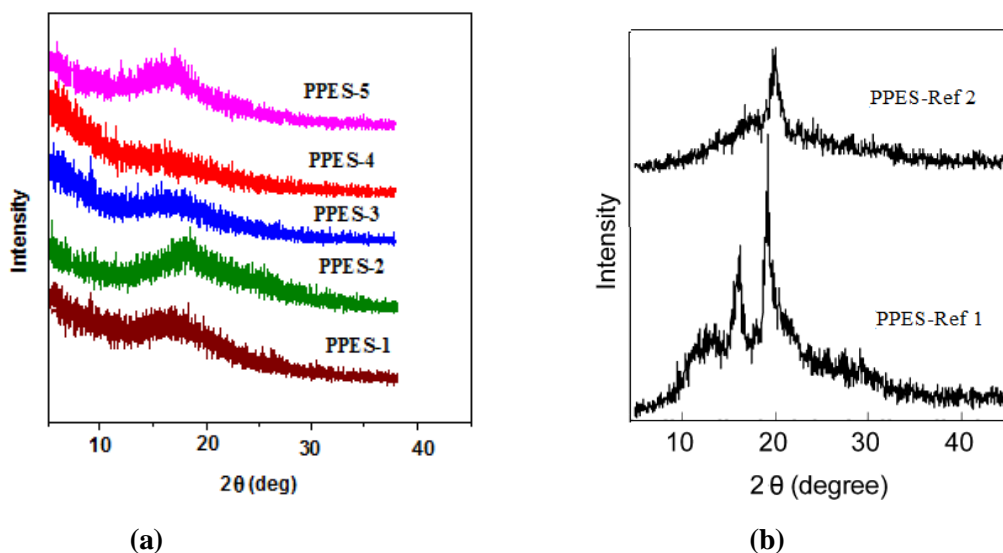
Figure5a.5 **(a) X-Ray diffractograms of aromatic polyesters containing pendent propargyloxy groups. (b) (top) aromatic polyester from BPA with IPC (bottom) aromatic polyester from BPA with TPC (X-Ray diffractogram of PPES-Ref 1 and PPES-Ref 2 are taken from reference 8)**

5a.5.5 *Thermal properties*

Thermal stability of polyesters was determined by TGA at a heating rate of 10 ^{o}C/ min under nitrogen and TG curves are shown in **Figure 5a.6**. The temperature at 10 % weight loss (T_{10}) values for polyesters were observed in the range 410-440 °C indicating their good thermal stability (**Table 5a.4**).
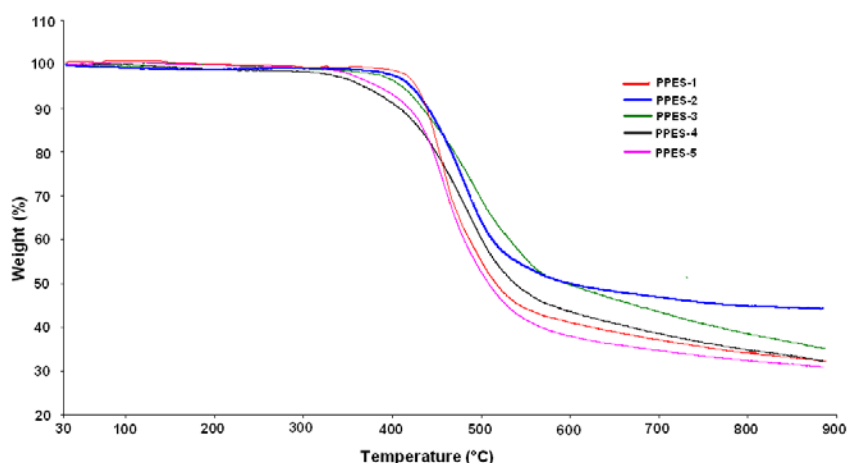
Figure 5a.6 TG curves of polyesters containing pendent propargyloxy groups

Table 5a.4 Thermal properties of aromatic polyesters containing pendent propargyloxy groups.

Sr. No.	Polyester	T_{10} (^{o}C) [a]
1	PPES-1	440
2	PPES-2	440
4	PPES-3	430
5	PPES-4	400
6	PPES-5	410

a : Measured by TGA at a heating rate of 10 °C/min in nitrogen.

To determine Tg by DSC analysis, polyesters were heated from 50 °C to 210 °C at a heating rate of 10 °C/minute. In DSC analysis, temperature was limited to 210 °C as propargyloxy groups present in the polymers are reported to undergo crosslinking reaction in the temperature range 220-350 °C.[9, 10] In DSC scans, polyesters exhibited a featureless trace up to a temperature of 210 °C and Tg was not detected. It is reasonable to presume that Tg values of these polyesters are above 210 °C based on the Tg value (244 °C) of the reference polyester derived from 4, 4'-(1-phenylethane-1,1-diyl)diphenol and TPC.[7]

5a.6 *Non-isothermal curing studies*

Thermal characteriscics of polyesters containing pendent propargyloxy groups were studied by DSC in nonisothermal mode. During the first heating scan, the DSC trace of PPES-1 (**Figure 5a.7**) showed exothermic peak maximum at around 270 °C, in which the exotherm starts at 220 °C. The heat released (325 J/g) is attributed to the formation of chromene followed by the curing. However, no obvious exotherm was observed in the second heating scan indicating that the crosslinking got completed during the first scan.
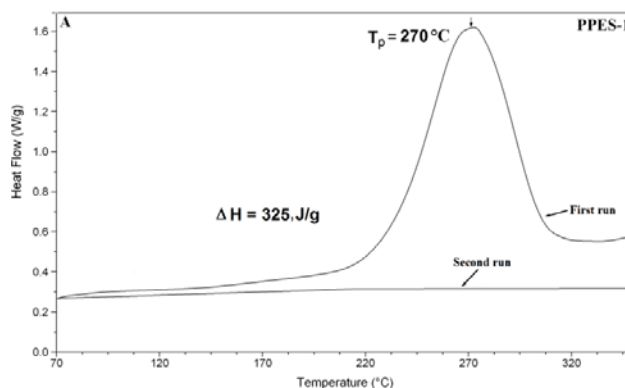
Figure 5a.7 DSC curves of polyester (PPES-1) containing pendent propargyloxy groups

Similarly DSC plots of PPES-2 to PPES-5 (**Figure 5a.8)** exhibited a broad exotherm that begins at around 220 °C, reaches a maximum at around 270 °C and finishes at around 330 °C. The cure characteristics of polyesters containing propargyloxy groups are compiled in **Table 5a.5**
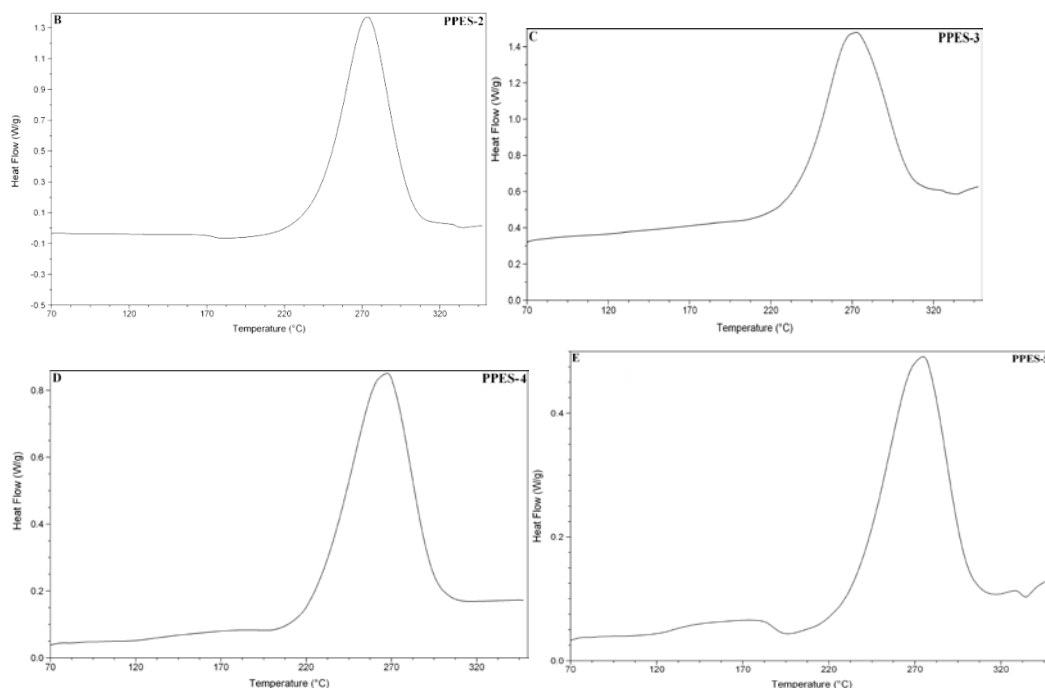
Figure 5a.8 DSC curves of polyesters (PPES-2 - PPES-5) containing pendent propargyloxy groups

Table 5a.5 Cure characteristics of polyesters containing propargyloxy groups

polyester	Composition of Bisphenols (mol%)		Diacid Chloride (mol%)		T_0 (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
	BPA	Pro-BPA	IPC	TPC				
PPES-1	0	100	100	0	220	270	330	325
PPES-2	0	100	0	100	220	270	330	326
PPES-3	0	100	50	50	220	270	330	262
PPES-4	50	50	100	0	225	275	330	186
PPES-5	75	25	100	0	225	275	330	103

T_o – Cure onset temperature, T_p – Maximum cure (peak) temperature
T_f – Final cure temperature, ΔH – Enthalpy of curing
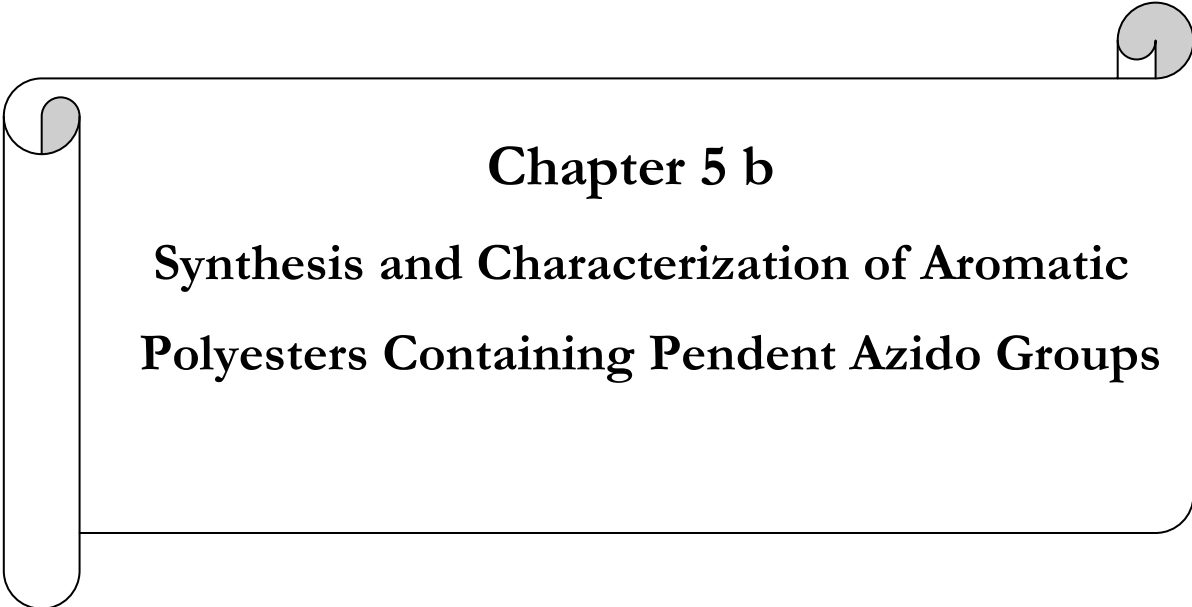
All the thermograms showed a single exotherm which corresponds to the curing reactions of polyesters. The peak cure temperature for the series of polyesters containing pendent propargyloxy groups do not seem to depend on the degree of functionalization (**Table 4a.a**) which indicated the similar cure behavior of these polyesters. ΔH of polyesters was in the range 103-325 J/g with a gradual increase with increase in the content of Pro-BPA.

5a.7 Conclusions

1. Medium molecular weight aromatic polyesters containing pendent propargyloxy groups were obtained from 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl) ethane in combination with bisphenol A and diacid chloride systems by phase transfer catalyzed interfacial polycondensation technique.

2. Polyesters were found to be soluble in common organic solvents such as dichloromethane, chloroform and tetrahydofuran. Tough, transparent and flexible films of polyesters could be cast from chloroform solution of polyesters.

3. Wide-angle X-ray diffraction patterns of polyesters indicated their amorphous nature.

4. The curing of polyesters containing pendent propargyloxy groups occurred in the temperature range 220–330 °C. The percentage incorporation of propargyloxy functionalities in the polyesters did not alter the cure onset and the cure peak temperature during the curing process.

5. The heat of cure reaction of polyesters was in the range of 103 – 326 J/g. Increase in ΔH was observed with increase in the content of propargyloxy functional groups in the polyesters.

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Chapter 5 b

Synthesis and Characterization of Aromatic Polyesters Containing Pendent Azido Groups

5b.1 Introduction

Polymers containing pendent azido groups are of great interest as azido group is very versatile and can be involved in several types of coupling reactions, the most popular being the copper-catalyzed 1,3-dipolar cycloaddition with alkyne derivatives, often called click chemistry to form triazole derivatives.[1-5] Azido-functionalized materials can serve as convenient 'reactive' platforms for the post-synthesis or post-functionalization for the introduction of a broad range of functionalities into the polymers *via* appropriately substituted alkynes.[1, 6-11]Organic azides have been widely used for crosslinking because azido groups can easily decompose under thermal or photochemical conditions to nitrogen gas and reactive nitrenes that undergo insertion reactions.[12-15] Azido groups can also be transformed into versatile functional groups such as amines, triazenes, etc.[7] The last decade has seen an increase in both the number and a variety of reports that exploit the properties and the reactivities of azido-functionalized polymers.[16, 17]

Aliphatic polyesters and polycarbonates containing pendent azido groups have been the subject of intensive research owing to their suitability for chemical modifications and potential applications in biomedical field. However, aromatic polyesters containing pendent azido groups have not been investigated in detail except for their mention in the patent literature.[18]

Therefore, our study is based on the polycondensation of a N_3-containing bisphenol viz; 4,4'–(5-azidopentane-2,2-diyl)diphenol with aromatic diacid chlorides to obtain clickable aromatic (co)polyesters. Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A copolyester containing 30 mol percent 4,4'–(5-azidopentane-2,2-diyl)diphenol monomer was used for click reaction with phenyl acetylene as a representative example.

5b.2 Experimental

5b.2.1 Materials

4,4'–(5-Azidopentane-2,2-diyl)diphenol   (AZ-BPA) was synthesized as described in **Chapter 3.** 4,4'-(1-Phenylethane-1,1-diyl)diphenol (P-BPA) (Aldrich) was sublimed under reduced pressure prior to use. Benzyltriethyl ammonium chloride (BTEAC), *N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) and copper bromide (CuBr) were purchased from Aldrich and were used as received. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were synthesized from terephthalic acid and isophthalic acid, (Aldrich), respectively using excess thionyl chloride in the presence of *N,N*-dimethylformamide (DMF) as a catalyst and were purified by distillation under reduced pressure.[19] Dichloromethane (S.D.Fine Chemicals) was dried over calcium hydride and then distilled. Other solvents were purified according to standard procedures.[20]

5b.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured with 0.5 % (w/v) solution of polyester

in chloroform at $30 \pm 0.1 \, ^{o}C$ using an Ubbelohde suspended level viscometer.

Solubility of aromatic polyesters was determined at 3 % (w/v) concentration in different solvents at room temperature.

Molecular weights of the polyesters were measured on ThermoFinnigan make gel permeation chromatograph (GPC) using the following conditions: column – polystyrene - divinylbenzene (10^5 Å to 50 Å), detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in chloroform (5 mL) and filtered through 0.45 µ filter.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using CDCl$_3$ as a solvent.

X-Ray diffractograms of polyesters were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / min. Ddried polymer films or powder was used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 10 ^{o}C / min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) analysis was carried out on TA instrument DSC Q10, at a heating rate of 10 °C / min in nitrogen atmosphere.

5b.3 Preparation of aromatic polyesters containing pendent azido groups
5b.3.1 Synthesis of homopolyesters containing pendent azido groups

A representative procedure for synthesis of homopolyesters is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed 4,4'–(5-azidopentane-2,2-diyl)diphenol (0.8 g, 2.68 x 10^{-3} mol) dissolved in 1M NaOH (12 mL). The reaction mixture was stirred at 10 °C for 1h. Thereafter, BTEAC (0.10mg) was added to the reaction mixture. The solution of isophthaloyl chloride (0.54 g, 2.68 x 10^{-3} mol) dissolved in dichloromethane (20 mL) was added in one lot to the reaction mixture and the reaction mixture was stirred vigorously at 2000 rpm at 10 ^{o}C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and reprecipitated into methanol:water (1:1, v/v) mixture (1000 mL). Polymer was filtered, washed with methanol and dried at 50 ^{o}C under reduced pressure for two days.

5b.3.2 Synthesis of aromatic copolyesters containing pendent azido groups

A representative procedure for synthesis of copolyesters is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed 4,4'–(5-azidopentane-2,2-diyl)diphenol (1 g, 3.36 x 10^{-3} mol), 4,4'-(1-phenylethane-1,1-diyl)diphenol (2.32 g, 7.84 x 10^{-3} mol) dissolved in 1M NaOH (24 mL). The reaction mixture was stirred at 10 °C for 1h. Thereafter, BTEAC (152 mg) was added to

the reaction mixture. The solution of isophthaloyl chloride (2.27 g, 11.[22] x 10^{-3} mol) dissolved in dichloromethane (20 mL) was added in one lot to the reaction mixture and was stirred vigorously at 2000 rpm at 10 $^{\circ}$C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and precipitated into methanol:water (1:1, v/v) mixture (1000 mL). Polymer was filtered, washed with methanol and dried at 50 $^{\circ}$C under reduced pressure for two days.

5b.3.3 Click reaction of azido functionalized polyester with phenyl acetylene

To a Schlenk tube equipped with a magnetic stirring bar were placed AZ-PES-4 (0.20 g, 2.23 x 10^{-3} mmol), phenyl acetylene (0.0059 g, 5.7 x 10^{-2}), PMDETA (0.0034 g, 1.81 X 10^{-4} mol), CuBr (0.0027 g, 1.88 x 10^{-4} mol) and DMF (10 mL). The tube was degassed by three freeze-pump-thaw cycles and sealed under nitrogen atmosphere. The reaction mixture was stirred at 50 $^{\circ}$C for 24 h. After completion of the reaction time, the reaction mixture was diluted with chloroform (150 mL) and then passed through a column of neutral alumina to remove metal salts. The reaction mixture was concentrated and precipitated into methanol. The filtrate was dried under vacuum at room temperature for 12 h to obtain the modified polyester.

5b.4 Results and discussion

5b.4.1 Synthesis of aromatic polyesters containing pendent azido groups

Interfacial polycondensation of 4,4'–(5-azidopentane-2,2-diyl)diphenol with IPC or TPC or IPC:TPC (50:50, mol %) was conducted in dichloromethane/water solvent system with BTEAC as a phase transfer catalyst to obtain aromatic polyesters bearing pendent azido groups. Copolyesters were synthesized by polymerization of a mixture of 4,4'–(5-azidopentane-2,2-diyl)diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC. 4,4'-(1-Phenylethane-1,1-diyl)diphenol was chosen as the bisphenol component in order to ensure that the prepared polyesters were soluble in common organic solvents. The use of 4,4'–(5-azidopentane-2,2-diyl)diphenol was to provide azido functionalty to the polyester for further modification. In copolyester synthesis, the loading percentage of azido group was varied by adjusting the molar ratios of 4,4'–(5-azidopentane-2,2-diyl)diphenol in the feed during polymerization (**Table 5b.1**). Interfacial polycondensation was carried out at low temperature (10 $^{\circ}$C) and is particularly suitable as at that temperature the azido group is stable and there is no risk of decomposition of the monomeric units.[21]

Scheme 5b.1 illustrates synthesis of polyesters from 4,4'–(5-azidopentane-2,2-diyl) diphenol and aromatic diacid chlorides.
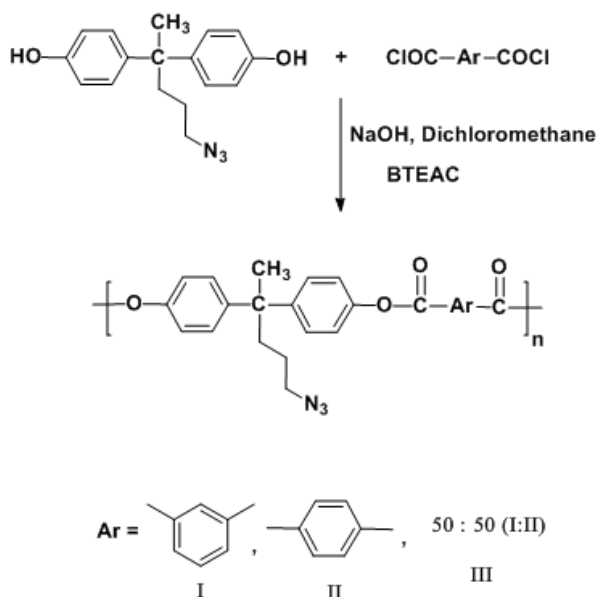
Scheme 5b.1 Synthesis of polyesters from 4,4'–(5-azidopentane-2,2-diyl)diphenol and aromatic diacid chlorides

Scheme 5b.2 illustrates synthesis of copolyesters from a mixture of 4,4'–(5-azidopentane-2, 2-diyl)diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC.

Where, m = mol of AZ-BPA

n = mol of P-BPA
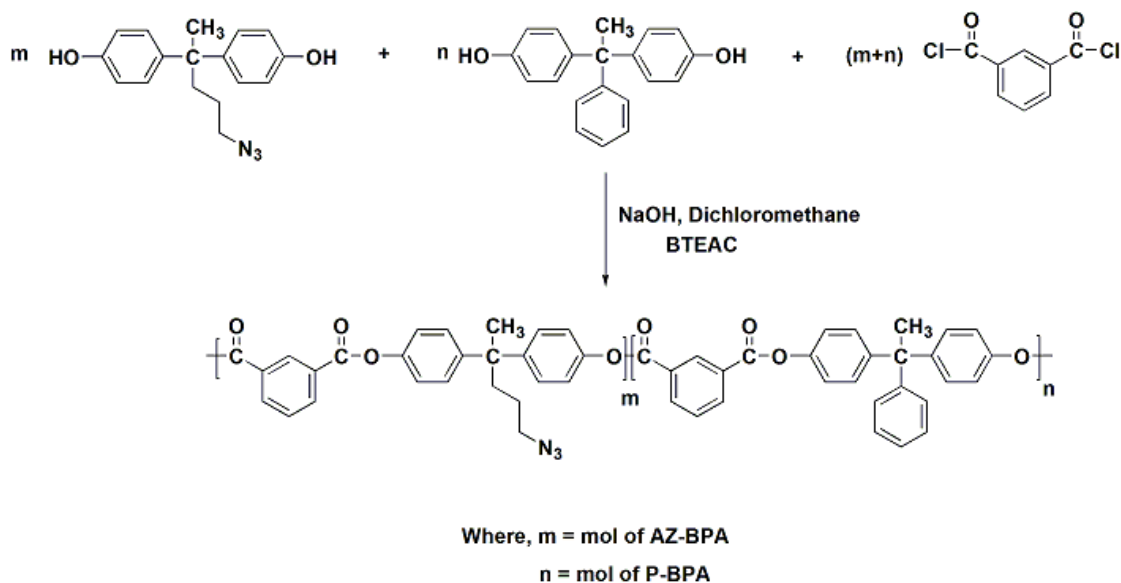
Scheme 5b.2 Synthesis of copolyesters from a mixture of 4,4'–(5-azidopentane-2, 2-diyl) diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC

Polyesters were isolated as white fibrous materials with inherent viscosities in the range 0.73-1.64 dL/g indicating formation of medium to high molecular weight polymers. Number average molecular weights (Mn) of polyesters were in the range 58,900-1,17,100 with polydispersity index in the range 1.9-2.3. Tough, transparent and flexible films of polyesters could be cast from their solutions in chloroform.

Table 5b.1 Synthesis of aromatic polyesters containing pendent azido groups

Polyester	Composition of Bisphenol (mol %)		Diacid Chloride (mol %)		η_{inh} [a] dL/g a	Molecular weight [b]		Mw/ Mn
	AZ-BPA	P-BPA	IPC	TPC		Mn	Mw	
AZPES-1	100	0	100	0	1.38	91,200	20,06,00	2.2
AZPES-2	100	0	0	100	1.25	1,17,100	2,37,400	2.0
AZPES-3	100	0	50	50	1.0	75,200	1,62,200	2.1
AZPES-4	30	70	100	0	0.73	85,500	1,57,400	1.9
AZPES-5	20	80	100	0	0.85	58,900	1,37,600	2.3
AZPES-6	10	90	100	0	1.64	1,90,400	3,67,500	2.0

a: η_{inh} of polyester was measured with 0.5 % (w/v) solution in chloroform at $30 \pm 0.1\ ^{\circ}C$.
b: Measured on GPC in chloroform; polystyrene was used as the calibration standard.
`

5b.4.2 Structural characterization

The structural characterization of polyesters was done by using FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

FT-IR spectrum of polyester derived from 4,4'–(5-azidopentane-2,2-diyl) diphenol and IPC is reproduced in **Figure 5b.1**. The appearance of characteristic absorption band at 2099 cm^{-1} for asymmetric stretching vibration of azido group indicated the incorporation of azido groups in the polyester. Ester carbonyl band of polyester appeared at 1740 cm^{-1}.
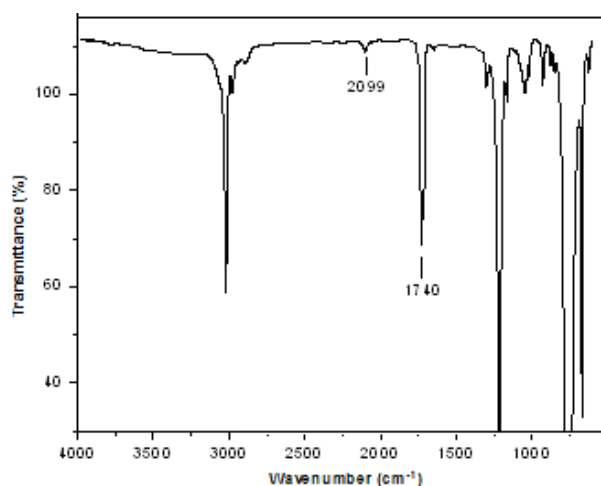
Figure 5b.1 FT-IR spectrum of polyester from 4,4'–(5-azidopentane-2,2-diyl)diphenol and IPC (AZPES-1)

A representative ^{1}H-NMR spectrum of the polyester AZPES-1 (**Table 5b.1, entry 1**) is reproduced in **Figure 5b.2.**
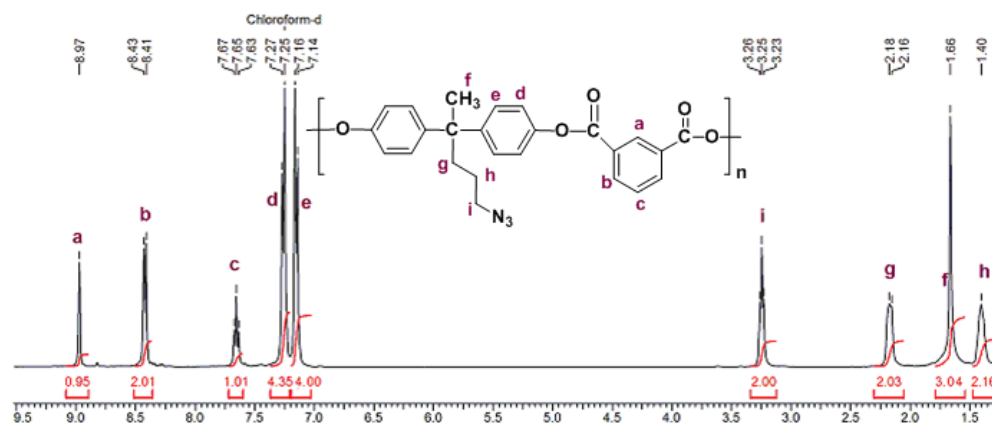
Figure 5b.2 **^{1}H-NMR spectrum (CDCl$_3$) of polyester from 4,4'–(5-azidopentane-2,2-diyl) diphenol and IPC (AZPES-1)**

The proton "a" flanked by ester carbonyl groups appeared as a singlet at 8.97 δ ppm. The protons "b" exhibited a doublet at 8.42 δ ppm. The proton "c" exhibited a triplet at 7.65 δ ppm. The doublets appeared at 7.26 and 7.15 δ ppm are due to protons "d" and "e", respectively. The triplet at 3.25 δ ppm corresponds to methylene protons "i" attached to azido group. The peaks appeared in the range 2.18-2.16 δ ppm are due to methylene protons "g". The methyl group protons "f" attached to bridge carbon exhibited a singlet at 1.66 δ ppm. The peaks appeared in the range 1.45-1.30 δ ppm are due to methylene protons "h".

