SYNTHESIS AND CHARACTERIZATION OF HOMO AND COPOLY(ARYL CARBONATE)S *VIA* CARBONATE INTERCHANGE REACTION

A thesis submitted to the

UNIVERSITY OF POONA

for the degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

by

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DEDICATED TO MY PARENTS

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CERTIFICATE

*This to certify that the work incorporated in this thesis entitled "**Synthesis and Characterization of Homo and Copoly(aryl carbonate)s via Carbonate Interchange Reaction**" submitted by **Sukhendu Bikash Hait** was carried out by him under my supervision at the National Chemical Laboratory. Such material as obtained from other sources has been duly acknowledged in the thesis.*

S. Sivaram

Date : 24 November 1997
Place : Pune

Dr. S. Sivaram
(Research Guide)

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my deep sense of gratitude to my research supervisor and architect of this thesis, Dr. S. Sivaram, for his consistent inspiration, constructive guidance and immense encouragement at all stages of my work. Without his critical evaluation and deep rooted knowledge, this thesis would not have become a reality. His enthusiasm, dedication and approach to science has instilled a sense of confidence in me.

I would also like to thank Dr.J.C. Sehra, Dr. V. S. Iyer, Dr. T.P. Mohandas, Dr. P.P. Wadgaonkar, Dr. C. Ramesh, Dr.(Mrs.) B. Garnaik, Dr. R.A. Kulkarni, Dr.(Mrs.) S.B. Idage, Dr. B.B. Idage, and Dr. B.B. De for helpful discussions from time to time.

I take the pleasure in expressing my sincere thanks to my labmates Mr. A.A. Gunari, Mr. A.S. Jadhav, Dr. C.V. Avadhani, Dr.(Ms.) R.S. Kshiti, Dr. A.G. Shaikh, Neeta, Bindu and Anjali for maintaining a cordial atmosphere in the laboratory. I would also like to thank my colleagues Biswajit, Radhakrishnan, Nabin, Balu, Rajesh, Phukan, Shruti, Subarna, Saptarshi, Mahua, Parag, Nirmala, Sandhya, Ramanathan, Viswaprasad, Raghu and Yanjarappa for maintaining a very friendly atmosphere.

Special thanks are due to my friends Sourav, Sanjib, Bindu, Sanjoy, Debasis, Nepu, Tapan, Pampa, Soumen, Snigdha, Indra, Laska, Paramantapa, Brahma, Prasanta, Shyamal, Goutam, Krishanu, Tanya, Tilu, Tomalda, Malayda, Nikhilda, Manas, Surojit, Rasidul, Anil, Priya, Sundar, Bikash, Anjan, Karuna, Trushar, Uday and all other friends at NCL for making my stay at Pune memorable.

I gratefully acknowledge Shaikh, Gracy, Suryawanshi, Kakade, Zine and Murugan for their special help.

Whatever I am and whatever I intend to be in future is due to the goodwill and unstinted support that I have received from my mother, maternal uncle, brother, sisters, brothers in law, and all my family members. Their kind cooperation helped me to pursue the Ph. D. study and no words are enough to acknowledge them.

I thank the Director, NCL for providing infrastructural facilities and CSIR, New Delhi for financial support.

(Sukhendu Bikash Hait)

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GLOSSARY

BPA	4,4′-Isopropylidene diphenol (bisphenol A)
CH_2Cl_2	Dichloromethane
$CHCl_3$	Chloroform
$CuSO_4$	Copper sulphate
DAC	Diallyl carbonate
DBC	Di-n-butyl carbonate
DMC	Dimethyl carbonate
DPC	Diphenyl carbonate
DPE	Diphenyl ether
DSC	Differential scanning calorimeter
DSS	Disodium salt of BPA
HCl	Hydrochloric acid
EC	Ethylene carbonate
HEEP	Hydroxyethyl ether of phenol
HQ	Hydroquinone
IDT	Initial decomposition temperature
K_2CO_3	Potassium carbonate
KOH	Potassium hydroxide
MEK	Methyl ethyl ketone
NaOH	Sodium hydroxide
$NaHCO_3$	Sodium bicarbonate
NH_4Cl	Ammonium chloride
OBZ (B)	Tetrabutyl ammonium hydrogen *o*-nitro-bibenzoate
PBZ (B)	Tetrabutyl ammonium hydrogen *p*-nitro-bibenzoate
PC	Poly(aryl carbonate)s
PET	Poly(ethylene terephthalate)s
T_g	Glass transition temperature
T_m	Melting temperature
$Ti(OBu)_4$	Tetrabutyl titanate
$Ti(OPr)_4$	Tetrabutyl titanate
TGA	Thermogravimetric analysis
TMAM	Tetramethyl ammonium maleate
η_{inh}	Inherent viscosity
$[\eta]$	Intrinsic viscosity
XRD	X-ray diffraction

ABSTRACT

Aliphatic carbonates were synthesized from ethylene carbonate and alcohols using zeolites as catalyst. The results were compared with conventional metal-based catalyst systems, used for such reactions. The rate of carbonate interchange reaction using a zeolite catalyst was found to be significantly faster compared to the tetra-n-butyltitanate catalyst. With a KL type zeolite, 90% conversion of ethylene carbonate was obtained within 2 h, whereas, in case of titanium catalyst 82% conversion was obtained after 12 h.

The model reaction of ethylene carbonate with phenol using different catalysts were also examined to understand the effect of reaction conditions on the nature of the reaction. It is observed that at or above 160 °C, decarboxylation is the main reaction with basic catalysts. The reaction of bisphenol A with ethylene carbonate leads to polymers with both ether and carbonate linkages.

Low molecular weight poly(aryl carbonate) oligomers could be chain extended in the solid state under defined conditions to high molecular weight polymers ($\bar{M}_v >$ 60,000). This technique removes the limitations of the melt phase process for producing poly(aryl carbonate)s with wide range of molecular weights. Influence of various reaction parameters, such as, type of reactor used, time, temperature, catalyst, initial crystallinity, initial molecular weight and initial end group concentration on the rate of solid state polymerization were studied in a fluidized bed reactor. The changes in crystallinity and melting temperature of poly(aryl carbonate) synthesized by solid state polymerization was explored. It is proposed that solid state polymerization of poly(aryl carbonate) involves simultaneous occurrence of chain extension as well as increase in crystallinity (increase in T_m). Kinetic parameters for the solid state polymerization reaction were evaluated. Chemical reaction was found to be rate-controlling step in the solid state polymerization. The Arrhenius relationship was found to be

$$k = 1.41 \times 10^8 \exp(-4807/RT), h^{-1}.$$

Branched poly(aryl carbonate)s, were synthesized by solid state polymerization technique. The amount of branching agent incorporated in the polymer was determined quantitatively using HPLC after saponification of the polymer. The branching reactions were found to be quantitative under these conditions.

The synthesis of poly(ester-carbonate)s was successfully achieved using solid state polymerization techniques. The polymerization was carried out using poly(aryl carbonate)s and poly(aryl ester)s or poly(ethylene terephthalate) oligomers in presence of a catalyst below 230 ^{0}C. Prior to solid state polymerization, the oligomer mixtures were crystallized using ethyl acetate or acetone. The product was analyzed by ^{1}H NMR, DSC and viscosity. It is proposed that solid state polymerization of two chemically distinct oligomers involves ester-carbonate interchange reaction with simultaneous chain extension. The results established that carbonate-ester interchange reaction can occur at appreciable rate at as low a temperature as 240 ^{0}C in the solid state.

Different bis(hydroxyethyl ether)s were synthesized from bisphenols and ethylene carbonate. They were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. Poly(ether-carbonate)s were synthesized using bis(hydroxyethyl ether) of bisphenols and bisphenol A with diphenyl carbonate by the melt phase carbonate interchange reaction. Structure-property relationships were examined in poly(ether carbonate). With increasing content of bis(hydroxyethyl ether) in the copolymer, the T_g of the polymer was found to decrease.

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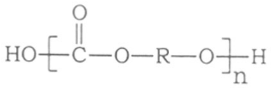
CHAPTER I

GENERAL INTRODUCTION

1.1 INTRODUCTION:

Poly(carbonate)s are defined as linear polyesters of carbonic acid having the general formula



$$HO\left[\overset{\overset{O}{\|}}{C}-O-R-O\right]_n H$$

Depending on the nature of R group poly(carbonate)s are subdivided as aliphatic, aliphatic-aromatic or aromatic poly(carbonate).

Poly(aryl carbonate) resins were first prepared by Einhorn[1] in 1898 by reacting simple diols, such as hydroquinone, resorcinol and catechol, with phosgene in pyridine. However, due to the insoluble and intractable nature of these polymers, they remained uncharacterized. Four years later, attempts were made by Bischoff and Von Hendenstroem[2] to react these diols with diphenyl carbonates. Their efforts, too, remained unsuccessful for the same reasons. Thus the subject of aromatic poly(carbonate)s remained dormant and unexplored during the next fifty years.

In the early 1930's, interest in general poly(carbonate)s was renewed by Carothers and van Natta[3] who demonstrated the preparation of low melting, low molecular weight microcrystalline aliphatic poly(carbonate)s using two synthetic approaches:

i. transesterification of aliphatic dihydroxy compounds with diethyl carbonate

ii. ring opening polymerization of cyclic carbonates of aliphatic dihydroxy compounds.

The transesterification work was extended by Peterson[4] (1940) to make low melting high molecular weight films and fibers using 1,6-hexanediol and dibutyl carbonate. By 1941, the first commercially viable poly(carbonate) was introduced by Pittsburg Plate Glass Company (PPG). This material was a liquid casting resin intended for use as a surface coating in fiber or optical applications. This crosslinkable resin, designated as CR-39 was derived from the allyl ester of diethylene glycol carbonate. Further, peroxide initiated reaction produces a scratch-resistant, transparent plastic.

The evolution of the field continued with the reexamination of the aromatic derivatives. In 1953, about fifty years after Einhorn's discovery, aromatic poly(carbonate)s were rediscovered, independently by Schnell[5] at

Bayer, A.-G., Germany and by Fox[6] at General Electric, USA. They synthesized poly(carbonate) using bisphenol A as the diol. Both the groups synthesized poly(aryl carbonate), almost simultaneously, based on bisphenol A using entirely different routes. The Bayer process was based on the solution phosgenation of bisphenol A in pyridine whereas, General Electric's technology was based on the melt phase carbonate interchange reaction of bisphenol A with diphenyl carbonate.

Many other bisphenols were investigated for the synthesis of poly(carbonate)s. It was observed that with the exception of impact strength every other property of the bisphenol A poly(carbonate) was surpassed individually by other poly(carbonate)s. But no resin had the right combination of performance, manufacturing ease and economy that the original bisphenol A poly(carbonate) resin enjoyed. Hence, bisphenol A poly(carbonate) remains the most sought after poly(aryl carbonate) even today.

Poly(aryl carbonate)s especially those based on 4,4′-isopropylidene diphenol (bisphenol A, BPA) are a class of important engineering plastics which are characterized by superior impact strength, high heat distortion temperature and glass like transparency.[7] The wide ranging applications include glazing, electrical and electronic components, household appliances, housings for sophisticated instruments, sports goods and shatter-proof windows for automobiles and aircrafts. Since their discovery in the early sixties, these polymers have shown substantial growth worldwide and accounts for 1.5 million tons of annual production in industrywith a projected growth rate of 8-10% per annum.[8,9] Much of the future growth is being propelled by automotive application and optical recording media.[9,10]

With such wide range of applications, unusual combination of properties, excellent price/performance balance and access to variation in the chemical and physical properties, bisphenol A poly(carbonate) has emerged as one of the most important engineering thermoplastics.

1.2. SYNTHETIC ROUTES TO POLY(ARYL CARBONATE)S:

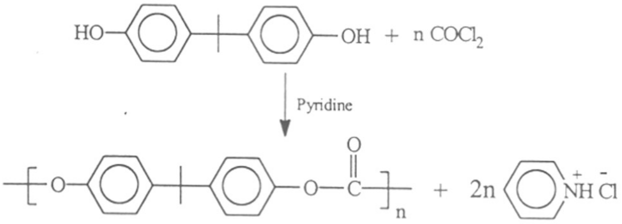
Poly(aryl carbonate)s are generally synthesized by either of the following routes.

1. A phosgene route involving (solution, interfacial or ring opening) polymerization of bisphenol A with phosgene.

2. A nonphosgene route involving melt phase carbonate interchange reaction of bisphenol A with dialkyl or diaryl carbonate.

1.2.1 Solution polymerization: [11]

Solution polymerization was one of the earliest processes to be pursued commercially. In this process bisphenol A is phosgenated in a mixture of pyridine and anhydrous chlorinated hydrocarbon solvents (such as, dichloromethane) wherein, the former acts as an acid acceptor as well as a condensation catalyst by forming a salt like adduct which is substantially more reactive (**Scheme 1.1**).



***Scheme 1.1** : Synthesis of poly(aryl carbonate)s using solution polymerization*

The molecular weight of the resulting poly(aryl carbonate)s are primarily influenced by the reaction temperature, the quantity of pyridine used, the rate of phosgene addition, and the presence of chain terminators. Excess of pyridine and a slow addition of the last 5 to10% of the phosgene favor higher molecular weight poly(aryl carbonate)s. The reaction is moderately rapid and is completed within couple of hours. After the reaction the polymer solution is repeatedly washed with aqueous acid and water, to remove pyridine as its hydrochloride. Precipitation from aliphatic hydrocarbon solvent followed by filtration and drying provides the polymer as a white dry powder.

Merits of solution polymerization:

i. Moderate reaction rate.

ii. Polymers of all grades, *viz.*, injection molding, extrusion and film forming grades can be prepared by this technique

Demerits of solution polymerization:

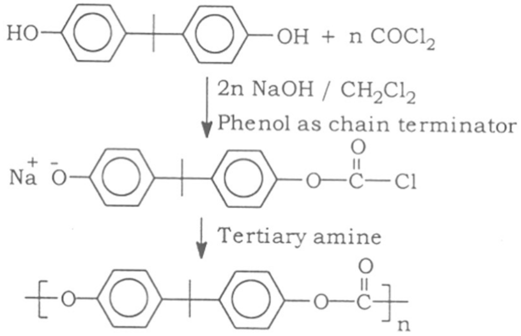
i. The process entails use of toxic and hazardous chemicals like pyridine and phosgene as well as a chlorinated hydrocarbon solvent.

ii. Difficulty in the removal of last traces of pyridine/pyridinium hydrochloride from the polymer solution.

iii. Polymer produced by this process is contaminated with unreacted bisphenol A.

1.2.2 Interfacial polymerization:[12]

A successful modification of the above process was the interfacial polymerization. A major portion of the world's poly(aryl carbonate)s are produced *via* this process. In this technique bisphenol A and specific chain terminating monofunctional phenols are dissolved in aqueous caustic and the organic phase (dichloromethane) is used to dissolve phosgene. The reaction occurs at the boundary between the two immiscible solvents (**Scheme 1.2**).



***Scheme 1.2** : Synthesis of poly(aryl carbonate)s using interfacial polymerization*

Initially, the organic solvent serves as solvent for the phosgene, and in the course of the reaction it also dissolves the aryl chloroformates and oligocarbonates formed in this process. In the second stage, the aryl chloroformates and oligo(carbonate)s are condensed to high molecular weight poly(aryl carbonate)s by means of tertiary amine catalysts (triethylamine or tri-n-propylamine). Vigorous agitation and a pH of 8-10 are maintained to yield very high molecular weight poly(aryl carbonate)s. Using reaction temperatures of about 0 to 40 ^{0}C, poly(aryl carbonate)s with molecular weights upto $\bar{M}_v$ = 2,00,000 can be synthesized by this method.

Merits of interfacial polymerization:

i. The reaction is fast and is completed within an hour.

ii. Reaction is carried out at ambient temperature.

iii. Relatively simple reactor design.

iv. Polymers of all grades, viz., injection molding, extrusion ($\bar{M}_v$ ~ 20-40,000) and film forming grades ($\bar{M}_v > 40,000$) can be easily prepared by varying the ratio of diols to monofunctional phenols.

Demerits of interfacial polymerization:

i. The process involves use of toxic, hazardous phosgene and environmentally unfriendly chlorohydrocarbon as a solvent.

ii. The process involves complex sequence of operations, such as, concentration, distillation, steam distillation, nonsolvent precipitation for both polymer as well as for the solvent.

iii. The process involves formation of chlorine containing by-product such as HCl and sodium chloride, which need to be removed as it has a corrosive effect on the downstream processing equipment. Furthermore, residual sodium in ppm levels has a deleterious effect on the properties of poly(aryl carbonate)s.

iv. The interfacial polymerization technique can not be used to prepare poly(aryl carbonate)s of diphenols (which are alkali insoluble) and liquid crystalline monomers (as they tend to precipitate at low conversions).

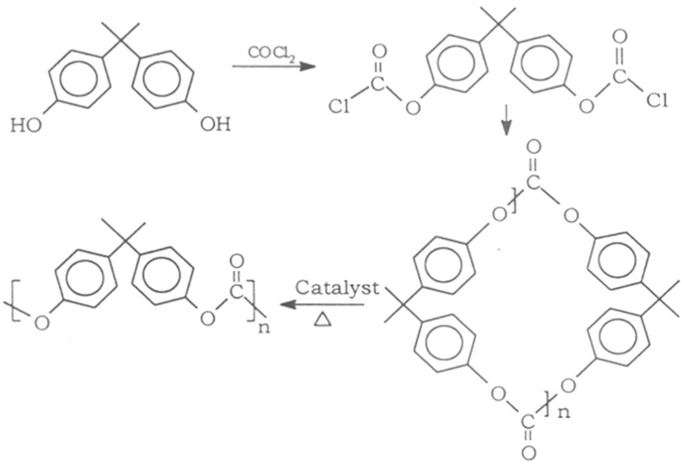
1.2.3 Ring opening polymerization of oligopoly(aryl carbonate)s:[13]

Although cyclic carbonates have been known for about 60 years, the first preparation of cyclic oligomeric carbonates took place in mid 1960's. Schnell and Bottenbruch[14] reported the synthesis of the cyclic tetramer of bisphenol A and of other bisphenols using classical high dilution procedures. The process involved slow addition of a mixture of bisphenol A to its bischloroformate in dichloromethane over a period of several hours in pyridine (which also absorbs HCl) such that a final product concentration of 0.5 M is reached. The method resulted in yields of cyclic tetramer with mp = 375 °C, in yields as high as 21%. The tetramer was isolated by a series of precipitation and crystallization. It is also reported that the cyclic tetramer could be polymerized at its melting point, affording very high molecular weight poly(carbonate). A few years later Prochaska[15] and Moody[16] reported the precipitation of the cyclic trimer of bisphenol A under similar conditions using either phosgene or bisphenol A bischloroformate in the presence of pyridine.

However, the utility of ring opening polymerization as an alternative route to the commercial synthesis of poly(aryl carbonate)s has been limited for two reasons.

a) Procedures for the synthesis of cyclic carbonates were nonselective resulting in low yields, necessitating tedious fractionations and b) polymerization and processing were hampered by the high melting points (>350 ^{0}C) of the individual cyclics.

Recently, Brunelle *et al.*[17] reported the first successful synthesis of low molecular weight cyclic oligomer of poly(aryl carbonate)s, wherein the selectivity of the cyclic to linear was raised to 10,000 : 1 by a novel pseudo dilution technique. Analysis of cyclics indicated that the cyclics ranged from dimer to about hexanosamer (n = 26) with about 90% of the material having a degree of polymerization less than 10 (**Scheme 1.3**).



Scheme 1.3 *: Synthesis of poly(aryl carbonate)s via ring opening polymerization*

The cyclic oligomer could be polymerized to very high molecular weight linear polymers at 250 ^{0}C ($\bar{M}_w$ = 3,00,000) using NBu_4BPh_4 as catalyst. The polymerization reactions were characterized by a very low heat of reaction and almost complete conversion of oligomeric species to linear polymers.

Merits and demerits of ring opening polymerization:

The ring opening polymerization of cyclic oligo(carbonate)s offers high potential to produce very high molecular weight poly(aryl carbonate)s ($\bar{M}_v$ = 1,00,000-3,00,000). This process has the following desirable features.

i) Molecular weight can be controlled by suitably adjusting the [cyclic]/[initiator] ratio.

ii) Absence of by-products allows the use of reactive processing techniques in which cyclic oligomer is directly polymerized into final objects by extrusion or molding.

iii) Block copolymers of poly(carbonate)/polydimethylsiloxane[18] and poly(carbonate)/polystyrene can be synthesized using one of the block as the initiating species.