^{1}H-NMR spectrum of copolyester derived from a mixture of 4,4'–(5-azidopentane-2,2-diyl)diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC is reproduced in **Figure 5b.3.**
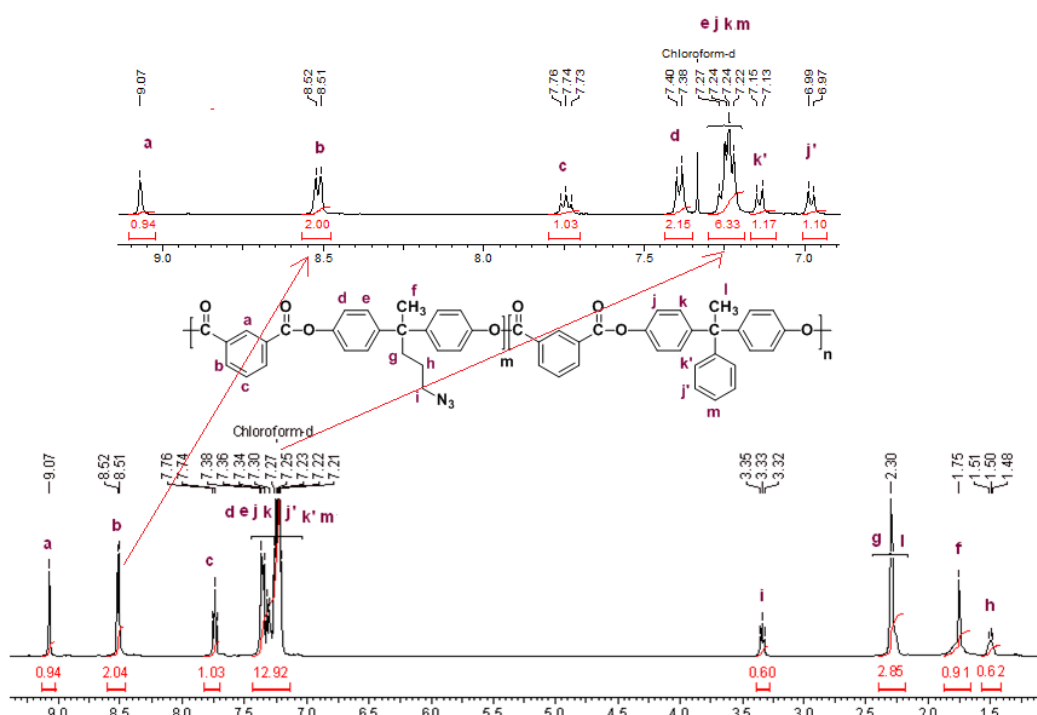
Figure 5b.3 **^{1}H-NMR spectrum (CDCl$_3$) of copolyester from a mixture of 4, 4'–(5-azidopentane-2, 2-diyl) diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC (AZPES-4)**

The proton "a" flanked by ester carbonyl groups exhibited a singlet at 9.07 δ ppm. The protons "b" appeared as a doublet at 8.52 δ ppm. The protons "j'" appeared as a doublet at 7.98 δ ppm. The proton "c" exhibited a triplet at 7.74 δ ppm. The doublet displayed at 7.39 δ ppm is due to protons d. The multiplet in the range of 7.27-7.22 δ ppm is due to protons "e", "j", "k" and "m". The doublet appeared at 7.14 δ ppm corresponds to protons "k'". The triplet at 3.33 δ ppm is due to methylene protons "i" adjacent to the azido group. The peaks of protons "g" and "l" merged together and appeared in the range 2.40-2.20 δ ppm. The methyl group protons "f" exhibited a singlet at 1.75 δ ppm. The multiplet appeared in the range 1.51-1.48 δ ppm is due to protons "h".

^{13}C-NMR spectrum of polyester obtained from 4,4'–(5-azidopentane-2,2-diyl) diphenol and IPC along with assignments of the carbon atoms is shown in **Figure 4b.4.**
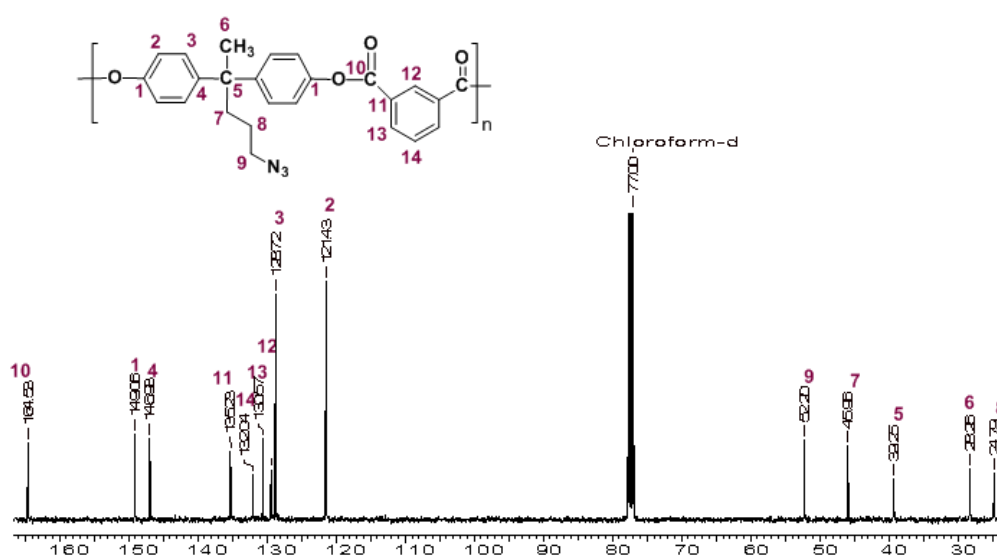
Figure 5b.4 ^{13}C NMR spectrum (CDCl$_3$) of polyester from 4,4'–(5-azidopentane-2,2-diyl) diphenol and IPC

The above characterizations confirmed the formation of polyesters with chemical structures shown in scheme **Scheme 5b.1,** and **Scheme 5b.1** that is, formation of polyesters with azido functional units.

The copolymer composition in terms of AZ-BPA and P-BPA was calculated by comparing the integration of ^{1}H NMR resonance of protons 'f' at 1.75 δ ppm (-CH$_3$ from AZ-BPA) and protons "l" at 2.30 δ ppm (CH$_3$ from P-BPA). As methyl protons "l" and methylene protons "g" attached to bridge carbon atoms merged together, the integration of "l" was determined by subtracting the corresponding integration of "g" from the total integration value at 2.30 δ ppm. As presented in **Table 5a.2**, the calculated amounts of the incorporated AZ –BPA agreed well with the feed ratios.

Table 5b.2 Copolyester composition determined from ^{1}H NMR spectra

Copolyester	Feed AZ -BPA, mol %	Observed AZ -BPA, mol %
AZPES-4	30	29
AZPES-5	20	20
AZPES-6	10	11

5b.4.3 Solubility of polyesters

Solubility of polyesters was tested in various organic solvents at 3 wt % concentration and the results are summarized in **Table 5b.3.** Polyesters were soluble in common organic solvents such as dichloromethane, chloroform, THF and aprotic polar solvents such as NMP, DMAc, etc. The reference polyesters derived from BPA with IPC **and** BPA with TPC **are** reported to be insoluble in the above mentioned solvents.[22] The improved solubility of AZPES-1 to AZPES-3 results from the presence of the azido containing alkyl side-chains which hinders close chain packing and also provides additional "handle" for interaction with solvents.

Table 5b.3 Solubility data of aromatic (co)polyesters containing pendent azido groups

Polyester	CHCl$_3$	DCM	THF	m-cresol	Pyridine	DMF	NMP	DMAc	DMSO
AZPES-1	++	++	++	++	++	++	++	++	--
AZPES-2	++	++	++	++	++	++	++	++	--
AZPES-3	++	++	++	++	++	++	++	++	--
AZPES-4	++	++	++	++	++	++	++	++	--
AZPES-5	++	++	++	++	++	++	++	++	--
AZPES-6	++	++	++	++	++	++	++	++	--

++: soluble, --: insoluble

5b.4.4 X-Ray diffraction studies

WAXD patterns of polyesters showed broad halo over the range $2\theta \approx 10\text{-}35^{o}$ in the wide angle region indicating that polyesters were amorphous (**Figure 5b.5**). The amorphous nature of polyesters AZPES-1, AZPES -2 and AZPES-3 could be attributed to the presence of pendent alkyl

chain with azido groups in the polyesters which disrupt the chain packing of polyesters. In contrast to these results, polyesters derived from BPA with TPC and BPA with IPC are reported to be partially crystalline in nature.[23] The amorphous nature of polyesters AZPES-4 to AZPES-6 could be attributed to the co-operative effect of pendent azido group containing alkyl chain and phenyl rings in distrupting the closed chain packing.
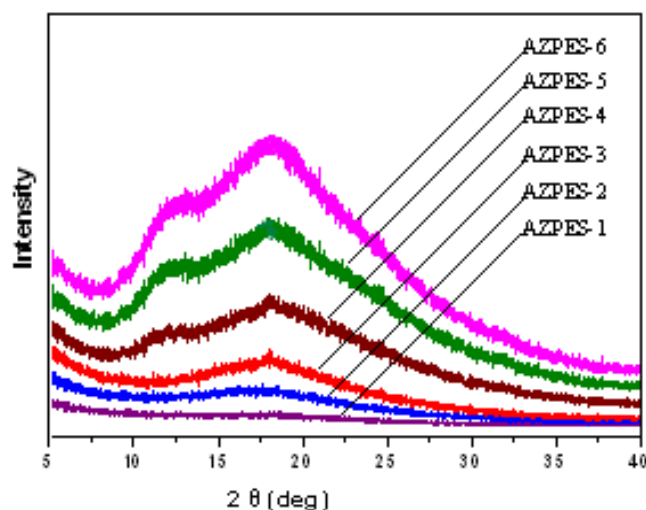
Figure 5b.5   X-Ray diffractograms of aromatic polyesters containing pendent azido groups

5b.4.5 Thermal behavior of polyesters

Thermal stability of polyesters containing pendent azido groups was studied by thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate 10 ^{o}C/min [**Figure 5b.6 (A)**]. A representative TG and differential thermogravimetric (DTG) analysis curve of AZPES-3 is reproduced in **Figure 5B.6(B).**

The thermal decomposition of polyesters containing pendent azido groups took place in three steps. The first step of the decomposition occurs in the temperature range 225–310 °C having a mass loss of around 10 %, 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 pendent azido groups. [3, 24] The second and third stage of decomposition could presumably be attributed to the cleavage of alkyl groups and breakdown of the polyester backbone.
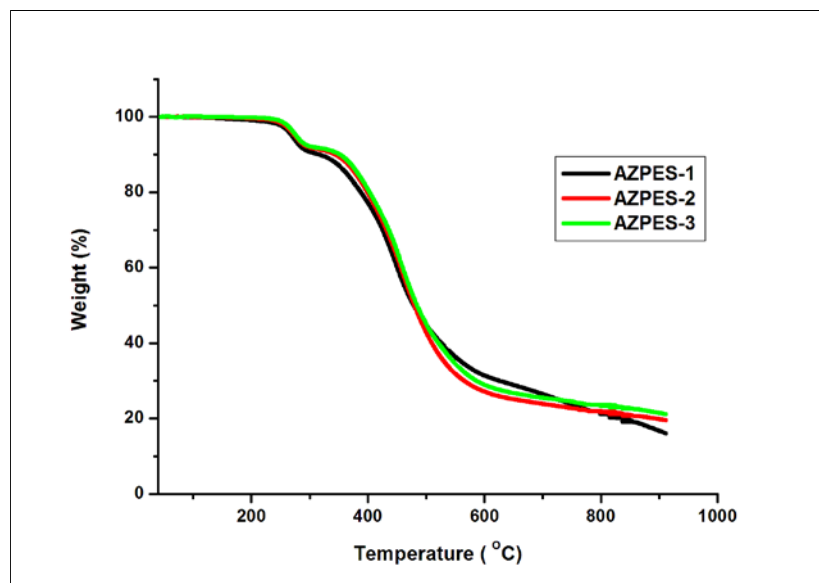
Figure 5b.6 (A) TG curves of polyesters containing pendent azido groups
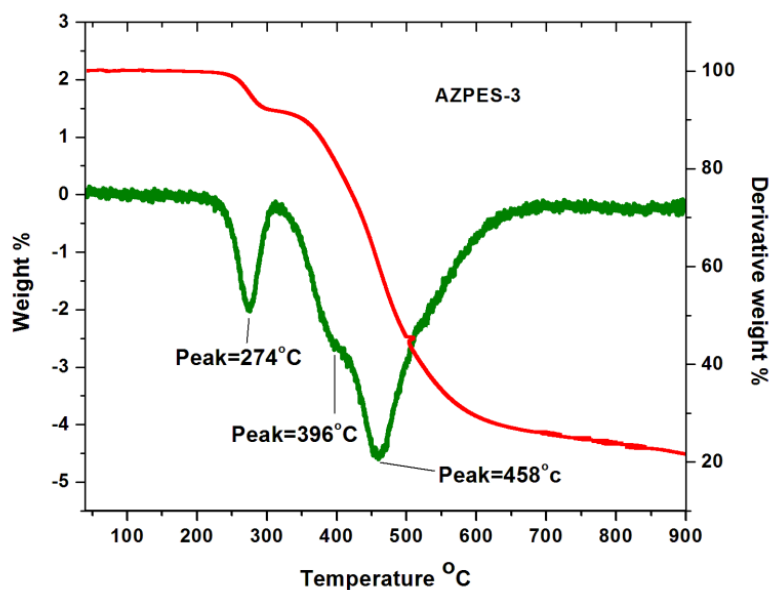
Figure 5b.6 (B) TG and DTG curves of polyester (AZPES-3) containing pendent azido groups

Glass transition temperature (Tg) values of polyesters derived from 4,4'–(5-azidopentane-2,2-diyl)diphenol with aromatic diacid chlorides were determined by DSC (**Figure 5b.7, Table 5b.4).**
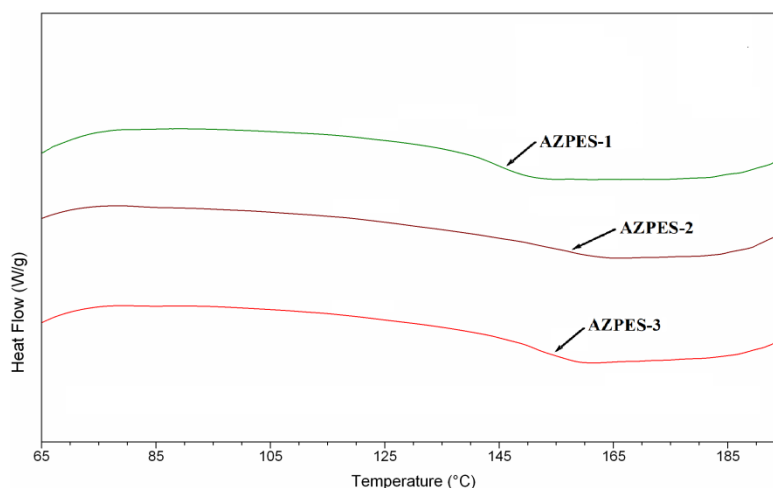
Figure 5b.7 DSC curves of polyesters containing pendent azido groups

DSC curves of polyesters AZPES-1, AZPES-2 and AZPES-3 obtained from second heating scan upto 200 ºC at a heating rate of 10 ºC / minute showed Tg at 144 ºC, 158 ºC and 151 ºC, respectively. A comparison of this data with literature Tg values of polyesters from BPA-TPC,(210 ºC) BPA-IPC (181 ºC) and BPA-TPC+IPC(197 ºC)[22] indicated that there is a drop in glass transition temperature of polyesters by the incorporation of pendent alkyl chain with azido groups. The lowering of Tg of these polyesters is ascribed to increase in backbone torsional freedom due to the presence of the pendent alkyl chain with azido groups. A similar observation has been reported for polyesters containing pendent alkyl chain with ester group based on diphenolic acid (DPA) and IPC (140- 149 °C).[25]

Table 5b.4 Tg values of aromatic polyesters containing pendent azido groups

Sr. No.	Polymer	Tg (°C) [a]
1	AZPES-1	144
2	AZPES-2	158
4	AZPES-3	151

a : Measured by DSC at a heating rate of 10 °C/min in nitrogen.

5b.5 *Functionalization of polyester containing pendent azido groups by phenyl acetylene.*

In our study, phenyl acetylene was chosen as a model compound to react with copolyester (AZPES-4) containing pendent azido groups (**Scheme 5b.3**).
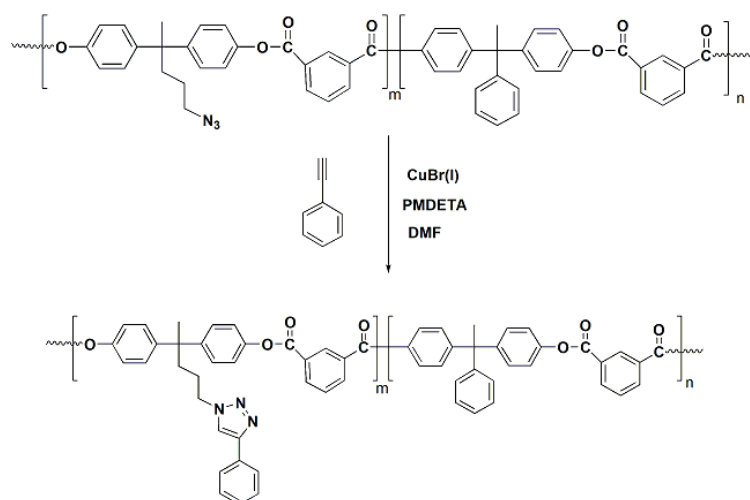
Scheme 5b.3 Azide-alkyne click reaction between aromatic polyester containg pendent azido groups and phenyl acetylene

A click reaction between AZPES-4 (1eq) and phenyl acetylene (2 eq) (**Table 5b.1**, entry 4) was performed using CuBr/PMDETA as the catalyst in DMF at 50 °C for 24 h. After passing through a neutral alumina column to remove metal salt and precipitating in methanol, the obtained clicked copolyester was characterized by ^{1}H-NMR and FT-IR spectra. ^{1}H-NMR spectra of AZPES-4 along with the modified polyester are shown in **Figure 5b.8**.
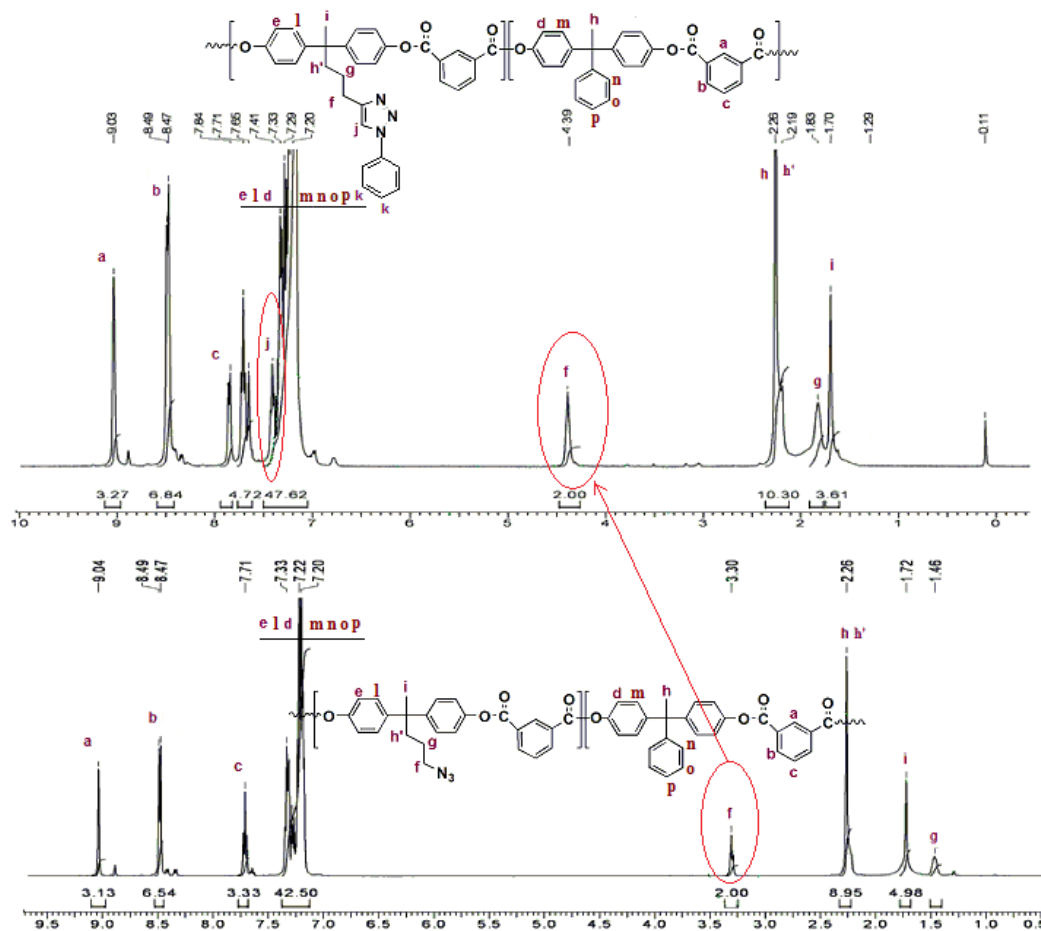
Figure 5b.8 ^{1}**H-NMR spectra (CDCl₃) of polyester containing pendent azido groups (bottom) before and (top) after functionalization**

As shown in **Figure 5b.8**, a new peak appeared at 7.41 δ ppm which could be attributed to the characteristic proton of five membered triazole ring. The peak "f" corresponding to methylene protons adjacent to azido group at 3.30 δ ppm (lower spectrum) is shifted to 4.39 δ ppm (upper spectrum) upon triazole formation, indicating click reaction has been achieved efficiently.

The success of click reaction was confirmed by FT-IR spectroscopy (**Figure 5b.9**) The disappearance of the absorption peak at 2093 cm^{-1} associated with the azido group evidenced the quantitative functionalization.
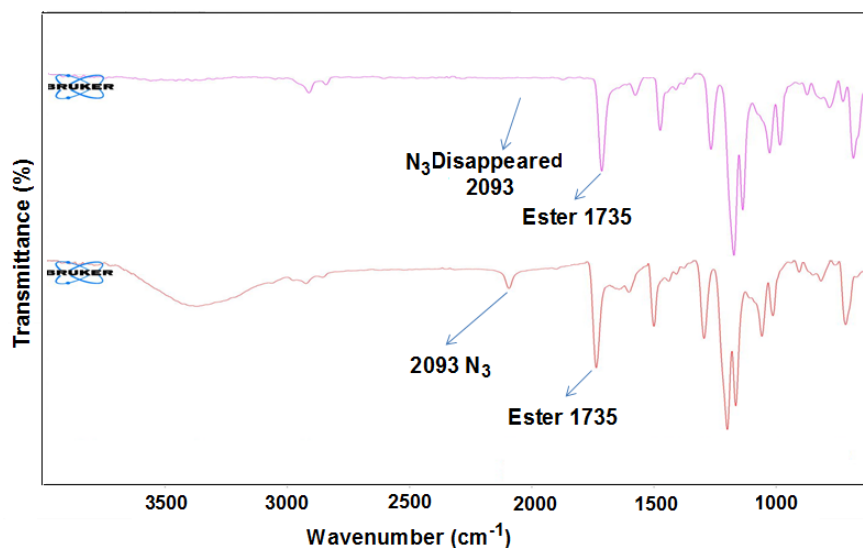
Figure 5b.9 FT-IR spectra of polyester containing pendent azido groups before (bottom) and after functionalization (top).

A myriad of functional alkynes for further modification of azido containing polymers are commercially available. For instance, glycidyl propargyl ether (Fluka), propargyl alcohol (Acros) propiolic acid (Acros), 2- methyl-1-buten-3-yne (Aldrich), trimethyl (propargyl) silane (Acros) and so on. These diverse functional alkynes could be reacted with azide side chain-functionalized polyesters *via* click reaction and a series of corresponding side chain functionalized polymers could be obtained.

5b.6 Conclusions
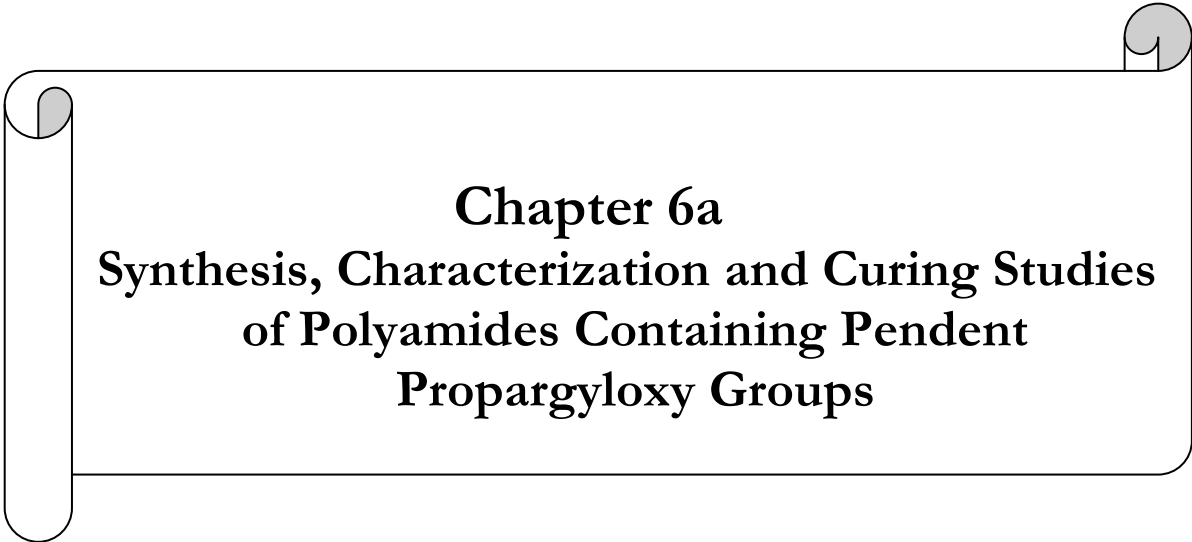
1. "Clickable" polyesters containing pendent azido groups were successfully synthesized from bisphenol containing azido functional group and 4,4'-(1-phenylethane-1,1-diyl)diphenol with aromatic diacid chlorides by interfacial polycondensation technique.

2. Polyesters were found to be soluble in chloroform, dichloromethane, pyridine, *m*-cresol, etc.

3. Tough, transparent and flexible films could be cast from solutions of polyesters in chloroform.

4. The post-functionalization of the polyester was successfully performed *via* a copper-catalyzed Huisgen 1,3-dipolar cycloaddition with phenyl acetylene. Complete conversion

of the pendent azide functionalities to triazoles was confirmed by FT-IR and ^{1}H-NMR analysis.

5. This concept of functionalization of polyester is believed to afford new class of material with easily adaptable physical properties by making use of readily accessible alkynes or polymer containing alkyne groups.

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Chapter 6a
Synthesis, Characterization and Curing Studies of Polyamides Containing Pendent Propargyloxy Groups

6a.1 Introduction

Polyamides are an important class of synthetic polymers widely used in industry as membrane materials, as tire cord in tires of automobiles, aircrafts, in circuit boards, coatings, adhesives, packaging materials, foams, and biomedical aids.[1-4] Such important applications of polyamides are possible as a result of the design of polymer properties tailored to exert distinct functions.[5-7] As polyamides are mostly prepared by step-growth polymerization between diacids or derivatives and diamines, proper combination of these components determines the unique and on-demand properties of final products.[6]

For many specific applications, polyamides should have functionalities which allow tuning of their properties. The functionalization of polyamides can be accomplished either by introducing functional groups into the monomer with further step-growth polymerization or afterwards on the end product.[6, 8] The former approach is preferred because incorporation of functional groups into monomer is experimentally more feasible. These functional groups can be used as modification sites for further post-functionalization especially by click chemistry approach.[9, 10] Thus, the combination of step-growth polymerization and click chemistry has contributed significantly to the development of aliphatic polyamides containing pendent functional groups. Except for aromatic polyamides containing pendent maleimide moieties, to the best of our knowledge there are no reports on aromatic polyamides containing the popular pendent clickable groups such as propargyloxy, azido or allyloxy.[8]

This work reports synthesis of aromatic polyamides containing pendent propargyloxy groups derived from diacid chloride *viz;* 5-(propargyloxy)isophthaloyl chloride with 4, 4'-oxydianiline. Copolyamides were synthesized by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride and 4, 4'-oxydianiline.

Polyamides were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies. Curing characteristics of polyamides containing pendent propargyloxy groups were studied using DSC in nonisothermal mode. The primary objective of the study was to synthesize clickable polyamides containing pendent propargloxy groups and hence thermal stability studies were not undertaken.

6a.2 Experimental

6a.2.1 Materials

5-(Propargyloxy)isophthaloyl chloride (P-IPC) was synthesized as described in **Chapter 3**. 4, 4'-Oxydianiline (ODA) (Aldrich) was sublimed before use. Isophthaloyl chloride (IPC) was synthesized from isophthalic acid (Aldrich) using excess thionyl chloride in the presence of N, N-dimethylformamide (DMF) as a catalyst and was purified by distillation under reduced pressure.[11] 1-methyl-2-pyrrolidinone (NMP) (S. D Fine Chemicals) was dried over calcium hydride and distilled under reduced pressure. Pyridine (Merck, India) was purified by distillation

over KOH and stored over KOH. The solvents were of reagent grade quality and were purified prior to use according to reported procedures.[12]

6a.2.2 Measurements

Inherent viscosity (η_{inh}) of polyamides was measured on 0.5 % (w/v) solution of polyamide in DMAc at 30 ± 0.1 ^{o}C using an Ubbelohde suspended level viscometer.

Solubility of aromatic polyamides was determined at 3 % (w/v) concentration in different solvents at room temperature.

Molecular weight of polyamides was measured on ThermoFinnigan make gel permeation chromatography (GPC) and a RI Detector. The eluent was DMF containing lithium bromide (LiBr) [0.1% (w/v)]. Polystyrene standard was used as the reference. Polyamide sample (5 mg) was dissolved in DMF (5 mL) and filtered through 0.45 µ filter.

FT-IR spectra of polyamides were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using DMSO-*d6* as a solvent.

X-Ray diffractograms of polyamides were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / min. Dried polymer films or powder was used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 10 ^{o}C / min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) analysis was carried out on TA instrument DSC Q10, at a heating rate of 10 °C / min in nitrogen atmosphere.

6a.3 Synthesis of polyamides containing pendent propargyloxy groups
6a.3.1 Synthesis of homopolyamide containing pendent propargyloxy groups

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirrer bar and a nitrogen inlet tube were placed 4,4'-oxydianiline (0.84 g, 4.20 x 10^{-3} mol), NMP (7 mL), pyridine (1.50 mL) and 5-(propargyloxy)isophthaloyl chloride (1.08 g, 4.20 x10^{-3} mol) solution in NMP (7 mL).The reaction mixture was stirred at room temperature for 6 h under nitrogen atmosphere. The viscous reaction mixture was poured into excess of methanol when a fibrous precipitate was obtained which was filtered and washed thoroughly with methanol. Polymer was dried at 75 °C for 12 h under vacuum.

6a.3.2 Synthesis of aromatic copolyamides containing pendent propargyloxy groups

A representative procedure for synthesis of copolyamides is described below.

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirrer bar and a nitrogen inlet tube were placed 4,4'-oxydianiline (1.5 g, 7.48 x 10^{-3} mol), NMP (11 mL), pyridine

(1.8 mL) and 5-(propargyloxy)isophthaloyl chloride (0.57 g, 2.23 x10^{-3} mol) and isophthaloyl chloride (1.05 g, 5.85 x10^{-3} mol) solution in NMP (10 mL). The reaction mixture was stirred at room temperature for 6 h under nitrogen atmosphere. The viscous reaction mixture was poured into excess of methanol when a fibrous precipitate was obtained which was filtered, washed thoroughly with methanol and hot water. Polymer was dried at 75 °C for 12 h under under vacuum.

6a.4 Curing studies of polyamides

6a.4.1 DSC analysis

DSC measurements were performed on TA Instrument (Q10) supported by TA Universal Analysis software for data acquisition. Polyamide sample (5 mg) was sealed in hermetic aluminum pans and experiments were performed under a nitrogen flow of 50 mL / min. In nonisothermal studies, polyamides were subjected to a dynamic DSC scan at the heating rate of 10 °C/min. The enthalpy of curing (ΔH_T) was determined from the area under the exothermic curve. The cure onset temperature (T_o) was considered as the intercept of slope of baseline and tangent of curve leading to peak of transition (**Figure 6a.1**).

(A)   **(B)**
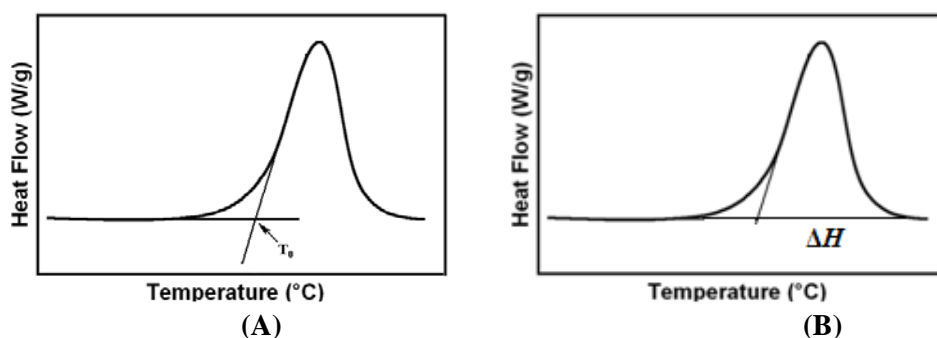
Figure 6a.1 Theoretical DSC curves illustrating (A) cure onset temperature (B) total

enthalpy of curing (ΔH)

6a.5 Results and discussion

6a.5.1 Synthesis of polyamides containing pendent propargyloxy groups.

Polyamides containing pendent propargyloxy groups were synthesized by low temperature solution polycondensation reaction of 5-(propargyloxy)isophthaloyl chloride and 4, 4'-oxydianiline in NMP as a solvent and pyridine as an acid acceptor at room temperature (**Scheme 6a.1**). Copolyamides were also synthesized by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with 4, 4'-oxydianiline (**Scheme 6a.2**). The monomer feed ratios varied from 5% to 30%. 5-(propargyloxy)isophthaloyl chloride content. 5-(Propargyloxy)isophthaloyl chloride was chosen as the diacid chloride component so that the resulting copolyamides with propargyloxy functional groups could serve as useful candidates for further post-functionalization.
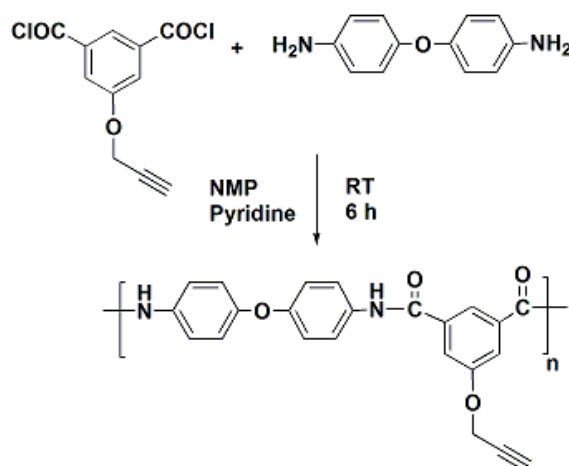
Scheme 6a.1 Synthesis of polyamide from 5-(propargyloxy)isophthaloyl chloride and ODA
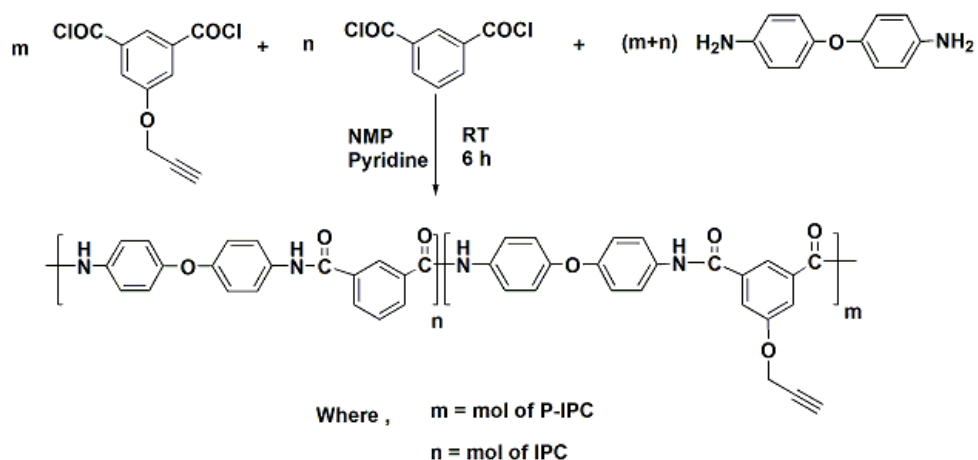
Scheme 6a.2 Synthesis of copolyamides from a mixture of 5-(propargyloxy)isophthaloyl chloride and IPC with ODA

Table **6a.1** lists the results of inherent viscosity measurements and GPC analysis of obtained polyamides.

Table 6a.1 Synthesis of aromatic (co)polyamides containing pendent propargyloxy groups

Polyamide	(Diamine) (mol %)	Diacid chloride (mol%)		η_{inh} [a] (dl/g)	Molecular weight [b]		Mw/Mn
		IPC	P- IPC		Mn	Mw	
PPA-1	ODA	00	100	0.65	1,07,500	2,68,700	2.5
PPA-2	ODA	70	30	0.73	1,15,600	2,54,300	2.2
PPA-3	ODA	80	20	1.02	1,37,300	2,87,700	2.1
PPA-4	ODA	90	10	0.65	88,700	2,04,200	2.3
PPA-5	ODA	95	5	0.52	72,400	1,59,200	2.2

a: η_{inh} of polyamides was measured with 0.5% (w/v) solution of polyamide in DMAc at 30 ±0.1°C.
b: Measured by GPC in DMF containing LiBr ; polystyrene was used as the calibration standard.

Inherent viscosity of polyamides was in the range 0.52-1.02 dl/g indicating formation of medium to high molecular weight polymers. As far as molecular characterization is concerned, polyamides PPA-1 to PPA-5 displayed Mn in the range 72,400-1,37,300 and polydispersities in the range 2.1-2.5 as determined by GPC measurements (**Table 6a.1**). Tough, transparent and flexible films of polyamides could be cast from their solutions in DMAc.

6a.5.2 Structural Characterization

Polyamides were characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

A representative FT-IR spectrum of polyamide based on 5-(propargyloxy)isophthaloyl chloride and 4, 4'-oxydianiline is shown in **Figure 6a.2**.

FT-IR spectrum of polyamide showed –NH stretching frequency as a broad band at 3286 cm^{-1}. The amide-I band, associated with stretching vibration of the carbonyl group, appeared at 1657 cm^{-1}. The amide-II band, ascribed to the coupling of the –N-H bending and –C-N stretching of -C-N-H group, appeared at 1536 cm^{-1}. The characteristic absorption band at 2129 cm^{-1} (C≡C) confirmed the incorporation of propargyl group in polyamide.
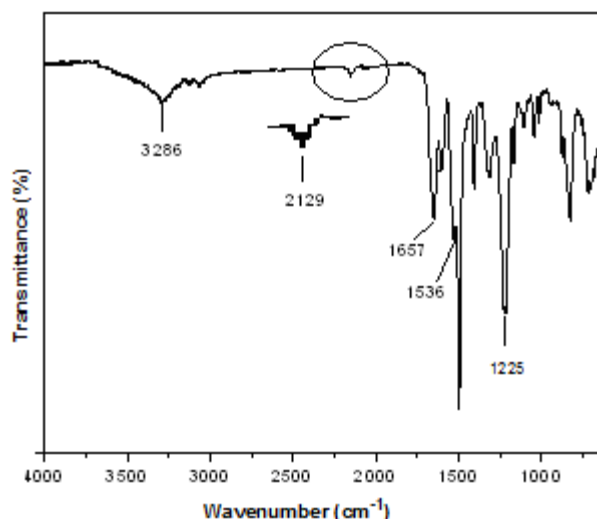
Figure 6a.2 FT-IR spectrum of polyamide (film) derived from 5-(propargyloxy)isophthaloyl chloride and ODA (PPA-1)

^{1}H-NMR spectrum of polyamide derived from 5-(propargyloxy)isophthaloyl chloride and 4, 4'-oxydianiline along with assignments is reproduced in **Figure 6a. 3.**
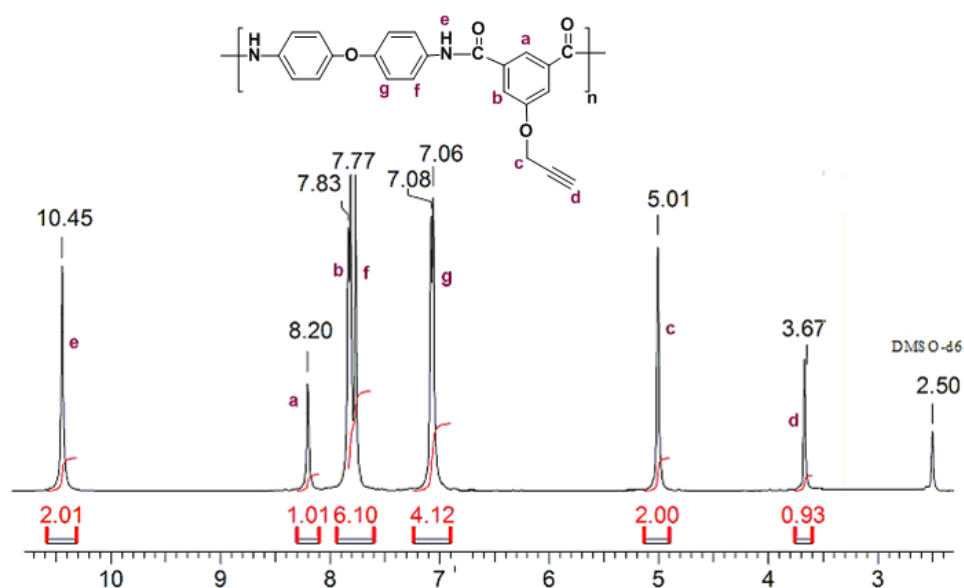
Figure 6a.3 ^{1}H-NMR spectrum (DMSO-d$_6$) of polyamide from 5-(propargyloxy)isophthaloyl chloride and ODA (PPA-1)

The peak appeared at 10.45 δ ppm is due to –NH of amide group. The proton "a" exhibited a singlet at 8.20 δ ppm. The peaks displayed in the range of 7.83-7.77 δ ppm are due to protons "b" and "f". The aromatic protons "g" exhibited a doublet at 7.07 δ ppm. The peak appeared at 5.01 δ ppm is due to methylene protons "c". The triplet appeared at 3.67 δ ppm due to proton "d" of propargyl group.

^{1}H-NMR spectrum of copolyamide derived from a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with 4, 4'-oxydianiline along with assignments is shown in **Figure 6a.4.**
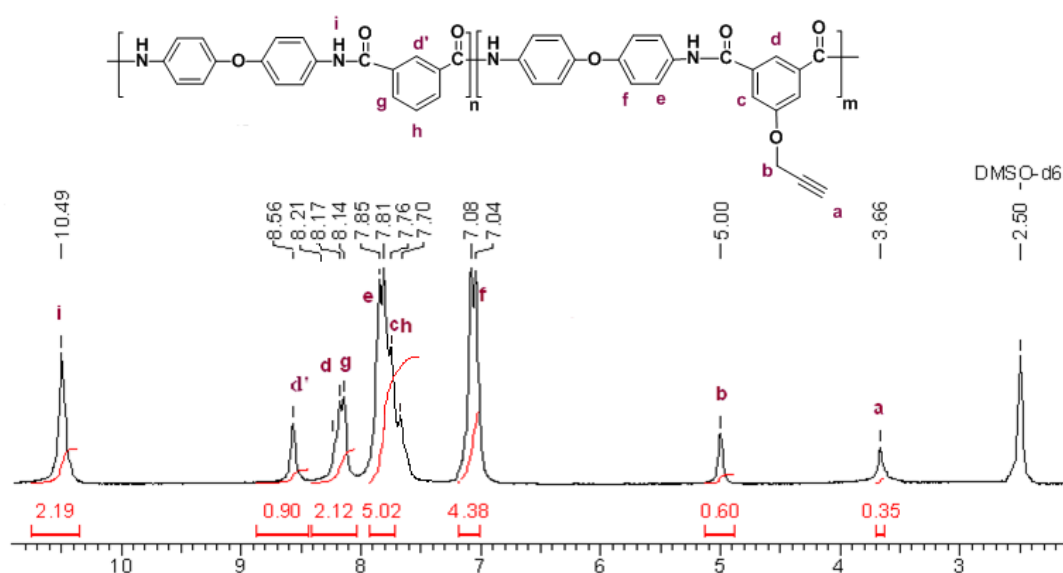
Figure 6a.4 ^{1}H NMR spectrum (DMSO-d$_6$) of copolyamide from a mixture of 5-(propargyloxy)isophthaloyl chloride and IPC with ODA (PPA-2)

The peak appeared at 10.49 δ ppm is due –NH of amide group. The aromatic proton "d'" flanked by amide carbonyls exhibited a singlet at 8.56 δ ppm. The peaks displayed in the range

8.21-8.14 δ ppm are due to protons "d" and "g". The peaks appeared in the range 7.85-7.70 are due to protons "e", "c" and "h". The protons "f" exhibited a doublet at 7.06 δ ppm. The peak displayed at 5.0 δ ppm is due to methylene protons "b". The triplet appeared at 3.66 δ ppm is due to proton "a" of propargyl group.

The compositions of copolyamides were determined by ^{1}H-NMR spectroscopy. For determination of composition, integration of the signal "b" at 5.0 δ ppm (C≡C-CH_2-) from P-IPC was compared with the integration of signal "d'" at 8.56 ppm from IPC. As presented in **Table 6a.2**, composition calculated by ^{1}H-NMR spectra was in excellent agreement with the feed values.

Table 6a.2 Copolyamide composition determined from ^{1}H NMR spectra

Copolyamide	Feed P-IPC, mol %	Observed P-IPC, mol %
PPA-2	30	30
PPA-3	20	21
PPA-4	10	10
PPA-5	5	6

^{13}C-NMR spectrum of polyamide obtained from 5-(propargyloxy)isophthaloyl chloride and 4, 4'-oxydianiline along with assignments of the carbon atoms is shown in **Figure 6a.5**.
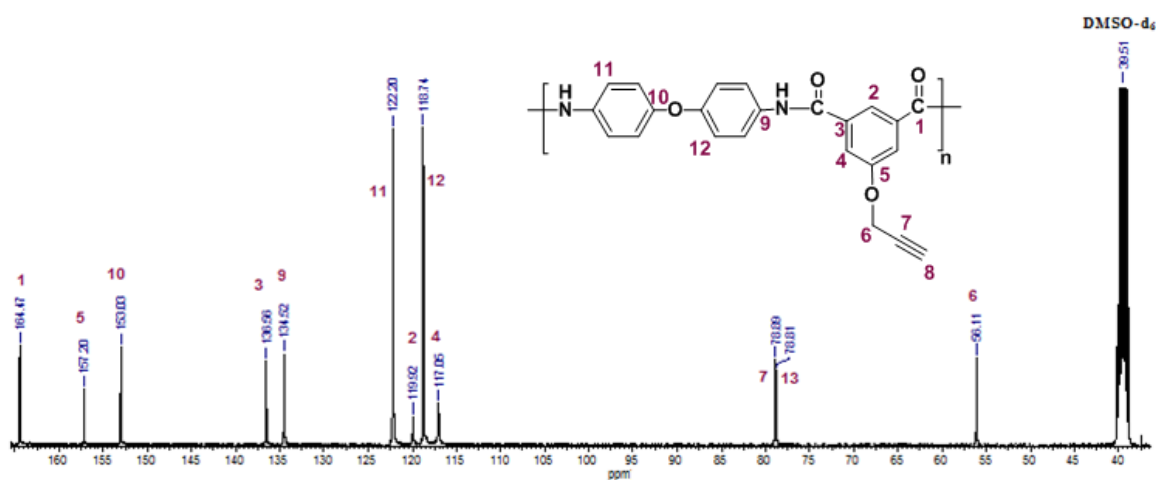
Figure 6a.5 ^{13}C-NMR spectrum (DMSO-d_6) of polyamide from 5-(propargyloxy)isophthaloyl chloride and ODA

6a.5.3 Solubility of polyamides

Solubility of polyamides was tested in various organic solvents at 3 wt % (w/v) concentration and the data is summarized in **Table 6a.3**.

Table 6a.3: Solubility data of polyamides containing pendent propargyloxy groups

Polyamide	IPC mol %	P-IPC mol %	ODA mol %	CHCl₃	THF	DMF	DMAc	NMP	Pyridine	DMSO
PPA-1	00	100	100	--	--	++	++	++	++	++
PPA-2	70	30	100	--	--	++	++	++	++	++
PPA-3	80	20	100	--	--	++	++	++	++	++
PPA-4	90	10	100	--	--	++	++	++	++	++
PPA-5	95	5	100	--	--	++	++	++	++	++
*PPA-Ref1	100	00	100	--	--	--	++	++	--	--

++ : soluble, -- : insoluble, *PPA-Ref1: Polyamide derived from ODA with IPC, data taken from reference [13]

Polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and DMSO at room temperature and did not dissolve in chloroform and THF. It is reported that polyamide derived from ODA with IPC is soluble in DMAc and NMP but not soluble in DMF, pyridine and DMSO at room temperature.[13] These results indicated that incorporation of pendent propargyloxy groups contributed to improvement in solubility characteristics due to disruption of the closed chain packing.

6a.5.4 X-Ray diffraction studies

Wide-angle X-ray diffraction (WAXD) patterns of polyamides containing pendent propargyloxy groups are shown in **Figure 6a.6 (A).** Polyamides exhibited a broad halo over the range 2θ ≈10-35°, indicating their amorphous nature. In contrast of this, polyamide derived from ODA with IPC (PPA-Ref1) is reported to be partially crystalline in nature [**Figure 6a.6 (B)**].[14] Apparently, the introduction of pendent propargyloxy groups in polyamide interfere with the dense chain packing, thus resulting in their amorphous nature.

(A)   **(B)**
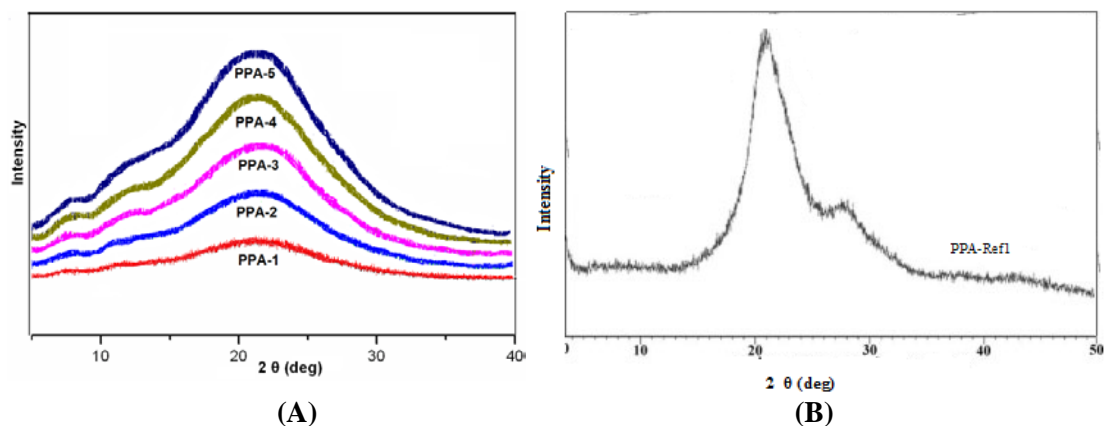
Figure 6a.6 X-Ray diffractograms of (A) aromatic polyamides containing pendent
propargyloxy groups (B) aromatic polyamide derived from ODA with IPC
(X-Ray diffractogram of PPA-Ref1 was taken from reference 14)

6 a.5.5 Thermal properties of polyamides

To determine Tg by DSC analysis, polyamides were heated from 50 °C to 210 °C at a heating rate of 10 °C/minute. In DSC analysis, temperature was limited to 210 °C as propargyloxy groups present in the polymers are reported to undergo crosslinking reaction in the temperature range 220-350 °C. In DSC scans, polyamides exhibited a featureless trace up to a temperature of 210 °C and there was no evidence of glass transition in all the polyamides upto a temperature of 210 °C. It is reasonable to presume that Tg values of these polyamides are above 210 °C based on the Tg value (280 °C) of the reference polyamide derived from 4, 4'-oxydianiline with isophthaloyl chloride.[5]

6a.6 Non-isothermal curing studies of polyamides

Nair et.al[15] studied the cure characteristics of bispropargyl ethers in catalyzed and uncatalyzed nonisothermal mode. The authors reported that in uncatalyzed conditions, both the Claisen rearrangement and the subsequent curing reaction (**Scheme 4a.3, Chapter 4a**) occur within a single exotherm in the range 200-350 °C.

In the present case, the cure characteristics of polyamides containing pendent propargyloxy groups were studied in uncatalyzed conditions in nonisothermal mode using DSC. The representative DSC curves of PPA-1 (**Figure 6a.7**) exhibited an exothermic peak maximum at 275 °C during the first DSC heating scan. It was observed that the cure onset was 220 °C and reaches to completion around 320 °C with the total heat of cure reaction of 278 kJ/mol. This irreversible peak can be accounted for the crosslinking reaction.
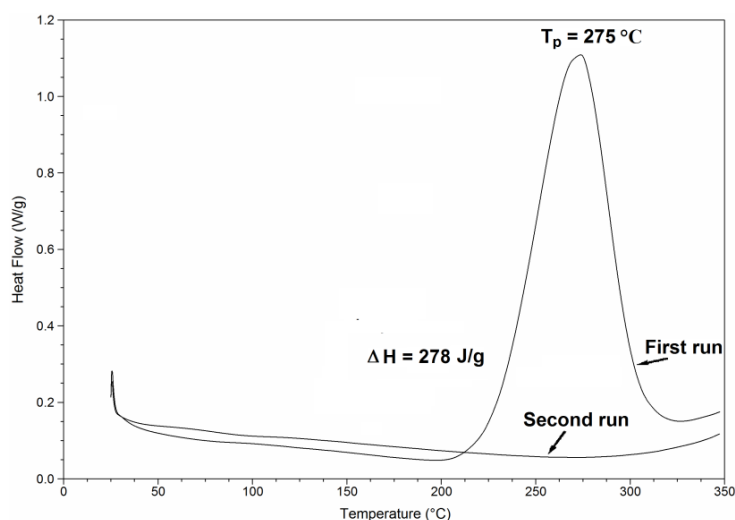
Figure 6a.7   DSC curves of polyamide (PPA-1) containing pendent propargyloxy groups. (first run) scanned from 50 – 350 °C @ 10 °C/min, (second run) rescanned from 50 – 350 °C @ 10 °C/min

DSC curves of polyamides containing propargyloxy groups are reproduced in **Figure 6a.8**. The data regarding cure onset temperature (T_o),cure   peak temperature (T_p) and cure final temperature (T_f) of uncatalyzed curing from DSC curves for PPA-1 to PPA-5 are collected in **Table 6a.4.**
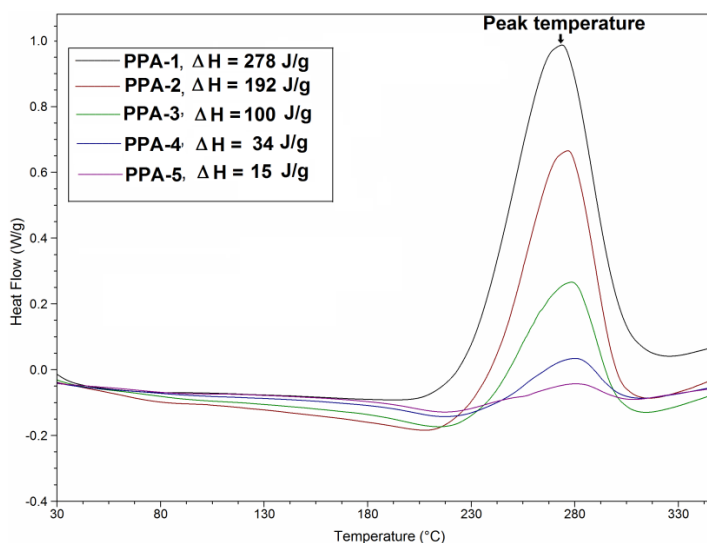
Figure 6a.8 DSC curves of polyamides (PPA-1 to PPA-5) containing pendent propargyloxy groups

Table 6a.4 Cure characteristics of polyamides containing pendent propargyloxy groups

Sr.No.	Polyamides	T_0 (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
1	PPA-1	220	275	320	278
2	PPA-2	220	275	315	192
3	PPA-3	220	280	315	100
4	PPA-4	220	280	315	34
5	PPA-5	220	280	315	15

T_o – Cure onset temperature, T_p – Cure peak temperature, T_f – Final cure temperature,
ΔH – Enthalpy of curing

The cure reactions of all the propargyloxy containing polyamides occurred in the temperature range 220-320 °C which indicates their similar cure behavior. ΔH was in the range of 15-278 J/g. ΔH values increased as the composition of P-IPC content was increased. This could be attributed to the increase in crosslinked density with increase in the propargyloxy groups content.
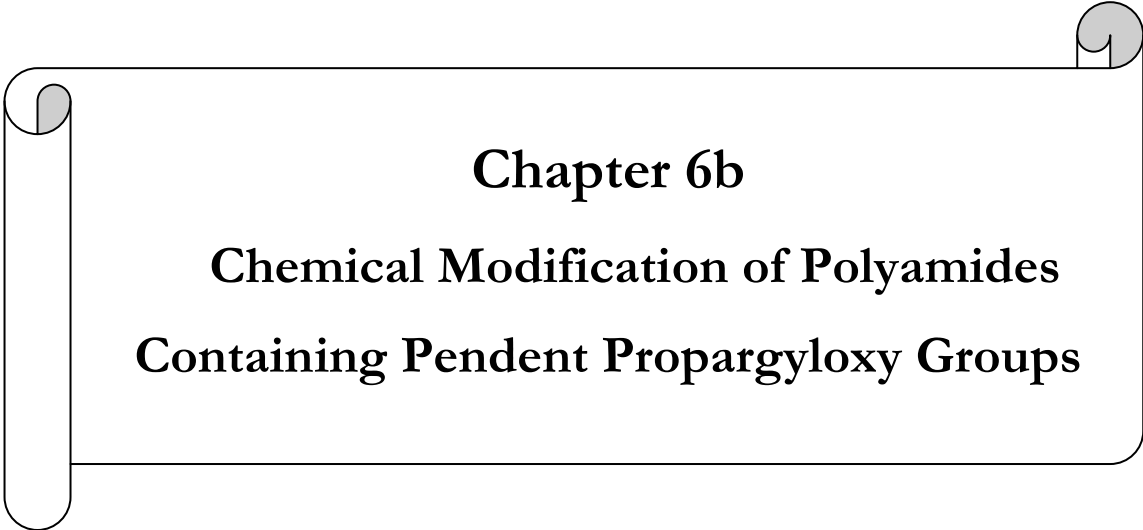
6a.7 Conclusions

1. A new clickable polyamide containing pendent propargyloxy groups was synthesized by polycondensation of 5-(propargyloxy)isophthaloyl chloride and 4, 4'-oxydianiline. A series of clickable copolyamides were also synthesized from a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with 4, 4'-oxydianiline.

2. Polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and DMSO. Tough, transparent and flexible films of polyamides could be cast from DMAc solution.

3. The curing of polyamides occurred in the temperature range 220–320 °C. The percentage incorporation of propargyloxy functionalities into the polyamides did not influence the cure onset and the cure peak temperature during the thermal curing process.

4. The heat of cure reaction of polyamides was observed in the range 15 – 278 J/g . Increase in ΔH was observed with increase in the content of propargyloxy functional groups into the polyamides.

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Chapter 6b

Chemical Modification of Polyamides

Containing Pendent Propargyloxy Groups

6b.1 Introduction

The azide-alkyne click reaction has recently been exploited as a useful protocol for functionalization of polymers such as polyurethanes, aliphatic polyamides, aliphatic polycarbonates, aliphatic polyesters, etc.[1-12] However, functionalization of aromatic polyamides by azide-alkyne click chemistry approach has not been studied.[2, 13-15]

The post-functionalization approach is demonstrated herein for polyamides containing pendent propargyloxy groups (PPA-2), synthesized in **chapter 6a**) by azide - alkyne click reaction using azides *viz;* 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, $PEG_{550}-N_3$, $PEG_{1000}-N_3$).

The efficiency of the post-functionalization of polyamide by click reaction was confirmed by FT-IR and ^{1}H-NMR spectroscopy. Polyamide modified by1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene were further characterized by UV-Vis, and fluorescence spectroscopy techniques while polyamides obtained by grafting with azido-terminated polyethylene glycol monomethyl ether were characterized by contact angle measurements, polarized optical microscopy (POM) and scanning electron microscopic (SEM) techniques.

6b.2 Experimental

6b.2.1 Materials

Polyamide containing pendent propargyloxy groups (PPA-2) was synthesized as described in **Chapter 6a.** 1-(4-Azidobutyl)pyrene (PY-N_3), 9-(azidomethyl)anthracene (An-N_3) and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, $PEG_{550}-N_3$, $PEG_{1000}-N_3$) were synthesized as described in **Chapter 4 b.**[16] N, N-Dimethylformamide (DMF) was of reagent grade and was distilled prior to use as per literature procedure.[17] Copper sulphate and sodium ascorbate (Loba Chemie) were used as received. Other solvents were purified according to standard procedures. [18]

6b.2.2 Measurements

FT-IR spectra were recorded using polyamide films on a Perkin-Elmer 883 spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrophotometer at resonance frequency of 400 MHz using using DMSO-d_6 as a solvent.

Contact angle measurements were carried out on GBX Contact angle meter by sessile drop method. A 5 wt. % solution of the respective polymers were drop-cast onto a glass slit. Water was used as the wetting liquid.

Ultraviolet–Visible (UV–Vis) spectra of polyamide solutions in DMF were recorded on Perkin-Elmer Lambda 950 UV/Vis Spectrometer.

Fluorescence measurements of polyamide solutions in DMF were carried out using a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Polarized optical microscopy images of polymer surface morphology of the polyamide was determined by optical photography using an image analyzing system consisting of a microscope (XSZ single zoom microscope), a CCD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro-Plus.

The surface morphology of polyamides was observed with a scanning electron microscope at 15 kV (SEM, JEOL JSM-5410LV).

6b.3 Functionalization of polyamides containing pendent propargyloxy groups with 1-(4-azidobutyl)pyrene

A representative procedure for click reaction between copolyamide (PPA-2) and 1-(4-azidobutyl)-pyrene is described below.