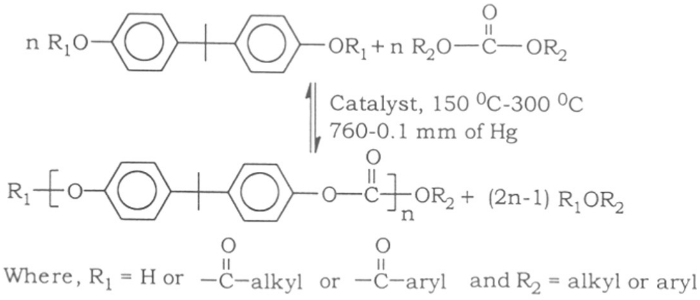
iv) Functionalized poly(carbonate)s can also be synthesized starting from a functionalized bisphenol.[19] However, in certain cases, the method failed to achieve cyclics in very high yield.[20]

v) The method can not produce copoly(carbonate)s of aliphatic-aromatic poly(carbonate).

The interfacial process was widely used, till the mid 80's, for the synthesis of poly(aryl carbonate)s. The melt phase carbonate interchange process did not gain commercial significance owing to the fact that diphenyl carbonate (DPC), used as a carbonate source was itself synthesized by the reaction of phosgene with phenol. But with the advent of alternative process routes to DPC, the situation has undergone a drastic change. DPC can now be produced by a carbonate interchange reaction of dimethyl carbonate (DMC) with phenol.[21] DMC in turn is accessible by oxidative carbonylation of methanol[22] or by the reaction of ethylene carbonate with methanol.[23] The latter process shifts the DMC process to carbon dioxide, which is even more environmentally benign than carbonylation reactions. Efforts have also been made towards the synthesis of DPC by oxycarbonylation of phenol or by direct condensation with carbon dioxide.[24] However, these efforts have met with little success. Thus, with DMC becoming a large volume commodity chemical and with the growing global concern over the use of both phosgene and chlorohydrocarbon solvent in industrial processes, there has been a resurgence[25] of interest in nonphosgene based process for the preparation of poly(aryl carbonate)s.

1.2.4 Melt phase carbonate interchange reaction:

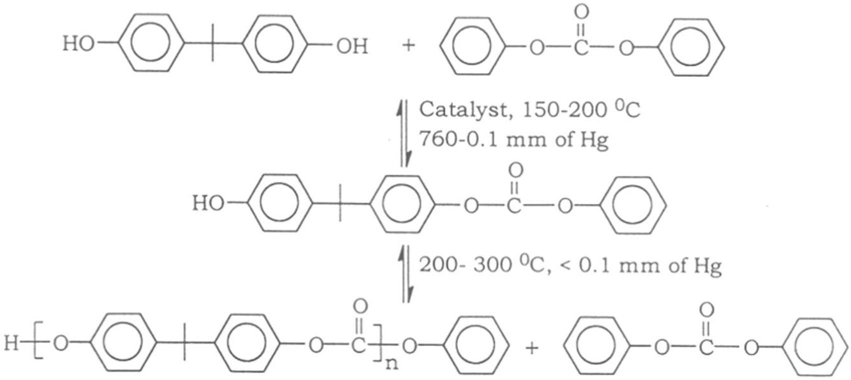
The synthesis of poly(aryl carbonate)s by non-phosgene route involves a carbonate interchange reaction either with diaryl carbonates such as diphenyl carbonates, or with dialkyl carbonates, such as, dimethyl carbonate/diethyl carbonate or dibutyl carbonate (**Scheme 1.4**).[26]



Scheme 1.4 : Synthesis of poly(aryl carbonate)s via melt phase carbonate interchange reaction

1.2.4.1 Carbonate interchange reaction with diphenyl carbonate (DPC):

The melt phase carbonate interchange reaction of bisphenol A with DPC has been extensively investigated.[7,27] It is conducted in two stages (**Scheme 1.5**).



Scheme 1.5 : Carbonate interchange reaction of bisphenol A and diphenyl carbonate

Initially, the polymerization is carried out in an inert atmosphere at 150 to 200 °C under 20 to 40 mm of Hg pressure, till the evolution of phenol ceases. Then temperature is gradually raised from 200 to 300 °C with a reduction of pressure to 0.1 mm of Hg to increase the yield of phenol, and correspondingly, the molecular weight of the polymer. It is observed that during the carbonate interchange reaction, mono(phenyl carbonate) of bisphenol A is formed, followed by its self condensation to high molecular weight polymer.[28] The melt viscosity of the polymer increases rapidly with molecular weight making agitation difficult. Hence, the final stages of polymerization is conducted in a specially designed equipments (wiped film evaporators, helicon reactors and multiple stage vacuum vented extruders) with superior heat and mass transfer to obtain characteristic polymer of η_{inh} = 0.60 dL/g in chloroform at 30 ^{0}C, $\bar{M}_v$ > 30,000. The rate of polymerization depends on the rate of removal of phenol, which is expedited by the simultaneous application of heat and vacuum.

Nature of catalysts and additives:

Reaction of bisphenol A with DPC is a thermodynamically favored reaction. Catalysts play an important role in the melt phase carbonate interchange reaction of BPA with diaryl carbonates. In practice, catalyst in the concentration range of 0.001 to 0.1 wt% (based on BPA) is usually added for optimum results. A desirable catalyst is expected to exhibit the following features.

i) high activity ii) high efficiency iii) should not cause thermal degradation of bisphenol A iv) residual catalyst in the polymer must neither cause nor catalyze degradation (thermal and hydrolytic) of the polymer during processing or use, nor contribute to loss of optical properties.

The types of catalysts used for the melt phase carbonate interchange reactions are given as follows:

A) Acidic catalysts:

Acidic catalysts were found to be less suitable for carbonate interchange reaction. In general, acids such as boric acid, p-toluene sulfonic acid and zinc chloride are found to be less effective, hence not preferred. However, few sulfonic and phosphoric acids have been reported to give a color free poly(aryl carbonate)s.[29]

B) Organometallic catalysts:

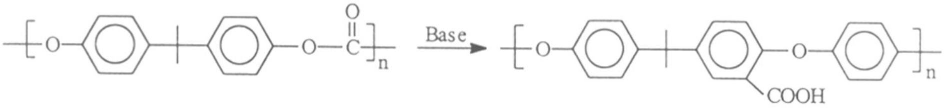
Organometallic catalysts are another class of catalysts used for carbonate interchange reaction. They are generally derived from Ti, Sn, Mn, etc. These catalysts generally produce colored poly(aryl carbonate)s. Manganese compounds display lower activity and result in discolored poly(aryl carbonate)s when used in large quantities, owing to their insolubility in poly(aryl carbonate)s melt.[30] In addition, other metal compounds such as manganese salts and lead salts[31] increase the sensitivity to atmospheric oxygen. The molded articles obtained from poly(aryl carbonate)s produced with these salts, gradually become brown in air, especially at elevated temperatures. Organotitanium catalysts like titanium alkoxides are found to yield dark yellow colored melts even in the absence of atmospheric oxygen.[32] It is likely that the decomposition of bisphenol A occurs concurrently because of the longer reaction time required for bisphenol A to displace the DPC from its titanium metal complex.

C) Basic catalysts:

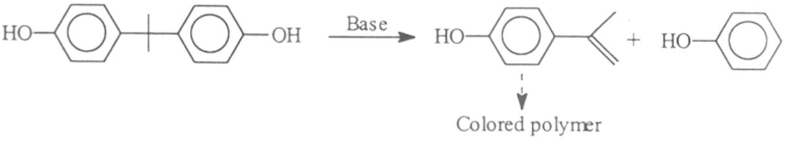
Basic catalysts are found to accelerate the carbonate interchange reactions significantly. The following types of basic catalysts have assumed importance.

i) Alkali and alkaline earth metals:

The alkali metal bases derived from lithium and sodium are found to induce rapid carbonate exchange reaction of bisphenol A with DPC. It is expected that use of alkali and alkaline earth metals involved formation of more reactive bisphenol A salt. However, the common feature of all the basic catalysts belonging to alkali and alkaline earth metals is their propensity towards unwanted side reactions.[7] The two major side reactions in the melt phase carbonate interchange reaction of bisphenol A and DPC involve an analogous Kolbe-Schmitt reaction (**Scheme 1.6**) and the decomposition of bisphenol A at temperatures exceeding 150 °C, which competes with the exchange reaction to yield a highly reactive unwanted phenol (**Scheme 1.7**) monomer known for giving coloured polymers.[33]



Scheme 1.6 *: Kolbe-Schmitt reaction*



Scheme 1.7 *: Decomposition of bisphenol A in presence of base at higher temperature*

The catalyst and temperature dependent Kolbe-Schmitt reaction in poly(aryl carbonate) is concerned with the rearrangement of carbonate ester group to carboxylic acid on aromatic nuclei, which on further esterification results in branched polymer. The Kolbe-Schmitt reaction has been demonstrated with DPC in presence of sodium carbonate.[34] The extent of branching due to

Kolbe-Schmitt reaction is decreased considerably by reducing the concentration of the catalyst. One can quantify the branch unit per molecule by chemical degradation of the poly(carbonate) and its subsequent estimation by HPLC.[35]

ii) Boron containing compounds:

The alkali metal catalysts of fluoroboric acid are reported to form color free and thermally stable poly(aryl carbonate)s. For instance, potassium borohydride[36] has been widely used for the synthesis of bisphenol A based poly(carbonate) and copoly(aryl carbonate)s, which are used for making optical disks with high transparency, low water absorption and high dimensional stability.

iii) Organosilanes and germanium oxide:

Organosilanes,[37] especially tetraphenyl silane have been found to yield a polymer of viscosity average molecular weight higher than 40,000 with good transparency. Germanium dioxide[38] is reported to yield a color free polymer of good thermal stability.

iv) Hypernucleophilic organic bases:

Recently, basic catalysts (hypernucleophilic bases[39]) such as guanidine, 4-dimethyl aminopyridine and imidazole, which are sufficiently volatile or a composite catalyst system comprising of hypernucleophilic and an alkali metal or an alkaline earth metal (or VB elements) compound is reported to give a high molecular weight transparent poly(aryl carbonate). For instance, combination of dimethyl aminopyridine or imidazole[40] with potassium acetate is reported to give a highly active catalyst system for the melt phase carbonate interchange reaction of bisphenol A with DPC. It is presumed that a mechanism similar to nucleophilic catalysis occurs, wherein, the alkali metal carboxylates act as a proton acceptor.

v) Quarternary ammonium and phosphonium salts:

Recently, significant research has been focused on the identification of a catalyst, which apart from exhibiting high activity, also produces polymers with improved thermal and hydrolytic stability as well as good color. In this regard, certain classes of quaternary ammonium or phosphonium based catalysts have received wide spread attention.[41]

The major advantage of these catalysts is that they avoid the use of additional additives for obtaining color free polymers. Among quaternary salts, emphasis is placed on the derivatives of nitrogen. Trimethylphenyl ammonium chloride[53] is reported to produce a poly(aryl carbonate) of viscosity average molecular weight of about 29,000 with good whiteness and improved thermal stability. Quaternary ammonium hydroxides in conjunction with boric acid or alkylphenylsulphonates[42] or methyl borate[43] gave poly(aryl carbonate) with good transparency, high thermal stability and yellowing resistance.

Recently, a new class of quaternary ammonium hydrogen biscarboxylates[44] have been reported to produce poly(carbonate) with good color and thermal stability. They are a 1:1 complex of tetrabutyl ammonium carboxylate and its conjugate acid and the unique feature of these catalysts is that the basicity of these catalysts can be fine tuned. In addition they are non-metallic, crystalline, shelf-stable and nonhygroscopic.

The poly(aryl carbonate) synthesized using these catalysts showed improved thermal properties in comparison to those based on metal containing catalysts [such as, bisphenol A disodium salt and $Ti(OBu)_4$]. The improved thermal stability of poly(aryl carbonate) derived using bioxyanion catalysts has been ascribed to the self extinguishing nature of these catalysts, i.e., these catalysts showed onset of degradation at temperatures greater than 200 °C leaving no residue at 300 °C. It was also found that amongst the bioxyanions poly(aryl carbonate) derived using tetrabutylammonium hydrogen-bis-o-nitrobenzoate and tetrabutylammonium hydrogen-bis-p-nitrobenzoate, showed significantly higher initial decomposition.

1.2.4.2 Carbonate interchange reaction with dialkyl carbonate:

1.2.4.2a Carbonate interchange reaction of bisphenol A with dialkyl carbonate:

The melt phase carbonate interchange reaction based on bisphenol A and diphenyl carbonate is an equilibrium reaction but free of unfavorable thermodynamic constraints. However, this reaction has the following drawbacks.

a) Complete removal of high boiling phenol by distillation is difficult and the residual phenol in poly(aryl carbonate)s affects its properties.

b) Diphenyl carbonate is a relatively expensive chemical.

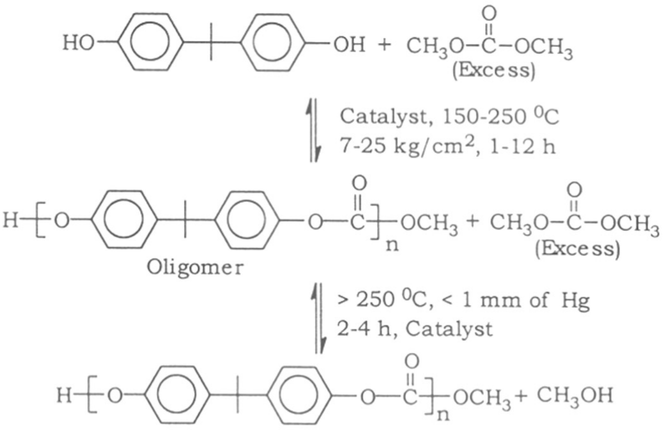
Therefore, the synthesis of poly(aryl carbonate)s by the carbonate interchange reaction of bisphenol A with dimethyl carbonate has assumed great interest[45] because dimethyl carbonate, which is precursor of diphenyl carbonate, is more readily available and is relatively inexpensive. However, the reaction of dimethyl carbonate with aromatic hydroxy compounds is thermodynamically unfavorable owing to its very low K_{eq} of 3×10^{-4} at 453 K.[46] Therefore, the practical efficiency of this reaction is determined largely by the availability of efficient catalysts. Acids do not display good catalytic activity and organic bases promote decarboxylation resulting in the simple alkylation of phenols. Organometallic compounds of tin and titanium have proven to be especially useful and have been widely studied. In fact, similar catalysts are also used for the synthesis of diphenyl carbonate from phenol and dimethyl carbonate.[47]

Due to the low boiling point of dimethyl carbonate (bp 90 ^{0}C) the reaction should be carried out under pressure and in stoichiometric excess of the aromatic diol. It is likely that strong complexes of organometallic compounds with dimethyl carbonate would permit easy reaction with bisphenol A. The use of tin and titanium catalysts for the synthesis of poly(aryl carbonate)s is described in the following sections.

i) Tin compounds:

The reaction is generally carried out in two stages. In the first stage, excess of dimethyl carbonate is continuously supplied to the system and by-product methanol is removed as an azeotrope with dimethyl carbonate under a pressure of 7 to 25 kg/cm^2 and at a temperature range of 160 to 250 ^{0}C with a varying reaction time of 1 to 12 h. An oligocarbonate of $\overline{M}_n$ = 300-1500 is obtained. In the second stage, post-polymerization is carried out using the same catalyst and at temperatures >250 ^{0}C and under a pressure of < 1 mm of Hg. The resulting poly(carbonate)s have a molecular weight in the range of 10,000 to 40,000 (**Scheme 1.8**).

Yamazaki *et al.*[48] first attempted the synthesis of poly(aryl carbonate)s by carbonate interchange reaction of bisphenol A with di-n-butyl carbonate using dibutyltin dibutylate as a catalyst. The reaction was carried out at 180 to 250 ^{0}C and at 0.5 mm of Hg pressure for 5.5 h. The molecular weight of the polymer obtained was 4,600. It was also concluded that higher temperature would increase the molecular weight of the polymer. The reaction between bisphenol A and diethyl carbonate using ethyl(tristiniso-octylate) as catalyst was carried out in presence of excess phenol.[76] The reaction was conducted at 150-180 °C with continuous addition of diethyl carbonate and removal of byproduct ethanol for 63 h. It is believed that diphenyl carbonate, initially formed, by the reaction of diethyl carbonate with phenol is actually undergoing carbonate interchange reaction. The oligocarbonate thus obtained was further polymerized at 250-270 °C/0.03 mm of Hg to yield a polymer of molecular weight 56,000.



***Scheme 1.8** : Carbonate interchange reaction of bisphenol A with dimethyl carbonate*

Another approach to poly(carbonate) synthesis using dimethyl carbonate involves the conversion of bisphenol A to its bis(methyl carbonate).[49-52]

In an attempt to better understand the relative reactivity of mono and bis(methyl carbonate), Shaikh and Sivaram[53] have synthesized, separated and characterized these two compounds obtained *via* carbonate interchange reaction of bisphenol A with dimethyl carbonate at atmospheric pressure using tetrabutyl-1,3-diphenoxy distannoxane as catalyst.[54] Mono and bis(methyl carbonate)s of bisphenol A were polymerized using distannoxane as a catalyst. It was observed that bis(methyl carbonate) of bisphenol A gave high molecular weight polymer[54] whereas the corresponding mono(methyl carbonate) furnished only a low molecular weight oligomer. This conclusively establishes the higher reactivity of bis(methyl carbonate) containing monomer or oligomer. Moreover, presence of mono(methyl carbonate) of bisphenol A or oligomers terminated with hydroxyl groups at both ends are likely to inhibit the polymerization. So, it is evident that the carbonate interchange reaction between hydroxyl group of bisphenol A and dimethyl carbonate as well as self-condensation between methyl carbonate end groups is feasible in presence of tin catalysts.

ii) Titanium and other compounds:

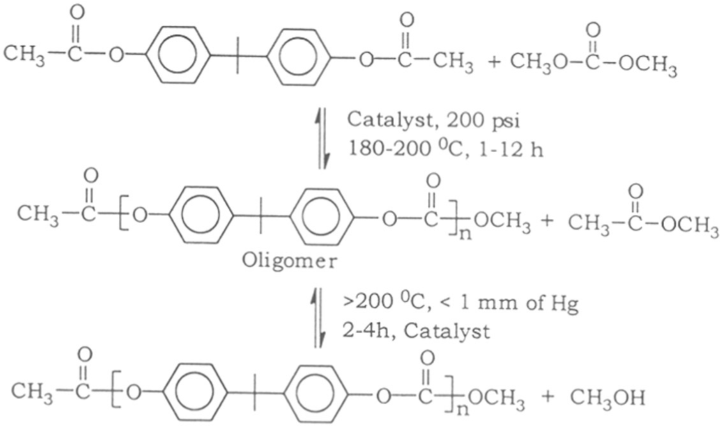
Compounds such as potassium borohydride,[55] sodium methoxide[56] and antimony trioxide,[57] are reported as useful catalysts for carbonate interchange reaction of bisphenol A with dimethyl carbonate in patent literature. But these results are surprising as organic bases generally promote decarboxylation reaction. Carbonate interchange reaction of bisphenol A with diethyl carbonate (DEC) using $Al(OPh)_3$ and $Ti(OBu)_4$ as catalysts at 125-200 ^{0}C was also reported.[58] Poly(aryl carbonate)s were obtained with extremely low molecular weight (η_{red} = 0.1 dL/g). In another attempt bis(methyl carbonate) of bisphenol A was also self polymerized[59] using zinc diacetate as catalyst at 240 ^{0}C for 30 h and a polymer of molecular weight 11,000 was obtained.

1.2.4.2b Carbonate interchange reaction of bisphenol A diesters with dialkyl carbonate:

The thermodynamically unfavorable reaction of bisphenol A and dimethyl carbonate is overcome by converting bisphenol A to bisphenol A diacetate. This reaction occurs *via* an interchange reaction between ester and carbonate groups with the formation of unreactive alkylester (methyl acetate) and is also promoted by various catalysts.

i) Titanium Compounds:

The reaction is generally conducted using titanium compounds such as alkoxides or aryloxides. This is a two stage process with the removal of methyl acetate followed by polymerization. For example, the reaction of bisphenol A diacetate with dimethyl carbonate at 200 ^{0}C and 200 psi in presence of $Ti(OPh)_4$[60] catalyst yielded an oligomer with degree of polymerization, 2-4, which on further condensation at 280 ^{0}C/1 mm of Hg gave poly(carbonate) of viscosity average molecular weight 20,000 (**Scheme 1.9**). Although the reaction of DMC with bisphenol A diester is thermodynamically more favored it suffers from certain disadvantages, such as, the need for conversion of bisphenol A to its diacetate and difficulty in recycling the byproduct methyl acetate. The ester-carbonate interchange reaction between bisphenol A diacetate and dimethyl carbonate is enhanced by the addition of phenyl acetate[61] using $Ti(OBu)_4$ catalyst.