To a Schlenk tube equipped with a magnetic strirring bar were added PPA-2 (1 eq), 1-(4-azido-butyl)pyrene (3 eq), copper sulphate (0.05 eq), sodium ascorbate (0.1 eq) and DMF (10 mL). The tube was degassed by three times freeze-pump-thaw cycles then sealed under vacuum. The reaction mixture was stirred at 60 ºC for 24 h. The reaction mixture was diluted with DMF (200 mL) and then passed through a column of neutral alumina to remove metal salt. The solution was concentrated and precipitated into methanol to remove the remaining catalyst and excess of the azide and then dried under vacuum at room temperature for 12 h for further characterizations.

6 b.4 Results and discussion

6b.4.1 Functionalization of polyamides containing pendent propargyloxy groups with azides

The copper catalyzed ($CuSO_4/Na_{asc}$) alkyne-azide click reaction (CuAAC) was applied to synthesize post-functionalized polyamides by reaction between polyamide containing pendent pendent propargyloxy groups (PPA-2, **chapter 6a**, entry 2) with azides *viz*., $PEG_{550}-N_3$, PEG_{1000}-N_3, $PY-N_3$ and $An-N_3$ in DMF solvent at 60 °C for 24 h. After passing through neutral alumina to remove metal salt and precipitating in methanol, the obtained functionalized polyamides were characterized.

Scheme 6b.1 illustrates functionalization of polyamide *via* azide-alkyne click reaction. 1-(4-Azidobutyl)pyrene and 9-(azidomethyl)anthracene were selected as the azide precursors for chemical modification to introduce photophysical properties to the polyamide where as azido-terminated polyethylene glycol monomethyl ether was chosen as the azide precursors to tune the specific surface properties of the polyamide.
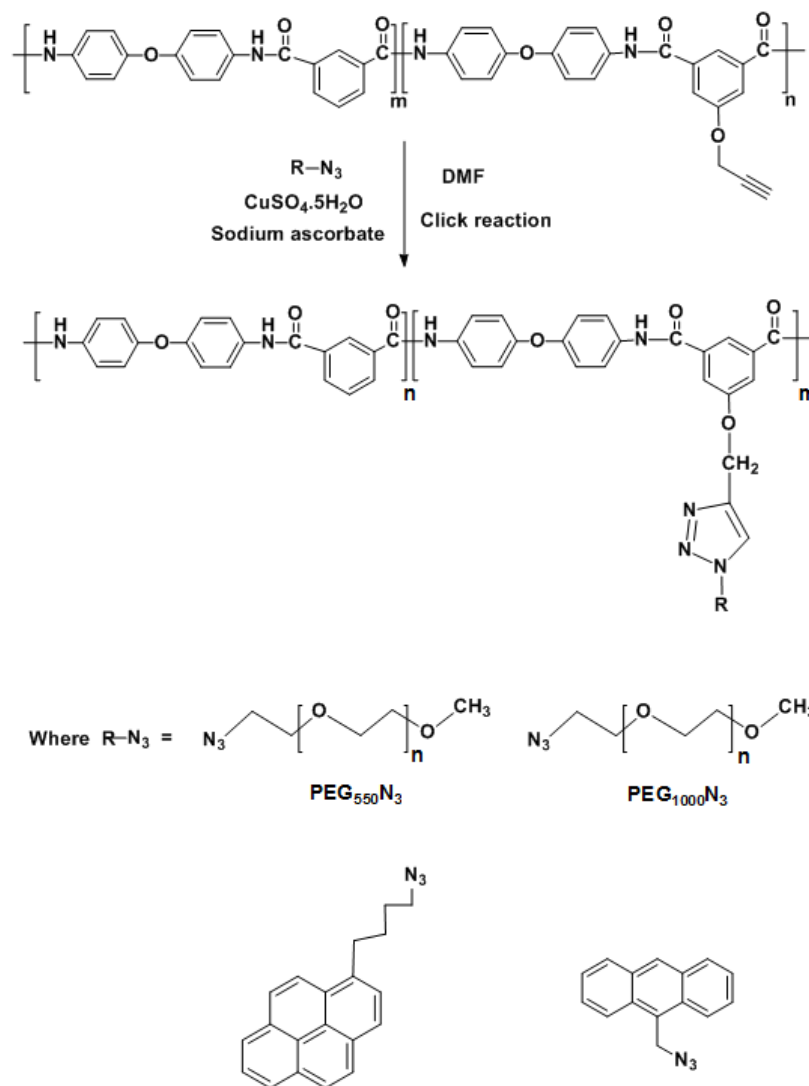
Scheme 6b.1 The general scheme of copper-catalyzed azide-alkyne click reaction between polyamide containing pendent propargyloxy groups and azides

6b.4.1.1 Functionalization of polyamide with PEG-N$_3$ via azide-alkyne click reaction

6b.4.1.1.1 Structural characterization

Polyamides functionalized with PEG (PPA-PEG$_{550}$, PPA-PEG$_{1000}$) were characterized by FT-IR, ^{1}H-NMR spectroscopy, contact angle measurements, polarized optical microscopy and SEM.

FT-IR spectra of the functionalized polyamide (PPA-PEG$_{550}$) along with PEG$_{550}$-N$_3$ and parent polyamide (PPA-2) are shown in **Figure 6b.1**. The absorption peak at 2129 cm^{-1} (C≡C) ascribed to propargyl group completely disappeared after click reaction indicating quantitative click reaction.
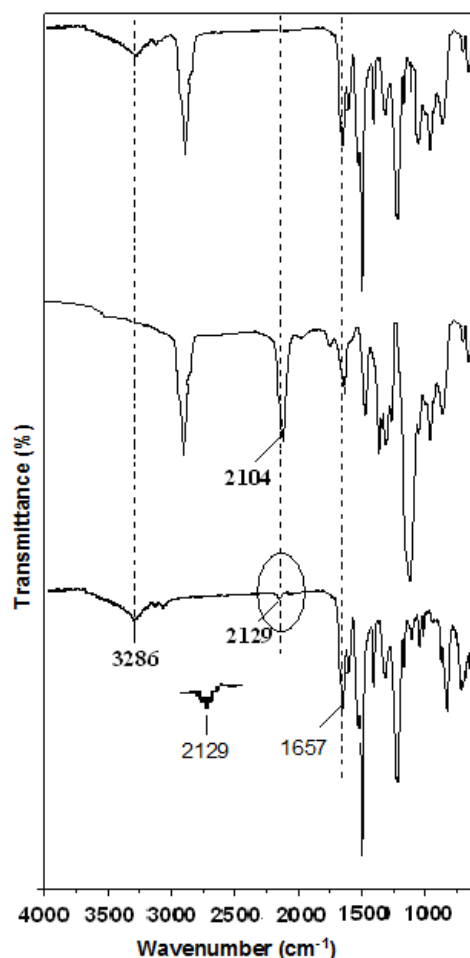
Figure 6b.1 FTIR spectrum of (lower) PPA-2 (middle) PEG$_{550}$ –N$_3$ (upper) PPA-PEG$_{550}$

^{1}H-NMR spectra of the parent polyamide (PPA-2) along with the polyamide functionalized with PEG$_{550}$-N$_3$ are reproduced in **Figure 6b.2.** Success of the click reaction was confirmed by the complete disappearance of the signal at 3.66 δ ppm from propargyl groups and the appearance of a new proton signal originating from the formed triazole ring at 8.25 δ ppm. The shifting of methylene protons of propargyl from 5.0 δ ppm to 5.34 δ ppm also confirmed the quantitative azide-alkyne click reaction. Further, new peaks ascribed to PEG chain appeared at 4.56 δppm, 3.82 δ ppm, 3.46-3.35 δ ppm and 3.21 δ ppm.
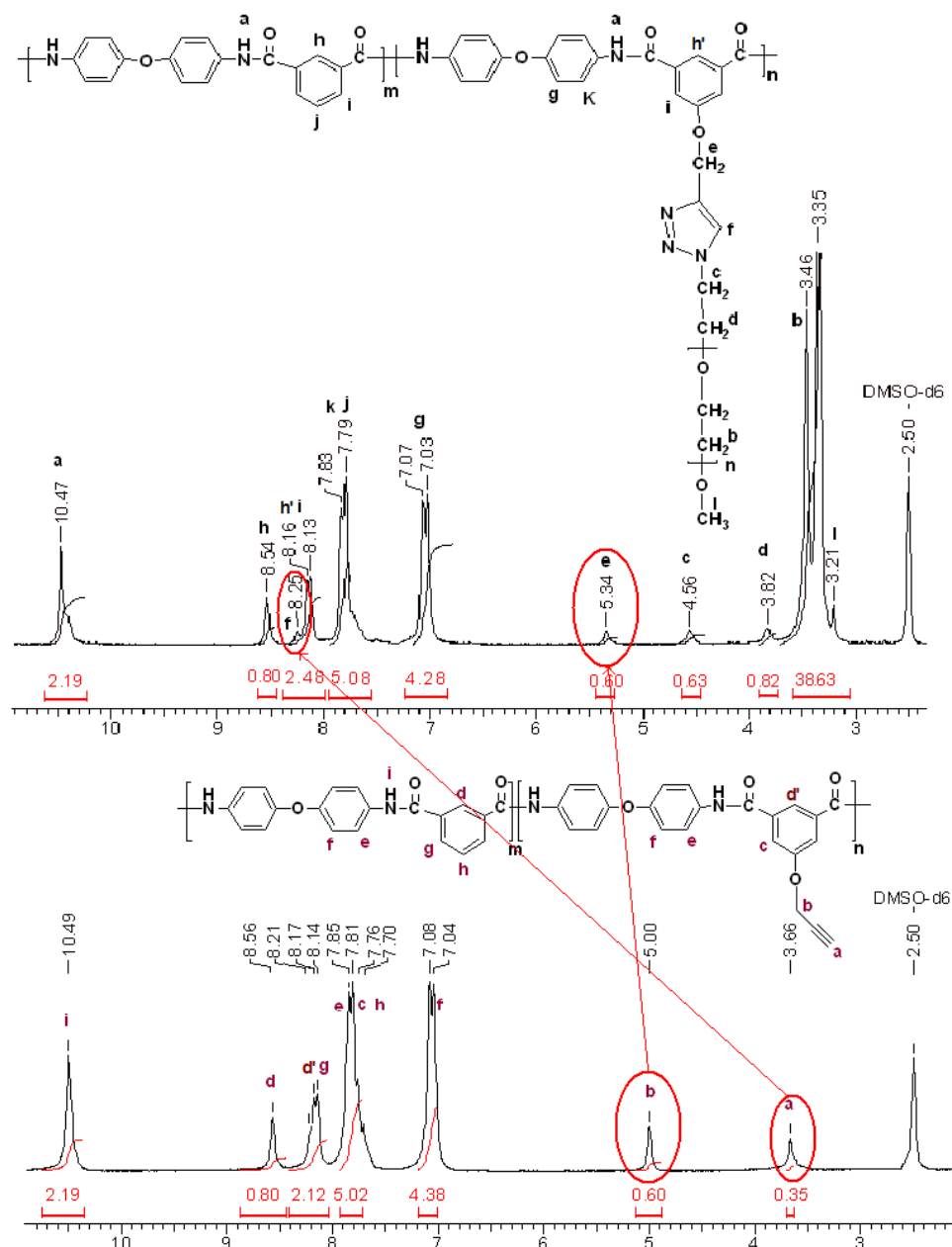
Figure 6b.2 ^{1}H-NMR spectra (DMSO-d$_6$) of (bottom) PPA-2 (top) PPA-PEG$_{550}$

A similar observation was drawn from the click reaction between polyamide containing pendent propargyloxy groups (PES-2) and PEG$_{1000}$-N$_3$. The complete disappearance of FT-IR absorption peak at 2120 cm^{-1} (C≡C) and 3300 (≡CH) ascribed to propargyl group confirmed the successful click reaction (spectrum not shown) which is further supported by ^{1}H-NMR spectroscopy where the complete disappearance of signal at 3.66 δ ppm from propargyl groups and the appearance of a new proton signal originating from the formed triazole ring at 8.25 δ ppm confirmed the quantitative click reaction (spectra not shown).

6b.4.1.1.2 Contact angle measurement

Water contact angle measurements were performed on drop-cast films of polyamide grafted with PEG_{550}-N_3 to evaluate the hydrophilicity of the polyamide before and after grafting**.** Contact angle images of PPA-2 and PEG_{550} grafted PPA-2 are shown in **Figure 6b.3**. Contact angle of grafted polyamide was lower (44°) than that parent polyamide (82°), possibly due to better spatial arrangement of the hydrophilic PEG moiety to the polyamide surface which increases its hydrophilicity.

Figure 6b.3 Water droplet on polyamide PPA-2 (a) before and (b) after PEG_{550} grafting

Surface morphology of parent polyamide and PEG grafted polyamide films were examined by polarized optical microscopy and SEM analysis (**Figure 6b.4** and **Figure 6b.5**). The results showed that PEG_{550} grafted polyamide has smoother surface than the parent polyamide. The explanation to these differences (between **Figure 6b.4** and **Figure 6b.5)** could be attributed to the individual capabilities for adopting different conformations and molecular packing.

(a)   (b)
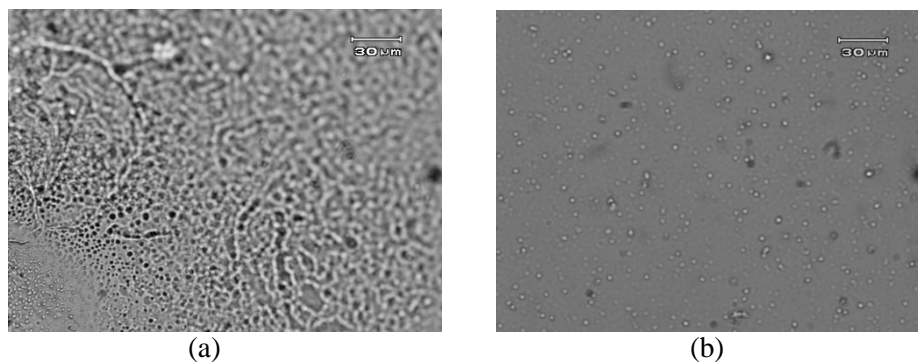
Figure 6b.4 Polarized optical microscopy images of polyamide (a) before and (b) after PEG_{550}-N_3 functionalization

(a)   (b)
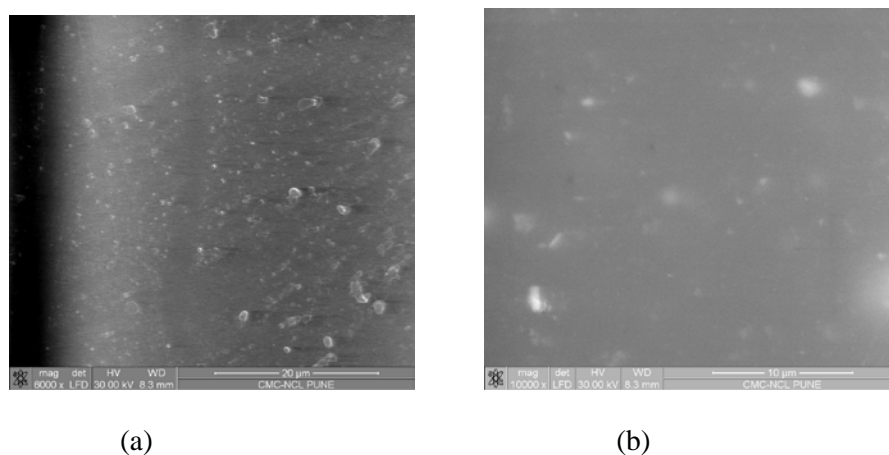
Figure 6b.5   SEM micrographs of polyamide (a) before and (b) after PEG_{550}-N_3 functionalization

6b.4.1.2 Polyamide functionalized with 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene via click reaction

6b.4.1.2.1 Structural characterization

The efficiency of the click reaction between polyamide containing pendent propargyloxy groups and PY-N_3 or An-N_3 was confirmed by FT-IR, ^{1}H-NMR spectroscopy, UV-Vis, and fluorescence spectroscopy techniques.

FT-IR spectra of 1-(4-azidobutyl)pyrene grafted polyamide *via* azide-alkyne click reaction are reproduced in **Figure 6b.6**. The complete disappearance of C≡C absorption peak at 2129 cm^{-1} was observed after the click reaction which confirmed the quantitative click reaction.
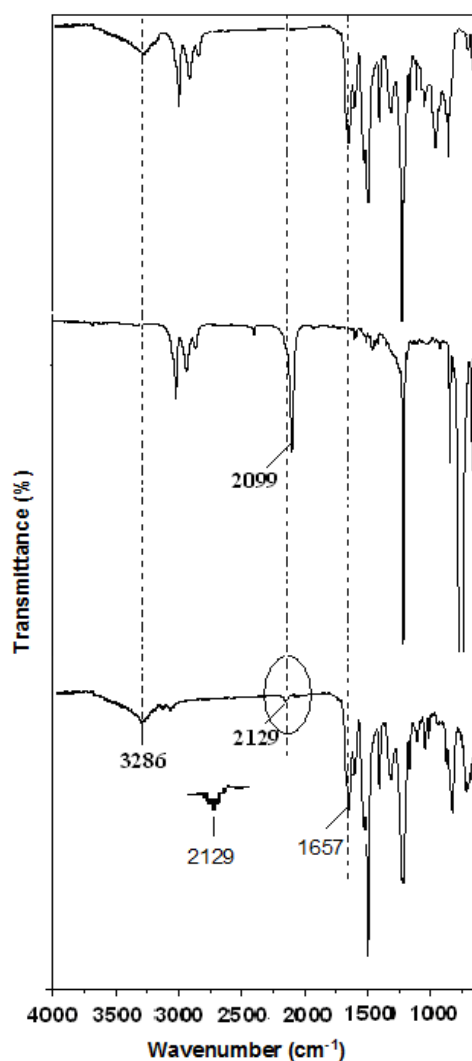
Figure 6b.6 FT-IR spectra of functionalized polyamide *via* azide-alkyne click reaction (Lower) PPA-2, (middle) PY –N_3, (upper) PPA-2 functionalized with PY –N_3 (PPA-2-PY)

Similarly in 9-(azidomethyl)anthracene grafted polyamide the complete disappearance of C≡C absorption peak at 2129 cm^{-1} confirmed the success of the click reaction (spectra not shown)

Click recation between polyamide containing pendent propargyloxy groups and PY-N_3 and An-N_3 was further supported by ^{1}H-NMR spectra (**Figure 6b.7**)
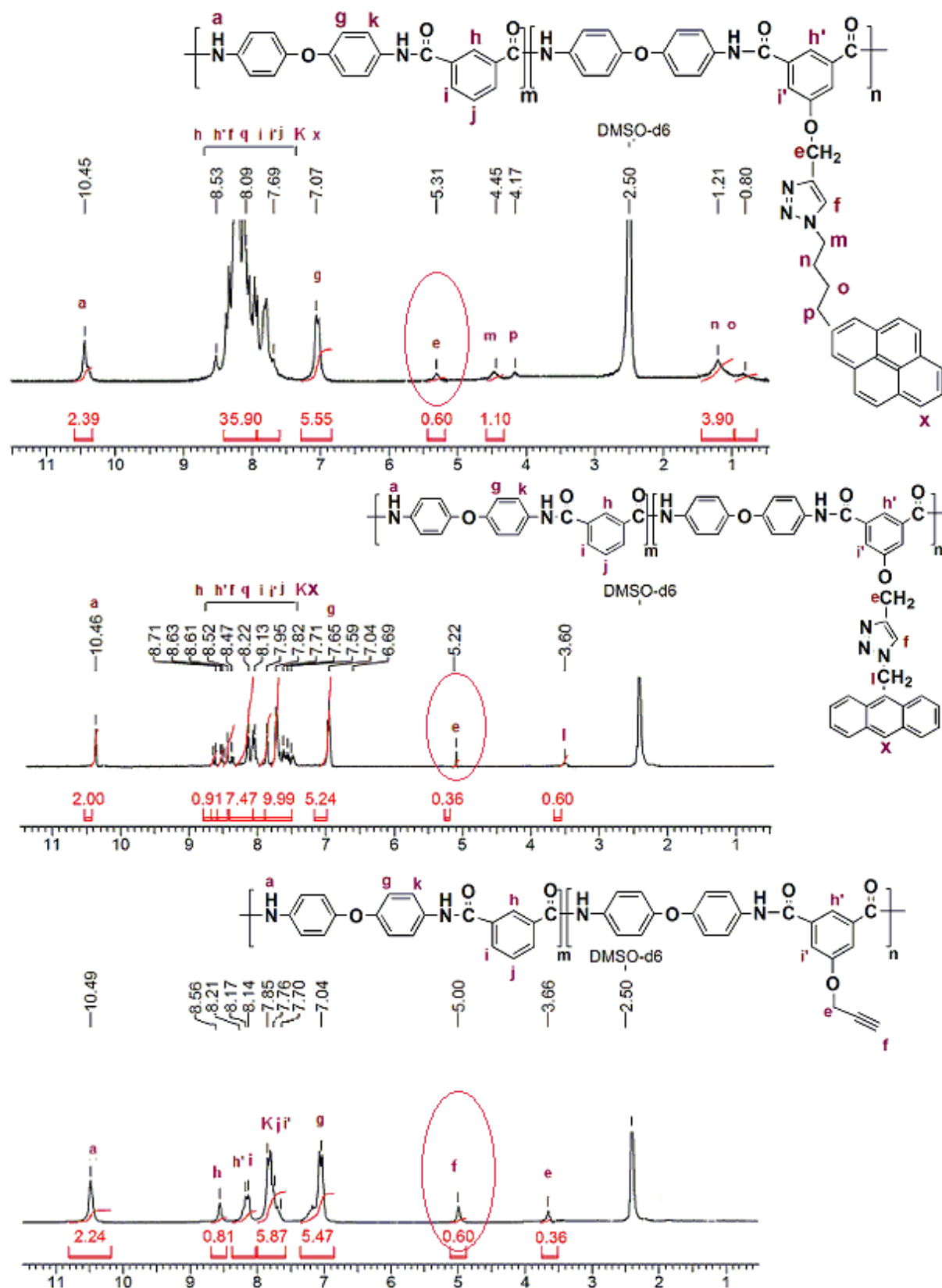
Figure 6b.7 ^{1}**H-NMR spectra (DMSO-d$_{6}$) (lower) PPA-2, (middle) PPA-An, (upper) PPA--PY**

Click reaction between polyamide containing pendent propargyloxy groups and PY-N$_{3}$ or An-N$_{3}$ was shown to proceed quantitatively as the complete disappearance of the alkyne proton at

3.66 δ ppm was observed. The shifting of methylene protons adjacent to propargyl, from 5.0 to 5.28 in case of PY-N$_3$ and 5.0 to 5.31 δ ppm in case of An-N$_3$ also confirmed the click reaction. The attachment of the pyrene units were further proved by the appearance of the characteristic aromatic peaks of pyrene and anthracene in aromatic region **(Figure 6b.7)**.

6b.4.1.2.2 *Photophysical properties of polyamides functionalized with 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene*

Polyamides functionalized with PY-N$_3$ and An-N$_3$ were further characterized by the absorption and fluorescence spectroscopy. UV-Vis absorbance peaks at 315, 330 and 345 nm are typical peaks of pyrene chromophore [**Figure 6b.8 (a)**] where as the maximum absorption peak at 275 nm is of anthracene-clicked polymer [**Figure6b.8 (b)**].

(a)   (b)
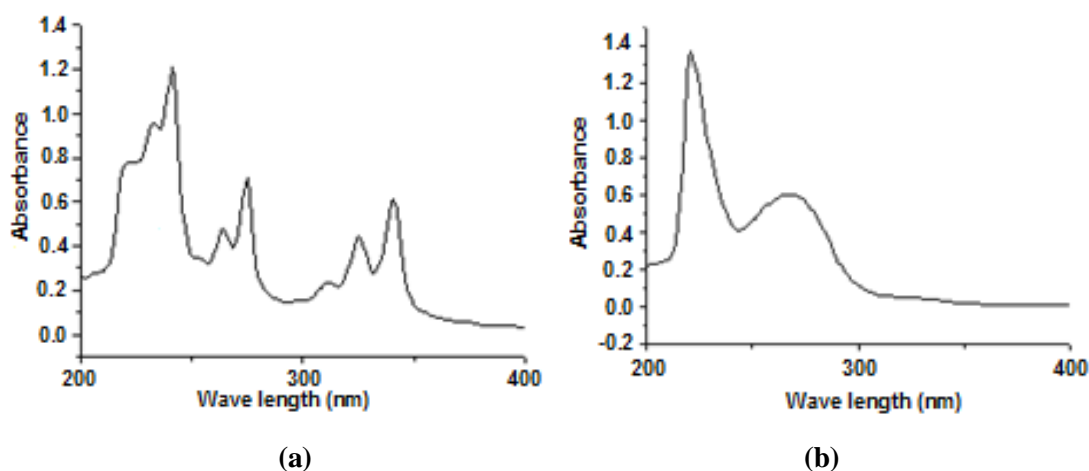
Figure 6b.8 UV-Vis absorbance profiles of (a) PPA-PY (b) PPA-An (0.00001 wt % (w/v) concentration in DMF)

Additional evidence for the functionalization can be obtained from fluorescent spectroscopy. Polyamide functionalized with PY-N$_3$ and An-N$_3$ showed spectral emission at 485 nm and 440 nm, respectively **(Figure 6b.9)**. These emissions of the pyrene and anthracene fluorophores[19, 20] confirmed the functionalization of polyamide *via* click reaction.

(a)   (b)
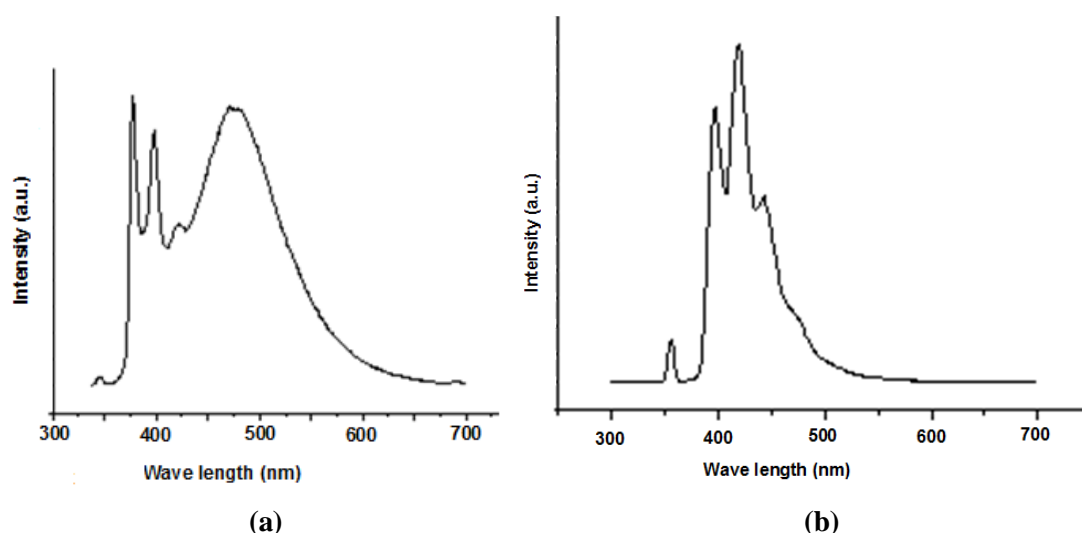
Figure 6b.9 Solution fluorescence emission spectra of (a) PPA-PY (0.00001 wt % (w/v)

concentration in DMF (b) PPA-An (0.0001 wt % (w/v) concentration in

DMF)

The post-functionalization of the pendent propargyl groups in the polyamide backbone *via* CuAAC was shown to be highly efficient. Importantly, it could be extended for the post-functionalization reaction to other azides containing moieties useful in a wide variety of applications. So this strategy allows the synthesis of several functional polymers from a single reactive polymer.
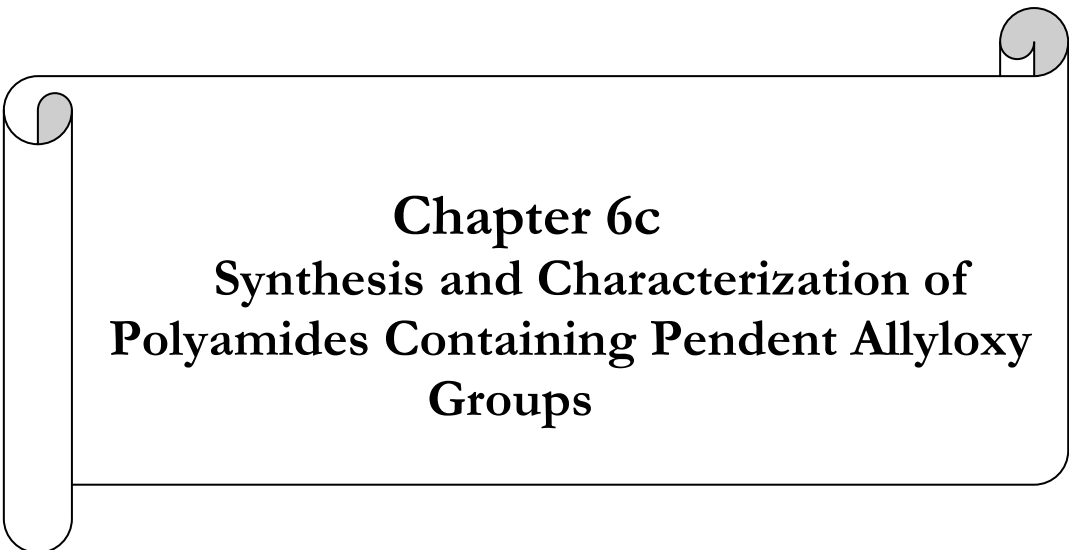
6b.5   Conclusions

1.   The azide-alkyne click reaction turned out to be a very efficient reaction to functionalize aromatic polyamide containing pendent propargyloxy groups with interesting hydrophilic and fluorescent compounds under mild condition to introduce photophysical properties and surface properties to the polyamide.

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Chapter 6c
Synthesis and Characterization of Polyamides Containing Pendent Allyloxy Groups

6c.1 Introduction

Polymers containing pendent allyl(oxy) groups are of interest as they provide a versatile option to ready functionalization *via* radical addition of thiols, epoxidation, halogenations and hydroboration, among others.[1-6] Specifically, thiol-ene click reaction is of enormous utility in chemical modification due to its advantages which include metal-free reaction condition, high conversion, ability to initiate these reactions by variety of methods under mild conditions, and ready availability of an enormous range of thiols. Aliphatic polymers such as polyesters, polycarbonates, polyurethanes and polyamides containing pendent allyl(oxy) groups have been reported in the literature [7-14] 5-(Allyloxy)isophthaloyl chloride was considered as a useful monomer for synthesis of aromatic polyamides containing clickable allyloxy groups.

We report herein synthesis of polyamides by polycondensation of a diacid chloride *viz;* 5-(allyloxy)isophthalic acid, with commercially available diamines *viz;* 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline and 4,4'-(hexafluoroisopropylidene)dianiline. Copolyamidess were also synthesized by polycondensation of a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline.

Polyamides were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies. The primary objective of the study was to synthesize clickable polymides containing pendent allyloxy groups and hence thermal characterization studies were not undertaken.