Scheme 1.9 *: Carbonate interchange reaction of bisphenol A diacetate with DMC*

Equimolar amounts of phenyl acetate and bisphenol A diacetate are used and a two step polymerization is carried out at 220-290 °C/1 mm of Hg pressure. In this reaction a poly(carbonate) of η_{inh} = 0.61 dL/g was obtained. It is assumed that in the initial stage, phenyl acetate interchanges with bisphenol A diacetate and is converted to bisphenol A diphenate, which undergoes faster exchange with dimethyl carbonate affording a high molecular weight poly(carbonate). Prepolymer prepared by the reaction of bisphenol A diacetate with dimethyl carbonate using $Ti(OPh)_4$ catalyst can be converted to higher molecular weight by solid state polymerization.[62] Recently, the carbonate-ester interchange reaction between bisphenol A diacetate and dimethyl carbonate using $Ti(OPh)_4$ catalyst has been studied in detail by Deshpande *et al.*[63] They examined the effect of a number of parameters, such as, time, catalyst concentration and reaction temperature on the degree of polymerization and percentage of carbonate end groups in oligo(aryl carbonate)s and established the dependence of molecular weight of poly(aryl carbonate) upon the composition of the oligomer. Oligomer with higher acetate end groups gave a low molecular weight polymer whereas oligomers with higher carbonate end groups gave higher molecular weight polymer.

ii) Other compounds:

The ester-carbonate interchange reaction between bisphenol A diacetate and dimethyl carbonate has also been reported to occur in the presence of potassium borohydride as a catalyst.[64] The reaction was carried out at 160 °C for 1 h and the oligomer thus obtained was post polymerized at 240-280 °C under vacuum to a colorless transparent poly(carbonate) of molecular weight 35,000.

Merits of melt phase carbonate interchange reaction:

a) The process involves use of non-hazardous organic carbonates.

b) By-product, such as, phenol or methanol can be recycled.

c) No solvent recovery step is necessary and handling of chlorinated solvent is eliminated.

Demerits of melt phase carbonate interchange reaction:

a) The process entails the use of higher temperature (200 to 300 °C) and relatively longer reaction time.

b) Side reactions can occur at such high temperatures leading to inferior quality poly(aryl carbonate)s as compared to those prepared by interfacial technique. This occurs especially when process is not carefully controlled.

c) It requires reactors with complex design to maintain a very high vacuum and agitation at a very high temperature range for a longer period of time.

d) Due to long reaction time the chances of discoloration of the polymer are also high which affects the quality of the poly(aryl carbonate).

e) It is difficult to produce poly(aryl carbonate) that is fully end capped with *p-tert*-butylphenyl end groups and of higher molecular weights.

f) It is difficult to produce resins of higher molecular weight due to prohibitively high melt viscosities encountered in the reactor.

1.3 CARBONATE INTERCHANGE REACTION WITH ETHYLENE CARBONATE:

Carbonate interchange reaction using ethylene carbonate has not been widely studied due to the occurrence of decarboxylation during the process, except in the case of synthesis of aliphatic carbonates. Sakai *et al.*[65] have reported the carbonylation of butylstannyl alkoxide catalyst with ethylene carbonate under nitrogen atmosphere to give the corresponding dialkyl carbonate in 27-73% yield. The higher alkyl carbonates were synthesized by the carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compounds.[47] Most of the patent informations reveal the use of basic inorganic compounds,[66-68] organic bases[69] and phase transfer catalysts.[70] All these catalysts were used in the range of 0.01 to 0.1% by weight based on the reaction mixture. Reaction temperatures were varied from 175 to 225 ^{0}C, where lower temperature led to low yields, even with relatively longer reaction time.

Carbonate interchange reactions of ethylene carbonate with aliphatic hydroxy compounds were also catalyzed by organometallic catalysts.[71-74] All the reactions were conducted under homogeneous condition with or without the use of solvent and good yields of corresponding carbonates were obtained. Recently, Texaco Chemical Co.[75] has developed a process based on the carbonate interchange reaction of ethylene carbonate with methanol to the co-synthesis of dimethyl carbonate and ethylene glycol.

Basic ion exchange resin[76] containing quaternary ammonium group was also used for the synthesis of dialkyl carbonate from ethylene carbonate and aliphatic hydroxy compounds. For example, dimethyl carbonate is produced from ethylene carbonate and methanol by passing through Dowex MSA-1 at 100 ^{0}C under 7 kg/cm^2 gauge in 48% conversion and 99.1% selectivity.

Recently, Tatsumi *et al.*[77] reported the synthesis of dimethyl carbonate from ethylene carbonate and methanol using TS-1 as solid base catalyst exchanged with aqueous K_2CO_3 (**Table 1.1**).

Table 1.1 : Synthesis of DMC catalyzed by various TS-1 compounds

Catalyst	K (wt%)	K/Ti	EC conversion (%)	DMC yield (%)
H-TS-1	0	0	0.11	0
UT-TS-1	1.1	0.46	43	26
K-TS-1	1.9	0.69	68	57

They compared the results of UT-TS-1 (untreated TS-1), H-TS-1 (TS-1 treated with NH_4Cl, 1.0 M) and K-TS-1 (TS-1 treated with 0.5 M K_2CO_3), which showed that the activity of K-TS-1 was much higher than UT-TS-1, whereas H-TS-1 showed negligible activity. From this result, they concluded that the activity of this reaction is not due to the titanium in TS-1 but to the potassium exchanged silanol, Si-O-K, which lies mostly adjacent to titanium in the MFI framework.

The available patent information on carbonate interchange reaction of ethylene carbonate with hydroxy compounds is given in **Table 1.2.**

Table 1.2 : Carbonate interchange reaction of EC with alcohols

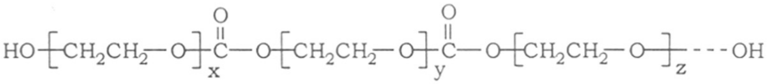
Chem. Abstr. No./Company /Patent No.	Hydroxy compd.	Catalyst	Reaction condn. time(^{0}C)/time(h)/pr (kg/cm^2)	Product	Yield (%)
76:99140z (Dow Chemical Co.) US 3,642,868	C_2H_5OH	C_2H_5ONa	175/3/103	DEC	13
90:168058g (Bayer A.G.) DE 2,740,242 (1979)	CH_3OH	NaOH	reflux/1.5/na	DMC	na
90:186365j (Bayer A.G.) DE 2,740,243 (1979)	CH_3OH	$ClCH_2CO_2Na$	150/2/na	DMC	60
90:186366k Bayer A.-G. DE 2,740,251 (1979)	CH_3OH	Tl_2O_3	150/0.5/na	DMC	25
92:214901t (Nisso Petrochem. Ind. Co. Ltd.) JP 79,148,726 (1979)	C_4H_9OH	$Ti(OC_4H_9)_4$	120/5/na	DBC	68
93:147990k (Nisso Petrochem. Ind. Co. Ltd.) JP 80, 64,551 (1980)	C_4H_9OH	Ph_3P	120/5/na	DBC	65
93:149791m (Nisso Petrochem. Ind. Co. Ltd.) JP 80, 64,550 (1980)	C_2H_5OH	$ZnCl_2$, Et_3N	reflux/5/na	DEC	70
110:74823g (Asahi Chem. Ind. Co. Ltd.) JP 63 238,043 (1988)	CH_3OH	Anion exchange resin (Dowex SA-1)	100/na/7	DMC	48
116:193723h (Asahi Chem. Ind. Co. Ltd.) JP 04 09,356 (1992)	CH_3OH	PbO	100/1/na	DMC	38
121:258494j (Nippon Shokubai Co. Ltd.) EP 599,287 (1994)	CH_3OH	Y-oxide	100/2	DMC	32
122:105257e (Nippon Catalytic Chem. Ind.) JP 06,239,806 (1994)	CH_3OH	ZnO	100/2.5	DMC	32
123:9072r (Chiyoda Chem. Eng. Constraction Co.) JP 07,48319 (1995)	CH_3OH	K-exchanged A-type zeolite	50/2	DMC	56
124:260370w (Mitsubishi Kogaku K.k., Japan, JP 07,330,685 (1995)	CH_3OH	Sm_2O_3	40/2/2	DMC	58
125:33164j (Mitsubishi Chem. Corp., Japan, JP 08,59,558 (1996)	CH_3OH	Bi_2O_3	140/2/2	DMC	59
125:33165k (Mitsubishi Chem. Corp., Japan, JP 08,59,559 (1996)	CH_3OH	MnO	140/2/2	DMC	69

Contd.

Chem. Abstr. No./Company/ Patent No.	Hydroxy compd.	Catalyst	Reaction condn. time(⁰C)/time(h)/pr (kg/cm²)	Product	Yield (%)
125:33166m (Mitsubishi Chem. Corp., Japan, JP 08,59,560 (1996)	CH_3OH	ZnO	140/2/2	DMC	38
125:33183q (Mitsubishi Chem. Corp., Japan, JP 08,73,410 (1996)	CH_3OH	$ZnCO_3$	140/2/2	DMC	67
125:33184r (Mitsubishi Chem. Corp., Japan, JP 08,73,411 (1996)	CH_3OH	CdO	140/2/2	DMC	69
125:221200s(Mitsubishi Chem. Corp., Japan, JP 08,176,071 (1996)	CH_3OH	Mixed metal oxide (Co, Y, Ce, Pr, Nd)	120/3	DMC	29

na = Data not available

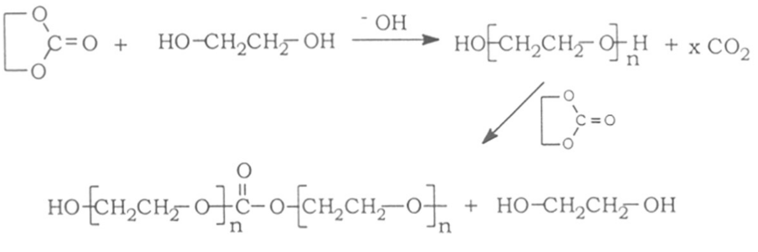
Ethylene carbonate can also form aliphatic poly(carbonate) under special condition.[78] Thus, relatively low molecular poly(carbonate)s of the general formula with hydroxyl end groups can be obtained from ethylene carbonate when heated



$$HO\!-\!\left[CH_2CH_2\!-\!O\right]_x\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O\!-\!\left[CH_2CH_2\!-\!O\right]_y\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O\!-\!\left[CH_2CH_2\!-\!O\right]_z\!-\!-\!-OH$$

under pressure at approximately 250 ⁰C in the presence of 0.01-0.2 mol% (based on EC) of a compound with at least two active hydrogen atoms such as ethylene glycol and an alkaline catalyst.

The pressure increases during the reaction because of the splitting off of carbon dioxide. Apparently, this reaction is not a polymerization of the 5-membered cyclic carbonate, but the ring first splits off carbon dioxide to form polyglycol ethers. These poly(glycol ether)s can transesterify with additional cyclic carbonate to form alkylene glycol and carbonic acid esters (**Scheme 1.10**).



***Scheme 1.10** : Reaction of ethylene carbonate with ethylene glycol*

The ring opening polymerization of ethylene carbonate and other 5-membered cyclic carbonates have been described in several papers.[79-81] The polymerization proceeds by the partial elimination of carbon dioxide and result in poly(oxyethylene-co-ethylene carbonate)s. Vogdanis and Heitz *et al.*[82] reported that polyethylene carbonate is not accessible from ethylene carbonate by the variation of temperature and concentration using metal alkoxide due to the positive enthalpy (ΔH_p = 125.6 KJ/mol) of polymerization.

Carbonate interchange reaction of ethylene carbonate with aromatic hydroxy compound is complicated due to the occurrence of decarboxylation reaction. Kuran *et al.*[83] have studied the reaction of dipotassium diphenolates with 5-membered cyclic carbonates and α,ω-dihalocompounds in the presence of 18-crown-6. They showed that the formation of poly(ether carbonate)s with various content of carbonate linkages or polyethers depending on the kind of diphenolate and dihalo compounds used and the reaction temperature.

Based on a study of polymerization of aliphatic cyclic carbonates, Kricheldorf and Weegen-Schulz concluded that, Lewis acid complexes of cyclocarbonate are involved in polymerization.[84] They employed several Lewis acids, such as, BBr_3, BCl_3, BF_3, $SbCl_5$ for the complexation study. Ethylene carbonate did not form any complex with BF_3. The complexation of the carbonyl group with cyclic carbonates was confirmed by solid ^{1}H NMR ^{13}C NMR, FT-IR spectra and elemental analysis. Upon heating, these complexes react in two different ways. First, they cause ring opening with halogen transfer in a stoichiometric reaction followed by decarboxylation to form a γ-haloalkanol. This reaction is typical for BCl_3 and BBr_3. Secondly; when the complex is heated with a large excess of monomers, they initiate the polymerization of cyclocarbonates. It was suggested that this polymerization follows a cationic mechanism resulting in decarboxylation and poly(carbonate)s with ether groups are formed. The complexes of BF_3, $SnCl_4$ and $SbCl_5$ were typical examples of this reaction pattern. They also suggested that the polymerization could also involve an insertion mechanism yielding pure poly(carbonate)s. The complexes of $TiCl_4$ were typical example of this reaction pattern

In a separate study,[85] the authors have conducted bulk polymerization of cyclotrimethylene carbonate (TMC) using either $TiCl_4$ or $SbCl_5$ as initiator and poly(carbonate)s with high yields (>90%) were obtained in both the cases. But the $\overline{M}_w$ never exceeded above 75,000 by this process. $SbCl_3$ in contrast with

$TiCl_4$ does not cause decarboxylation at temperatures below 150 ^0C and furnished the poly(carbonate) free of ether linkages. Both the initiators yield poly(carbonate)s with more -CH_2Cl than -CH_2OH end groups.

1.4 BRANCHED POLY(ARYL CARBONATE)S:

1.4.1 Introduction:

Branched poly(aryl carbonate)s are important in applications such as structural sheets and blow molding.[86] The excellent fit of branched poly(aryl carbonate) in the market place is ascribable to its outstanding property profile, especially glass like transparency, thin section toughness, high heat resistance, and shear sensitivity.[87]

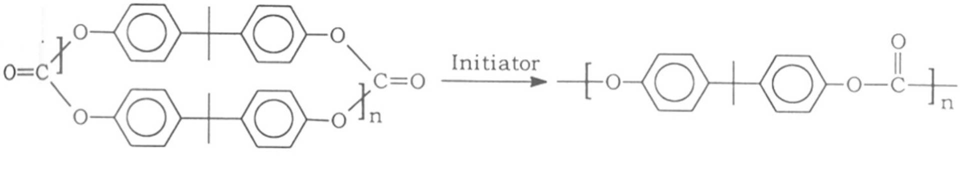
Branched poly(aryl carbonate)s are used primarily in the production of twin wall sheets, which is one of the largest applications areas of poly(aryl carbonate)s.[88] The incorporation of small amount of branching agent gives branched poly(aryl carbonate)s, whereas, larger amount leads to crosslinked poly(carbonate)s. The boundary between branched and crosslinked poly(carbonate)s primarily depends on solubility.

The rheological behavior of branched poly(aryl carbonate)s differ from that of linear poly(carbonate)s. The former exhibits pronounced structural viscosity. The non-Newtonian flow makes it possible to obtain poly(carbonate)s with a sufficiently high melt viscosity for extrusion. Melt viscosity decreases to the low range required for injection molding when the shear rate is increased.

1.4.2 Synthesis of branched poly(aryl carbonate)s:

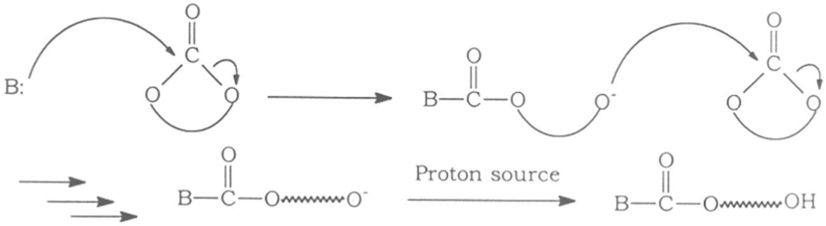
Branched poly(aryl carbonate)s are synthesized using interfacial polymerization or melt polymerization technique used for linear poly(aryl carbonate)s, by the addition of a small amount of branching agent along with the monomers.

Krabbenheft and Boden[89] synthesized branched poly(aryl carbonate)s with high shear sensitivity by ring opening polymerization of cyclic oligomeric carbonate in the melt phase using 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) as the branching agent. The general reaction for the preparation of linear bisphenol A poly(carbonate) *via* ring opening polymerization is illustrated in **Scheme : 1.11**.



Scheme 1.11 : Synthesis of bisphenol A poly(carbonate) via ring opening polymerization

The reaction, which is conducted in solution or in the melt at an elevated temperature, is initiated by various anionic species, such as, phenyl-lithium or lithium phenoxide.[90] A key mechanistic feature of the ring opening polymerization technique is that the substituted phenoxide anions are the propagating species as shown in **Scheme : 1.12**.

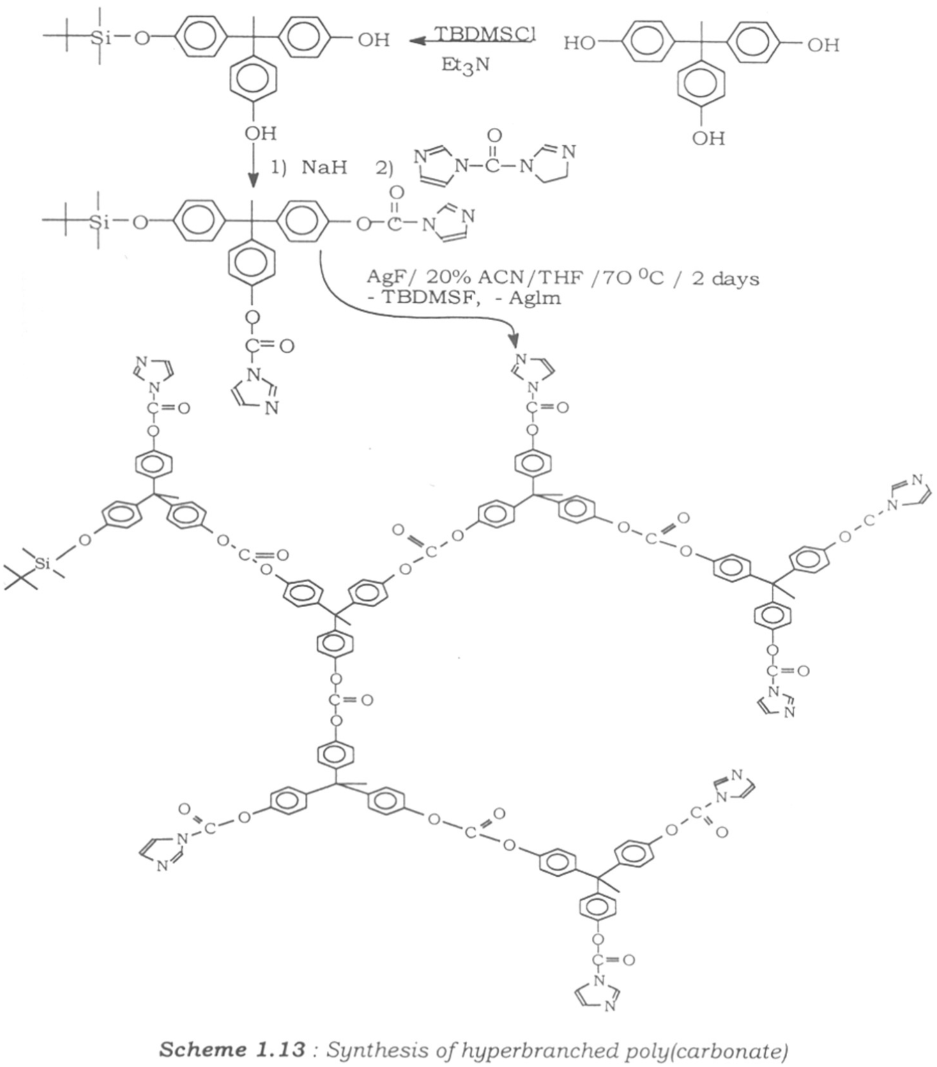


Scheme 1.12 : *Mechanism of ring opening polymerization*

Thus, it becomes a simple matter to prepare branched poly(aryl carbonate)s by incorporating suitable tri- and tetra-functional reagents in the ring opening polymerization reaction. Two generic types of branching agents have been used to prepare branched bisphenol A poly(carbonate) via ring opening polymerization of cyclic oligomeric carbonates. They are, i) chain terminating agents and ii) chain propagating agents. By using 1,3,5-tris(chloromethyl)-2,4,6-triethyl benzene and sodium phenoxide as initiator a branched poly(carbonate) having melt index ratio 2.25 was obtained. In the absence of the branching agent the melt index ratio is 1.3.