6c.2 Experimental

6c.2.1 Materials

5-(Allyloxy)isophthalic acid (A-IPA) was synthesized as described in **Chapter 3**. Diamines, *viz;* 1,4-phenylenediamine (*p*-PD), 4,4'-oxydianiline (ODA), 4,4'-methylenedianiline (MDA) and 4,4'-(hexafluoroisopropylidene)dianiline (HFDA) and isophthalic acid (IPA) all received from Aldrich, were purified by sublimation under reduced pressure. Triphenyl phosphite (TPP), received from Aldrich, was purified by distillation under reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) (S. D. Fine Chemicals) was dried over calcium hydride and distilled under reduced pressure. Pyridine (Merck, India) was purified by distillation over KOH and stored over KOH. Anhydrous lithium chloride (Aldrich) was dried at 180 °C for 8 h under reduced pressure. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[15]

6c.2.2 Measurements

Inherent viscosity (η_{inh}) of polyamides was measured on 0.5 % (w/v) solution of polyamide in DMAc at $30 \pm 0.1^{\circ}$C using an Ubbelohde suspended level viscometer.

Solubility of aromatic polyamides was determined at 3 % (w/v) concentration in different organic solvents at room temperature.

Molecular weight of polyamides was measured on ThermoFinnigan make gel permeation chromatograph (GPC), detector-RI, room temperature. The eluent was *N, N*-dimethylformamide (DMF) containing lithium bromide (LiBr) [0.1% (w/v)]. Polystyrene was used as the calibration standard. Polyamides sample (5 mg) was dissolved in DMF (5 mL) and filtered through 0.45 μ filter.

FT-IR spectra were recorded using polyamides films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using DMSO d_6 as a solvent.

X-Ray diffractograms of polyamides were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

6c.3 Synthesis of polyamides containing pendent allyloxy groups

A representative procedure for the synthesis of polyamide is described below.

Into a 200 mL three-necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring bar, were placed NMP (30 mL), 5-(allyloxy)isophthalic acid (A-IPA) (0.83 g, 1.35 x 10^{-3} mol), isophthalic acid (0.20 g , 1.20 x 10^{-3} mol), 4,4'-oxydianiline (0.5 g, 2.55 x 10^{-3} mol), lithium chloride (1 g), triphenyl phosphite (3.08 g, 9.98 x 10^{-3} mol) and pyridine (7.50 ml). The reaction mixture was stirred at 120 °C for 8 h. The viscous reaction mixture was poured into methanol (800 mL) when a fibrous precipitate was obtained which was filtered and washed thoroughly with hot water. Polymer was dried at 50 °C for 12 h under reduced pressure.

6c.4 Results and discussion

6c.4.1 Synthesis of polyamides derived from diacid monomer containing pendent allyloxy groups

As outlined in **Scheme 6c.1,** a series of clickable polyamides was synthesized by phosphorylation polycondensation of 5-(allyloxy)isophthalic acid with commercially available aromatic diamines *viz;* 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline or 4,4'-(hexafluoroisopropylidene)dianiline in NMP solution containing lithium chloride using triphenyl phosphite and pyridine as condensing agents. Copolyamides were also synthesized by polycondensation of a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline (**Scheme 6c.2**). 5-(Allyloxy)isophthalic acid was chosen as the diacid component to introduce pendent allyloxy functionalty in polyamides for further modification. The synthesis of

polyamides with varying mol percent of allyloxy functionalities was achieved by varying the molar ratio of 5-(allyloxy)isophthalic acid in the feed during copolymerization.
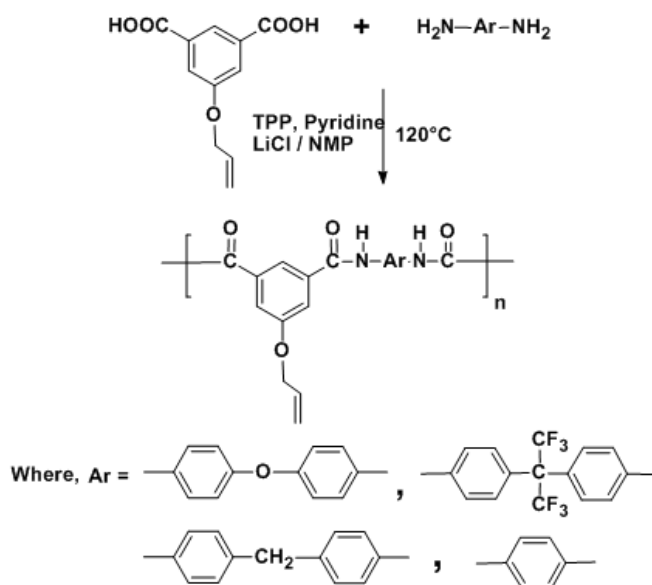
Scheme 6c.1 Synthesis of polyamides from 5-(allyloxy)isophthalic acid and aromatic diamines
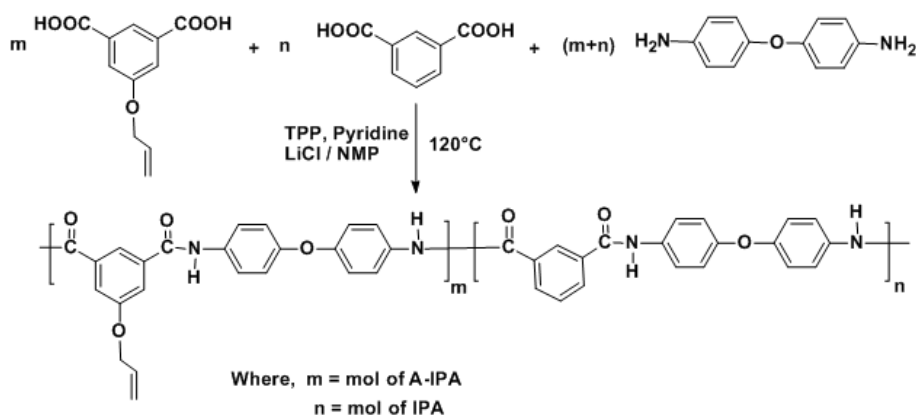
Scheme 6c.2 Synthesis of copolyamides from a mixture of 5-(allyloxy)isophthalic acid and IPC with ODA

The direct polycondensation technique reported by Yamazaki *et al* is a well accepted and useful laboratory method for the synthesis of polyamides.[16, 17] This method involves the one-pot polycondensation of aromatic diamines with aromatic diacids in the presence of an aryl phosphite such as triphenyl phosphite and an organic base such as pyridine. The addition of inorganic salts such as LiCl improves the solubility of polymer and the maximum attainable molecular weights. The advantage of this method is that it avoids the use of moisture-sensitive diacid chlorides.

It is reported that aromatic Claisen rearrangement occurs in the temperature range of 150-220 °C. Therefore, the polycondensation reactions were carried out at 120 °C at which there is practically no possibility of Claisen rearrangement of 5-(allyoxy)isophtahlic acid monomer and the formed polymer. This presumption was subsequently verified from NMR spectroscopic

measurements of the synthesized polyamides. The polymerizations were homogeneous throughout the reaction and afforded viscous polymer solutions. Polyamides were isolated by precipitating the reaction mixture in excess methanol. The results of synthesis of polyamides are presented in **Table 6c.1 and Table 6c.2.**

Table 6c.1 Synthesis of polyamides containing pendent allyloxy groups

Polyamide	Diamine	Diacid	η_{inh}, dl/g[a]	Molecular weight[b]		Mw/Mn
				Mn	Mw	
PA-1	H_2N—⬡—O—⬡—NH_2	A-IPA	0.73	96,000	2,11200	2.2
PA-6	H_2N—⬡—C(CF_3)(CF_3)—⬡—NH_2	A-IPA	0.81	99,000	2,47,500	2.5
PA-7	H_2N—⬡—CH_2—⬡—NH_2	A-IPA	0.65	1,07,000	2,46,100	2.3
PA-8	H_2N—⬡—NH_2	A-IPA	0.65	1,03,000	2,47,200	2.4

a: η_{inh} was measured with 0.5% (w/v) solution of polyamide in DMAc at $30 \pm 0.1^{\circ}$C;
b**:** Measured on GPC in DMF containing LiBr; polystyrene was used as the calibration standard.

Table 6c.2 Synthesis of copolyamides containing pendent allyloxy groups

Polyamide	Diamine	Diacid (mol %)		η_{inh} dl/g[a]	Molecular weight[b]		Mw/Mn
		IPA	A-IPA		Mn	Mw	
PA-2	ODA	25	75	1.0	1,08,600	2,28,000	2.1
PA-3	ODA	70	30	0.76	1,00,600	2,31,300	2.3
PA-4	ODA	80	20	1.21	1,28,000	2,94,400	2.3
PA-5	ODA	90	10	0.82	1,02,300	2,45,500	2.4

a: η_{inh} was measured with 0.5% (w/v) solution of polyamide in DMAc at $30 \pm 0.1^{\circ}$C;
b**:** Measured on GPC in DMF containing LiBr; polystyrene was used as the calibration standard.

Polyamides were isolated as white fibrous materials with inherent viscosity in the range 0.65-1.21 dL/g. Number-average molecular weights (Mn) of polyamides were in the range 96,000-1,28,000 with polydispersity index in the range 2.1-2.5. Inherent viscosity and GPC data indicated the formation of medium to reasonably high molecular weight polyamides. Tough, transparent, and flexible films of polyamides could be cast from their solutions in DMAc.

6c.4.2 Structural characterization

The formation of polyamides was confirmed by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

FT-IR spectrum of polyamide derived from 5-(allyloxy)isophthalic acid and 4,4'-oxydianiline is reproduced in **Figure 6c.1**.
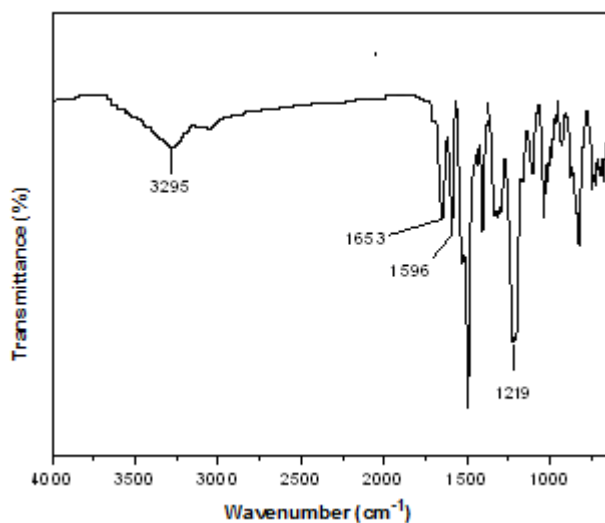
Figure 6c.1 FT-IR spectrum of polyamide derived from 5-(allyloxy)isophthalic acid and ODA (PA-1)

FT-IR spectrum of polyamide showed –NH stretching frequency as a broad band at 3295 cm^{-1}. The amide-I band, associated with stretching vibration of the carbonyl group, appeared at 1653 cm^{-1}. The amide-II band, ascribed to the coupling of the –N-H bending and –C-N stretching of -C-N-H group, appeared at 1596 cm^{-1}.

^{1}H-NMR spectrum of polyamide derived from 5-(allyloxy)isophthalic acid and 4,4'-oxydianiline along with assignments is shown in **Figure 6c.2.**
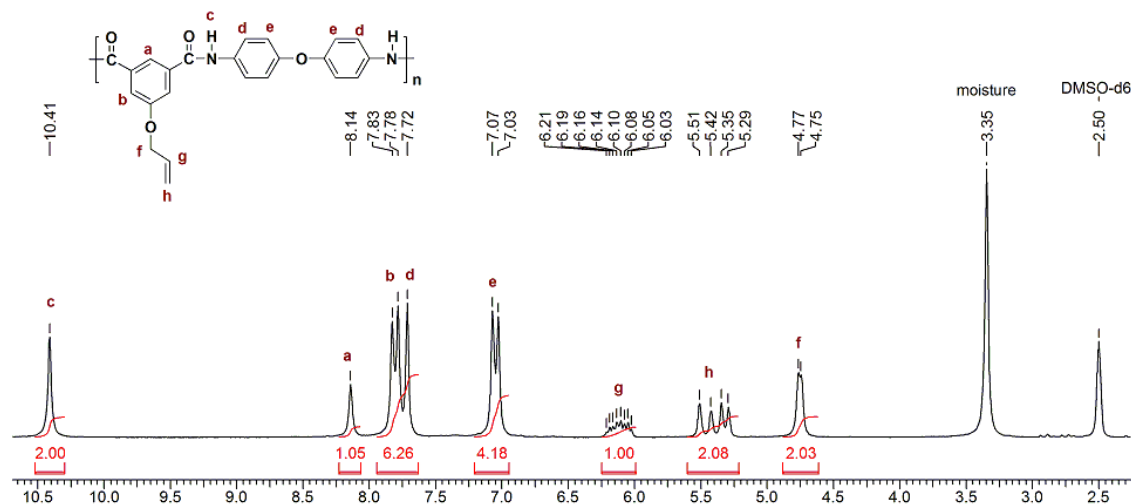
Figure 6c.2 ^{1}H-NMR spectrum of polyamide (DMSO-d$_6$) from 5-(allyloxy)isophthalic acid and ODA (PA-1)

The peak appeared at 10.41 δ ppm is due to -NH of amide groups. The proton "a" flanked by amide groups exhibited a singlet at 8.14 δ ppm. The peaks displayed in the range 7.83-7.78 δ ppm are due to protons "b" and "d". The doublet appeared at 7.05 δ ppm is due protons "e". The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range

6.21-6.03 δ ppm, and 5.51-5.29 δ ppm which correspond to proton "g" and protons "h", respectively. The protons "f" appeared as a doublet at 4.76 δ ppm.

¹H-NMR spectrum of copolyamide from a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline along with assignments is shown in **Figure 6c.3.**
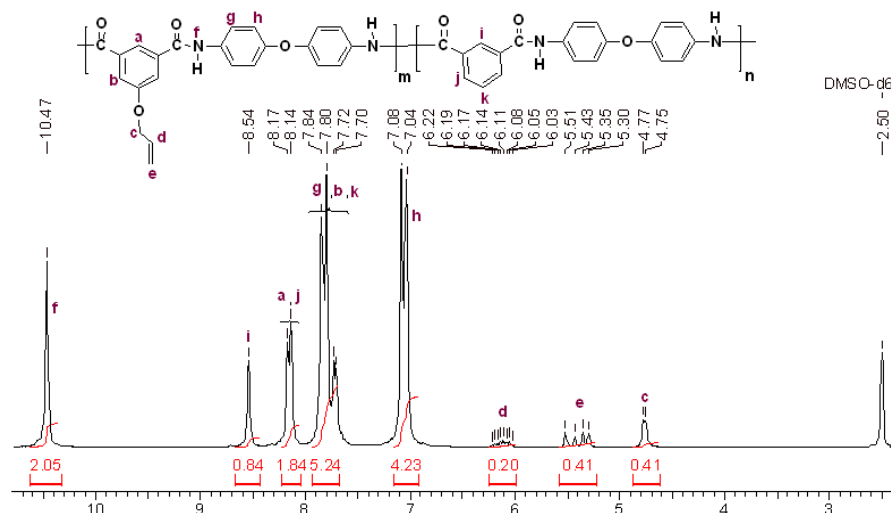
Figure 6c.3 ¹H-NMR spectrum of copolyamide (DMSO-d₆) from a mixture of

5(allyloxy)isophthalic acid and IPC with ODA (PA-4)

The peak appeared at 10.47 δ ppm is due to –NH of amide group. The proton "i" flanked by amide groups exhibited a singlet at 8.54 δ ppm. The peaks appeared in the range 8.17-8.14 δ ppm are due to protons "a" and "j". The peaks displayed in the range 7.84-7.70 δ ppm are due to protons "g", "b" and "k". The proton "h" appeared as a doublet at 7.06 δ ppm. The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range 6.22-6.03 δ ppm, and 5.51-5.30 δ ppm which correspond to protons "d" and "e", respectively. The protons "c" exhibited a doublet at 4.76 δ ppm.

¹³C NMR spectrum of polyamide obtained from 5-(allyloxy)isophthalic acid and 4,4'-oxydianiline along with assignments of the carbon atoms is shown in **Figure 6c.4.**
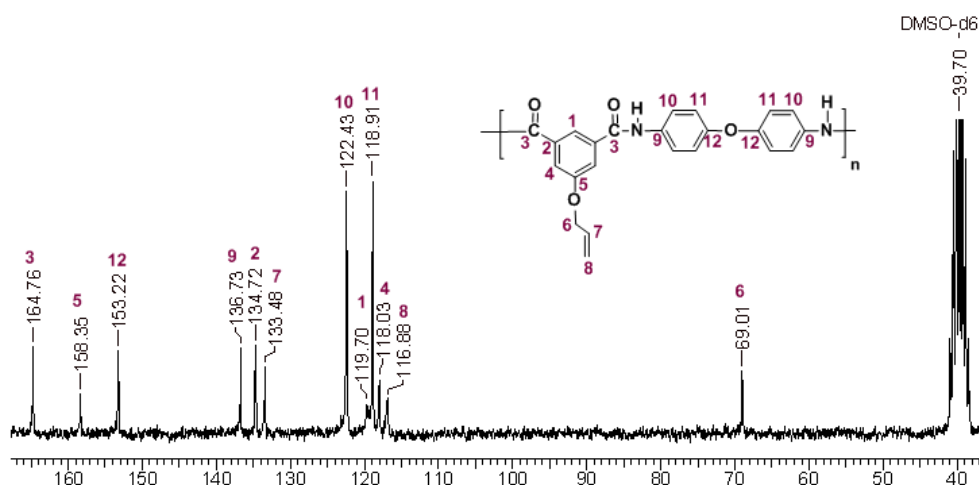
Figure 6c.4 ¹³C-NMR spectrum of polyamide (DMSO d6) obtained from 5-(allyloxy) isophthalic acid and ODA (PA-1)

Thus, FT-IR, ^{1}H and ^{13}C-NMR spectra confirmed the formation of polyamides with the chemical structure shown in **Scheme 6c.1** and **Scheme 6c.2,** that is, formation of polyamides with pendent allyloxy groups in the backbone. The perfect agreement between integration of aromatic proton flanked by amide carbonyls and methylene protons of allyloxy groups indicated that there was no detectable thermal Claisen rearrangement in these systems.

6c.4.3 Solubility of polyamides

Solubility of polyamides was tested in various organic solvents at 3 wt % (w/v) concentration and data is summarized in **Table 6c.3.**

Table 6c.3 Solubility data of polyamides containing pendent allyloxy groups

| Polyamide | Diacid (mol %) | | Diamine | CHCl$_3$ | THF | DMF | DMAc | NMP | Pyridine | DMSO |
	IPA	A-IPA								
PA-1	0	100	ODA	--	--	++	++	++	++	++
PA-2	25	75	ODA	--	--	++	++	++	++	++
PA-3	70	30	ODA	--	--	++	++	++	++	++
PA-4	80	20	ODA	--	--	++	++	++	++	++
PA-5	90	10	ODA	--	--	++	++	++	++	++
PA-6	0	100	HFDA	--	--	++	++	++	++	++
PA-7	0	100	MDA	--	--	++	++	++	++	++
PA-8	0	100	*p*-PD	--	--	++	++	++	++	++
PPA-Ref1	IPC	0	ODA	--	--	--	++	++	--	--

+ + : soluble; - - :insoluble, PPA-Ref1: polyamide derived from ODA and IPC[18] (solubility data was taken from reference 18)

Polyamides containing pendent allyloxy groups were soluble in DMF, DMAc, NMP, pyridine and DMSO and were insoluble in chloroform and THF. It is reported that polyamide derived from ODA with IPC is soluble in DMAc and NMP but not soluble in DMF, pyridine and DMSO whereas polyamides derived from *p*-PD or MDA with IPC are reported to be not soluble in the above mentioned solvents.[18] This result indicates that the incorporation of allyloxy groups in the polyamides backbone enhanced the solubility of polyamides. This is due to the disturbance in the dense chain packing of the polymer by the pendent groups, which, in turn, facilitates the penetration of the solvent molecules resulting in improved solubility.

6c.4.4 X-Ray diffraction analysis

Wide-angle X-ray diffraction (WAXD) patterns of polyamides containing pendent allyloxy groups exhibited a broad halo over the range $2\theta \approx 10\text{-}35^{o}$ indicating their amorphous nature (**Figure 6c.5**). In contrast, polyamide derived from ODA with IPC (PPA-Ref1) is reported to be partially crystalline in nature (**chapter 6a, Figure 6a.5**).[19] This clearly indicates that the pendent allyloxy groups are responsible for disrupting chain packing in polyamides, thus resulting in their amorphous nature.
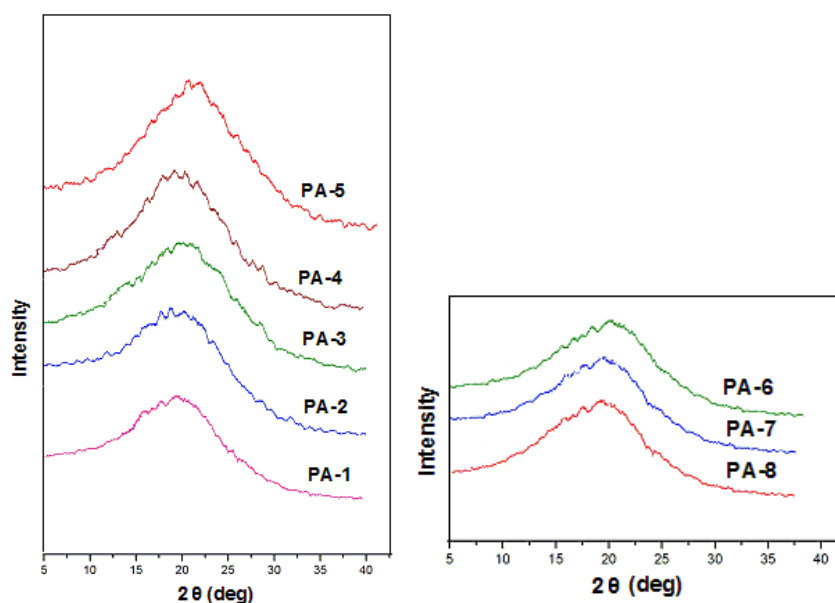
Figure 6c.5 Wide angle X-ray diffractograms of aromatic polyamides containing pendent allyloxy groups
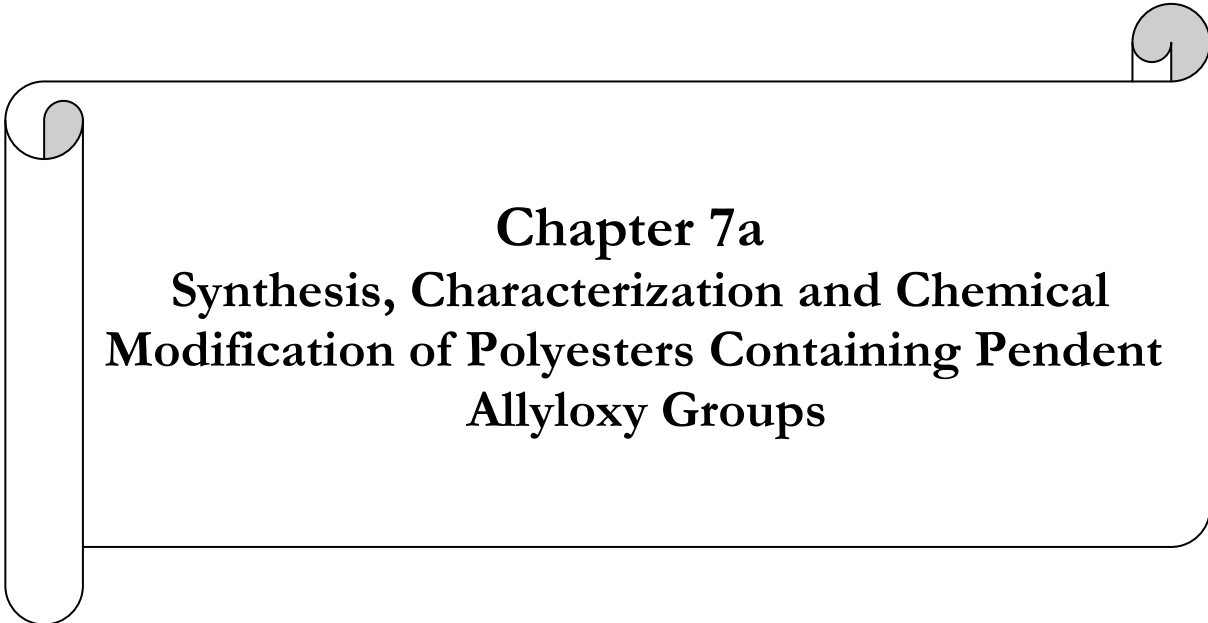
6c.5   Conclusions

1. Clickable polyamides containing pendent allyloxy groups were synthesized from 5-(allyloxy)isophthalic acid and various aromatic diamines using Yamazaki reaction. Copolyamides were also synthesized from a mixture of 5- (allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline.

2. Inherent viscosities of polyamides were in the range 0.65- 1.2 dL/g indicating the formation of medium to reasonably high molecular weight polymers.

3. Polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and DMSO. Tough, transparent and flexible films of polyamides could be cast from DMAc solution.

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Chapter 7a
Synthesis, Characterization and Chemical Modification of Polyesters Containing Pendent Allyloxy Groups

7a.1 Introduction

The click philosophy, as introduced by Sharpless and coworkers, has been heavily exploited in polymer and material sciences by means of the copper-catalyzed azide-alkyne cycloaddition (CuAAC) and has led to a convenient approach to synthesize functionalized polymers.[1, 2] Due to the toxicity of copper and the risk inherent in working with azides, a growing interest has risen in thiol-ene chemistry, which works under mild conditions and is copper- and azide- free.[3-8] One of the greatest utilities of thiol– ene click chemistry is rapid modification of existing polymers to tailor physical, mechanical, optical, solubility, and other key properties over a wide range, in high yield. In recent years, significant effort has been expanded towards polymer functionalization using thiol–ene free-radical reactions.[7, 9-12]

Allyl group is an important functional group. As a consequence of its unsaturation, allyl groups provide versatile option for ready functionalization *via* radical addition of thiols, epoxidation, halogenations, and hydroboration among others.[9, 13-17]

This chapter describes synthesis of allyloxy functionalized polyester by polycondensation of a diacid chloride containing pendent allyloxy group *viz*; 5-(allyloxy)isophthaloyl chloride and commercially available bisphenol A. Copolyester was also synthesized by polycondensation of a mixture of 5-(allyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy. Copolyester containing 25 mol % 5-(allyloxy)isophthaloyl chloride was post-functionalized using four different thiols *viz;* 1-butanethiol, 2-mercaptoethanol, 3-mercaptopropanoic acid and 11-marcaptoundecyl phosphoric acid *via* thiol-ene click reaction.

The functionalized polyesters were characterized by FT-IR and ^{1}H-NMR spectroscopy.

The primary objective of the study was to synthesize clickable polyesters containing pendent allyloxy groups and their post-functionalization and hence thermal stability studies were not undertaken.

7a.2 Experimental

7a.2.1 Materials

5-(Allyloxy)isophthaloyl chloride (A-IPC) was synthesized as described in **Chapter 3.** Bisphenol A (BPA), 2-mercaptoethanol, 1-butanethiol, 3-mercaptopropionoic acid, 11-mercaptoundecyl phosphoric acid and benzyltriethyl ammonium chloride (BTEAC) (Aldrich) were used as received. Isophthaloyl chloride (IPC) was synthesized from isophthalic acid, (from Aldrich, USA), using excess thionyl chloride in the presence of *N, N*-dimethylformamide (DMF) as a catalyst and was purified by distillation under reduced pressure.[18] 2,2'-Azobisisobutyronitrile (AIBN), received from Fishers scientific, was recrystallized from methanol before use. Dichloromethane (S. D. Fine Chemicals) was dried over calcium hydride and distilled. Other solvents were purified according to standard procedures.[19]

7a.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured on 0.5 % (w/v) solution of polyester in chloroform at 30 ± 0.1^{o}C using an Ubbelohde suspended level viscometer on Schott Gerate CK-160 automatic viscometer.

Solubility of polyesters was determined at 3 % (w/v) concentration in different solvents at room temperature.

Molecular weight of polyesters was measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: column – polystyrene - divinylbenzene (10^5 Å to 50 Å), Detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in chloroform (5 mL) and filtered through 0.45 µ filter.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using CDCl$_3$ as a solvent.

7a.3 Synthesis of aromatic polyester containing pendent allyloxy groups
7a.3.1 Synthesis of homopolyester containing pendent allyloxy groups

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed bisphenol A (1.32 g, 5.76 x 10^{-3} mol) dissolved in 1M NaOH (12 mL). The reaction mixture was stirred at 10 °C for 1h. Thereafter, BTEAC (0.45 g) was added to the reaction mixture. The solution of 5-(allyloxy)isophthaloyl chloride (1.5 g, 5.76 x 10^{-3} mol) dissolved in dichloromethane (40 mL) was added in one lot to the reaction mixture and was stirred vigorously at 2000 rpm at 10 ^{o}C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and reprecipitated in methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 ^{o}C under reduced pressure for two days.

7a.3.2 Synthesis of aromatic copolyester containing pendent allyloxy groups

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an additional funnel were placed bisphenol A (1.4 g, 6.14 x 10^{-3} mol) dissolved in 1M NaOH (12.3 mL). The mixture was stirred at 10 °C for 1h. Thereafter, BTEAC (0.16 g) was added to the reaction mixture. The solution of 5-(allyloxy)isophthaloyl chloride (0.39 g, 1.5 x 10^{-3} mol) and isophthaloyl chloride (0.93 g, 4.6 x 10^{-3} mol) dissolved in dichloromethane (40 mL) was added in one lot to the reaction mixture and was stirred vigorously at 2000 rpm at 10 ^{o}C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and reprecipitated in methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 ^{o}C under reduced pressure for two days.

7a.3.3 A representative procedure for functionalization of copolyester containing pendent allyloxy groups with 1- butanethiol (APES-CL1)

Into an ampoule, polymer APES-2 (1eq), 1-butanethiol (3 eq) and AIBN (0.05 eq) were dissolved in THF (12 mL). The reaction mixture was degassed *via* three freeze-pump-thaw cycles, and subsequently sealed. The ampoule was heated at 60 ºC for 24 h with stirring. After completion of the reaction, the product was precipitated into methanol (200 mL), washed thoroughly with methanol and dried under reduced pressure at 50°C for two days.

Click reaction of copolyester with other thiols *viz*; 2-mercaptoethanol, 3-mercaptopropanoic acid and 11-marcaptoundecylphosphoric acid, was carried out using a similar procedure to obtain APES-CL1, APES-CL3 and APES-CL4, respectively.

7a.4 Results and discussion

7a.4.1 Synthesis of polyesters containing pendent allyloxy groups

Clickable polyester possessing pendent allyloxy groups was synthesized by phase transfer-catalyzed interfacial polycondensation of 5-(allyloxy)isophthaloyl chloride (A-IPC) and BPA. Copolyester from a mixture of 5-(allyloxy)isophthaloyl chloride (A-IPC) and IPC with BPA was also synthesized. A-IPC was chosen as diacid chloride because it introduced pendent allyloxy groups into the polymer for further functionalization *via* thiol-ene click reaction using thiol containing molecules or thiol containing polymeric chains.

Scheme 7a.1 illustrates synthesis of polyester from 5-(allyloxy)isophthaloyl chloride and BPA.
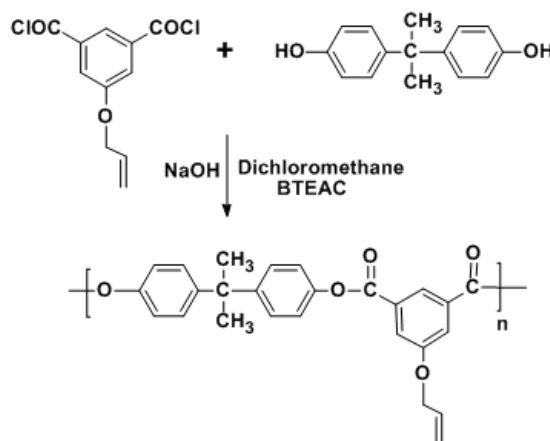
Scheme 7a.1 Synthesis of polyester from 5-(allyloxy)isophthaloyl chloride and BPA

Scheme 7a.2 illustrates synthesis of copolyester from a mixture of 5-(allyloxy)isophthaloyl chloride and IPC with BPA.
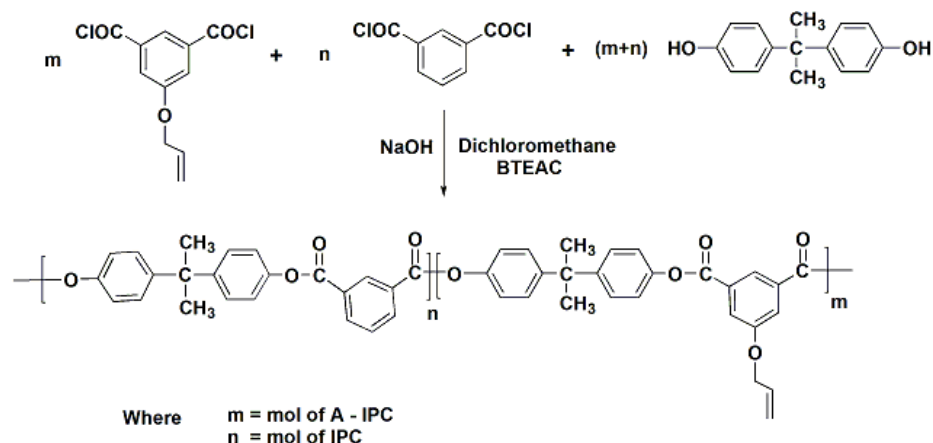
Scheme 7a.2 Synthesis of copolyester from a mixture of 5-(allyloxy)isophthaloyl chloride and IPC with BPA

The results of polymerizations are summarized in **Table 7a.1.**

Table 7a.1 Synthesis of aromatic (co)polyesters containing pendent allyloxy groups

Polyester	Bisphenol A (mol %)	IPC (mol %)	A-IPC (mol %)	η_{inh} [a] (dL/g)	Molecular Weight [b] Mn	Mw	Mw/Mn
APES-1	100	0	100	0.50	18,100	36,500	2.0
APES-2	100	75	25	0.72	31,900	66,500	2.1

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

Inherent viscosity of homopolyester and copolyester was 0.50 and 0.72 dL/g, respectively. Number average molecular weight (Mn) of homopolyester and copolyester was 18,100 and 31,900 with polydispersity index of 2.0 and 2.1, respectively. Tough, transparent and flexible films of polyesters containing pendent allyloxy groups could be cast from their solutions in chloroform.

7a.4.2 Structural characterization

The formation of polyesters was confirmed by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

FT-IR spectrum of polyester derived from a mixture of 5-(allyloxy)isophthaloyl dichloride and IPC with BPA is reproduced in **Figure 7a.1**.
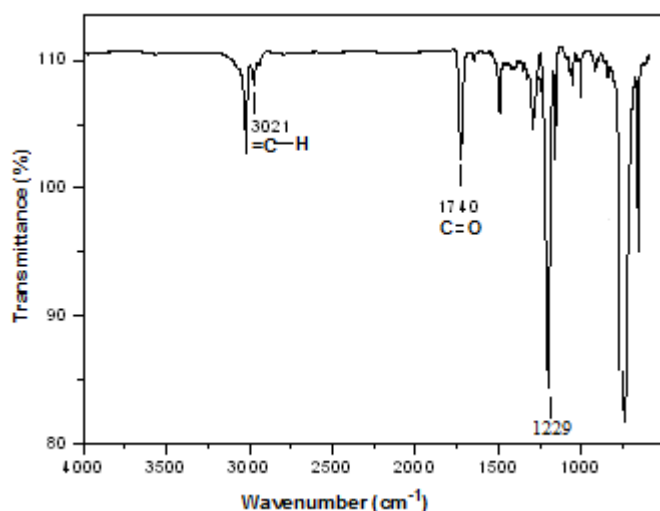
Figure 7a.1 FT-IR spectrum of polyester from a mixture of 5-(allyloxy)isophthaloyl chloride and IPC with BPA

      The incorporation of allyloxy groups was evidenced by the presence of characteristic band of =C-H which appeared at 3021cm^{-1}. Ester carbonyl band of polyester was observed at 1740 cm^{-1}. Absorption band corresponding to C-O-C stretching was observed at 1229 cm^{-1}.

      ^{1}H-NMR spectrum of polyester derived from a mixture of 5-(allyloxy)isophthaloyl chloride and IPC with BPA along with assignments is shown in **Figure 7a.2**
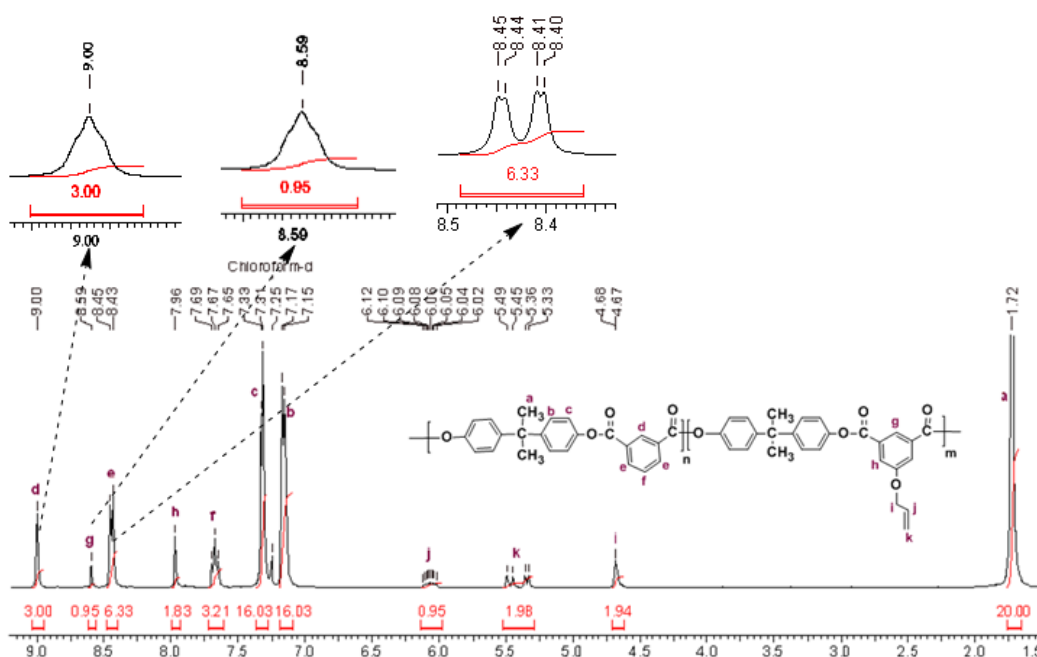
Figure 7a.2 ^{1}H-NMR spectrum (CDCl$_3$) of copolyester from a mixture 5-(allyloxy)isophthaloyl chloride and IPC with BPA

      The protons "d" and "g" flanked by ester carbonyl groups appeared as triplets at 9.0 and 8.59 δ ppm, respectively. The protons "e" exhibited doublet of doublet at 8.42 δ ppm. The peak appeared at 7.96 is due to the protons "h". The proton "f" exhibited a triplet at 7.67 δ ppm. The doublets at 7.31 and 7.16 δ ppm are due to protons "c" and "b", respectively The presence of

allyloxy functionality was confirmed by the appearance of multiplets in the range 6.12- 6.02 δ ppm, and 5.49-5.33 δ ppm corresponding to proton "j" and "k", respectively. The doublet at 4.60 δ ppm corresponds to proton "i". The protons of methyl group attached to bridge carbon exhibited a singlet at 1.72 δ ppm.

In copolyester, the allyloxy comonomer was quantified by integration of the signal ''g'' at 8.59 δ ppm from A-IPC in relation to the signal 'd' at 9.0 δ ppm from IPC encountered in ^{1}H-NMR spectrum (**Figure 7a.2).** As presented in **Table 7a.2**, A-IPC content was consistent with the feed ratio.

Table 7a.2 Copolyester composition determined from ^{1}H-NMR spectra

Copolyester	Feed A-IPC, mol %	Observed A-IPC, mol %
APES-2	25	24

^{13}C-NMR spectrum of polyester from a mixture of 5-(allyloxy) isophthaloyl chloride and IPC with BPA along with the assignments of carbon atoms is shown in **Figure 7a.3**
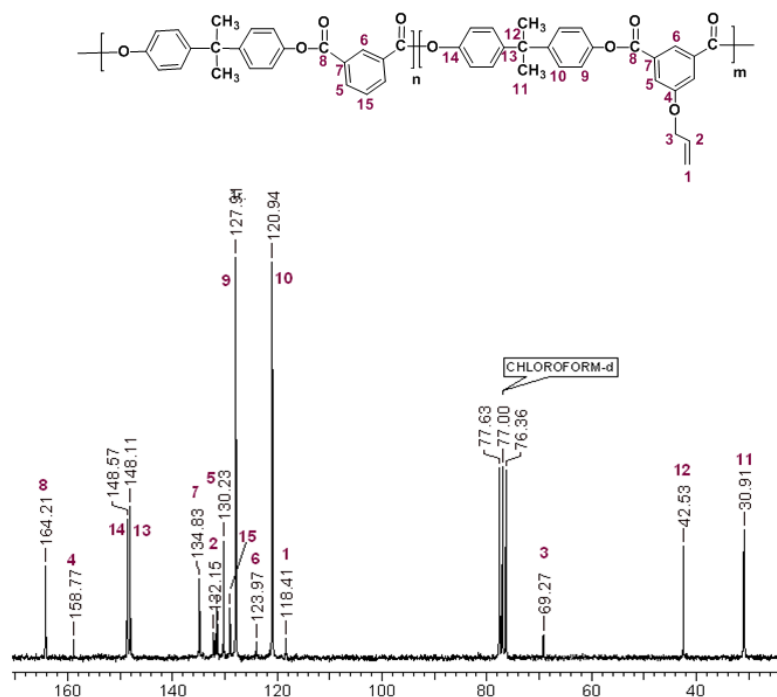
Figure 7a.3 ^{13}C-NMR spectrum (CDCl₃) of copolyester from a mixture of 5-(allyloxy) isophthaloyl chloride and IPC with BPA

7a.4.3 *Solubility of polyesters*

Solubility data of polyesters in different organic solvents at 3 wt % (w/v) is shown in **Table 7a.3**. Both the polyesters were completely soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran and aprotic polar solvents such as NMP and DMAc.

In contrast to these results, aromatic polyester synthesized from isophthaloyl chloride and bisphenol A is reported to be not soluble in the above organic solvents.[20, 21] These results indicated that the incorporation of pendent allyloxy groups into the polymer interrupted the chain packing, which resulted into improved solubility.

Table 7a.3 Solubility data of aromatic polyesters containing pendent allyloxy groups

Polyester	BPA (mol %)	Diacid chloride (mole %)		$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-cresol
		A-IPC	IPC								
APES-1	100	100	00	++	++	++	++	++	++	++	++
APES-2	100	25	75	++	++	++	++	++	++	++	++

++ : soluble,   -- : insoluble
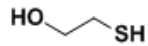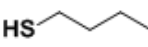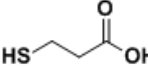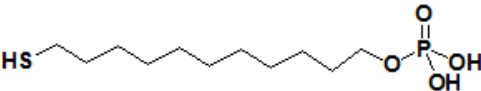
7a.5 Chemical modifications of polyester containing pendent allyloxy groups

The obtained polyesters containing allyloxy functional groups could be used in thiol-ene click reaction with various thiols to provide functional polyesters. To evaluate the efficiency of functionalization of the copolyester containing pendent allyloxy groups, the functionalization was carried out by free-radical induced thiol-ene click reaction between allyloxy group of the copolyester (1 eq) and various thiols (3 eq) in tetrahydrofuran solvent using AIBN as a free radical initiator **(Scheme 7a.3)**. Four different thiols were used, *viz* 1-butanethiol, 2-mercaptoethanol, 3-mercaptopropanoic acid and 11-marcaptoundecyl phosphoric acid. The results of functionalizations are summarized in **Table 7a.4.**
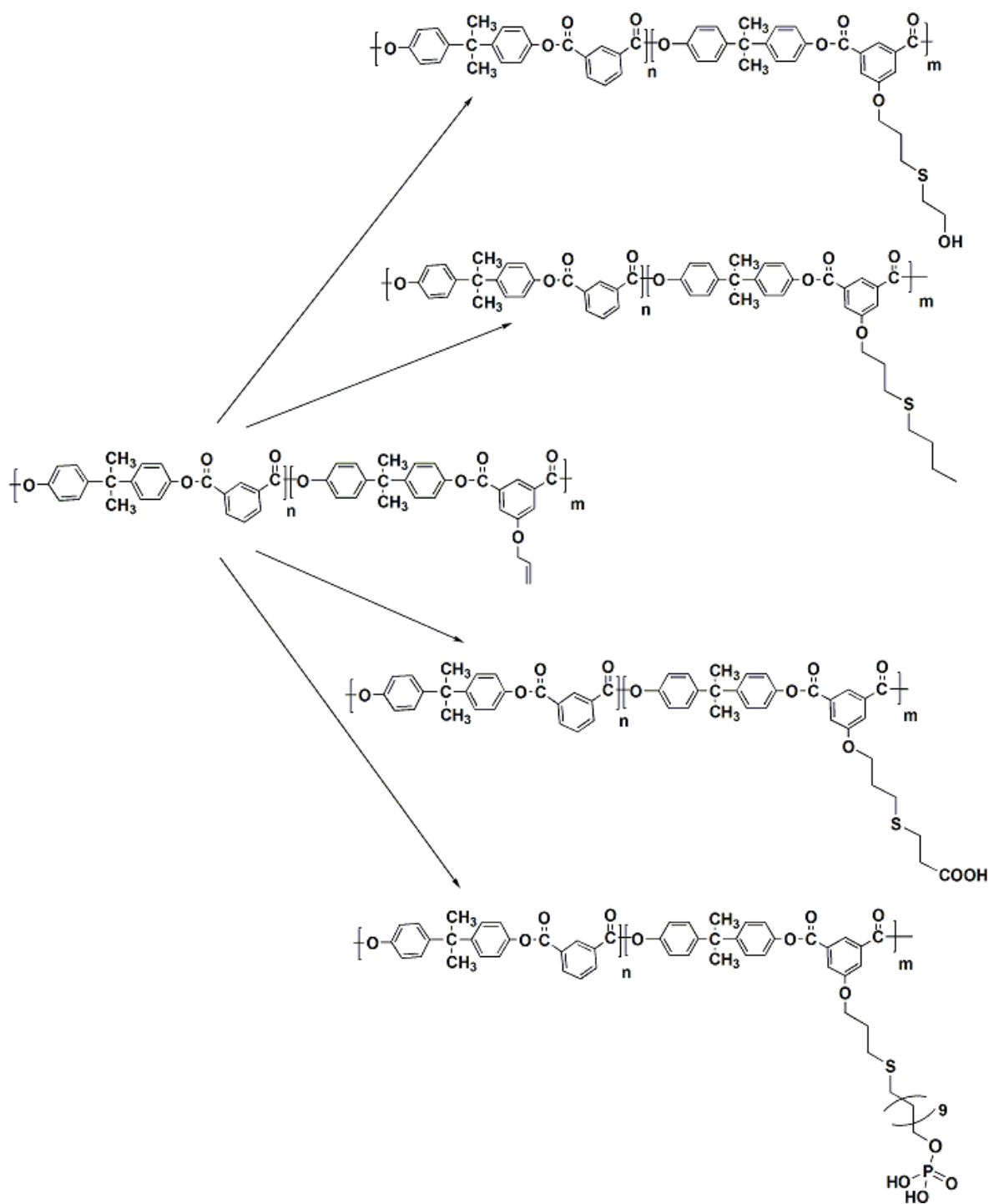
Scheme 7a.3 Thiol-ene click reaction of allyloxy containing polyester with various thiols

Table 7a.4 Functionalization of copolyester (APES-2) by thiol-ene click reaction

Sr. No.	Functionalized polyester	Thiol	Molecular Weight [a] Mn	PDI
1	APES-CL1	HO⌒SH	33100	2.2
2	APES-CL2	HS⌒⌒	32600	2.5
3	APES-CL3	HS⌒C(=O)OH	33000	2.5
4	APES-CL4	HS⌒⌒⌒O-P(=O)(OH)OH	35200	2.6

Starting polymer: APES-2, Mn = 31,900, Reaction conditions: APES-2 (1eq), thiol (2 eq), AIBN (0.05 eq)

a: Determined by GPC using chloroform as a solvent, calibrated with polystyrene standard,

The resulting functionalized polyesters were characterized by FT-IR and ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of the APES-2 along with those of the modified polyesters are shown in **Figure 7a.4,** The peaks in the range 5.31-5.97 and 5.50-4.66 δ ppm, for APES-2 (bottom spectrum) highlighted the presence of the ene bond. The signals associated with the C=C bonds completely disappeared in clicked products, thereby confirming that the click reaction proceeded to completion in all the cases.

The new peaks appeared at 4.51, 10.05 and 3.58 δ ppm indicated the presence of hydroxyl, carboxylic and phosphoric acid groups in respective modified polyesters *via* thiol-ene click reaction.
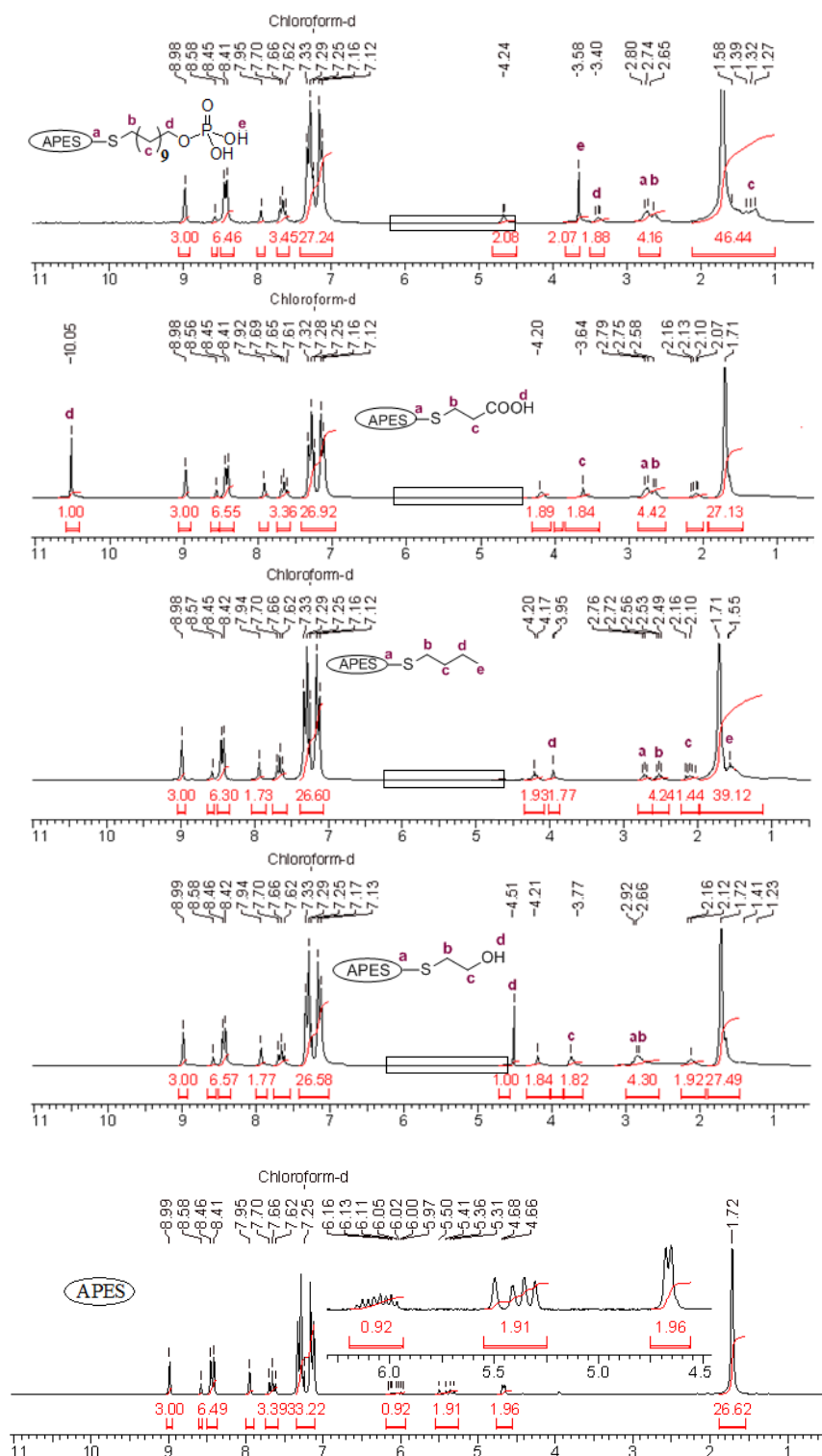
Figure 7a.4 ^{1}**H-NMR spectra (CDCl$_3$) of (l) APES-2 (ll) functionalized with 2-mercaptoethanol (lll) with 1- butanethiol (lV) with 3-mercaptopropanoic acid (V) with 11-mercaptoundecyl phosphoric acid**

Further evidence of successful functionalization is also provided by FT-IR spectra (**Figure7a.5**). After functionalization by 2-mercaptoethanol, 1-butanethiol, 3 mercaptopropanoic acid and 11-marcaptoundecylphosphoric acid, new absorptions bands attributed to the stretching vibration of OH [**Figure 7a.5 (ll)**], COOH [**Figure 7a.5 (IV)**], and phosphoric acid [**Figure 7a.5**

(V)], appeared at 3500, 2400-3200 and 1078 cm^{-1} while the absorption attributed to the stretching vibration of double bond of starting copolymer at 3021 cm^{-1} was absent [**Figure 7a.5 (I)**].
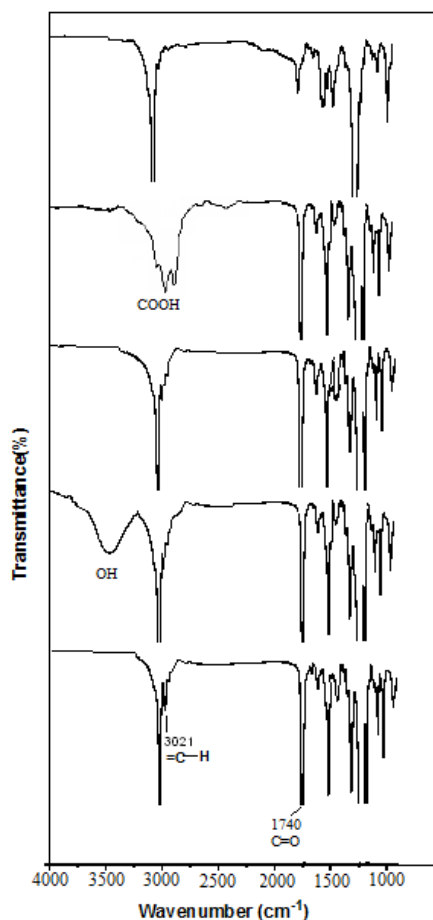
Figure 7a.5 FT-IR spectra for (I) APES-2 (II) functionalized with 2-mercaptoethanol (III) with1- butanethiol (IV) with 3-mercaptopropanoic acid (V) with11-mercaptoundecyl phosphoric acid

Thus, FT-IR and ^{1}H-NMR spectral analysis confirmed the quantitative functionalization of the polymer under mild condition. As a large number of thiols are commercially available. So the optimized reaction could be extended to the modification of these commercially available thiols as well as polymers with thiol groups to prepare a wide range of functional polymers.

7a.6 Conclusions

1. Clickable polyesters containing pendent allyloxy groups were successfully synthesized from 5-(allyloxy)isophthaloyl chloride, isophthaloyl chloride and bisphenol A by phase-transfer catalyzed interfacial polycondensation method.

2. Polyesters were found to be soluble in chloroform, dichloromethane, pyridine, *m*-cresol etc. Tough, transparent and flexible films could be cast from solutions of polyesters in chloroform.

3. Copolyester containing 25 mol% pendent allyloxy functionality was successfully functionalized by four different thiols *viz*; 2-mercaptoethanol, 1- butanethiol, 3-

mercaptopropanoic acid and 11-mercaptoundecyl phosphoric acid *via* thiol-ene click reaction technique under mild conditions.

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Chapter 7b

Synthesis and Characterization of Polyesters

Containing Pendent Pentadecyl Chains

7b.1 Introduction

Aromatic polyesters are an important class of high performance polymers. High thermal stability, solvent resistance and good mechanical properties of these polymers make them possible to meet the demands of the modern industry in the areas of aviation, automobile, electronics, etc.[1,2] However, most aromatic polyesters encounter processing difficulties due to their high glass transition temperatures or melting temperatures coupled with insolubility in common organic solvents.[3,4] Therefore, development of aromatic polyesters for various applications with improved processability is an important goal. Several approaches have been implemented to improve solubility and processability of aromatic polyesters.[5-23] These include:

1. Insertion of flexible spacers in the polymer backbone.
2. Incorporation of bent or 'crank-shaft' units along the backbone.
3. Appending bulky side groups or flexible side chains.

The incorporation of flexible side chains along the polymer backbone has been demonstrated to improve solubility of polyesters. This is due to disturbance in dense chain packing of the polymer chains by flexible side chains which, in turn, increases the free volume. In this context, asymmetrically substituted diacid chloride monomer, *viz.,* 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride (CPPBC) containing pentadecyl chain was considered as a useful monomer for synthesis of aromatic polyesters with improved processability characteristics.

In the present work, a new series of aromatic polyesters was synthesized by polycondensation of diacid chloride containing pendent flexible pentadecyl chain *viz,* CPPBC with aromatic bisphenols, namely*,* bisphenol A, 4,4'-(perfluoropropane-2,2-diyl)diphenol, and 4,4'-(1-phenylethane-1,1-diyl)diphenol. Two series of copolyesters were also synthesized by (i) polycondensation of bisphenol A with a mixture of CPPBC and TPC and (ii) polycondensation of bisphenol A with a mixture of CPPBC and IPC in order to study the effect of incorporation of pendent pentadecyl chains on the solubility and thermal properties of polyesters.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of incorporation of pentadecyl chains on the polymer properties was investigated

7b.2 Experimental

7b.2.1 Materials

4-(4-(Chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride (CPPBC) was synthesized as described in **Chapter 3.** 2,2-Bis(4-hydroxyphenyl)propane (bisphenol-A or BPA), (hexafluoroisopropylidene)diphenol (HFBPA), and 1,1'-bis(4-hydroxyphenyl)-1-phenylethane (BisP-AP) (Aldrich) were sublimed under reduced pressure prior to use. Benzyltriethyl ammonium chloride (BTEAC) (Aldrich) was used as received. Isophthaloyl chloride (IPC) and terephthaloyl

chloride (TPC) were synthesized from isophthalic acid and terephthalic acid, respectively (Aldrich), using excess thionyl chloride in the presence of *N,N*-dimethylformamide (DMF) as a catalyst and were purified by distillation under reduced pressure.[24] Dichloromethane (S. D. Fine Chemicals) was dried over calcium hydride and distilled. Other solvents were purified according to standard procedures.[25]

7b.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured on 0.5 % (w/v) solution in chloroform at 30 ± 0.1 ^{o}C using an Ubbelohde suspended level viscometer.

Solubility of polyesters was determined at 3 % (w/v) concentration in different solvents at room temperature.

Molecular weight of polyesters was measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: column – polystyrene - divinylbenzene (10^5 Å to 50 Å), detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in chloroform (5 mL) and filtered through 0.45 µ filter.

FT-IR spectra were recorded using polyester films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H measurement using CDCl$_3$ as a solvent.

X-Ray diffractograms of polyesters were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2°/min. Dried polymer films or powder was used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 10 ^{o}C/min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) analysis was carried out on TA instrument DSC Q10, at a heating rate of 10 °C/min in nitrogen atmosphere.

7b.3 Synthesis of aromatic polyesters containing pendent pentadecyl chains
7b.3.1 Synthesis of homopolyesters containing pendent pentadecyl chains

A representative procedure for synthesis of polyesters is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel, were placed bisphenol A (0.450 g, 1.98 x 10^{-3} mol) dissolved in 1M NaOH (3.94 mL). The mixture was stirred at 10 ^{o}C for 1h. Thereafter, BTEAC (0.12 g) was added to the reaction mixture. The solution of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride (1 g, 1.98 x 10^{-3} mol) in dichloromethane (20 mL)was added in one lot to the reaction mixture and the reaction mixture was stirred vigorously at 2000 rpm at 10 ^{o}C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and precipitated into

methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 °C under reduced pressure for two days.

7b.3.2 Synthesis of copolyesters containing pendent pentadecyl chains

A representative procedure for synthesis of copolyesters is described below.

Into a 200 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel, were placed bisphenol A (1.4 g, 6.14 x 10^{-3} mol) dissolved in 1M NaOH (12.3 mL). The mixture was stirred at 10 °C for 1h. Thereafter, BTEAC (0.16 g) was added to the reaction mixture. The solution of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride 0.39 g, 1.53 x 10^{-3} mol) and isophthaloyl chloride (IPC) (0.93 g, 4.6 x 10^{-3} mol) in dichloromethane (40 mL) was added in one lot to the reaction mixture and the reaction mixture was stirred vigorously at 2000 rpm at 10 °C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. Polymer was dissolved in dichloromethane (20 mL) and precipitated into methanol:water (1:1, v/v), (1000 mL) mixture. Polymer was filtered, washed with methanol and dried at 50 °C under reduced pressure for two days.