Three chain propagating branching agents, 12,12'-(1,3'-dipropanediyl)bis-[2,10-dimethyl-12H-dibenzo[d,g][1,3] dioxocin-6-one], 1,1,1-tris(4-hydroxy phenyl) ethane (THPE) and bis(2,4-dihydroxyphenyl)sulfide (0.5 mol%) have separately been used along with tetrabutyl ammonium tetraphenyl borate (0.1 mol%) as initiator for the synthesis of branched poly(aryl carbonate)s and a melt index ratio of 2.33, 2.49 and 2.66 (0.05 mol% initiator) respectively was obtained. Again, using THPE as a branching agent it was observed that the shear sensitivity is directly proportional to the level of branching agent and inversely proportional to the level of initiator.

Recently, Bolton and Wooley[91] reported the synthesis of hyperbranched poly(carbonate) by the polymerization of A_2B type of monomer derived from 1,1,1-tris(4-hydroxyphenyl)ethane (THPE). Protection of one of the triphenol by a *tert*-butyldimethylsilyl group followed by conversion of the remaining two phenolic groups to carbonylimidazolide functionalities gave the A_2B type monomer. This was polymerized *via* the anhydrous removal of the silicon protecting group and subsequent reaction of the phenoxide with a carbonylimidazolide moiety. The reaction is represented in **Scheme 1.13**.



***Scheme 1.13** : Synthesis of hyperbranched poly(carbonate)*

A large proportion of the literature for the synthesis of branched poly(carbonate) *via* melt phase are in patents, which are listed in **Table1.3**.

Table 1.3 : Synthesis of branched poly(aryl carbonate)s via melt phase carbonate interchange reaction

Sr No.	Chemical Abstract No./ Patent assignee	Branching monomer	Features
1	103/105721j General Electric Co EP 140341 (1985)	Triphenyl-trimellitate	[η] = 0.67 Melt index ratio = 14
2	112/21778a General Electric Co. US 4888400 (1989)	1,1,1-Tris(4-hydroxy phenyl) ethane	Melt index ratio = 2.67, useful for blow molding.
3	114/165620n General Electric Co. EP 400478 (1990)	1,1,1-Tris(4-hydroxyphenyl) ethane.	Poly(carbonate)s have high melt strength and high shear sensitivity.
4	115/51051t General Electric Co. US 4959422 (1990)	Triglycidyl isocyanurate	Mw = 65,000, MWD = 4.6 and melt viscosity = 171,500 P.
5	117/112261b Nippon GE plastics K.K. JP 0489824 (1992)	1,1,1-Tris(4-hydroxyphenyl) ethane.	-
6	121/301661a GE Plastics, Japan Ltd. JP 06 136112 (1994)	α-Methyl-α,α',α''-tris(4-hydroxyphenyl)-1,4-diethyl benzene	Polycarbonates with good heat and water resistant, color and moldability
7	122/315983q Daicel Chem. Ind. Ltd. EP 622 418 (1994)	1,1,1-Tris(4-hydroxyphenyl) ethane.	Polycarbonate with η_{inh} = 0.34 dL/g with YI = 1.2
8	126/186847 General Electric Co. USA US 5597887 (1997)	-	2.1-10 mol% poly-functional agent based on the total carbonate units with blow moldable grade

1.4.3: Characterization of branched poly(aryl carbonate)s:

Dobkowski and Brzeinski[92] characterized branched poly(aryl carbonate) using GPC and viscometric method. They have used 2,4-bis(4-hydroxycumyl) phenol (BPX) and 1,3,5-trihydroxybenzene (THF) as branching agent and the amount of branching agent was varied from 0 to 1.5 mol%. The branching factor was calculated by empolying the equation $g_v = \bar{M}_{vg}^*/\bar{M}_v^*$. Where $\bar{M}_v^*$ is the apparent viscosity-average molecular weight calculated from the measured [η] according to the Mark-Houwink equation for linear polymers. {$[\eta] = K \bar{M}^a$, where, $K = 12 \times 10^{-5}$ and $a = 0.82$} and $\bar{M}_{vg^*}$ is the apparent viscosity-average molecular weight calculated from the GPC data for the same constant a. The value $g_v = 1$, is obtained for the linear polymer and $g_v > 1$ for the branched polymer. Hence, branching factor g_v, determined by GPC / viscometry can be considered as an adequate measure of long chain branching.

Bartosiewicz *et al.*[93] have also characterized branching in bisphenol A poly(carbonate) by fractionation, gel permeation chromatography and light scattering.

Boden and Krabbenheft[89] characterized branched poly(carbonate)s by measuring the melt index ratio (MIR) and complex melt viscosity (R*). They showed that higher the MIR and R*, higher the shear sensitivity. The shear sensitivity is directly related to the branching agent incorporated.

Bolton and Wooley[91] characterized hyperbranched poly(aryl carbonate)s by a branching factor determined by silylation of the phenol-terminated polymer with *tert*-butyldimethylsilyl chloride, followed by degradation of the carbonate linkages by the reaction with lithium aluminum hydride and analysis of the product by HPLC. The structural characterization was performed by ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis. Molecular weight of the products was determined by GPC.

1.5 SOLID STATE POLYMERIZATION OF POLY(ARYL CARBONATE)S: AN OVERVIEW

Solid state polymerization is defined as a post polymerization technique in which chain extension of a suitable semicrystalline prepolymer is carried out by heating it above the glass transition temperature but below melting temperature. The general reaction scheme can be depicted as follows:

$$P_1 + P_2 \rightarrow P_3 + B$$

Where P_1 and P_2 are polymer chains combining to form P_3 and B is a by-product, such as, phenol etc.

Solid state polymerization is a commonly practiced technique[94] to obtain high molecular weight crystalline polymers such as poly(ethylene terephthalate), nylon 6,6 etc. This technique has practical significance, as polymers of such high molecular weight cannot be generally produced in a stirred reaction, in melt due to their high melt viscosities. In this technique, polymerization is generally carried out by heating low or medium molecular weight semicrystalline prepolymers in the form of chips or powders in a stream of gas or under vacuum, at a temperature just below the polymer melting temperature. Under these conditions the functional groups are sufficiently mobile to undergo reactions with the elimination of by-products. It is generally accepted that the polymerization proceeds by step reactions in the amorphous regions of the semicrystalline prepolymer. For these equilibrium reactions characterized by low equilibrium constants, the removal of the by-product is necessary to build up high molecular weight chains. This involves diffusion through the particles and desorption of by-products from the particle surfaces.

The solid state polymerization rate is thus dependent on the chemical and physical processes. The factors governing this are (i) reaction temperature (ii) time (iii) particle size of the prepolymer (iv) initial crystallinity (v) end group concentration (vi) catalysts employed (vii) initial molecular weight of the prepolymer and (viii) the techniques used to eliminate the reaction by-products.

These factors are interrelated and also depend on the type of apparatus used.

(i) Reaction temperature:

Reaction temperature is one of the most important features affecting solid state polymerization. It is interrelated with almost all other aspects of the process. An increase in the temperature usually results in the increase of overall rate of the process as a consequence of the increment in both reaction and diffusion rates. This sometimes also changes the controlling step of the process. Too low a temperature leads to long reaction times. The lowest temperature at which the solid state polymerization takes place in a detectable manner depends on the polymer. Higher temperatures, on the other hand, favor undesired side reactions and cause problems related to particle sticking. Commonly, solid state polymerization is carried out at a temperature 10-40 ^{0}C below the polymer melting temperature. For polyamides and polyesters,[95,96] the temperature dependence of the molecular weight is fairly well represented (**Figure 1.1**). For nylon 6, the solid state reaction sets at a considerably lower temperature than for poly(ethylene terephthalate) (PET) (100-120 ^{0}C *vs* 160-180 ^{0}C). A strong increase in the rate can be observed at reaction temperatures close to the melting point (225 ^{0}C for nylon 6 and 265 ^{0}C for PET).

(ii) Reaction time:

Because of relatively high diffusion and chain mobility restrictions, solid state polymerization requires a much longer reaction time than the conventional melt or solution polymerization. The curves in **Figure 1.1** illustrate the effect of reaction time on the solid state polymerization process for nylon 6,6.[97] A characteristic feature of the curve is the absence of plateau formation. This indicates that no equilibrium state has been reached and this has been related to the use of a very low reaction temperature (the maximum reaction temperature is about 80 °C below the melting points of PET or nylon 66). However, if the solid state polymerization is carried out at a temperature around 5-15 °C below the melting point, a well-defined plateau can be observed. The two factors, namely, reaction temperature and reaction time generally function in opposite directions and thus compensates the effect of the one.

(iii) Particle size:

It is observed that the solid state polymerization rate increases on decreasing the particle diameter {surface/volume (s/v) ratio}. For this purpose the employment of a porous starting prepolymer is expected to speed up the process. Strong particle size effect is illustrated (**Figure 1.2**) for PET[98] and a similar dependence was also observed in other polycondensates.

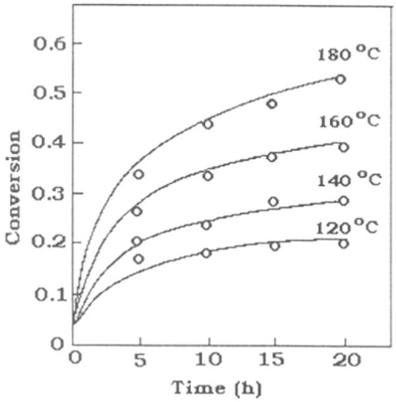


***Figure 1.1** : Effect of time/temperature on solid state polymerization of PET*

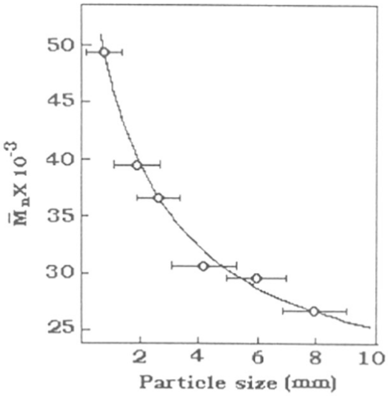


***Figure 1.2** : Effect of particle size on solid state polymerization of PET*

The particle size may, under certain conditions, change the reaction mechanism. For example, Griskey[97] demonstrated that for reaction temperatures below 106 °C, the rate controlling factor in solid state polymerization of nylon 6,10 is the chemical reaction, if the polymer is in powdered form, whereas, for particles of sizes larger than 0.33 cm it is diffusion controlled.

(iv) Initial crystallinity of the prepolymer:

As it is generally accepted that the solid state polymerization reactions take place in the amorphous regions, crystallinity of the starting polymer or oligomer controls the reaction rate. Chang[99] has demonstrated that under the same reaction conditions, higher the crystallinity lower is the rate of solid state polymerization This was attributed to the influence of crystallinity on the diffusivity of the reactive functional groups, wherein, the latter is proportional to the mass fraction of the amorphous phase (**Figure 1.3**). The contribution of the amorphous phase in semicrystalline polymers to the increase in the reaction rate has been well explained by Zimmerman[100] in his work on copolyamides. It was demonstrated that the rate of solid state polymerization of copolymer is much higher than the corresponding homopolycondensate. This is attributed to the diminished crystallisability of the copolymers. For the same reason, the synthesis of copolycondensates in the solid state (using crystalline monomer) proceeds at a higher rate than does the synthesis of the corresponding homopolycondensates under identical conditions. However, the crystallinity in the polymer prevents the agglomeration of particles, in contrast to amorphous polymers.

(v) End Group Concentration:

It is also one of the important factors affecting solid state polymerization reactions. Prepolymers with reactive functional groups in stoichiometric proportion exhibit optimal reactivity. For example, too high a concentration of carboxyl end groups[101] has been found to slow down solid state polymerization (**Figure 1.4**).

(vi) Reaction Medium:

The technique used to remove by-product is a less important factor than the preceding ones. Solid state polymerization can be conducted either under vacuum or in an inert gas atmosphere. Published data[102] reveal that the differences in the molecular weight, achieved by vacuum or inert gas techniques are insignificant, if the vacuum is not higher than 130 torr. Nevertheless, the choice between the two methods is usually made on the basis of general convenience and industrially, the choice is chiefly governed by the overall cost.

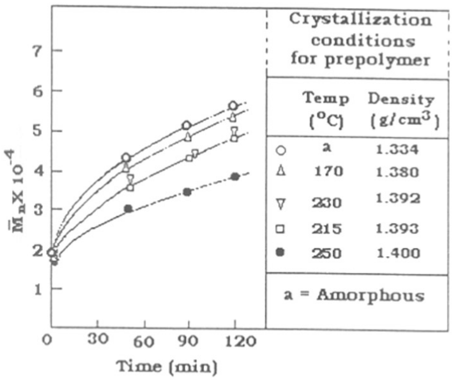


Figure 1.3 : *Effect of crystallinity on solid state polymerization*

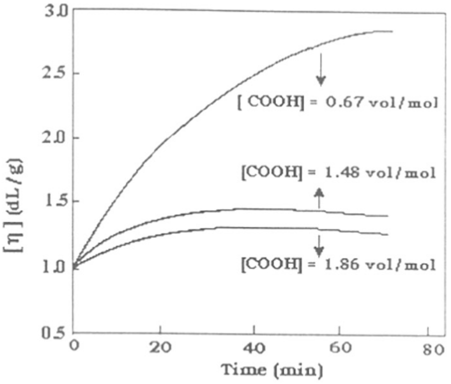


Figure 1.4 : *Effect of end group concentration on solid state polymerization*

However, when an inert gas is used, two aspects are usually considered, the nature of the gas and its flow rate. A comparison of the effectiveness of the different gases on the molecular weight increase of PET showed[103] that at 250 °C the effectiveness decreased from He to CO_2 to N_2. This has been attributed to higher solubility of CO_2 over N_2 in PET, wherein the latter helps it to effectively sweep the by-product from the polymer thereby increasing the rate of solid state reaction.

(vii) Catalysts and additives:

Catalysts and additives have also been found to have pronounced effect on the solid state polymerization rate. In addition to certain well-known transesterification catalysts other substances also behave either as catalysts or as inhibitors. For example, solid state polymerization[104] of p-acetoxybenzoic acid is catalyzed by substances of very different chemical composition, such as, boric acid, urea, benzidine, terephthalic acid, MgO, Na_2CO_3, camphor sulfonic acid and orthophosphoric acid. Other low molecular weight substances[105] such as TiO_2 having a pronounced inhibitory effect. Inert materials such as powders or beads of inorganic materials are added to prevent polymer particles from sticking during processing in order to enhance the solid state reaction.[106]

The salient features of solid state polymerization are (i) the prepolymer is handled in powdered (or chips) form, thus requiring a very simple reactor design (stationary bed reactors or rotary vacuum reactors), (ii) the reaction temperatures employed are very much lower than that of melt polymerization leading to a clean reaction devoid of side reactions or thermal degradation, (iii) very high molecular weight polycondensates inaccessible through a melt process can be prepared, and (iv) owing to considerable restriction on the mobility of chain segments and functional groups, solid state polymerization requires longer reaction time.

Recent years have shown a marked interest in the solid state polymerization of oligopoly(aryl carbonate)s by an efficient alternative nonphosgene route to synthesis of high molecular weight poly(aryl carbonate).[107] Iyer *et al.*[108] have recently demonstrated the solid state polymerization of oligopoly(aryl carbonate)s at temperatures ranging from 180-250 °C wherein, poly(aryl carbonate)s of inherent viscosity as high as 0.8 dL/g could be synthesized at 210 °C. On the basis of the results obtained, they found that solid state polymerization of poly(aryl carbonate)s involved occurrence of chain extension as well as increase in crystallinity. Examples of solid state polymerization covered in patents are presented in **Table 1.4**.

Table 1.4 : Solid state polymerization of oligopoly(aryl carbonate)s

Sr. No.	Chemical Abstract/ Patent Assignee	Method of crystallization	Features
1	110/155052g Asahi Chemical Industries Co. Ltd JP 63223035(1988)	Dissolving in methylene chloride and removing solvent	Dimethyl carbonate of BP-A was polymerized in the melt phase for 6 h/240 °C using dibutyl tin oxide to give prepolymer of molecular weight 6300, which was heated at 220°C to give a transparent polycarbonate having molecular weight 28,000 and 35,000 respectively after 15 and 22 h.
2	111/115963u Asahi Chemical Industries Co. Ltd. WO 89 02904 (1989)	--	BPA-DPC prepolymer ($\bar{M}_w$ = $3x10^3$-$2x10^4$) was solid state polymerized to give a polymer having $\bar{M}_w$ = $6X10^3$-$2X10^5$
3	113/192190h Asahi Chemical Industries Co. Ltd WO 90 07536 (1990)	Shearing from acetone	BP-A/PC oligomer (prepared from BP-A/DPC, $\bar{M}_n$ =4,000, % cryst = 28), heated from 180-220°C. PC ($\bar{M}_n$ = 13,000, %cryst = 45, T_m = 271°C) was obtained.
4	113/172973w Asahi Kasei Kogyo K K JP 02 155921 (1990)	Shearing from acetone	BP-A/PC oligomer ($\bar{M}_w$: 7800) was heated to 220 °C/2-5 mm of Hg/8 h. PC ($\bar{M}_w$ = 24,000) was obtained.
5	114/248039f Asahi Kasei Kogyo K. K. JP 0314830(1991)	--	BP-A/PC oligomer (prepared from BPA/DPC, $\bar{M}_w$ = 7,800) was heated to 220oC/3-4 mm/ 10h. PC ($\bar{M}_w$ = 25,200; T_m = 257°C, %cryst = 40) was obtained.

Contd.

Sr. No.	Chemical Abstract/ Patent Assignee	Method of crystallization	Features
6	115/208911y Asahi Chemical Industries Co. Ltd. JP 03 143920 (1991)	Shearing from acetone	BP-A/PC oligomer (prepared from BPA diacetate and DMC, $\bar{M}_n$ = 3500, %cryst = 25) was heated to 140-210^{0}C. PC ($\bar{M}_n$ = 12,000; $\bar{M}_w$ = 29,000, T_m = 268^{0}C) was obtained.
7	117/213245e Bayer A.-G DE 4104691. (1992)	Tempering	BP-A/PC oligomer (prepared from BP-A/DPC, η_{red} = 1.080dL/g) was heated to 180-220^{0}C/8 h. PC ($\bar{M}_v$ = 27,600) was obtained.
8	117/70557v Bayer A.-G. DE 481296(1992)	-	BP-A/PC oligomer (prepared from BP-A/$COCl_2$/phenol, $\bar{M}_n$ = 9,000) + Oligomer (prepared from BP-A/$COCl_2$, without phenol) was heated to 180-220^{0}C/8 h. PC ($\bar{M}_w$ = 24,800) was obtained.
9	117/27503n Asahi Kasei Kogyo K. K. JP 0453824 (1992)	-	BP-A/PC oligomer ($\bar{M}_n$ = 4000) was heated to 210^{0}C/10 mm using N_2 pulse. No sticky PC ($\bar{M}_n$ = 13,300) was obtained, whereas, without N_2 pulse sticky PC ($\bar{M}_n$ = 13,100) was obtained.
10	120:165294h CSIR-NCL US 5266659 (1993)	Starring the oligomer with disodium salt of BPA in $CHCl_3$, removing $CHCl_3$	BP-A/PC oligomer ($\bar{M}_n$ = 6425) with particle size oligomer with <710 μm was heated at 210 ^{0}C under N_2 using disodium salt of BP-A catalyst gave a polymer having $\bar{M}_n$ = 24,000 and η_{inh} = 0.47 dL/g in $CHCl_3$,
11	120:192620t CSIR-NCL EP 568740 (1993)	Starring the oligomer with disodium salt of BPA in $CHCl_3$, removing $CHCl_3$	BP-A/PC oligomer ($\bar{M}_n$ = 6425) was heated with BP-A disodiam salt at 200 ^{0}C/1 h under N, heating at 200 ^{0}C and 1mmHg for 4 h and heating 230oC/4 h gave a polymer having $\bar{M}_n$ = 46,900.
12	120:299593p Bayer A.-G DE 4233016 (1993)	-	BP-A/PC oligomer η_{rel} = 1.080) was crystd. and placed in a reflux vessel with undecane, using Zeolite K-Y in the extn. apparatus as a molecular sieve for the byproduct. After 180/1 h and 200/7 h, a crystalline polymer with η_{rel} = 1.254 was obtained
13	120:324492q Asahi Chemical Ltd. JP 05310905 (1993)	Stirring with acetone contg. 120 ppm water.	BP-A/PC oligomer ($\bar{M}_n$ = 3900) was subjected to SSP to give a cryst polymer with $\bar{M}_n$ = 48,000.
14	121:58263w Toray Industries JP 0656983 (1994)	Shearing from acetone	BP-A/PC oligomer was heated above T_g but above T_m to get a colorless trasparent polymer with $\bar{M}_n$ = 22,300 and $\bar{M}_w$ = 54,900.

Contd.

Sr. No.	Chemical Abstract/ Patent Assignee	Method of crystallization	Features
15	121:231665d Asahi Chemical Ind. JP 06 122758 (1994)	-	A white polycarbonate of $\bar{M}_n$ = 12,400, $\bar{M}_w$ = 28,420, crystallinity = 30% and terminal OH group content 14 mol% was prepared from BPA/DPC oligomer and diphenyl terephthalate
16	122:161705m Teijin Chemicals Ltd. JP 06322097 (1994)	Heated at170^{0}C/30 h	BP-A/PC oligomer ($\bar{M}_v$ = 4500) was heated at 200 ^{0}C and 1mm of Hg with increasing the temperature 240^{0}C /8 h to obtained PC with $\bar{M}_v$ = 19,500 with good color tone
17	127:34706r Idemitsu Petrochem. Co., Ltd., Japan JP 09 132,641 (1997)	Swollen with atm. contg. gaseous solvent	BPA-PC oligomer was heated in N-contg. Toluene to give a transparent PC with mp = 290 ^{0}C and $\bar{M}_v$ = 38,900
18	127:34707s Idemitsu Petrochem. Co., Ltd., Japan JP 09 136,949 (1997)	Dissolving in p-xylene at 250 ^{0}C and injected into H_2O to give spherical particle with 1.4 mm diameter and 29.8% cryst.	The polymer particle was polymerized in the solid state under n-heptane –*p*-xylene flow at 235 ^{0}C for 2 h to give a polymer with $\bar{M}_v$ = 51,230 and no color
19	127:51126u Idemitsu Petrochem. Co., Ltd., Japan JP 09 157, 950 (1997)	Swollen with atm. contg. gaseous solvent	The polycarboate's are manufd. By solid polymerization of crystallized spherical polycarbonate oligomers having waddel's
20	127:51160a Idemitsu Petrochem. Co., Ltd., Japan JP 09 143,257 (1997)	From *p*-xylene	100 g amorphous PC and 150 g crystallized PC ($\bar{M}_v$ = 6400) were press-moulded and pulverized to give a mixture which was polymerized in the atm. contg. Toluene folw and 50 vol% N_2 gas at 220 ^{0}C for 2 h to give a transparent PC having $\bar{M}_V$ = 31,700
21	127:51161b Idemitsu Petrochem. Co., Ltd., Japan JP 09 143,258 (1997)	Swollen with atm. contg. gaseous solvent	The PC oligomer ($\bar{M}_v$ = 4360) are polymerized in the solid state under p-xylene contg. 65% n-heptane at 210-220 ^{0}C for 2.5 h to give PC of $\bar{M}_v$ = 27,800
22	127:66339q Idemitsu Petrochem. Co., Ltd., Japan JP 09 136,950 (1997)	Swollen with atm. contg. gaseous solvent	An amorphous PC prepd. By transesterification of an arom. dihydroxy compd. with a diester of carbonic acid was polymerized in the solid state under a atm. contg. gaseous swollen solvent while prepolymer was kept in a fluid state
23	127:95756d Idemitsu Petrochem. Co., Ltd., Japan WO 97 19,975 (1997)	Swollen with an inactive solvent	Polycarbonate are manufactured in a process in which prepolymer having molar ratio of terminal carbonate group to hydroxyl group in the range of 1:4 to 4:1are swelled by an in active solvent

In solid state reaction an additional type of exchange process is observed, which involves the structural reorganization of random copolymers to multiple block copolymers, with increase in total crystalline mass. These are commonly referred to as crystallization induced reactions (CIR). Crystallization induced reaction of copolymers is a type of reaction wherein partially crystalline copolymer develops an increasingly blocky structure. The repeating units undergo isomerization or interchange reaction below melting point, in such a manner that the newly placed units of the crystallizable component are taken into the crystalline regions and become inaccessible to further reactions. This trend is just opposite to that found in the melt forming random copolycondensate. Lenz *et al.*[109] investigated the *cis-trans* photo isomerization reaction of 1,4-polybutadiene, having very high 1,4-*trans* content at temperatures below the melting point. Under appropriate conditions of the temperature and polymer composition, the reaction reverts to non-equilibrium behavior, which was attributed to the irreversible crystallization of repeating units after isomerization from *cis* to *trans* structures. The interpretation of the composition *vs* time behavior observed was based on the incorporation of *trans* units into crystalline regions on the lamellar fold surface. Furthermore, Lenz and Go[110] observed that random copolymers of *cis*- and *trans* 1,4-cyclohexylenedimethylene terephthalate underwent ester interchange reorganization at temperatures just below the melting point. This reorganization at temperatures just below the solid state is attributed to the conversion of random into a block copolymer, as evidenced by the change of copolymer properties. Replacement of *cis* by *trans* glycol units and subsequent irreversible expansion of the crystalline region is believed to be the driving force in this anti equilibrium ordering process. The above examples thus illustrate the effect of polymer structure and morphology on solid state reactions.

The salient features of crystallization induced reactions (CIR) are (i) restriction to copolymers having adequate type and content of crystallizable units, (ii) occurrence just below the melting point of the crystallizable unit, (iii) increament in crystalline domain sizes as well as in the sequence length of the crystallizable units, (iv) formation of a polymer with higher melting point and lower solubility, (v) a complex process of crystallization and reaction kinetics. At temperatures well below the melting point, the chemical reaction seems to be the rate controlling type whereas, crystallization process probably becomes the rate-controlling step when the melting point is approached.

1.5.1 Poly(aryl carbonate)s : Crystallinity and morphology

The crystallization of flexible chain molecule of sufficient structural regularity, is widely observed in both naturally occurring as well as synthetic macromolecular systems. Wide angle X-ray diffraction patterns have established that long-range three-dimentional order is a characteristic of polymer crystallinity and is thus similar to crystals of low molecular weight substances. However, a major difference exists between the two materials. In low molecular weight species individual molecules occupy equivalent points in each unit cell while in polymers the chain repeating units play the corresponding role. The special feature of the polymer structure is the covalent connectivity of the chain atoms and repeating units.

Generally, polymers are difficult materials to crystallise,[111] since crystalline order requires perfect juxtaposition of identical repeat units which is not easily realized in polymers. Moreover, because of the configurational entropy conditions, the polymeric chains tend to assume random coil conformations. Despite these constraints, some polymers are known to crystallize but their crystalline content or crystallinity or crystalline mass fraction is usually not very high. For instance, polymers crystallize with varying degree of crystallinity, i.e. after melt processing the crystallinity value can be as low as zero (amorphous), to as high as 90% or even higher depending upon the polymer. Further, these ordered structures are limited to small domain sizes, and their internal morphology is complex. Crystallizable polymers can thus be roughly divided into three classes according to their tendency to crystallize as follows:

i) Polymers which crystallize spontaneously and are impossible to obtain in an amorphous form even by quick quenching from the melt e.g., poly(ethylene).

ii) Polymers which are either crystalline or amorphous depending upon the experimental conditions e.g. poly(ethylene terephthalate).

iii) Polymers, which are difficult to crystallize and are normally produced only in an amorphous form e.g. polystyrene, poly(methyl methacrylate).

Bisphenol A polycarbonate is also a crystallizable polymer and belongs to class (iii). Bisphenol A polycarbonate can be crystallized by thermal or solvent treatment.

1.5.1a Crystallization from Melt:

Crystallization from the melt involves heating the polymer to temperature just 10 ^{0}C above T_m followed by annealing at comparatively lower temperature (10 to 50 ^{0}C less than T_m). In the melt crystallization process, polymer molecules are driven to uncoil from high entropy configurations. The driving force is the lowering of enthalpy as the molecular strands are bound together in crystalline array. There are two processes involved in the formation of crystallites and their subsequent transformation to spherulites. The two-stage process occurs by nucleation of spherulites of critical dimensions followed by their growth. The kinetics and mechanisms for these individual processes are described in detail.[112] Both these processes are temperature dependent, having their individual rates, generally governed by the expression,

$$G = G_o\, e^{(-E/RT)} e^{(-\Delta F/RT)}$$

Where, G is the growth rate, G_0 is a constant, E is the activation energy for transport across liquid solid interface, ΔF is the free energy formation of nuclei of critical size, and R is the gas constant. This leads to nucleation rate and the crystallization rate, which have maxima at a particular temperature as shown in the **Figures 1.5** and **Figure 1.6** respectively.

It is observed that there is a particular temperature for maximum growth rate. At temperatures close to T_g, the growth rate is mainly governed by the rate of transport in the melt whereas, at temperature close to T_m the growth is dominated by under cooling. This temperature[113] lies between T_g and T_m at which $T\text{-}T_g/T_m\text{-}T_g \sim 0.6$.

The overall rate of crystallization is usually described by Avrami equation.[114]

$$1\text{-}X_0 = V_{\propto}\text{-}\ V_t/\ V_{\propto} - V_0\, e^{(-ktm)}$$

Where, X_0 = mass fraction of crystallites, V_0 = volume of fully amorphous material, $V_{\propto}$ = volume of fully spherulite material, V_t = volume of the polymer at time t, m = Avrami coefficient which depends on the geometry of the growth and the nucleation; generally, $2 < m < 4$ and k = rate constant of the growth.

Table 1.5 : Half time crystallization of some common polymers with maximum crystallization rate

Sr. No.	Polymer	Crystallization temp (T), (°C)	Crystallization half time at T	Ref.
1.	Natural Rubber	30	2.5 h	111
2.	Poly(ethylene adipate)	55	3 min	112
3.	Poly(ethylene succinate)	106.5	4 min	113
4.	Poly(hexamethylene adipate)	264	5 sec	114,115
5.	Poly(ethylene terephthalate)	264	5 sec	116
6.	Poly(aryl carbonate)	190	8 days	117

From the table it can be seen that bisphenol A polycarbonate is a very difficult material to crystallize. At the temperature of maximum growth rate, poly(aryl carbonate) is ten thousand times slower than poly(ethylene terephthalate) and 5 x 10^5 times slower than polyethylene.[118] Hence, crystallization of bisphenol A polycarbonate from melt is not an attractive process for obtaining crystalline poly(aryl carbonate)s.

A method of hastening the crystallization rate from melt is by addition of certain substances which when incorporated in the polymer melt promote abundant nucleation of crystallites. These substances are called nucleating agents. In heterogeneous nucleation process the total interfacial free energy of the crystalline embryo is reduced by a foreign phase (nucleating agent) which provides a part of the interface to be formed. As a result the activation energy for nucleation is reduced leading to a further decrease in the degree of supercooling. The higher the preference of the crystalline phase to adsorb the foreign material rather than the liquid phase, the lower will be the energy of activation for nucleation. The amount of reduction in interfacial free energy is dependent on both the geometrical and chemical nature of the nucleating agent. Mercier *et al.*[119] observed that the alkali metal salts of many organic compounds such as sodium benzoate or phenolate are very efficient nucleating agents for bisphenol A polycarbonate. It was also observed that the crystallization of bisphenol A polycarbonate in the presence of an organic salt like sodium benzoate is characterized by several unusual features, such as, (i) enormous acceleration of the overall kinetics of crystallization. For instance, the crystallization half time at 230 °C of a bisphenol A polycarbonate sample nucleated by 1% sodium 2-chloro-4-nitrobenzoate is 10 min as compared with a minimum value of 18,000 min at 190 °C for unnucleated bisphenol A polycarbonate, (ii) the increase in melting point of the nucleated polymer to a temperature (300 °C) close to the thermodynamic melting point of bisphenol A polycarbonate (318 °C), (iii) higher (65%) crystallinity of nucleated bisphenol A polycarbonate was found, (whereas it never exceeded 30% for unnucleated bisphenol A polycarbonate), (iv) nucleated poly(aryl carbonate) once melted showed different crystallization kinetics.

Mercier *et al.*[120] showed some of the nucleating agents of bisphenol A polycarbonate and their effect on crystallinity and melting point after 15 min annealing at 180 °C (**Table 1.6**).

Table 1.6 : Crystallization of bisphenol-A polycarbonate : Degree of crystallinity and melting point after 15 min annealing at 180 °C

Nucleating substances (n)	0.1%		1%	
	%Crystallinity	T_m (°C)	%Crystallinity	T_m (°C)
Li benzoate	6.4	242	25	260
Na benzoate	36	298	41	270
Na parachlorobenzoate	13	293	66	301
Na parabromobenzoate	0.5	274	44	305
Na orthohydroxybenzoate	40	296	52	295
Na adipate	3.3	256	42	300
K adipate	0.2	295	74	301

All nucleating agents are salts of weak acids and strong base and therefore, besides their nucleating activity, they are also liable to induce polymer degradation[121] causing decrease in molecular weight (**Table 1.7**).

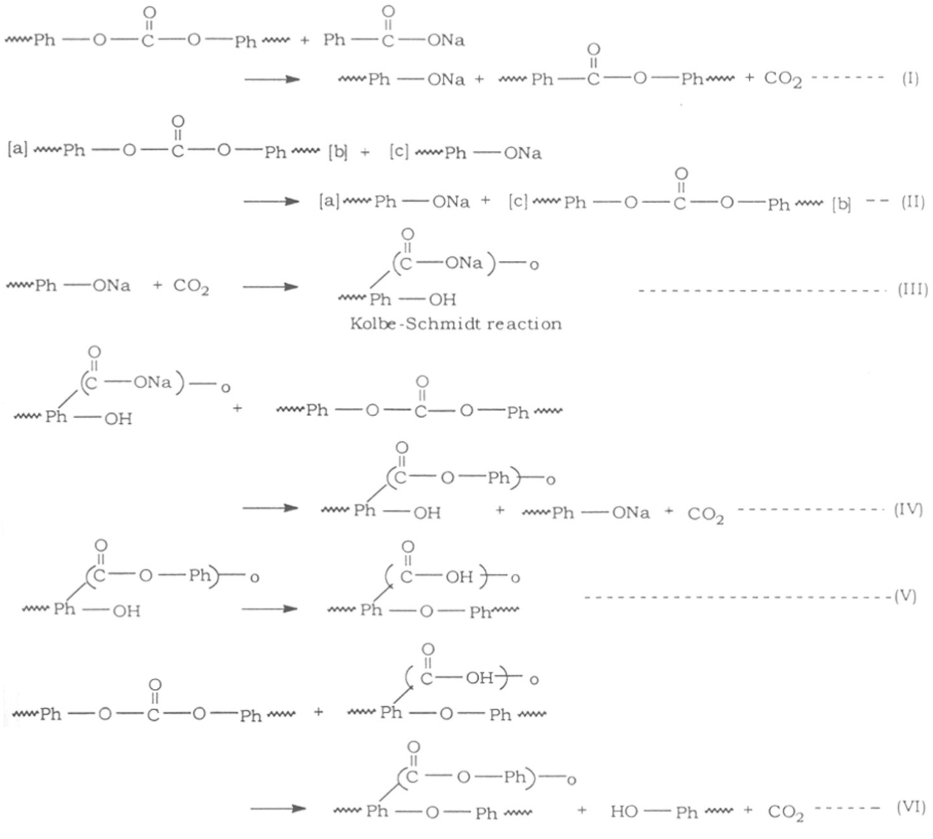
A mechanism was proposed by Mercier *et al.*[122] using polycarbonate/phenyl benzoate system (**Scheme 1.14**). Initially, the salts react with the carbonate groups of the polymer (eq. I). This lowers the number average molecular weight and produces ionic chain ends of the phenoxide type. A fast transesterification reaction is then produced by a continuous exchange between the phenoxide and the carbonate groups, affecting the molecular weight distribution until an equilibrium is attained (eq.II). In the presence of CO_2, the phenoxide terminated polycarbonate undergoes further chemical modification (formation of phenyl salicylate and phenyl phenoxy groups) leading to progressive crosslinking (eq. III-VI).

Table 1.7 : Stability of polycarbonate in presence of various nucleating agents

Nucleating agents	Melt viscosity* (poise)	Molecular weight (M_w)
Pure polycarbonate	7000	44000
Li benzoate	3200	28000
Na benzoate	2500	24000
Na parachlorobenzoate	2100	21000
Na parabromobenzoate	2500	24000
Na orthobromobenzoate	2300	23000
Na metachlorobenzoate	<1200	<15000
Na orthohydroxybenzoate	<1200	<15000
Na adipate	5600	39000
K adipate	6300	42000

** Melt viscosity after 8±1 min at 300 °C*

< Means viscosity or molecular weight inferior to the mentioned value.



***Scheme 1.14 :** Degradation of polycarbonate in presence of sodium benzoate*

The presence of a plasticizer causes the rate of primary crystallization to increase to a considerable extent (**Table 1.8**).

Table1.8 : Influence of the plasticizer on the crystallization rate of bisphenol A polycarbonate

Plasticizer	Chemical structure	Tg$_1$[a] (^{0}C)	Tg$_2$[b] (^{0}C)	t$_{0.5}$[c] (min)
Morflex 525	Trimellitic acid, tridecyloctyl ester	-75	95	95
Reomol ATM	Trimellitic acid, triisododecyl ester	-74	95	320
Santicizer 160	Phthalic acid, butyl-benzyl ester	-55	97	700
Reomol DIDA	Adipiic acid, diisodecyl ester	-	94	200
TTP	Tritolyl phosphate	-40	95	780
Arochlor	Chlorinated polyphenyl	-54	120	3600
Bromkal	Octabromodiphenyl	-90	127	3000

a) *Glass transition temperature of the plasticizer*
b) *Glass transition temperature of bisphenol A polycarbonate with 10% plasticizer*
c) *Half-crystallization time at 180 ^{0}C of 10% plasticized bisphenol A polycarbonate*

At 190 ^{0}C the half life crystallization time for polycarbonate is around 18,000 min. For polycarbonate plasticized with 5% Morflex 525 the half life-crystallization time is reduced to 1000 min and with 10% of the same plsticize, the value is only 150 min (**figure 1.8**). The effect of plasticizer and nucleating agent on the crystallization of poly(carbonate) was explained by Mercier *et al.*[117] (**Figure 1.9**).

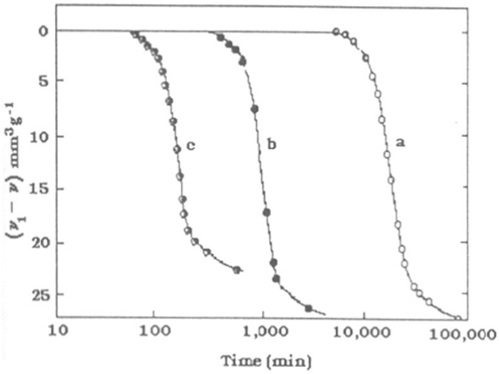


***Figure 1.8** : Crystallization of BPA-PC at 190 ^{0}C. Influence of plasticizer (a) Simple PC (b) PC with 5% trimellitic acid, tridecyloctyl ester (c) PC with 10% trimellitic acid, tridecyloctyl ester*

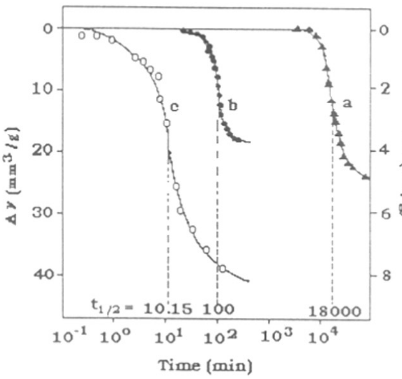


***Figure 1.9:** Crystallization kinetics (a) pure PC annealed at 190 ^{0}C (b) PC plasticized with 10% tri(n-decyl,n-octyl) trimellitate annealed at 170 ^{0}C (c) PC + 1% 2-Cl-4NO$_2$ benzoate annealed at 230^{0}C*

1.5.1b Solvent induced crystallization:

One of the methods of crystallizing a polymer involves the addition of suitable low molecular weight organic liquids. Investigations on the liquid induced crystallization have been carried out on polymers such as cellulose triacetate, poly(ethylene terephthalate), polysulfones, poly(methyl methacrylate) and poly(oxyphenylene).

Bisphenol A polycarbonate readily undergoes crystallization in presence of swelling agents[126-130] such as acetone, chloroform, dichloromethane, carbontetrachloride, xylene and others.