7b.4 Results and discussion

7b.4.1 Synthesis of aromatic polyesters containing pendent pentadecyl chains

In the present study, polyesters containing pendent pentadecyl chains and ether linkages in the backbone were synthesized in order to study the effect of incorporation of pentadecyl chains on the polymer properties such as solubility and thermal stability.

Polyesters were synthesized by interfacial polycondensation of 4-(4-(chlorocarbonyl) phenoxy)-2-pentadecylbenzoyl chloride in dichloromethane and aqueous solution of sodium salt of three commercially available bisphenols *viz*; bisphenol-A, (hexafluoroisopropylidene)diphenol and 1,1'-bis(4-hydroxyphenyl)-1-phenylethane using BTEAC as the phase transfer catalyst[26, 2] (**Scheme 7b.1**). Copolyesters were also synthesized from a mixture of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and TPC/IPC with bisphenol A (**Scheme 7b.2**).

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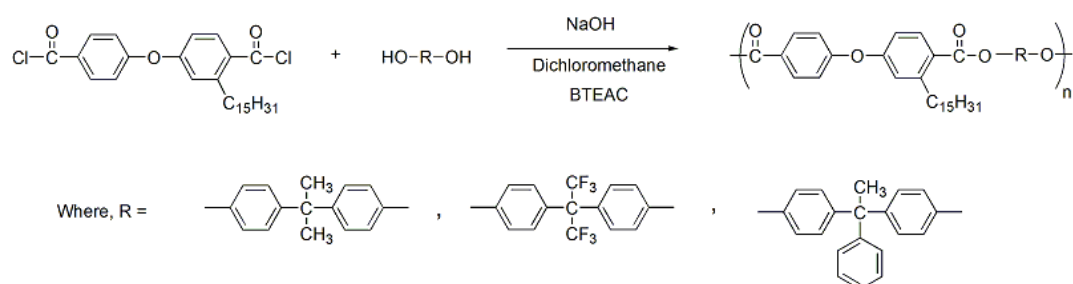
Scheme 7b.1 Synthesis of polyesters from 4-(4-(chlorocarbonyl)phenoxy)-2-

pentadecylbenzoyl chloride and bisphenols
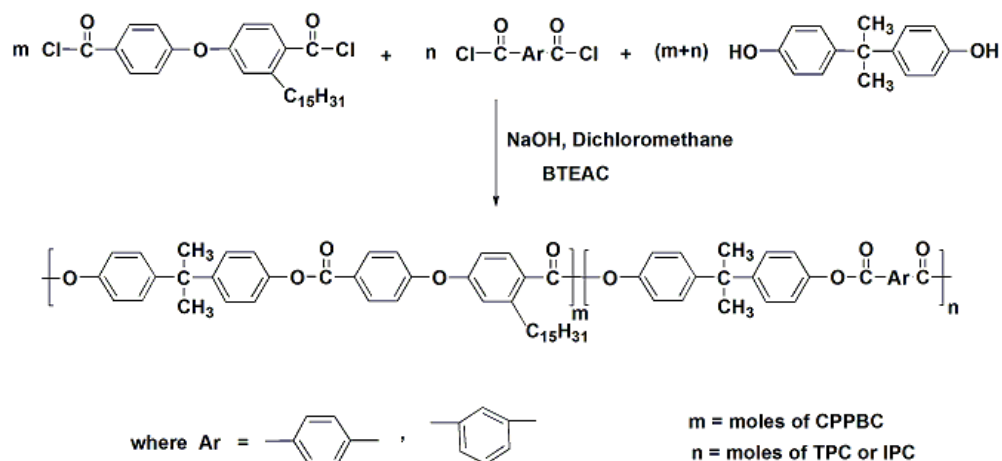
Scheme 7b.2 Synthesis of copolyesters from a mixture of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and TPC/ IPC with BPA.

The results of polymerizations are summarized in **Table 7b.1** and **Table 7b.2.**

Table 7b.1 Synthesis of aromatic polyesters containing pendent pentadecyl chains based on 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride

Polyester code	Polyester	η_{inh} (dL/g) [a]	Molecular Weight [b]		Mw/Mn
			Mn	**Mw**	
BPES-1		0.79	57,100	1,23,300	2.1
BPES-2		0.63	38,400	81,300	2.1
BPES-3		1.13	1,01,900	2,04,700	2.1

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

Table 7b.2 Synthesis of aromatic copolyesters containing pendent pentadecyl chains

Polymer	Bisphenol A (mol%)	CPPBC	TPC	IPC	η_{inh} [a] (dL/g)	Mn	Mw	Mw/ Mn
		Diacid chloride, (mol %)				Molecular weight[b]		
BPES-4	100	50	0	50	0.71	33,700	81,500	2.1
BPES-5	100	25	0	75	0.70	35,400	74,400	2.1
BPES-6	100	15	0	85	0.45	26,600	61,200	2.3
BPES-7	100	50	50	0	0.51	18,100	36,300	2.0
BPES-8	100	25	75	0	--[c]	--[c]	--[c]	--[c]

a: η_{inh} was measured with 0.5% (w/v) solution of polyester in chloroform at $30 \pm 0.1^{\circ}$C.

b: Measured by GPC in chloroform; polystyrene was used as the calibration standard.

c: ηinh and molecular weight could not be determined as polymer was insoluble in chloroform.

Polyesters exhibited inherent viscosity in the range 0.45 - 1.13 dL/g. Their molecular weight (Mn) and polydispersity index, determined by GPC, were in the range 18,100 - 1,01,900 and 2.0 -2.3, respectively. Except for BPES-8, tough transparent and flexible films of polyesters containing pendent pentadecyl chain could be cast from their solutions in chloroform.

7b.4.2 Structural characterization

The formation of polyesters was confirmed by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

FT-IR spectrum of polyester derived from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and BPA is reproduced in **Figure 7b.1**.
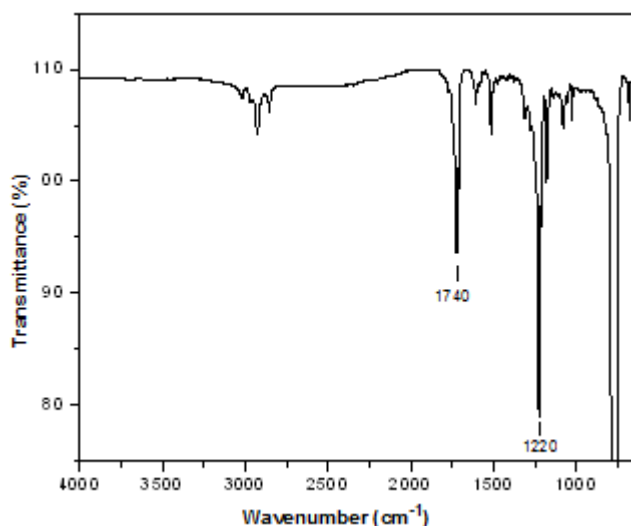
Figure 7b.1 FT-IR spectrum of polyester from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and BPA (BPES-1)

Ester carbonyl band of polyesters was observed at 1740 cm^{-1}. The band at 1220 cm^{-1} is attributed to C-O-C linkage.

^{1}H-NMR spectrum of polyester derived from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and bisphenol A along with assignments is shown in **Figure 7b.2.**
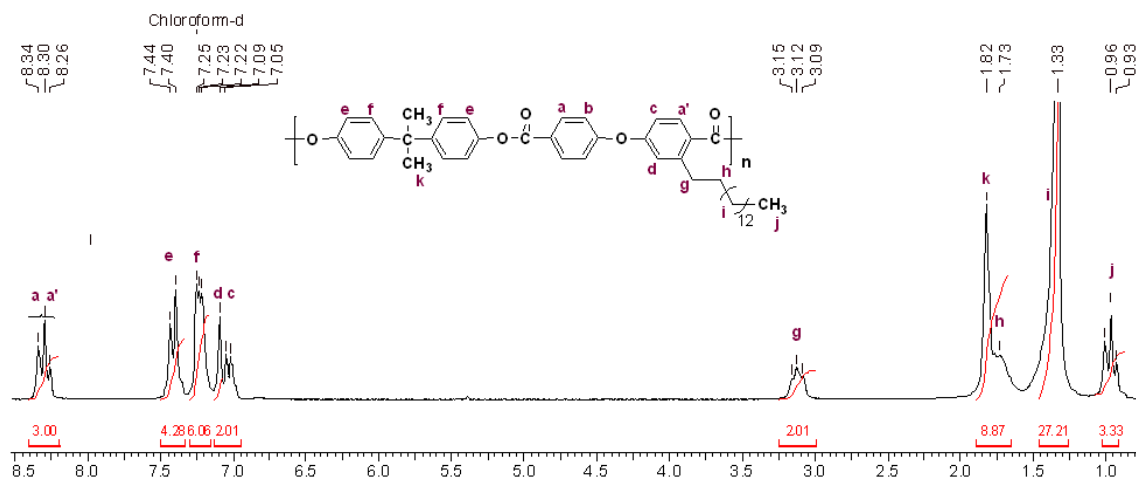
Figure 7b.2 ^{1}H-NMR spectrum (CDCl$_3$) of polyester from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and BPA (BPES-1)

The peaks appeared in the range 8.34-8.26 δ ppm are due to protons "a" and "a'". The doublets at 7.42 δ ppm and 7.24 δ ppm are due to protons "e" and "f", respectively. The proton "d" exhibited a singlet at 7.22 δ ppm. The peaks displayed in the range 7.09-7.05 δ ppm are due to protons "c+d". The methylene protons "g" appeared as a triplet at 3.12 δ ppm. The peaks in the range 1.82-1.73 δ ppm are due to methyl protons "k" and methylene protons "h". The methylene protons "i" appeared in the range 1.50-1.25 δ ppm. The triplet appeared at 0.93 δ ppm corresponds to methyl protons "j".

^{1}H-NMR spectrum of copolyester derived from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and IPC with BPA is shown in **Figure 7b.3.**
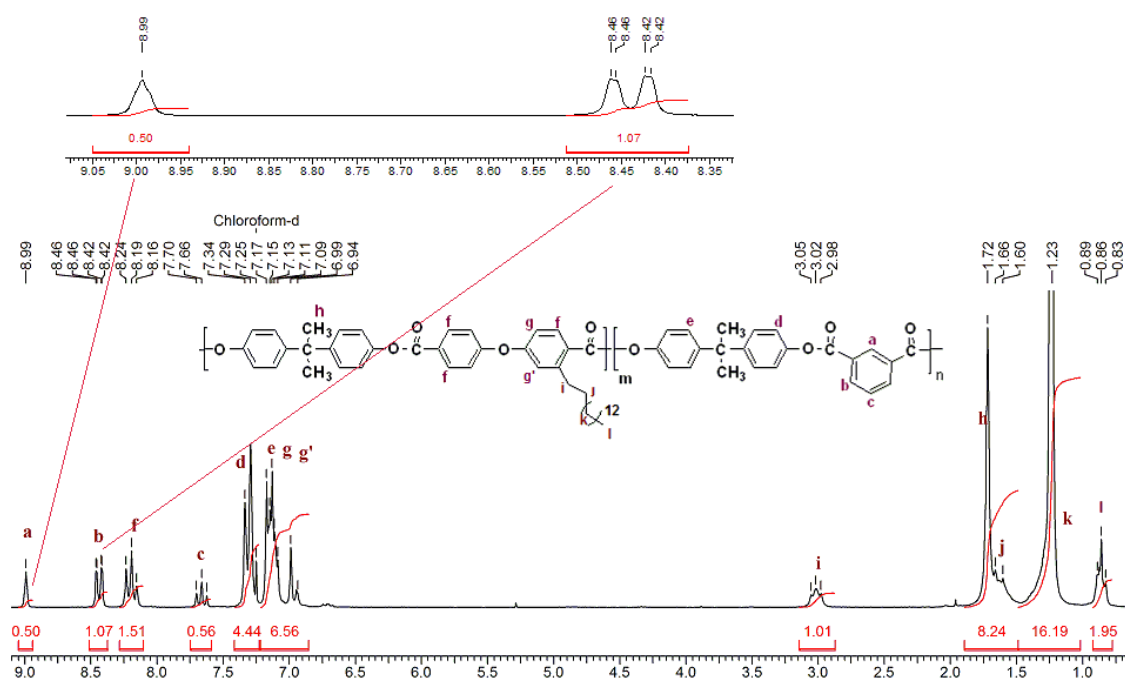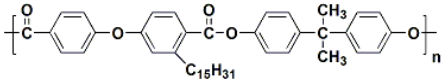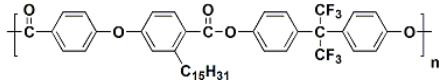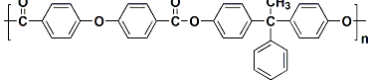
Figure 7b.3 ^{1}H-NMR spectrum (CDCl$_3$) of copolyester from a mixture of 4 -(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and IPC with BPA (BPES-4)

The proton "a" flanked by ester carbonyl groups appeared as a triplet at 8.99 δ ppm. The protons "b" exhibited doublet of doublet at 8.44 δ ppm. The protons "f" exhibited a triplet at 8.19 δ ppm. The triplet at 7.66 δ ppm is due to proton "c". The protons "d" appeared as a doublet at 7.34 δ. The peaks appeared in the range 7.17-6.94 δ ppm are due to protons "e","g" and "g'". The methylene protons "i" appeared as a triplet at 3.02 δ ppm. The methyl protons "h" and methylene protons "j" merged together and appeared in the range 1.72- 1.60 δ ppm. The peaks appeared in the range 1.25-1.23 δ ppm are due to protons "k". Methyl protons of the aliphatic chain appeared as a triplet at 0.86 δ ppm

7b.4.3 Solubility of polyesters

Solubility data of polyesters containing pendent pentadecyl chains in different organic solvents at 3 wt % (w/v) is summarized in **Table 7b.3** and **Table 7b.4.**

Table 7b.3 Solubility data of aromatic polyesters containing pendent pentadecyl chains

Polyester code	Polyester	CHCl₃	DCM	THF	Pyridine	m-Cresol	DMSO
BPES-1		++	++	++	++	++	--
BPES-2		++	++	++	++	++	--
BPES-3		++	++	++	++	++	--

++ : soluble, -- : insoluble

Table 7b.4 Solubility data of aromatic copolyesters containing pendent pentadecyl chains

Polyester code	Bisphenol A (mol %)	Acid chloride (mol %)			CHCl₃	DCM	THF	Pyridine	m-cresol
		CPPBC	TPC	IPC					
BPES-4	100	50	0	50	++	++	++	++	++
BPES-5	100	25	0	75	++	++	--	++	++
BPES-6	100	15	0	85	++	++	--	++	++
BPES-7	100	50	50	0	++	++	--	++	++
BPES-8	100	25	75	0	--	--	--	--	++

++ : soluble, -- : insoluble

Polyesters BPES-1, BPES-2 and BPES-3 derived from 4- (4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and BPA / HFBPA / BisP-AP were soluble in organic solvents such as

dichloromethane, chloroform, THF, pyridine and *m*-cresol. Polyester obtained from bis(4-hydroxyphenyl)ether and isophthaloyl chloride is reported to be not soluble in the above mentioned solvents[29] and is soluble in a mixture of phenol and tetrachloroethane. The analogous polyester BPES-1is easily soluble in common organic solvents indicating that presence of pendent pentadecyl chains is responsible for its improved solubility. An examination of solubility data of copolyesters indicated that incorporation of only 15 mol % of CPPBC was sufficient to impart solubility to IPC- based polyesters while incorporation of even 25 mol % of CPPBC was not sufficient to bring about solubility of TPC- based polyesters in common organic solvents. However, copolyester containing 50 mol % of CPPBC was soluble in common organic solvents. Thus, the improved solubility of synthesized polyesters could be attributed to weakening of the intermolecular interactions of polymer chains due to pentadecyl chains.

7b.4.4 X-Ray diffraction studies

Wide-angle X-ray diffractograms of polyesters containing pendent pentadecyl chains are reproduced in **Figure 7b.4**. X-Ray diffractograms of polyesters BPES-1 to BPES-3 exhibited a broad halo over the range 2θ≈10–30º indicating that the polyesters were amorphous in nature. It is reported that polyesters derived from BPA with TPC and BPA with IPC are partially crystalline in nature.[30, 31] Apparently, the introduction of pendent pentadecyl chains into the polyesters interfere with the dense chain packing thus resulting in their amorphous nature. Copolyesters BPES-4 to BPES-8 were found to be partially crystalline and the crystallinity decreased with increase in the content of pentadecyl substituted diacid chloride monomer *viz*; CPPBC.
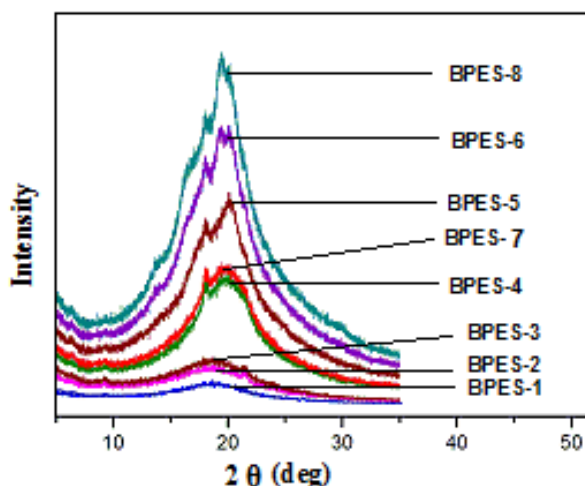
Figure 7b.4 X-Ray diffractograms of aromatic polyesters containing pendent pentadecyl chains

7b.4.5 Thermal behavior of polyesters

Thermal stability of polyesters was determined by TGA at a heating rate of 10 ºC/min under nitrogen atmosphere. TG curves of polyesters are reproduced in **Figure 7b.5** and **Figure 7b.6**. The temperature at 10 % weight loss (T_{10}) was calculated from TG curves and the values are

given in **Table 7b.5.** T_{10} values were in the range 425-455 ºC, indicating their good thermal stability.
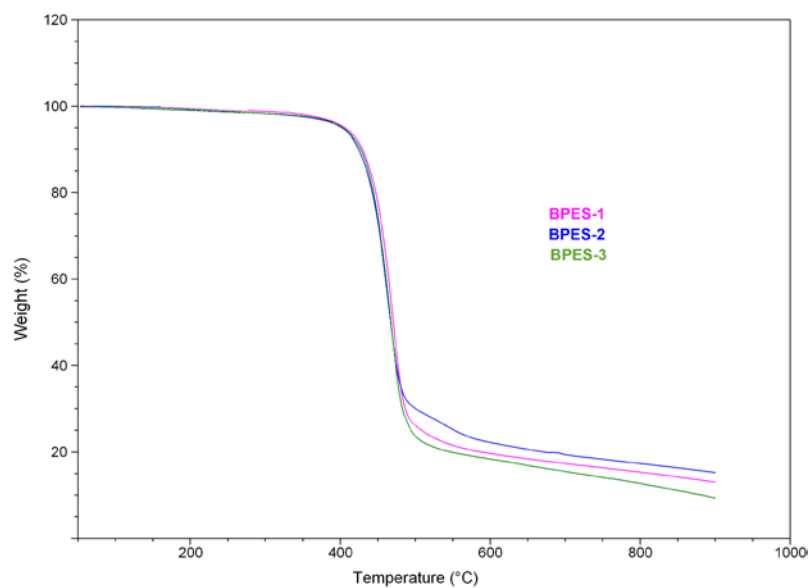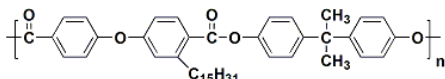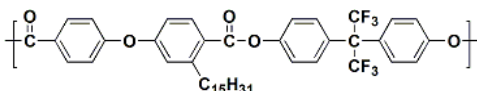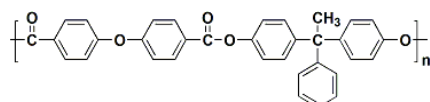
Figure 7b.5 TG curves of (co)polyesters containing pendent pentadecyl chains
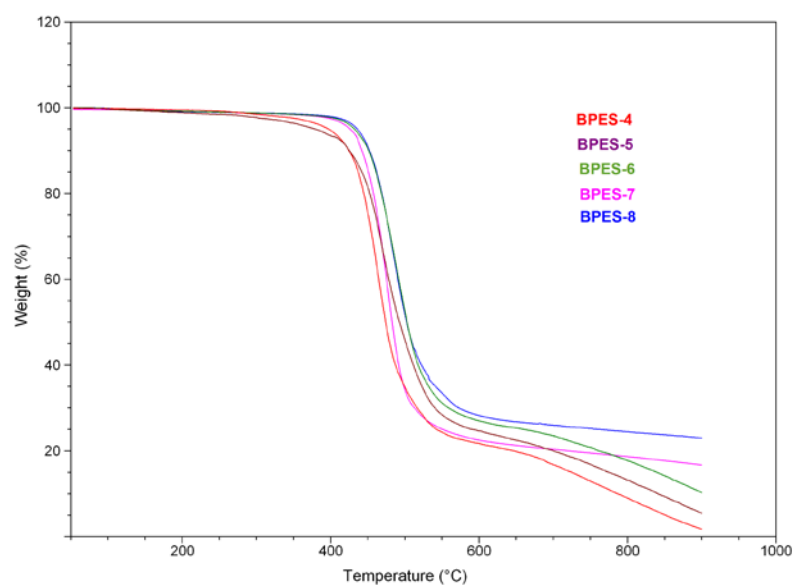
Figure 7b.6 TG curves of copolyesters containing pendent pentadecyl chains

Table 7b.5 Thermal properties of aromatic polyesters containing pendent pentadecyl chains

Polyester code	Polyester	Tg (°C)[a]	T$_{10}$ (°C)[b]
BPES-1		45	430
BPES-2		50	425
BPES-3		70	430

a : Measured on DSC at a heating rate of 10 °C/min. in nitrogen
b : Measured by TGA at a heating rate of 10 °C/min in nitrogen.

Table 7b.6 Thermal properties of aromatic copolyesters containing pendent pentadecyl chains

Polyester code	Bisphenol A (mol %)	CPPBC	Diacid Chloride, (mol %)		Tg (°C)[a]	T$_{10}$ (°C)
			TPC	IPC		
BPES-4	100	50	00	50	75	425
BPES-6	100	25	00	75	125	430
BPES-7	100	15	00	85	135	450
BPES-8	100	50	50	00	80	445
BPES-9	100	25	75	00	135	455

a : Measured on DSC at a heating rate of 10 °C/min. in nitrogen.
B : Measured by TGA at a heating rate of 10 °C/min in nitrogen.

DSC curves of polyesters are reproduced in **Figure 7b.7** an**d 7b.8.** Tg values obtained from the second heating scans at a heating rate of 10 °C / min are listed in **Table 7b.5** and **Table 7b.6.** Tg values of polyesters based on CPPBC with BPA/HFBPA/BisP-AP were in the range 45-70 °C. The increasing order of Tg generally corresponds to an increase in the rigidity and bulkiness of the bisphenol monomer. Tg values for the copolyesters obtained from CPPBC and IPC/TPC with BPA were in the range 75 – 135 °C. It should be noted that the *meta* substituted copolymers presented lower Tg values than corresponding *para*-substituted ones. It is reported that Tg values of the polyesters derived from BPA with TPC and BPA with IPC are 210 °C and 181 °C, respectively[29]. The depression in Tg of polyesters based on CPPBC could be attributed to the co-operative effect of decrease in rigidity of the polymer by increased degree of freedom available and decrease in intermolecular interactions caused by the chain separation effect. A large window between glass transition temperature (45-135 ^{o}C) and T$_{10}$ values (425-455 ^{o}C) was observed which offers polyesters a wide processing window.
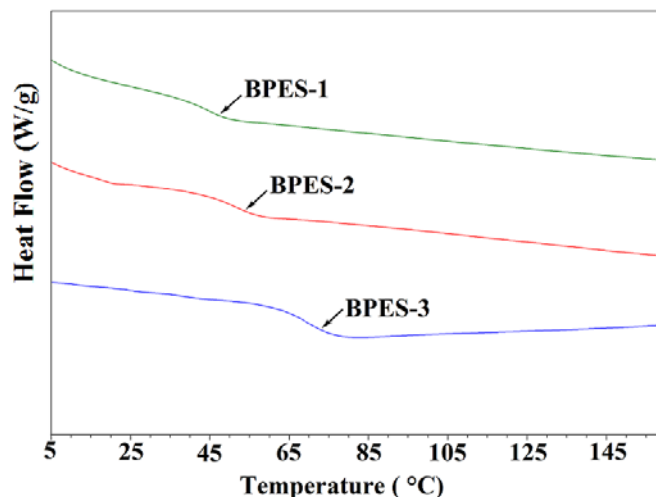
Figure 7b.7 DSC curves of polyesters containing pendent pentadecyl chains
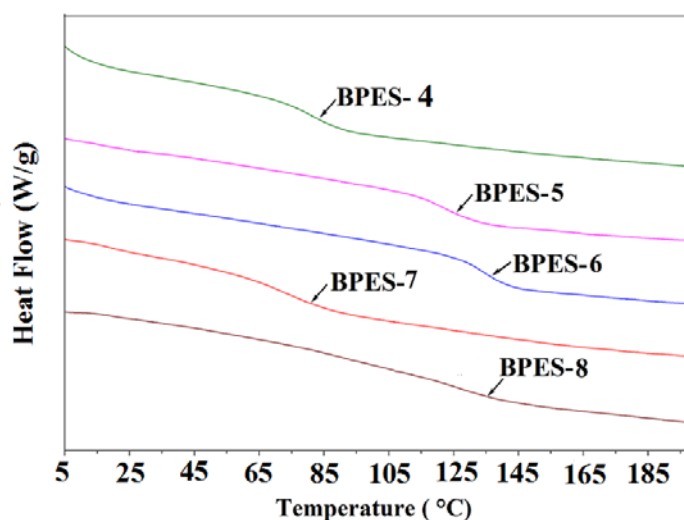
Figure 7b.8 DSC curves of copolyesters containing pendent pentadecyl chains

7b.5 Conclusions

1.   A series of polyesters containing pendent pentadecyl chains was synthesized from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride with bisphenols by phase transfer catalyzed interfacial polycondensation technique. Copolyesters were also synthesized from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and isophthaloyl chlorides/terephthaloyl chloride with bisphenol A.

2.   Most of the polyesters were found to be soluble in chloroform, dichloromethane, pyridine, *m*-cresol, etc.

3.   Tough, transparent and flexible films could be cast from solutions of polyesters in chloroform.

4.   DSC analysis showed that the pendent pentadecyl chains induced the depression of Tg (45-135 ºC).   A large window between glass transition temperature (45-135 ºC) and T_{10} values (425-455 ºC) was observed which offers polyesters a wide processing window.

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Chapter 8
Summary and Conclusions

8.1 Summary and Conclusions

The overall goal of the present work was to design and synthesize clickable aromatic polyesters and polyamides and study their post-functionalization *via* click chemistry approach. Towards this end, difunctional monomers containing suitable clickable groups, namely propargyloxy, allyloxy or azido functionality, were synthesized for step-growth polymerizaion. Additionally, difunctional monomers such as diacid chloride, diazides and a diamine containing pendent pentadecyl chain were synthesized.

Starting from commercially available 1,1,1-tris(4-hydroxyphenyl)ethane, 5-hydroxyisophthalic acid and 4,4'-bis(4-hydroxyphenyl)pentanoic acid, the following eight clickable difunctional monomers were synthesized.

1   1,1-Bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane

2   5-(Propargyloxy)isophthalic acid

3   5-(Propargyloxy)isophthaloyl chloride

4   5-(Propargyloxy)-1,3-diisocyanatobenzene

5   5-(Allyloxy)isophthalic acid

6   5-(Allyloxy)isophthaloyl chloride

7   5-(Allyloxy)-1,3-diisocyanatobenzene, and

8   4,4'–(5-Azidopentane-2,2-diyl)diphenol

Four difunctional monomers containing pendent pentadecyl chain were synthesized starting from 3-pentadecyl phenol, which in turn was obtained from CNSL-a renewable resource material.

9   2,4-Diazido-1-pentadecylbenzene

10   1-Azido-4(4-azidophenoxy)-2-pentadecylbenzene

11   4-(4-(Chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride

12   *N*-(4-Amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy)benzamide

Thus, twelve difunctional monomers were designed and synthesized *via* simple organic transformations. Of these, seven monomers (Sr. No. 1, 4, 7, 8, 9, 10 and 12) were synthesized for the first time. Monomers and intermediates involved in their synthesis were characterized by spectroscopic techniques such as FT-IR and NMR spectroscopy.

Difunctional monomers containing pendent propargyloxy or allyloxy group were utilized for the synthesis of clickable aromatic polyesters and polyamides. Aromatic polyesters containing pendent azido groups were synthesized based on bisphenol containing azido group. Diacid chloride containing pendent pentadecyl chain was utilized for the synthesis of aromatic polyesters.

Homopolyester containing pendent propargyloxy functionalities was synthesized by phase transfer-catalyzed interfacial polycondensation of 5-(propargyloxy)isophthaloyl chloride with bisphenol A. Copolyesters containing varying mol percent (25%, 50% and 75%) of 5-(propargyloxy)isophthaloyl chloride monomer containing pendent

propargyloxy group were synthesized by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A. Inherent viscosity of polyesters was in the range 0.90-1.33 dL/g. Medium to reasonably high molecular weight polyesters, soluble in common organic solvents such as chloroform, dichloromethane, THF, pyridine and *m*-cresol were obtained. Improvement in solubility of polyesters was observed by incorporation of pendent propargyloxy groups. Tough, transparent and flexible films of polyesters could be cast from chloroform solutions. The broad halo over the range $2\theta \approx 12–35°$ was observed for the polyesters in the wide angle X-ray diffraction patterns which revealed their amorphous nature. T_{10} values obtained from TG curves for polyesters were in the range 390-420 °C, indicating their good thermal stability. Glass transition temperature (*Tg*) of polyesters was in the range 146-170 °C. Curing behaviour of polyesters was studied in nonisothermal mode using DSC technique. DSC profiles of polyesters displayed a broad exotherm in the first scan, which began at about 220 °C and finished at 330 °C with a peak maximum temperature around 290 °C. In the second scan of DSC experiment, no trace of exothermic peak was observed indicating the cross-linking of the propargyloxy groups was completed during the first heating scan. The enthalpy of curing (Δ*H)* was determined from the area under the exothermic curve and was found to be in the range 118-413 J/g. Increase in ΔH was observed with the increase in the content of propargyloxy functional groups into the polyesters. Copolyester containing 50 mol percent of 5-(propargyloxy)isophthaloyl chloride monomer was post-functionalized by click reaction with five different azides *viz*; 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene, azido containing polymeric chains such as azido-terminated polystyrene (PS-N_3) and azido-terminated polyethylene glycol monomethyl ether of different molecular weights (Mn = 550, 1000 g/mol, PEG_{550}-N_3, PEG_{1000}-N_3) using copper catalyzed azide-alkyne click reaction. Quantitative functionalization was confirmed by FT-IR and ^{1}H-NMR spectroscopy. Thus, copper-catalyzed alkyne-azide click reaction turned out to be a very efficient reaction to functionalize aromatic polyesters under mild conditions for which no backbone degradation was observed. Polyesters functionalized with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene exhibited characteristics UV-Vis absorption peaks at 315, 330, 345, and 275 nm, respectively. The polyester functionalized with pyrene and anthracene derivatives showed spectral emission at 485 and 440 nm, respectively. Contact angle (CA) images of polyester grafted with PEG and PS derivatives showed a change in contact angle (CA changed from 88 º to 37 º and 88 º to 97 º, respectively). Decrease in contact angle of PEG grafted polyester is due to better spatial arrangement of the hydrophilic PEG moiety to the polyester surface whereas increase in contact angle of PS grafted polyester could be attributed to the attachment of hydrophobic PS moiety to the polyester.