There are two mechanisms proposed for this phenomenon. One of them is based on a lowering of glass transition[131] temperature and increase in chain mobility giving rise to increase in crystallization rate even below normal T_g Another view has been proposed as solvation and phase segregation of low molecular weight species[125a] (self-nucleation) giving rise to faster nucleation rate. However, the exact mechanism is not yet known.

Recently, Ji *et al.*[132] reported a rapid crystallization of poly(carbonate) by shock-cooling its very dilute benzene solution and then by sublimation of the solvent under vacuum. The degree of crystallinity of this treated polycarbonate was 42.5%.

A brief summary of each process of crystallization attempted so far for bisphenol A polycarbonate is given in **Table 1.9**.

Table 1.9 : Crystallization of bisphenol A polycarbonate

Sr. No.	Technique employed	Maximum crystallinity achieved (%)	Features	Ref.
1	Vapor induced crystallization	24 with CH_2Cl_2 and 23 with acetone	First swelling of PC 34-35% occurs followed by crystallization	128
2	Plasticization (trimellitic acid tridecyl octyl ester, Morflex)	20-21	Crystallization half time =100 min at 170 °C	124
3	Nucleation (o-Chlorobenzoate)	60	Crystallization half time =100 min at 170 °C	123
4	Nucleation (unplasticized)	-	T_m = 295-310 °C	120
5	Nucleation (Plasticized)	-	T_m = 210-260 °C	120
6	Vapor induced crystallization	60	T_m = 335 °C	130
7	Shock-cooling and freeze-drying method	42.5 (DSC) 46.4 (WAXD)	Polycarbonate with shock-cooling its very dilute benzene solution and then sublimation of the solvent under vacuum	132

1.5.1c Structure and morphology of poly(aryl carbonate)s synthesized via solid state polymerization:

Polymers crystallized from melt by chain folding mechanism forms a sheet like crystal structure called a lamella. These lamellae then arrange into superstructures leading to the formation of spherulites which are spherical domains containing radial outgrowth of lamella crystals. The crystalline symmetry in polymers is usually of the lower type i.e. triclinic ($a = b = c$ and $\alpha = \beta = \gamma$) e.g., poly(ethylene terephthalate), monoclinic ($a = b = c$ and $\alpha = \beta = 90^0 = \gamma$) e.g. poly(ethylene oxide). Sometimes it goes to higher level such as orthorhombic ($a = b = c$ and $\alpha = \beta = \gamma = 90^0$) e.g. polyethylene and hexagonal packing ($a = b = c$ and $\alpha = \beta = 90^0$, $\gamma = 120^0$) e.g. poly(tetrafluoroethylene). Prietchzsk[133] and Bonart *et al.*[134] have reported crystal structure of poly (aryl carbonate). Prietchzsk[133] has reported an orthorhombic type crystal structure whereas Bonart *et al.*[134] suggested a monoclinic type of crystal structure for the poly(aryl carbonate). The structures are determined by wide-angle x-ray diffraction for poly(aryl carbonate) crystallized from melt by heating isothermally at 190 ^{0}C for several days.

Iyer *et al.*[135] had also shown the development of structure and morphology of poly(aryl carbonate) synthesized by solid state polymerization using optical microscopy and wide angle X-ray diffraction. The crystallinity and the crystal structure of poly(aryl carbonate) obtained from solid state polymerization were investigated by wide angle X-ray scattering and differential scanning calorimetry. The wide angle X-ray diffraction (WAXD) of poly(aryl carbonate) obtained by solid state polymerization at different reaction times showed that it consists of major reflections occurring at diffraction angle of about 17^0 and very weak reflections on either side. Further, these various reflections, increase in intensity with the increase of solid state polymerization, indicating higher crystalline order. In order to confirm the occurrence of new peaks the WAXD was recorded on high intensity scale, which reveal that the major reflections in fact comprise of two components. Detailed analysis of WAXD was carried out by standard iterative technique. The comparison of d-values (interplanar spacing) with those reported for poly(aryl carbonate) by Prietchzsk[133] and Bonart *et al.*[134] suggests that the crystalline structure was distinctly different in the present case. Further analysis led to a conclusion that poly(aryl carbonate) obtained from solid state polymerization crystallized in orthorhombic configuration having lattice parameters of a = 12.1; b = 10.1 and c = 22.0 Å respectively.

It is quite likely that their method was not able to resolve completely all the peaks because of large intensity differences in various reflections. Crystallization in the present case, takes place along with the solid state reaction under restrictive conditions of chain mobility. This can alter the chain configuration due to different bond angles at the hinge atoms i.e. -O-C-O- group giving rise to different lattice parameters.

Fakirov et al[136] have suggested a process termed as "chemical healing" during the solid state polymerization reactions of heterochemical system such as nylon and poly(ethylene terephthalate). But such process is also possible in homochemical systems consisting of welding of two polymeric chains/crystalline domains at their interface. In the present context, however, this process occurs at microscopic domains rather than at macroscopic levels.

1.5.2 Kinetics of solid state polymerization:

The kinetics of the solid state polymerization reaction in linear polyesters and polyamides has been reported by several investigators.[97,99,141,137-147] Zimmerman first reported[100] the solid state polymerization of Nylon 6.6. The solid state polymerization is either diffusion or chemical reaction controlled depending on the flow rate of the carrier gas or the temperature. It was found that the rate of polymerization could be described by the equation,[148] $rate = kt^n$, Chen and Grisky[97] treated this combined chemical reaction and diffusion in more fundamental manner. They formulated equations for combined diffusion and chemical reaction in two distinct instances, *viz.* concerned solid state polymerization of polymer flakes or chips and polymer powder. The resulting solutions relate molecular weight changes to rate functions. Making use of elaborate technique for deriving the rate functions from the experimental data they studied solid state polymerization for nylon 6.6, nylon 6.10 and PET. The experiments were carried out in a fixed bed reactor, with a constant nitrogen flow, at temperatures from 120 to 200 °C and particle size from 0.095 to 0.21 cm. The specific reaction rate values are given in **Table 1.10**.

Table 1.10 : Arrhenius equation for nylon 6.6, nylon 6.10 and PET

Sr. No.	Polymer	Equation	Temperature range (°C)
1.	Nylon 6.6	$k = 1.39 \times 10^4 \exp(-10500/RT)$, $h^{-1/2}$	120-180
2.	Nylon 6.10*	$k = 1.68 \times 10^4 \exp(-13500/RT)$, h^{-1}	120-180
3.	PET	$k = 6.6 \times 10^4 \exp(42500/RT)$, h^{-1}	160-200

* *Where the chemical reaction controls that data was given.*

The authors[97] reached the following conclusions: chemical reaction is the rate controlling stage for the powders (average diameters 0.21 cm) nylon 6.6, PET, for nylon 6.10 and for larger nylon 6.10 particles (average diameter 0.33 cm) at temperatures of 160 °C or higher. Diffusion of by-products through the solid is the rate controlling stage for nylon 6.10 particles of 0.33 cm in diameter or more at temperatures 140 °C or less. The values of activation energy of different polymers are given in **Table 1.11**, where the Arrhenius relationship was examined for those cases where the chemical reaction is the rate controlling stage.

Table 1.11 : Activation energy of solid state polymerization for linear polyesters and polyamides

Polymer	Activation Energy (kcal/mole)	Temperature range (°C)	Ref.
Nylon 6	12.7	-	182
Nylon 6	5.18	160-228	188
Nylon 66	12.96	120-180	183
	10.96	120-180	138
Nylon 6-10	13.2	120-180	138
PET	30	210-260	140
	3.08	165-265	187
	29.87	200-240	190

Henderson *et al.*[142] investigated solid state polymerization of nylon 4.6 in a fluidized bed reactor, over a wide range of temperature, with nitrogen as a carrier gas. The experimental data were not comparable to any kinetic or diffusion model. The authors concluded that the diffusion of reactive end groups was the rate controlling stage. Polyamidation in the solid state of the same polymer was also investigated by Gaymans *et al.*[143] Along with the factors determining the rate of solid state polymerization reported by Gryskey *et al.*,[97] they considered two other factors *viz.* (i) diffusion of the reactive end groups and (ii) heat transfer. The experiments were carried out on low molecular weight nylon 4.6 in a fluidized bed reactor, with nitrogen as a carrier gas, in the temperature range of 190-280 °C. The authors concluded that the reaction rate is strongly dependent on the initial molecular weight with the main limiting stage being the diffusion of reactive end groups.

Chang[99] also studied the kinetics of the thermally induced solid state polymerization. Diffusion through a solid polymer (PET) is the rate controlling stage when the temperature is higher than 210 °C and the particle size is equal to or less than 100 mesh. This differs from Grisky's conclusion, wherein the chemical reaction is the controlling stage for the same polymer. This difference is likely due to the different temperature ranges studied. Comparing his results with Griskey's,[97] Chang[99] found that in both cases they appear to be reasonable because the mobility and reactivity of polymer chain ends are much more temperature sensitive than the diffusion process and the resistance to polymerization (due to diffusion) reduced as the particle size decreases. But, the almost equal rate of diffusion and chemical process led Schaaf *et al.*[147] to conclude that Chang's[99] considerations could not be valid for other systems.

1.6 PROPERTIES OF POLY(ARYL CARBONATE)S:

i) Structural characterisation:

The infrared spectra of PCs have the following absorptions : at 1770 cm^{-1} (C=O) at 1220 and 1235 cm^{-1} (C-O) and at 3595 cm^{-1} (phenolic OH).

The ^1H NMR spectra of poly(bisphenol A carbonate) shows a multiplet at 7. 25 ppm due to the 1,4 substituted phenyl ring hydrogens, and a singlet at 1.68 ppm due to the methyl hydrogens.

Crystallites in PCs can be detected using infrared spectroscopy. A weak absorption at a band width of 725 cm^{-1} corresponds to the crystallites. The ratio of the areas under the absorption band width of 725 cm^{-1} to 917 cm^{-1} gives the crystallinity index.

Two common methods for determining PC molecular weight and its distribution are size exclusion chromatography (GPC) and dilute solution method.[149] In some cases, a combination of these methods is used with low-angle laser light scattering (LALLS) to obtain molecular weight and molecular weight distribution. The dilute solution method is the best for determining viscosity average molecular weight, which can be converted from intrinsic viscosity by the Mark-Houwink-Sakurada relationship using known calibrants:

$$\eta = K \bar{M}_n{}^a$$

Where, K and a depend on the solvent and test temperature. Other methods to determine molecular weight are osmotic pressure, diffusion, and sedimentation.

ii) Stability:

PC is usually fabricated at high-melt temperatures (about 300 ^{0}C and above) where thermal degradation can occur particularly in the presence of basic or iron impurities. Yellowing is usually the first observation of thermal degradation,[150] followed by molecular weight degradation. Thermal degradation also has been demonstrated in PC by recycling in a capillary rheometer.[151] In this instance, the apparent shear viscosity decreased with increasing number of extrusions at 320 ^{0}C and at constant shear stress. The rate of thermal degradation depended on the applied shear stress. Thermal stabilizers for PCs are usually hindered phenols,[152] phosphonite,[153] phosphine, or phosphate[154] based compounds.

PC exhibits remarkable resistance to photo-oxidation.[155] However, with prolonged exposure to UV radiation, yellowing takes place. Photodegradation chemistry of PC has been studied with wavelengths of less than 285 nm (less than sunlight), which cause PC to undergo Photo-Fries rearrangements.[156-159] Degradation does not affect the layers beyond 250 mm from the surface but may cause embrittlement *via* surface crack formation. In some sheet applications, a coextruded poly(methyl methacrylate) (PMMA) coating layer with a UV absorber is used for stabilizer.[160,161] In the solid state, PC undergoes photo-oxidation in addition to chain scissions.[162-164] UV stabilizers are usually benzotriazoles and benzophenones, which can be applied by addition to a lacquer coating layer, solution embeddment on the PC skin,[165-169] or coextrusion.[170]

PC has an equilibrium moisture content of 0.9% at 25 °C, but it does not noticeably affect the mechanical integrity of the PC performance. Impurities in PCs may, however, react with water and cause degradation of the mechanical properties. Additives usually added to PCs may also accelerate the hydrolytic degradation of PC at temperatures above 60 °C. This process will eventually decrease both notched izod impact and molecular weight.[171]

iii) Optical properties:

The high percentage transmission, 87% at 550 nm and a refractive index of 1.584 of bisphenol A based poly(aryl carbonate) permit their utilization in optics and related fields.[172] Bisphenol A polycarbonate loses its transparency, and exhibits haziness when subjected to crystallization.[173] To improve the transparency for the preparation of optical discs, bisphenol A based polycarbonate are co-condensed with 2-5% of various aromatic diols. This removes nonhomogenities in the polymer, as it destroys any residual crystallinity. High transparency is needed to assure complete transmission of the laser beam with no optical distortion.

1.7 Purity criteria for the monomers bisphenol A and diphenyl carbonate for poly(aryl carbonate) synthesis:

Purity of the monomers (diphenyl carbonate and bisphenol A) is of prime importance for obtaining high molecular weight poly(aryl carbonate) by carbonate interchange reaction.

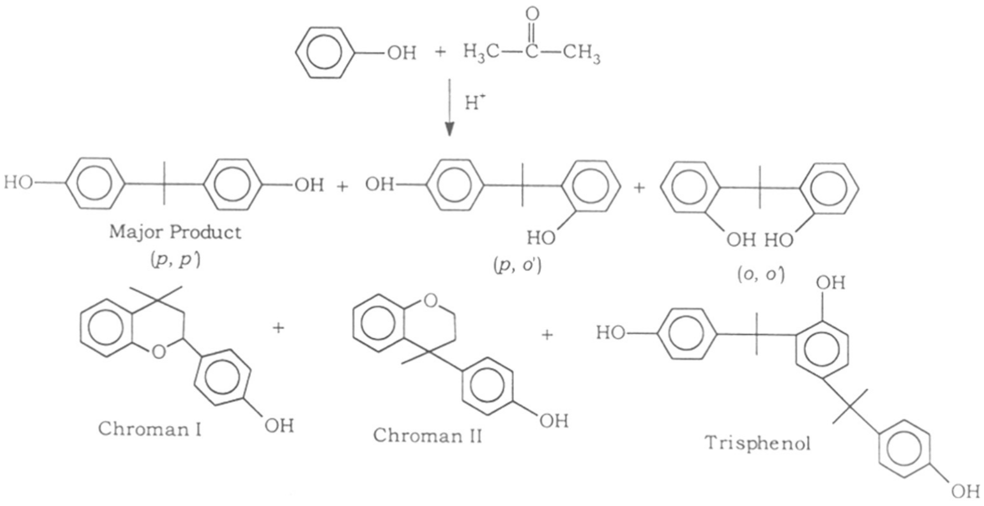
i) Diphenyl carbonate:

Diphenyl carbonate, is synthesized by the reaction of phenol dissolved in aqueous alkali with phosgene or by the reaction of dimethyl carbonate with phenol. It is usually produced in high purity (>99%). Typically, diphenyl carbonate employed for poly(aryl carbonate) synthesis should have sodium content less than 0.05 ppm and chloride ion less than 25 ppm.[174]

ii) Bisphenol A:

Bisphenol A is manufactured by condensation of phenol with acetone in the presence of an acidic catalyst in 90-95% yields. High purity bisphenol A (99.9%) is obtained by dual refining process. Due to high temperature, acidic nature of the reaction and because of poor selectivity in such reactions, several byproducts are formed. Commonly, occurring impurities[174,175] include, *o,p′*-isomer, *o,o′*-isomer, trisphenol and chroman I and chroman II (**Scheme 1.15**). The nature and the level of these impurities depends significantly on the conditions employed in the synthesis. Most of these impurities are high boiling and resulting from side reactions, pyrolysis and further addition/isomerization of the product. Furthermore, many of these impurities are detrimental to both the physical appearance and properties of poly(aryl carbonate). For instance, the *o,p′* and *o,o′*-isomers lead to polymers with kinks in the chain. Furthermore, the

2-hydroxy groups are sterically less accessible and thus of lower reactivity. Trisphenol can cause branching or even crosslinking and gelation, during polymerization at temperatures exceeding 300 °C. In addition, certain trace contaminants are also present which act as undesirable color bodies.



Scheme 1.15 : By-products during the reaction of phenol with acetone for the synthesis of bisphenol A

1.8 SYNTHESIS OF COPOLY(ARYL CARBONATE)S:

The carbonate linkage in organic polymers contributes to desirable physical properties such as high impact strength, high heat distortion temperature and good ductility. Therefore, copolymers containing arylcarbonate linkages have assumed importance as useful materials. Poly(ester-carbonate)s, prepared by melt blending of poly(ester)s and poly(aryl carbonate)s have aroused widespread interest in recent times. Similarly, use of flexible segments such as polyethers in carbonates are also of significant interest in extending the scope of applications of poly(aryl carbonate)s.

1.8.1 Poly(ester-carbonate)s:

1.8.1.1 Introduction:

Polyesters belong to the broad generic class of organic high molecular weight condensation polymers and are characterized by either regularly or randomly distributed ester group [-C(=O)-O-] in the main chain.[176] Linear polyester can be classified as poly(arylester) or poly(alkylester).

Poly(arylester)s[177] have excellent mechanical and themo-oxidative properties due to their ester linkages attached to the aromatic rings. However, the aromatic structure responsible for these attractive properties also makes these polymers difficult to process because of their relatively high glass transition temperature (T_g). Poly(alkylester)s[178] are generally highly crystalline polymers, chemically resistant and are lower in cost.

On the other hand poly(aryl carbonate)s based on bisphenol A is the corner stone of today's engineering thermoplastic due to its high clarity, heat resistance, impact strength and dimensional stability. Nonetheless, poly(aryl carbonate) consumers are demanding even higher levels of performance, particularly, with respect to heat distortion temperature, low-temperature impact strength, hydrolytic stability, sensitivity to sharp notches and chemical resistance while maintaining the price/performance ratio. Improvements towards this end are typically achieved by the incorporation of ester linkage in the matrix of poly(aryl carbonate)s.[179]

The family of polymers so formed, are known as copoly(ester-carbonate)s, having higher levels of performance without sacrificing the strength, modulus and optical characteristics of conventional bisphenol A poly(aryl carbonate). By varying the amount and type of terephthaloyl chloride comonomer and consequently, the ratio of carbonate to ester linkages a series of copolymer composition can be prepared, each with unique property profiles. Molecular weight variations can then be added to monomeric and stoichiometric considerations to produce custom tailored resins.

Aromatic poly(ester-carbonate)s, already promise to fill the gap between poly(aryl carbonate)s and specialty resins like polysulfone. The synthesis and properties of copoly(ester-carbonate)s were first described by Gouldberg.[180] They were first patented by the Chemische Werke Albert in 1957.[181]

Commercial production processes were developed in 1980 as a result of the increased requirements of the electronics industry, in particular, with regard to heat distortion resistance.[182] Aromatic copoly(ester-carbonate)s with glass transition temperatures between 150 °C to 190 °C have been commercialized by Bayer (Germany), General Electric Company (USA) and Unitika (Japan). These materials have found typical applications in the electrical, electronic, lighting, automobile, medical sectors and in household appliances.

1.8.1.2. Synthesis of poly(ester-carbonate)s:

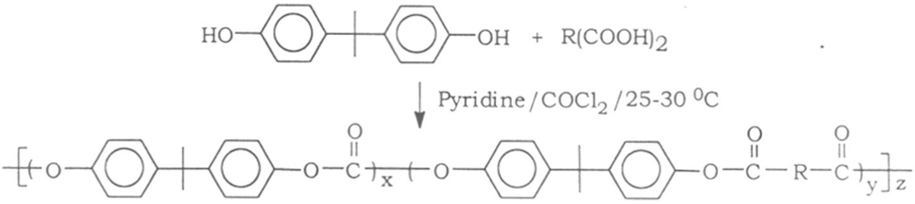
1.8.1.2a Poly(arylester-carbonate)s:

Poly(arylester-carbonate)s are synthesized by either using a phosgene route or by a nonphosgene route.

a) **Phosgene route**: In the phosgene route the copolymer can be prepared by solution or interfacial polymerization.

i) Solution polymerization:

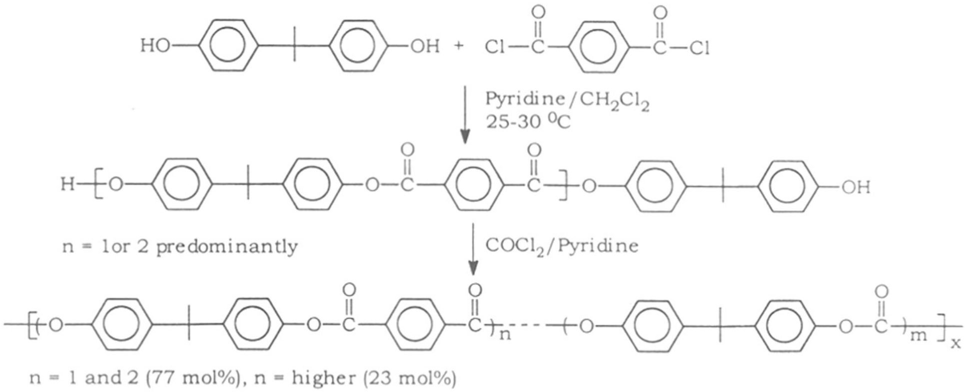
Gouldberg[180] was the first to prepare poly(arylester-carbonate)s by this method. In this process, a mixture of bisphenol A and a dicarboxylic acid was phosgenated in pyridine at room temperature. This led to a high yield with high molecular weight copolymer contain bisphenol A-poly(carbonate) and bisphenol A-dicarboxylate in the chain (**Scheme 1.16**).