A series of new aromatic polyesters possessing clickable propargyloxy functionalities was synthesized from 1,1-bis (4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and aromatic diacid chlorides *viz*; TPC, IPC and TPC+IPC (50:50, mol %) by phase transfer catalyzed interfacial

polycondensation technique. Copolyesters were synthesized by polycondensation of a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and bisphenol A with IPC. Inherent viscosities of polyesters were in the range 0.50-0.75 dL/g indicating formation of medium to reasonably high molecular weight polymers. Polyesters were soluble at room temperature in solvents such as chloroform, dichloromethane, THF, NMP, pyridine, DMF, etc. Tough, transparent and flexible films of polyesters could be cast from chloroform solutions. The broad halo over the range $2\theta \approx 15–25°$ was observed for polyesters in the wide angle X-ray diffraction patterns indicating their amorphous nature. T_{10} values obtained from TG curves of polyesters were in the range 410-440 °C indicating their good thermal stability. ΔH of curing reactions of polyesters studied by DSC in nonisothermal mode was observed in the range 103 – 326 J/g. Increase in ΔH was observed with increase in the content of propargyloxy functional groups into the polyesters.

New clickable aromatic polyesters were synthesized by phase transfer-catalyzed interfacial polycondensation of 4,4'–(5-azidopentane-2,2-diyl)diphenol with TPC, IPC, or TPC+IPC (50:50 mol %). Copolyesters containing varying mol percent (30%, 20% and 10%) of 4,4'–(5-azidopentane-2,2-diyl)diphenol monomer containing azido functionality were synthesized from a mixture of 4,4'–(5-azidopentane-2,2-diyl)diphenol and 4,4'-(1-phenylethane-1,1-diyl)diphenol with IPC. Inherent viscosities of polyesters were in the range 0.72-1.65 dL/g indicating formation of medium to reasonably high molecular weight polymers. The introduction of pendent alkyl chain with azido group brought about improvement in solubility and the polyesters were soluble in solvents such as chloroform, dichloromethane, THF, DMF, DMAc, NMP, pyridine and *m*-cresol. Tough, transparent and flexible films of polyesters could be cast from chloroform solutions. The broad halo over the range $2\theta \approx 10$-$35°$ was observed for polyesters in the wide angle X-ray diffraction patterns which indicated their amorphous nature. Glass transition temperature for polyesters derived from 4,4'–(5-azidopentane-2,2-diyl)diphenol with IPC, 4,4'–(5-azidopentane-2,2-diyl)diphenol with TPC and 4,4'–(5-azidopentane-2,2-diyl)diphenol with a mixture TPC and IPC (50:50, mol %) was 144, 158 and 151 °C, respectively. From TGA analysis it was observed that polyesters containing pendent azido groups underwent a mass loss of around 10 % in the temperature range 225–310 °C which corresponds to the theoretical mass loss due to release of nitrogen by decomposition of azido groups. As a model reaction, the post-functionalization of the copolyester containing 30 mol percent of 4,4'–(5-azidopentane-2,2-diyl)diphenol monomer was successfully performed *via* copper-catalyzed azide-alkyne click reaction using phenyl acetylene. Complete conversion of the pendent azido functionalities to triazoles was confirmed by FT-IR and ^{1}H-NMR spectroscopy. The compatibility of azido group with the low temperature polycondensation reaction and the versatile click chemistry that is enables makes 4,4'–(5-azidopentane-2,2-diyl)diphenol monomer uniquely suited

for preparation of functional polyesters and other polymers such as polycarbonates and poly(estercarbonate)s.

New clickable aromatic polyamide was synthesized from 5-(propargyloxy)isophthaloyl chloride and 4,4'-oxydianiline by low temperature solution polycondensation technique. Copolyamides containing varying mol percent (30%, 20% and 10%) of 5-(propargyloxy)isophthaloyl chloride monomer containing pendent propargyloxy functionality were synthesized from a mixture of 5 (propargyloxy)isophthaloyl chloride and IPC with 4,4'-oxydianiline. Polyamides had inherent viscosities in the range 0.52-1.0 dL/g. Polyamides were found to be soluble in solvents such as DMF, DMAc, NMP and pyridine. Tough, transparent and flexible films of polyamide could be cast from DMAc solutions. The enthalpy of curing (ΔH) of polyamides determined by DSC in nonisothermal mode was observed in the range 15–278 J/g. Increase in ΔH values was observed with the increase in the content of propargyloxy functional groups in the polyamides. Post-functionalization of copolyamide containing 30 mol percent of 5-(propargyloxy)isophthaloyl chloride monomer was performed *via* copper-catalyzed azide-alkyne click reaction, for which azides, *viz*; 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene as well as azido-terminated polyethylene glycol monomethyl ether of different molecular weights ($Mn = 550, 1000$ g/mol, $PEG_{550}N_3$, $PEG_{1000}-N_3$) were used. Quantitative functionalization was confirmed by FT-IR and ^{1}H-NMR spectroscopy. Polyamides functionalized with 1-(4-azidobutyl)pyrene and 9-(azidomethyl)anthracene exhibited characteristics UV-Vis absorption peaks at 315, 330, 345, and 275, respectively. Polyamides functionalized with pyrene and anthracene derivatives showed spectral emission at 485 and 440 nm, respectively. Contact angle (CA) images of polyamide grafted with PEG derivatives showed a change in contact angle (CA changed from 82 ° to 44 °). Decrease in contact angle of PEG grafted polyamide is due to better spatial arrangement of the hydrophilic PEG moiety to the polyamide surface. Polarized optical microscopy and SEM analysis showed that the polyamide modified with PEG has smooth surface than parent polyamide.

A series of clickable aromatic polyamides was synthesized by polycondensation of 5-(allyloxy)isophthalic acid with commercially available aromatic diamines *viz*; 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline and 4,4'-(hexafluoroisopropylidene) dianiline by Yamazaki reaction (phosphorylation reaction) at 120 °C. Copolyamides were synthesized from a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline *via* phosphorylation reaction. ^{1}H-NMR spectral analysis of polyamides indicated that the allyloxy groups remained intact during polymerization. Inherent viscosities of the polyamides were in the range 1.21-0.65 dL/g. Polyamides were found to be soluble in solvents such as DMAc, NMP, DMF, pyridine and DMSO. Wide angle X-ray diffraction patterns of polyamides showed broad halo over the range $2\theta \approx 10\text{-}35^\circ$ suggesting that polymers were amorphous.

New clickable aromatic polyester containing pendent allyloxy groups was synthesized by polycondensation of 5-(allyloxy)isophthaloyl chloride with BPA. A copolyester was also synthesized from a mixture of a mixture of 5-(allyloxy)isophthaloyl chloride and IPC with BPA. Inherent viscosity of homo- and co-polyester was 0.50 and 0.72 dL/g, respectively. Both the polyesters were found to be soluble in chloroform, DCM, THF, DMF, DMAc, NMP, pyridine, and *m*-cresol. Copolyester containing 25 mol percent of 5-(allyloxy)isophthaloyl chloride monomer was post-functionalized by four different thiols *viz;* 1-butanethiol, 2-mercaptoethanol, 3-mercaptopropanoic acid, 11-marcaptoundecyl phosphoric acid *via* thiol-ene click reaction. FT-IR and ^{1}H-NMR spectra of the resulting polymers confirmed the success of the thiol-ene click reaction.

A series of new aromatic polyesters was synthesized from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and aromatic bisphenols *viz*; bisphenol-A, (hexafluoroisopropylidene)diphenol, and 1,1'-bis(4-hydroxyphenyl)-1-phenylethane by phase transfer catalyzed interfacial polycondensation technique. Copolyesters containing pendent pentadecyl chains were synthesized by interfacial polycondensation of a mixture of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and IPC with bisphenol A. Inherent viscosities of (co)polyesters were in the range1.13-0.45 dL/g indicating formation of medium to reasonably high molecular weight polymers. Tough, transparent and flexible films of most of the polyesters could be cast from chloroform solutions. Homopolyesters obtained from 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and bisphenol A exhibited good solubility in solvents such as chloroform, dichloromethane, THF, pyridine and *m*-cresol. Copolyesters were found to be soluble in chloroform, dichloromethane, pyridine and *m*-cresol. Thus, improvement in solubility of polyesters was observed due to the presence of pendent pentadecyl chains. The broad halo over the range $2\theta\approx10$–$30°$ observed for the polyesters in the wide angle X-ray diffraction patterns revealed their amorphous nature .Tg and T_{10} values of the polyesters were in the range 45-135 °C and 425-455 °C, respectively. The observed large window between Tg and T_{10} values offers polyesters a wide processing window.

8.2   *Perspectives*

The present work on design and synthesis of clickable difunctional monomers, pentadecyl containing difunctional monomers, clickable polyesters and polyamides has opened up many prospects for the future work.

➢ The present work on synthesis of difunctional monomers has expanded the range of clickable monomers available for the synthesis of functionalized polymers by step-growth polymerization.

➢ Difunctional monomers containing propargyloxy, allyloxy or azido functionality *viz*; 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane, 4,4'–(5-azidopentane-2,2-diyl)diphenol, 5-(propargyloxy)isophthaloyl chloride and 5-(allyloxy)isophthaloyl chloride are particularly well suited for synthesis of a host of high performance polymers under mild polymerization conditions. Synthesis of high performance polymers requiring higher polymerization temperatures (150 °C and above) is not recommended as at that temperature side reactions such as decomposition of azido group, thermal Claisen rearrangement of allyloxy group and thermal crosslinking of propargyloxy group are possible.

➢ It would now be interesting to synthesize other step-growth polymers based on synthesized difunctional monomers. For example, aromatic diisocyanates containing pendent propargyloxy and allyloxy groups are potentially useful monomers for the synthesis of polyurethanes and polyureas.

➢ Random copolyesters or copolyamides containing both propargyloxy and allyloxy pendent groups could be prepared by copolymerization of corresponding diacid chlorides with diols or diamines, respectively. Copolymers containing propargyloxy and allyloxy groups could be modified by orthogonal click reactions with the appropriate reagents to obtain interesting functionalized/graft copolymers.

➢ Polyesters and polyamides containing pendent propargyloxy groups can be utilized for post-functionalization using various commercially available thiols *via* thiol-yne click reaction.

➢ Diverse commercially available functional alkynes such as glycidyl propargyl ether (Fluka), propargyl alcohol (Acros), propiolic acid (Acros), 2- methyl-1-buten-3-yne (Aldrich), trimethyl(propargyl)silane (Acros) could be reacted with polyesters containing pendent azido groups *via* the click reaction and a series of corresponding pendent functionalized polyesters could be obtained.

➢ Polyesters containing pendent azido functional groups could find potential application as photolithography materials.

➢ Polyamides functionalized by PEG could be useful as antifouling membrane materials.

➢ The diazide*s viz*; 2,4-diazido-1-pentadecylbenzene and 1-azido-4(4-azidophenoxy)-2-pentadecylbenzene are potentially useful monomers for synthesis of soluble polytriazoles by reaction with dialkynes *via* azide-alkyne click reaction. These triazoles could be further modified by reaction of triazole moieties with alkyl halides/tosylates to give polymeric forms of ionic liquids in the backbone.
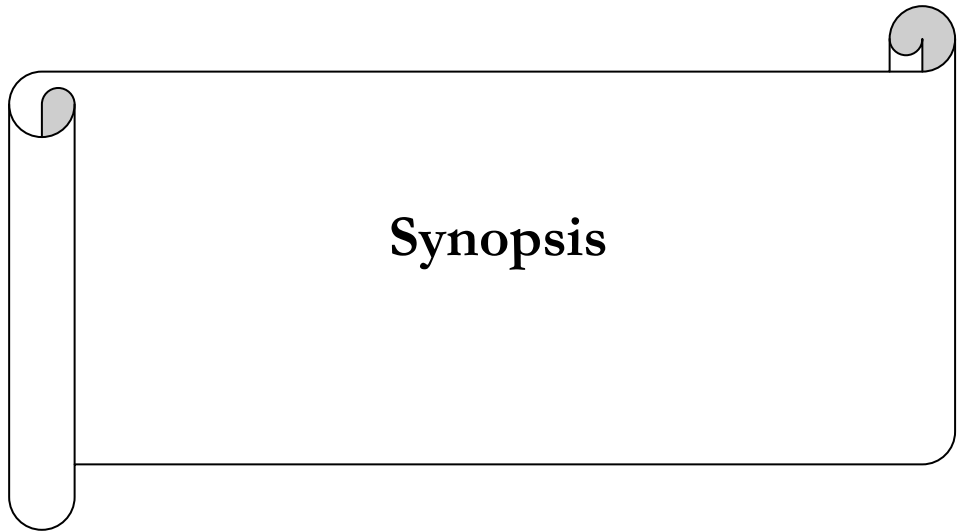
Synopsis

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Synopsis of Thesis Entitled

High Performance Polymers: Synthesis, Characterization and Chemical Modifications

</div>

Introduction

The post-polymerization modification is a powerful method for introducing new or altering existing functional groups on polymers.[1-12] In general, the technique is employed when (1) reaction conditions or catalyst necessary for polymerization are incompatible with the functional groups present on the corresponding monomer(s), (2) polymer isolation and/or processing is inhibited by the desired functionality, or (3) a means to rapidly prepare a diverse library of materials from a single polymeric precursor is desired. This broad range of applications provides the development of new reactions for modifying polymers. An ideal reaction for this purpose should have the following criteria: (1) it must not compromise the structural integrity of the polymer (i.e., chain scission and other degradative side reactions should not occur), (2) it should proceed with a high yield, and (3) to minimize applicability, it should utilize a structurally diverse range of reagents that are commercially or readily available.

The reactions that fulfil the requirement of these conditions are classified under click chemistry. The term click chemistry was first introduced by K. Barry Sharpless and co-workers,[13-20] who defined click chemistry 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). The required process characteristics include simple reaction conditions (ideally, the process should be insensitive to oxygen and water), readily available starting materials and reagents, the use of no solvent or a solvent that is benign (such as water) and simple product isolation. Purification, if required, must be by non- chromatographic methods, such as crystallization or distillation, and the product must be stable under physiological condition.[21-32] Examples of click Reaction include: azide-alkyne, thiol-ene, tertiary-amine catalyzed thiol-isocyanate, nitrile oxide-alkyne reactions, etc. Various approaches have so far been reported for synthesizing functionalized aliphatic polyesters and polyamides. However, functionalization of aromatic polyesters and polyamides *via* click chemistry approach has not been widely investigated.

Therefore, our approach is focused on a combination of step growth polymerization and click chemistry to obtain functionalized aromatic polyesters and polyamides. The first objective of this research was to develop a synthetic scheme that would allow the introduction of clickable functional groups such as pendent propargyloxy, allyloxy or azido groups into high performance polymers such as polyesters and polyamides. The approach involved synthesis of propargyloxy, allyloxy or azido group containing bisphenols, isophthalic acids, isophthaloyl chlorides and diisocyanates. The second objective of the present work was to synthesize aromatic polyesters and polyamides containing pendent propargyloxy, allyloxy or azido groups and study the effect of incorporation of these groups on solubility properties of polymers. The post-functionalization of

the synthesized aromatic polyesters and polyamides containing pendent propargyloxy, azido or allyloxy groups by alkyne- azide and thiol-ene click reaction, respectively was investigated in brief.

Another objective of the work was to synthesize diazides, diacidchloride and aromatic diamine containing pre-formed amide-linkages and possessing pendent pentadecyl chain starting from Cashew Nut Shell Liquid (CNSL)- a renewable resource material.

With the above objectives, the following specific work was chosen for the thesis.

Objectives of the present thesis:

1. Design and synthesis of aromatic diacids, diacid chlorides and diisocyanates containing pendent propargyloxy or allyloxy group starting from 5-hydroxyisophthalic acid–– a commercially available chemical.

2. Design and synthesis of bisphenols containing pendent propargyloxy or azido group starting from commercially available chemicals, *viz*; 1,1,1-tris(4-hydroxyphenyl)ethane and 4,4'-bis(4-hydroxyphenyl)pentanoic acid, respectively.

3. Design and synthesis of diazides, diacid chloride and diamine starting from 3-pentadecyl phenol which in turn is obtainable from CNSL- a renewable resource material

4. Synthesis and characterization of high performance polymers such as aromatic polyesters and polyamides containing pendent propargyloxy*,* allyloxy or azido groups and to study the effect of incorporation of these pendent groups on solubility properties of polymers.

5. To investigate curing studies of polyesters and polyamides containing pendent propargyloxy groups by differential scanning calorimetry (DSC) in nonisothermal mode.

6. Post-functionalization of the synthesized aromatic polyesters and polyamides containing pendent propargyloxy, azido or allyloxy groups by alkyne- azide and thiol-ene click reaction, respectively

7. Synthesis and characterization of aromatic polyesters containing pendent pentadecyl chains and study the effect of incorporation of pentadecyl chains on solubility and thermal properties of polyesters.

The thesis has been divided into the following eight chapters.

Chapter 1: Introduction and Literature Survey

A brief review of literature on chemical modification of polymers with an emphasis on click chemistry modifications of polymers containing pendent functional groups is presented in chapter 1.

Chapter 2: Scope and Objectives

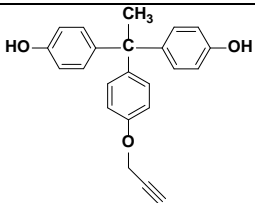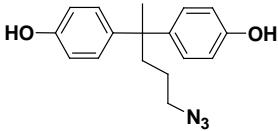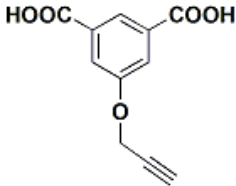Scope and objectives of the present work are described in this chapter.
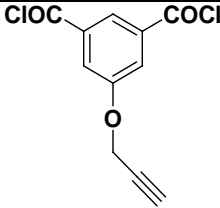
Chapter 3: Synthesis and Characterization of Difunctional Monomers Containing Pendent Propargyloxy, Allyloxy, Azido Group or Pentadecyl Chain.

This chapter provides a study on

i)   Synthesis of *meta*-oriented aromatic diacids, diacid chlorides and diisocyanates containing pendent propargyloxy or allyloxy group starting from 5- hydroxyisophthalic acid.

ii)   Synthesis of aromatic bisphenol containing pendent propargyloxy or azido group starting from 1,1,1-tris(4-hydroxyphenyl)ethane and 4, 4'-bis(4-hydroxyphenyl)pentanoic acid, respectively.

iii)   Synthesis of diazides, diacid chloride and diamine monomer containing pendent pentadecyl chain starting from 3-pentadecyl phenol.

The difunctional monomers (**Tables-1-2**) and intermediates involved in their synthesis were characterized by FT-IR, ^{1}H and ^{13}C-NMR spectroscopy.

Table 1: List of monomers containing pendent propargyloxy, allyloxy or azido group

Sr. No.	Monomer structure	Monomer
1		1,1-Bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane
2		4,4'–(5-Azidopentane-2,2-diyl)diphenol
3		5-(Propargyloxy)isophthalic acid
4		5-(Propargyloxy)isophthaloyl chloride
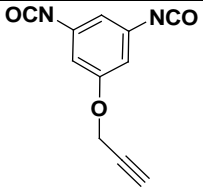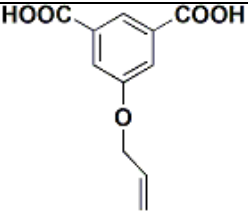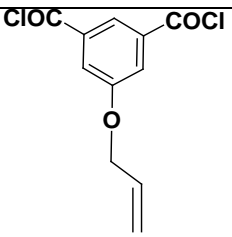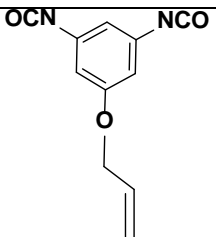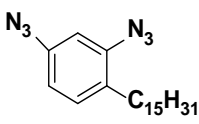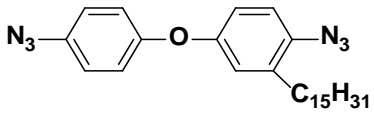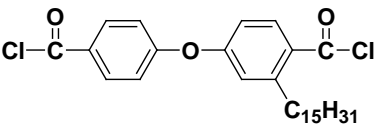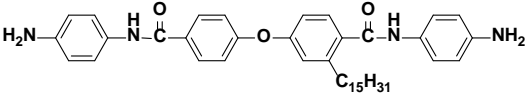
5		5-(Propargyloxy)-1,3-diisocyanatobenzene
6		5-(Allyloxy)isophthalic acid
7		5-(Allyloxy)isophthaloyl chloride
8		5-(Allyloxy)-1,3-diisocyanatobenzene

Table 2: List of monomers containing pendent pentadecyl chain

Sr. No.	Monomer structure	Monomer
9		2,4-Diazido-1-pentadecylbenzene
10		1-Azido-4(4-azidophenoxy)-2-pentadecylbenzene
11		4-(4-(Chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride

12		*N*-(4-Amino-3-pentadecyl)-4-(4-((4-aminophenyl)carbamoyl)phenoxy) benzamide

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Chapter 4: Synthesis, Characterization, Curing studies and Chemical Modification of Polyesters Containing Pendent Propargyloxy Groups

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This chapter is sub-divided into two sections:

Chapter 4a: Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy Groups

This section describes:

i. Synthesis of clickable aromatic polyester containing pendent propargyloxy groups by interfacial polycondensation of 5-(propargyloxy)isophthaloyl chloride with bisphenol A.

ii. Synthesis of copolyesters by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, TGA and DSC. This section also describes the curing studies of polyesters containing pendent propargyloxy groups by DSC in nonisothermal mode. The enthalpy of curing of polyesters was computed using DSC technique.

Chapter 4 b: Chemical Modification of Polyesters Containing Pendent Propargyloxy Groups

This section deals with chemical modifications of polyester containing pendent propargyloxy groups by azide-alkyne click reaction using azides *viz*; 1-(4-azidobutyl)pyrene, 9-(azidomethyl)anthracene, azido-terminated polystyrene (PS-N$_3$) and azido-terminated polyethylene glycol monomethyl ether (PEG-N$_3$), of different molecular weights (PEG$_{550}$N$_3$, PEG$_{1000}$-N$_3$). FT-IR, ^{1}H-NMR spectroscopy, GPC, contact angle measurements, UV-Vis spectra and fluorescence measurement techniques were used to characterize the functionalized polyesters.

Chapter 5: Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy or Azido Groups

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This chapter is divided into two sections:

Chapter 5 a: Synthesis, Characterization and Curing Studies of Polyesters Containing Pendent Propargyloxy Groups

This section describes:

i. Synthesis of polyesters containing pendent propargyloxy groups by polycondensation of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and isophthaloyl chloride or terephthaloyl chloride.

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ii. Synthesis of copolyester containing pendent propargyloxy groups by polycondensation of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane with a mixture of isophthaloyl chloride and terephthaloyl chloride.

iii. Synthesis of copolyesters containing pendent propargyloxy groups by polycondensation of a mixture of 1,1-bis(4-hydoxyphenyl)-1-(4'-propargyloxyphenyl)ethane and bisphenol A with isophthaloyl chloride.

Polyesters were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies and TGA. This section also describes curing studies of these polyesters by DSC in nonisothermal mode. The enthalpy of curing of polyesters was computed using DSC technique.

Chapter 5 b: Synthesis and Characterization of Polyesters Containing Pendent Azido Groups

This section deals with:

i. Synthesis of polyesters containing pendent azido groups by polycondensation of 4, 4'–(5-azidopentane-2, 2-diyl)diphenol with isophthaloyl chloride or terephthaloyl chloride

ii. Synthesis of copolyester by polycondensation of 4, 4'–(5-azidopentane-2, 2-diyl)diphenol with a mixture of isophthaloyl chloride and terphthaloyl chloride.

iii. Synthesis of copolyesters by polycondensation of a mixture of 4, 4'–(5-azidopentane-2, 2-diyl) diphenol and 4, 4'-(1-phenylethane-1, 1-diyl)diphenol with isophthaloyl chloride.

Polyesters were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, DSC and TGA. Selected polyester was chemically modified with phenyl acetylene *via* azide-alkyne click reaction. FT-IR and ^{1}H-NMR spectroscopy was used to characterize the functionalized polyester.

Chapter 6: Synthesis, Characterization, Curing Studies and Chemical Modification of Polyamides Containing Pendent Propargyloxy or Allyloxy Groups

This chapter is divided into three sections:

Chapter 6 a: Synthesis, Characterization and Curing Studies of Polyamides Containing Pendent Propargyloxy Groups

This section describes:

i. Synthesis of polyamide containing pendent propargyloxy groups by polycondensation of 5-(propargyloxy)isophthaloyl chloride with 4,4'-oxydianiline.

ii. Synthesis of copolyamides by polycondensation of a mixture of 5-(propargyloxy)isophthaloyl chloride and isophthaloyl chloride with 4,4'-oxydianiline

Polyamides were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies. This section also describes the curing studies of polyamides containing pendent propargyloxy groups. The enthalpy of curing of polyamides was computed using DSC technique.

Chapter 6 b: Chemical Modification of Polyamides Containing Pendent Propargyloxy Groups.

This chapter describes the chemical modification of polyamide containing pendent propargyloxy groups by azide-alkyne click reaction using azides *viz*; 1-(4-azidobutyl)pyrene, 9-(azidomethyl) anthracene and azido-terminated polyethylene glycol monomethyl ether (PEG-N$_3$), of different molecular weights (PEG$_{550}$N$_3$, PEG$_{1000}$-N$_3$). The functionalized polyamides were characterized by FT-IR, ^{1}H-NMR, contact angle measurements, UV-Vis spectra, fluorescence techniques, polarized optical microscopy (POM) and scanning electron microscopy techniques (SEM).

Chapter 6 c: Synthesis and Characterization of Polyamides Containing Pendent Allyloxy Groups

This section deals with:

i. Synthesis of polyamides containing pendent allyloxy groups by polycondensation of 5-(allyloxy)isophthalic acid with diamines, *viz*; 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylene dianiline and 4,4' (hexafluoroisopropylidene)dianiline.

ii. Synthesis of copolyamides by polycondensation of a mixture of 5-(allyloxy)isophthalic acid and isophthalic acid with 4,4'-oxydianiline.

Polyamides were characterized by inherent viscosity measurements, GPC, solubility tests, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy and X-ray diffraction studies.

Chapter 7: Synthesis, Characterization and Chemical Modification of Polyesters Containing Pendent Allyloxy Groups or Pentadecyl Chain

This chapter is divided into two sections:

Chapter 7 a: Synthesis, Characterization and Chemical Modification of Polyesters Containing Pendent Allyloxy Groups

This section describes:

i. Synthesis of polyester containing pendent allyloxy groups by polycondensation of 5-(allyloxy)isophthaloyl chloride with bisphenol A.

ii. Synthesis of copolyester by polycondensation of a mixture of 5-(allyloxy)isophthaloyl chloride and isophthaloyl chloride with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, solubility tests, GPC, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy. This section also describes chemical modification of copolyester containing pendent allyloxy groups *via* thiol-ene click reaction using four different thiols *viz;* 1-butanethiol, 2-mercaptoethanol, 3-mercaptopropanoic acid and 11-marcaptoundecyl phosphoric acid. FT-IR and ^{1}H-NMR spectroscopy was used to characterize the functionalized polyesters.

Chapter 7 b: Synthesis and Characterization of Polyesters Containing Pendent Pentadecyl Chains

This chapter describes:

i. Synthesis of polyesters containing pendent pentadecyl chains by polycondensation of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride with bisphenols *viz*., bisphenol-A, (hexafluoroisopropylidene)diphenol and 1,1'-bis(4-hydroxyphenyl)-1-phenylethane.

ii. Synthesis of copolyesters by polycondensation of a mixture of 4-(4-(chlorocarbonyl)phenoxy)-2-pentadecylbenzoyl chloride and IPC or 4-(4-(chlorocarbonyl)-phenoxy)-2- pentadecylbenzoyl chloride and TPC with bisphenol A.

Polyesters were characterized by inherent viscosity measurements, solubility tests, GPC, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, X-ray diffraction studies, DSC and TGA.

Chapter 8: Summary and Conclusions

This chapter summarizes the results and describes salient conclusions of the investigations reported in this thesis.

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Savita Kumari   **Prakash .P.Wadgaonkar**
(Research Student)   **(Research Guide)**

List of Publications

1. Synthesis and characterization of hyperbranched polyesters and polyurethane coatings.
   Savita kumari, Aswini K. Mishra, Dipak K. Chattopadhayay and K. V. S. N. Raju.
   J. Polym. Sci., Part A: Polym. Chem. **2007**, 45, 2673.

2. Organically modified montmorillonite hyperbranched polyurethane–urea hybrid composites
   Savita Kumari, Aswini K. Mishra, A.V.R. Krishna and K.V.S.N. Raju.
   Prog. Org. Coat. **2007,** 60, 54.

3. A facile strategy for synthesis of α, α'-heterobifunctionalized poly(ε-caprolactones) and poly(methyl methacrylate)s containing ''clickable'' aldehyde and allyloxy functional groups using initiator approach
   Prakash S. Sane, Bhausaheb V. Tawade, Indravadan Parmar, **Savita Kumari**, Samadhan Nagane and Prakash P. Wadgaonkar
   J. Polym. Sci., Part A: Polym. Chem. **2013**, 51, 2091.

4. Synthesis and characterization of clickable aromatic polyesters containing pendent azido groups using step-growth polymerization approach.
   Savita Kumari, Samadhan S Nagane and Prakash P. Wadgaonkar
   (To be C*ommunicated*)

5. Synthesis and characterization of clickable aromatic polyesters containing pendent propargyloxy groups and their functionalization by click chemistry.
   Savita Kumari, Mahadev Halhalli, Mahesh Biyani and Prakash P. Wadgaonkar
   (To be C*ommunicated*)

Presentations

1. Presented poster entitled "Synthesis and characterization of polyesters containing pendent pentadecyl chains" during MACRO 2009, held at Indian Institute of Technology, Chennai, in March 2009.

2. Presented poster entitled "Synthesis, characterization and curing studies of polyesters containing pendent propargyloxy groups" during MACRO 2010, held at Indian Institute of Technology, New Delhi, in December 2010.