Scheme 1.16: *Synthesis of poly(arylester-carbonate)s using solution polymerization*

It was postulated that control of the carboxylate / carbonate ratio can be easily accomplished by varying bisphenol/diacid ratio and that random or block structures could be achieved through proper choice of the order of addition of the reactants.

Latter a successful modification of the solution polymerization was performed by Prevosek *et al.*[183] They have synthesized poly(arylester-carbonate)s from bisphenol, diacid chlorides and phosgene. This method provided easier control of polymer composition, sequence distribution of monomers, quantitative incorporation of the dicarboxylic acid unit into the copolymer and absence of undesirable side reactions (**Scheme 1.17**).



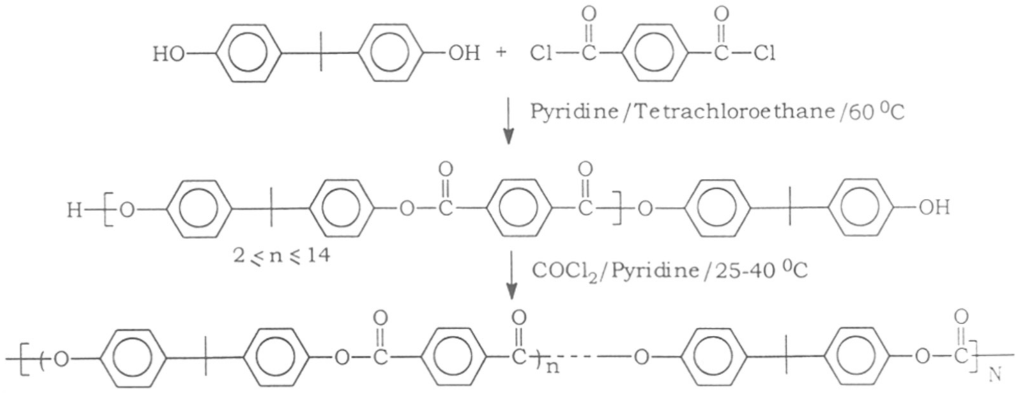
n = 1or 2 predominantly

n = 1 and 2 (77 mol%), n = higher (23 mol%)

***Scheme 1.17** : Synthesis of poly(arylester-carbonate)s using solution polymerization*

The copolymers synthesized by this method were random where ester and carbonate units were present in equimolar ratio.

Bosnyak *et al.*[184] prepared alternating block copoly(arylester-carbonate)s in a two step procedure. First the hydroxy terminated bisphenol A terephthalate and isophthalate blocks with $\bar{M}_n$'s ranging from 2,000 to 5,000 were made by reacting an excess of bisphenol A with the appropriate acid chloride in tetrachloroethane at 60 °C for 12 h. A solution of recovered poly(aryl ester) and excess pyridine was phosgenated at temperatures between 25 to 40 °C until a desired solution viscosity was obtained. The reaction procedure is shown in **Scheme 1.18** with isophthaloyl chloride as an example.



***Scheme 1.18 :** Synthesis of poly(arylester-carbonate)s using solution polymerization*

Merits of solution polymerization:

i. Quantitative incorporation of the dicarboxalic acid into the polymer is possible avoiding undesirable side reactions such as anhydride formation.

ii. Alternating block to fairly random copolymers can be prepared.

Demerits of solution polymerization:

i. This method involves the use of toxic and hazardous chemicals

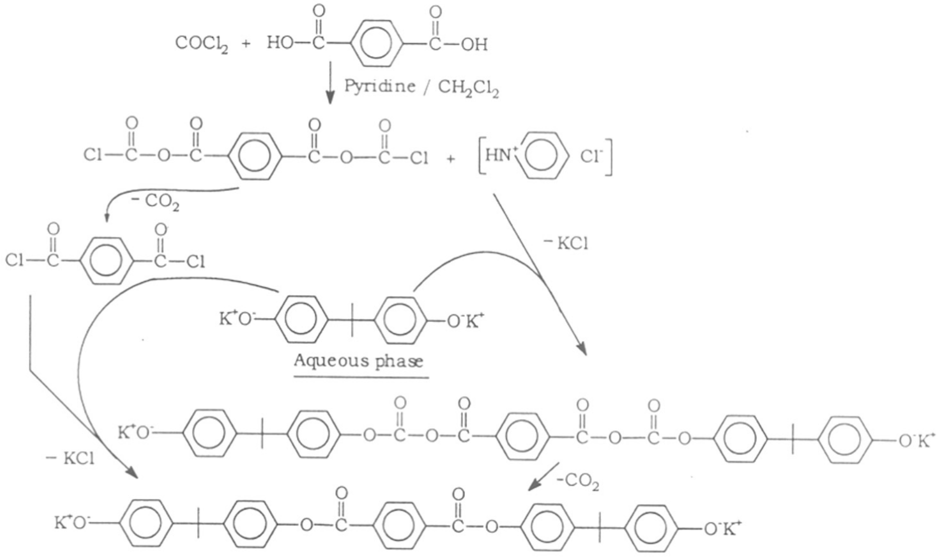
ii. Removal of undesirable contaminants, such as, pyridine, is a difficult job.

ii) Interfacial Polymerization:

Kolesnikov *et al.*[185] were the first to synthesize poy(arylester-carbonate)s by interfacial polymerization method. They have prepared poly(arylester-carbonate)s by reacting an aqueous alkaline solution of bisphenol A with a mixture of varying proportions of phosgene and terephthaloyl chlorides. They showed that yields of copoly(ester-carbonate)s increased as the mole ratio of phosgene to terephthaloyl chloride decreased.

Kochanowski synthesized poly(arylester-carbonate)s by reacting bisphenols in caustic soda solution with a dicarboxylic acid in an inert solvent in presence of a tertiary amine.[186] To this stirred solution phosgene was bubbled at room temperature maintaining pH in the range of 6 to 10.

Keohan *et al.*[187] studied the synthesis of poly(arylester-carbonate)s by interfacial polymerization in detail. The reaction was carried out at room temperature with tertiary amines like triethyl amine or pyridine. One of the major problems encountered in the synthesis of poly(arylester-carbonate)s by interfacial polymerization is to find a suitable solvent. The aromatic diacids and bisphenols are not soluble in many solvents. Therefore, carboxylic acids were allowed to react with phosgene and tertiary amine in the organic phase keeping bisphenols in the aqueous phase. Only low to moderate molecular weight copolymers with poor incorporation of ester units were obtained. In another attempt, dicarboxylic acids were allowed to react with phosgene and pyridine in the organic phase for some period of time and reaction was run with THF as a cosolvent for dissolving the bisphenols. This procedure also yielded low molecular weight copolymer with higher levels of ester units in the polymer matrix. It has been concluded that although this modified interfacial technique with THF may favor the ester units formation but at the same time it may also inhibit the coupling with carbonate linkages and formation of poly(carbonate) block. The sequence reaction occurring in poly(arylester-carbonate) formation is shown in **Scheme 1.19**.



Scheme 1.19 : *Synthesis of Poly(arylester-carbonate)s via interfacial polymerization*

Merits of interfacial polymerization:

i. Free from undesirable side reactions.

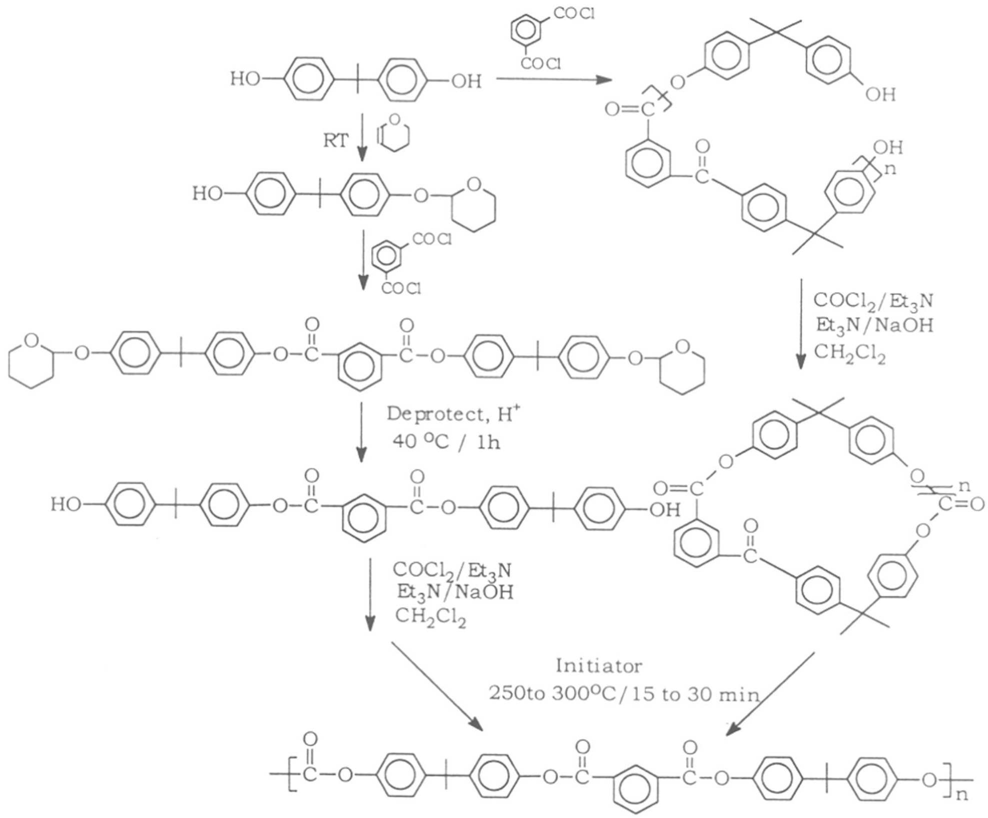
ii. Fast compared to solution polymerization.

Demerits of interfacial polymerization:

Involves the use of toxic and hazardous chemicals.

iii) Ring opening polymerization of cyclic(oligoester-carbonate)s:[188]

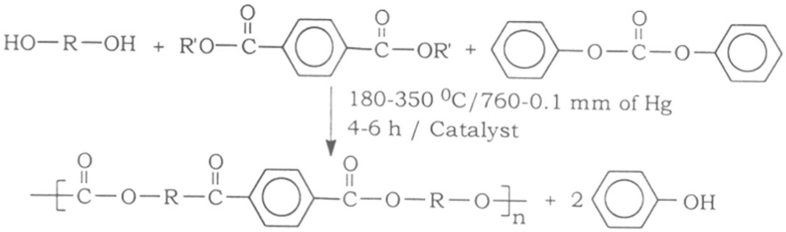
The synthesis of high molecular weight poly(arylester-carbonate)s from oligocyclic(ester-carbonate)s by ring opening polymerization is given in **Scheme 1.20**.



Scheme 1.20 : *Poly(arylester-carbonate)s formation by ring opening polymerization of cyclic oligo(arylester-carbonate)s*

iv) Melt phase reaction:

The melt phase ester-carbonate interchange reaction were generally carried out by the reaction of bisphenols with diaryl carbonate and diaryl ester of aromatic dicarboxylic acids in the temperature range 180 to 350 °C with subsequent reduction of pressure. in presence of suitable catalyst[189] (**Scheme 1.21**). Poly(arylester carbonate)s can be synthesized at higher reaction rates and under milder polymerization condition using activated diphenyl carbonate and diphenyl esters of aromatic dicarboxylic acids. For example, Brunelle *et al.*[190] has prepared poly(arylester carbonate)s of η_{inh} = 0.45 dL/g by polymerization of bisphenol A with bis(o-chlorophenyl carbonate) and bis(o-chlorophenyl isophthalate) using LiOH as catalyst and heating the reaction mixture at 100 °C for 15 min, at 200 °C for 15 min under 100 mm of Hg and at 240 °C for 5 min under 10 mm of Hg.

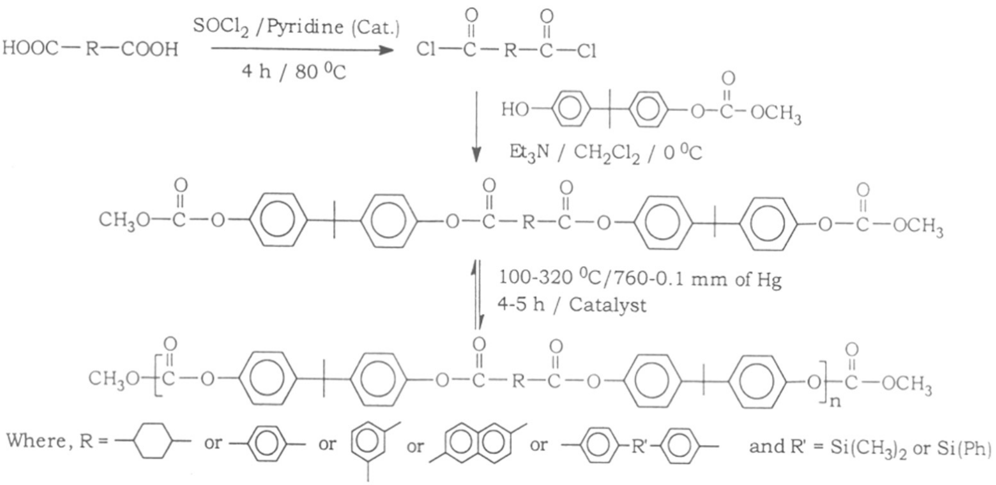


Scheme 1.21 *: Synthesis of poly(arylester-carbonate)s in the melt phase*

Poly(arylester-carbonate)s with η_{inh} = 0.63 dL/g has also been prepared by the polymerization of bisphenol A with dimethyl terephtahlate using phenyl methyl carbonate instead of diphenyl carbonate.[191] Phenyl methyl carbonate liberates substantially less phenol in this process.

In all these polymerization reactions, the ratio of carbonate to ester linkages vary significantly on the mole ratio of carboxylate ester to aromatic diol used and the particular carboxylate ester employed. The ratio of reactants employed will depend primarily on the particular polymer, the combination of polymer properties desired and the particular reactants employed. Compounds of tin, lead, titanium and alkaline earth metals are employed as polymerization catalysts.

Recently, Shaikh and Sivaram[192] have synthesized poly(arylester-carbonate)s *via* melt phase polymerization of diester carbonate monomers. First, they synthesized diester-carbonate monomers by the reaction of monomethyl carbonate of bisphenol A at 0 ^{0}C with various acid chlorides. The diester carbonate monomer derived from monomethyl carbonate and isophthaloyl chloride was polymerized using various catalyst systems in the temperature range 100 to 320 ^{0}C (**Scheme 1.22**). The order sequence of ester and carbonate groups in the copolymers were studied by ^{13}C NMR and except 1,4-cyclohexane (*trans*) moiety showed only one carbonyl signal due to ester and carbonate group in all the cases. From these results, the authors concluded that both the groups are in identical environment and hence the copolymer has a strictly alternating sequence of ester to carbonate groups, with a relative ratio of 2 : 1. A variety of copolymer with T_g ranging from 113 to 190 ^{0}C were prepared depending upon the type of the acid chloride moiety and composition of ester and carbonate groups. They also showed that the copolymers were thermally stable upto 300 ^{0}C.



Scheme 1.22 : *Synthesis of poly(arylester-carbonate)s in the melt phase*

Merits of melt phase polymerization:

The melt phase polymerization reaction is a versatile process enabling the synthesis of poly(arylester-carbonate)s with varying properties for specific applications.

Demerits of melt phase polymerization:

i) Diphenyl carbonate is an expensive raw material.

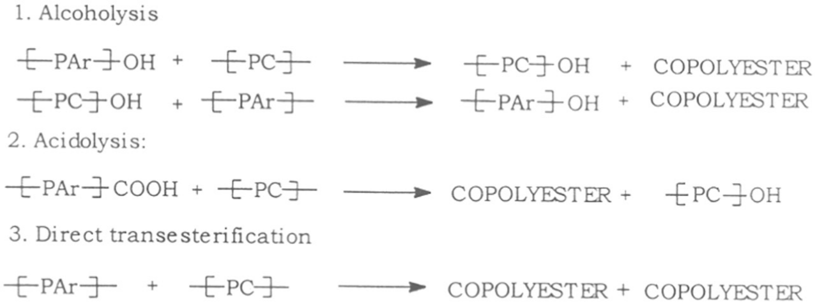
ii) The removal of byproduct phenol requires high temperature and reduced pressure in order to achieve high molecular weight polymer.

iii) The reactions are generally carried out at a temperature higher than 300 ^{0}C, where the degradation and side reactions may takes place.

v) Melt phase ester-carbonate interchange reaction between poly(aryl ester)s and poly(aryl carbonate)s:

Another important method for the preparation of poly(aryl ester-carbonate) is the melt phase ester-carbonate interchange reaction of poly(aryl ester)s and poly(aryl carbonate)s. Many attempts have been made to study the blends of bisphenol A poly(carbonate)s with poly(aryl ester)s. Mondragon *et al.*[193] prepared blends by melt processing and solution casting and examined them by differential scanning calorimetry and thermo opical analysis. Both the blends showed single T_g, which varied with the blend composition. It was concluded that both polymers are miscible over the full composition owing to negative enthalpy of mixing which was determined from the poly(aryl carbonate)s melting point depression. They also observed that interchange reactions are not appreciable during the melt processing of these blends. However, attention should be paid to the possible ester-carbonate interchage reaction, which can occur in such polymer blends and consequently resulting in a melting point depression. Devaux *et al.*[194] have shown the reactions between the two polymers in the melt by studying the reaction between the poly(aryl carbonate)s and diphenyl terephthalate / diphenyl isophthalate used as model compounds of a poly(carboxylate). The results from the kinetic studies indicated the presence of a ester-carbonate interchange reaction occurring without any catalyst.

The ester-carbonate interchange reaction furnishes copolymers with different levels of randomness and composition. This is a function of the temperature and residence time in the melt state as well as the percentage of each mixed polymer. Mainly three type of reactions occur in the melt phase reaction of poly(aryl carbonate)s and poly(arylester)s.[195] These reactions are alcoholysis, acidolysis and direct transesterification (**Scheme 1.23**). Devaux *et al.*[195a] concluded that for poly(aryl carbonate)-poly(butylene terephthalate) pair, the most likely mechanism of exchange reaction was direct ester-ester interchange reaction. Poly(arylester) is similar to PBT and, presumably, undergoes same type reaction.[196]



Scheme 1.23 *: Possible interchange reactions between poly(aryl carbonate)s and poly(aryl ester)s during melt blending process.*

Mondragon[197] and Nishi *et al.*[198] have studied the blends of bisphenol A poly(carbonate)s and poly(arylester)s in detail. Polymer blends with varying composition were prepared by casting films in dichloromethane solution at room temperature. Polymer blends were also prepared by melt mixing a desired composition in Brabender Plastograph at 250 to 290 ^{0}C. The miscibillity of these polymers were studied by differential scanning calorimetry, phase contrast microscopy with digital analysis system, FT-IR spectroscopy and cloud points for the PC/PAr/dichloromethane ternary systems, which led to the following conclusions.

i. PC/PAr is immiscible in the entire range of composition range at high temperature (220 to 270 °C). However, one can prepare an homogeneous blend by rapid evaporation of solvent due to the high T_g of the system.

ii. In this blend, interchange reaction can be induced under normal processing conditions.

iii. The exchange reaction can be controlled by adequate choice of the processing temperature, thus enabling the preparation of a copolymer at different residence times.

iv. All the mechanical properties of the copolymers that have been studied are higher than those of physical blends.

The melt blending of poly(carbonate) with poly(arylester) has also been described in a number of patents.[199]

Merits of exchange reaction:

Homogeneous blend with different composition can be easily obtained.

Demerits of exchange reaction:

As the polymers are subjected to heating above their melting points, due to difference in melt viscosity, polymer degradation can take place.

1.7.1.2b Synthesis of poly(alkylester-carbonate)s:

Poly(alkylester-carbonate)s are generally prepared by the melt mixing of the blend of homopolymers. Melt blending procedures are conducted with a variety of processing equipment at a temperature generally 5 to 20 °C higher than the melting temperature of the polyester. Mixing bowls, single screw and twin screw extruders are commonly used for melt mixing. The exchange reaction relates to intermolecular reactions that can occur between the functional groups of the polyester and the poly(aryl carbonate). Assuming that the end group of PC is a phenol and that of the polyester is either an alcohol or acid four reactions exist in the melt state.

- Midchain reaction between the polyester carbonyl and the PC carbonate group.
- Alcoholysis of the PC carbonate group by the polyester alcohol end group.

- Alcoholysis of the polyester carbonyl group by the PC phenol end group.
- Acidolysis of the PC carbonate group by the poyester end group.

A series of studies by Devaux *et al.*[195a,200-202] focussed on the role of these reactions in PC/PBT blends. After developing a statistical model to predict sequence distribution, Devaux *et al.*[200,201] proved that interchange reaction initially produces block copolymers and, as reaction proceeds, the sequence distribution shifts to that of a random copolymer.

Estimation of the initial reaction rates of the three remaining transreactions show that midchain reaction is 3-6 times greater than acidolysis or alcoholysis of PC by PBT end-groups. Additionally, the initial rate of midchain reaction in the presence of a titanium catalyst is estimated to be 60 times greater than that of the uncatalyzed blend.[195a] Thus, residual catalyst from the polyester synthesis can greatly increase the rate of midchain transreaction and facilitate the randomization process.

In PET/PC blends, introduction of titanium alkoxide catalysts leads to increase in the rate of midchain reaction, alcoholysis, and acidolysis of PC by the polyester end-groups.[203.] Here, unlike the PC/PBT blend, side reactions also play a significant role in the kinetics of reaction. It is likely that the ethylene carbonate sequence formed after exchange reaction is unstable and decomposes.[204] Due to this irreversible side reaction, interchange reaction is not an equilibrium process, hence the kinetic analysis to determine reaction rates must account for this.[205] Overall, kinetic studies of PBT/PC and PET/PC blends indicate that midchain reaction is the dominant reaction leading to randomization, particularly in the presence of residual catalysts such as titanium alkoxides. However, none of these studies directly correlates interchange reaction and phase-behavior results.

Qualitatively, it is known that transreaction in PC/PBT and PC/PET can produce miscible blends.[206,207] Quantitatively, there is little information relating the extent of trans-reaction to the phase behavior of PC/polyester blends. Interchange reaction leads to an interesting problem in regard to phase-behavior identification. In order to identify the equilibrium phase behavior, the temperatures of the blends must be elevated above the component T_gs and T_ms. However, at these temperatures, exchange reactions can occur, altering phase behavior. Without specific examination for the presence or absence of transreaction, phase-behavior results may not represent those of the pure blend, but may already be modified due to reactions. Thus in order to correctly identify phase behavior, care must be taken to minimize these reactions. One way to minimize reaction is to deactivate the catalysts used in the synthesis of the polyesters. Devaux *et al.*[208] report that phosphite compounds effectively inhibits the interchange reactions in PC/PBT blends containing titanium catalysts by complexation with it. The phosphite compound is not directly responsible for the decrease in reaction rate. The phosphite must first be converted to a phosphonate *via* hydrolysis.[207,209]

Unlike the previous attempt Fakirov *et al.*[210] studied the melting and crystallization induced sequential reordering in immiscible blends of poly(ethylene terephthalate) with poly(aryl carbonate). First, they annealed the blend in a DSC at 280 °C for various times, which reveals the complete disappearance of the crystallization or melting peak in the blends where the ratio of PET/PC repeating units is less than 5.7/1.0, Such an amorphization is attributed to the formation of random copolymer. This has been confirmed by ^{1}H NMR spectral measurements, the observations of one T_g in the range between the initial two T_g's and by solubility tests. The authors have further annealed the randomized samples at 235 and 245 °C i.e. below the melting point of PET, which resulted in a shift of T_g towards the T_g of PET as well as reappearance of the melting peak. This effect is accompanied by an eight-fold crystallinity increase in the equimolar blend compared to the randomized sample. They explained this regenerated crystallization as being due to the restoration of the blocks. Moreover, the competitive formation of a block copolymer by sequential reordering is driven by the crystallization of the PET blocks formed. It has also been shown that no randomization occurs with the blend composition ratio with repeating units of PET/PC > 5.7/1.0. It has been observed that when the annealing is performed at 165 °C for 300 min, where no significant exchange reactions are expected to occur, crystallization is not restored.

Ignatov *et al.*[211] reported that the catalyst residues present in PET promotes the exchange reactions during PC/PET reactive blending. In a separate study[212] it was established that the activity of the catalyst freshly added to polymers were much higher compared to that of the residues of the same type of catalysts remaining in the PET after its synthesis. On the basis of these results an innovative technique for PC/PET reactive blending by a one-step extrusion was developed by the authors.[213] They also compared the catalytic activity towards the exchange reactions in PET/PC system using various lanthanide compounds, titanium and calcium/antimony-based catalysts at a concentration of 0.063 mol% based on PET repeating unit.[214] The effect of reaction time on the extent of reaction was studied by selective solubility test coupled with ^{1}H NMR as well as by a selective degradation procedure for PC sequences, to observe the change in PET block length with time. The authors observed a progressive shift towards formation of larger amounts of the soluble or insoluble fraction with the progress of the exchange reaction. This is because the block copolymers resulting from exchange reactions have a different solubility due to the dominance of PC or PET blocks. PET blocks are present in the soluble fraction when the solubility of PC blocks prevails. PC blocks are present in the insoluble fraction when the prevailing effect is the insolubility of the PET blocks.

Among the catalysts employed terbium catalyst is the least active one, whereas titanium is the most active one. The authors also reported that lanthanide catalysts do not catalyze side reactions and, thus, does not give discoloration of the final product. From the above results it was concluded that series of PET/PC block copolymers with different block lengths and of improved quality can be synthesized by the use of a lanthanide catalysts, especially, those based on samarium, europium and cerium.

1.8.2 POLY(ETHER-CARBONATE)S:

1.8.2.1 Introduction:

Polyethers are industrially important polymer materials, having wide range of applications. The term polyether generally refers to those polymers in which ether linkage (C-O-C) is in the backbone.[215] They are known for their chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates and flexibility. Polyethers are generally used as prepolymer for polyurethane. The urethane industry produced 750 x 10^3 metric tons of polyurethane foams in 1983 from polyether polyols.[216]

Poly(aryl carbonate)s, on the other hand, possesses low tensile elongation, which can improved by the incorporation of aliphatic ether moiety in the matrix of poly(aryl carbonate).[217-221] This family of polymers are known as copoly(ether-carbonate), which can also be termed as soft poly(carbonate).

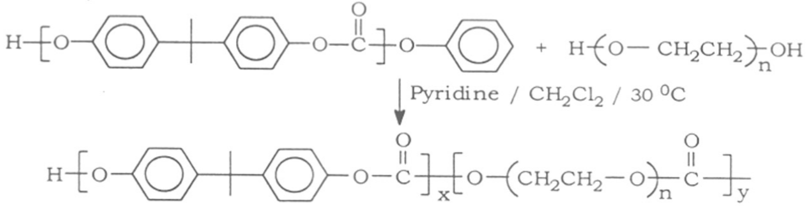
1.8.2.2 Synthesis of poly(ether-carbonate)s:

Poly(ether-carbonate)s are generally synthesized by phosgene route or by the non-phosgene route.

1.8.2.2a Phosgene route:

i) Solution Polymerization:

Goldberg[217] synthesized elastomeric block copoly(carbonate)s by reacting bisphenol A-poly(oxyethylene) glycol mixture in pyridine with phosgene at 30 °C (**Scheme 1.24**).

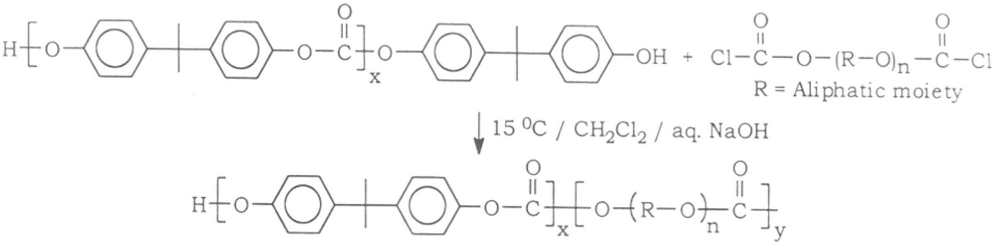


Scheme 1.24 : *Synthesis of poly(ether-carbonate)s using solution polymerization*

Copoly(carbonate)s derived from poly(oxyethylene) glycols (Carbowaxes) have been studied in detail for property-structure effects as a function of glycol molecular weight (1000-20,000) and copolymer composition (5-70 wt% or 0.3 to 10 mol% of a 4000 molecular weight glycol). The authors found remarkable strength (>700 psi) and snappy elasticity (>90% immediate recovery) of the copolymer with poly(oxyethylene) block concentrations greater than 3 mol%. These thermoplastic elastomers also exhibit high softening temperatures (>180 °C) and a tensile strength of about 700%. Both softening temperature and T_g varied linearly with the copolymer mole ratio over the composition ratio studied, with T_g displaying much greater polyether concentration sensitivity. A moderate molecular order, due to the bisphenol A poly(carbonate) segments rather than the normally crystalline polyether, was detected from the x-ray analysis. They also synthesized elastomeric carbonate-carboxylate tetrapolymer by partial replacement of carbonate with isophthalate, terephthalate or adipate linkages in polyether-bisphenol systems and observed a dramatic softening temperature depression due to the disruption of long bisphenol carbonate block sequences that exist in the simpler polyether glycol-bisphenol carbonate system.

ii) Interfacial polymerization:

Merrill[218] reported poly(ether-carbonate)s block copolymer using the interfacial technique. He prepared poly(ether-carbonate)s by reacting bisphenol A poly(carbonate) with phenolic end group in aqueous alkaline solution with bischloroformate of poly(ethyleneoxy) glycol or poly(tetrahydrofuran) in methylene chloride solution, where the chloroformate block was prepared by treating a polymer, terminated on each end by a primary hydroxyl group, with phosgene (**Scheme 1.25**).



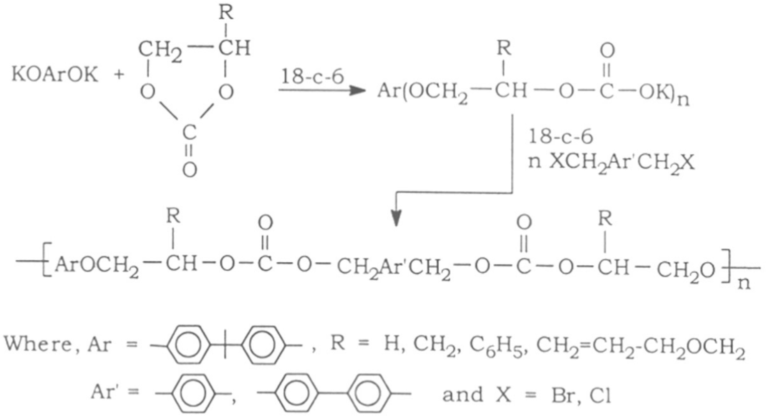
Scheme 1.25 *: Synthesis of block poly(ether-carbonate)s via interfacial polymerization*

He showed that the introduction of the flexible aliphatic poly(ether) blocks into the chain increase the mobility of the poly(carbonate) blocks and the poly(carbonate) blocks crystallize during short curing period at about 60 °C. The effect was reflected in considerably lowered T_g's.

Poly[tetrahydrofuran-poly(carbonate)] block copolymer, which is a elastomer, was capable of being cold drawn, after which it showed a tensile strength at break 100 kg /cm^2, elongation at break, 600% and recovery 95%. The elongation and recovery are comparable to those of gum rubber, the tensile strength being half that of gum rubber. The polymer can be cast into film or solvent-spun into fibers. Like an unvulcanized rubber, its thermal properties are good, owing to the high melting temperature of poly(carbonate). The glass transition temperature was considerably below 0 °C.

1.8.2.2b Melt phase reaction:

Rokicki *et al.*[83] synthesized poly(ether-carbonate) in the melt phase from α,ω-diphenolates, cyclic carbonates and dihalocompounds in presence of 18-crown-6 (**Scheme 1.26**).

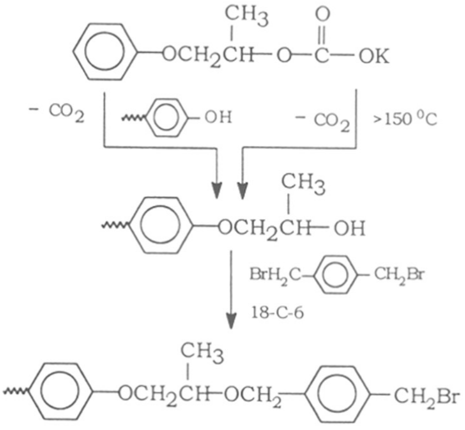


Scheme 1.26: *Synthesis of poly(ether-carbonate)s via melt phase*

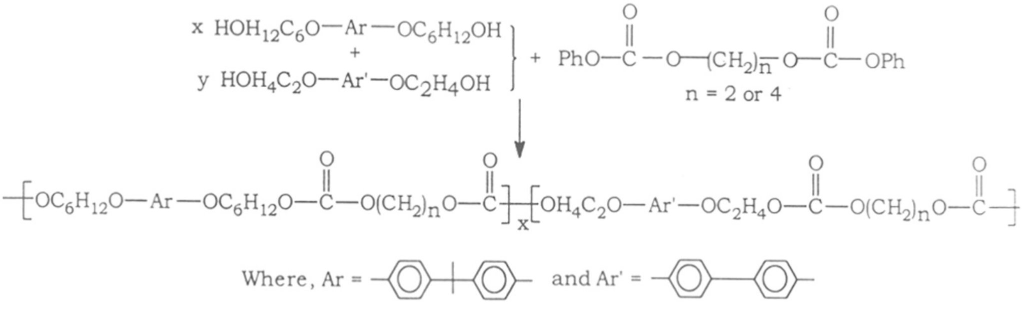
The formation of copolyether was confirmed by ^{1}H NMR and IR spectroscopic data. In the course of their study it was found that the formation of poly(ether-carbonate) depends on the purity of diphenol dipotassium salt. They also found that carbonate linkages content in the polymer was strongly dependent on the reaction temperature. At a temperature range of 100-120 ^{0}C the reaction with a participation of cyclic carbonate predominate due to the facile attack of phenolate anion on to the 1,3-dioxolan-2-one ring which resulted in the relatively high content of carbonate linkages in the product. They also observed that decreasing the temperature the formation of polymer with enhanced ether linkages content and at temperature of 70 ^{0}C and above 150 ^{0}C only polyether was obtained. The presence of free hydroxyl group in the salt also causes the decarboxylation side reaction (**Scheme 1.27**).

Sato *et al.*[219] synthesized liquid crystalline poly(carbonate) in the melt phase containing both aliphatic unit and ether linkages (**Scheme1.28**).

They showed that the copolymers with n = 4 are of high molecular weight, high yields and better solubility in organic solvents compared to the copolymer with n = 2. All the copolymers formed liquid crystal phases over the entire range of the composition. In the copolymers (n = 2) eutectic temperatures have been observed but with the copolymers (n = 4) the phase transition temperatures gradually increased with increasing content of the mesogenic unit. They have also compared the liquid crystal behavior of the copolymer with that of the polymer blends, which sowed that the latter form better aligned liquid crystal phases. From these results it has been concluded that the orientation of the mesogenic unit is disturbed by the polymer chain in the copolymer but in the polymer blends, the orientation was retained with interruption.



Scheme 1.27 : Different type of decarboxylation reactions, which can occur during the reaction



***Scheme 1.28** : Synthesis of liquid crystalline poly(ether-carbonate)s in the melt phase reaction*

1.9 PROPERTIES OF COPOLY(ARYL CARBONATE)S:

1.9.1 Properties of poly(ester-carbonate)s:

Copoly(arylester-carbonate)s combine poly(ester)'s chemical resistance properties with poly(carbonate)'s toughness, clarity and processability. The high temperature resistance of poly(carbonate) can be improved by the introduction of rigid aromatic ester units from terephthalate / isophthalate moiety and bisphenol A. The properties of poly(ester-carbonate)s vary depending upon the amount and type of phthaloyl moiety in the polymer. The various properties of poly(arylester-carbonate)s are discussed in the following paragraphs.[179]

a) Heat distortion temperature:

As measured by ASTM D 648 the heat distortion temperature (HDT) temperature of aromatic ester-carbonate copolymers improve with increasing ester content. Compared to the poly(carbonate) homopolymer, HDT can in fact, improve more than 10 ^{0}C depending on the ester loading.

b) Low temperature impact strength:

Notched Izod impact test run on injection molded bars of 1/8 inch thickness showed that at room temperature (21.1 ^{0}C), the impact strength of conventional bisphenol A poly(carbonate) is 16 kg-cm/cm. However, bisphenol A poly(carbonate) is quite brittle at -30 ^{0}C, as evidenced by its low impact strength. In contrast, the impact strength of the poly(aryl carbonate)s at room temperature ranges from that of the poly(carbonate) homopolymer down to 6 kgcm/cm, depending upon the ester content. At -30 ^{0}C, roughly 90 percent of the room temperature impact strength is maintained by the poly(arylester-carbonate)s copolymers throughout the ester content range studied.

c) Hydrolytic stability:

Poly(arylester-carbonate) has a hydrolytic stability significantly better than that of poly(carbonate), but not quite as good as polysulfones. The critical design stress level for poly(arylester-carbonate) is roughly two to three times higher than that of poly(aryl carbonate) and the hydrolytic stability improves with increasing ester content.

d) Optical properties:

Poly(arylester-carbonate)s show haze levels of less than two percent with a transmission value of 88 to 90 percent. A molded color is in the range of 3 to + yellowing index (YI) (ASTM D1925) for high ester content, untinted resins. Lower ester content poly(arylester-carbonate)s are close to typical poly(aryl carbonate) color at a 2.5 YI.

e) Flame retardency:

Poly(aryl carbonate)s have a UL 94 V-2 ignition-resistance rating similar to that of poly(aryl carbonate). Higher UL rating can be achieved through formulation with flame retardant additives. Measured limiting oxygen index is

38 for unmodified high ester content composition, a great improvement over the 27 rating for conventional poly(carbonate) is observed.

PC/PBT and PC/PET Blends:

Blend phase behavior and morphology are the key parameters relative to properties. As a result, much effort has been expended to determine the phase and morphological characteristics of these two blends. Overall, phase behavior depends on variety of factors, such as, preparation effects (melt blending vs. solution casting), solvent, analysis techniques, the extent to which equilibrium-phase behavior is reached (thermal history), component molecular weight, and interchange reaction.

Hobbs *et al.*[221] studied both melt and solution-cast PC/PBT blends. They reported nearly complete immiscibility for the samples cast from HFIP. Melt-blended samples exhibit partial miscibility in the PC-rich phase. Upon solution casting of these melt blends, the T_g shifted back to within a few degrees of the T_g of pure PC. Hobbs concluded that PC/PBT blends are partially miscible, with solvent effects causing the apparent immiscible behavior.

Kim and Burns[222] reported partial miscibility for PC/PBT blends prepared by both melt blending and solution casting from HFIP. Blend composition ratios vary from 70/30 to 30/70 (w/w). For composition ratios of 90/10, 20/80, and 10/90, miscible blends were reported. Additionally, it has been noted that the degree of partial miscibility is enhanced in the melt-processed samples.

Dielectric studies by Pratt and Smith[223,224] conducted on commercially available PC/PBT blends found evidence of partial miscibility. Morphological studies employing TEM were carried out to examine structure support the argument for partial miscibility in this system.[225] In a diffusion study, PBT fibrils growing across a sharp interface into a pure PC phase provide convincing evidence for partial miscibility.[226] In addition to this, phase behavior has been shown to depend on molecular weight, with miscibility being inversely proportional to molecular weight.[227]

The studies on PC/PET blends appear equally conflicting. From thermal analysis, complete miscibility in melt blends containing over 60% PET is reported by both Nassar *et al.*[228] and Murff *et al.*,[229] where partial miscibility is observed in compositions containing less PET. Linder *et al.*[230] examined a 25/75 (w/w) PC/PET blend cast from a 25/75 (w/w) HFIP/dichloromethane solution. Their carbon-carbon nuclear spin diffusion study indicated that the blend was homogeneously mixed at distances of 4.5-6 Å. DSC results obtained by Hanrahan *et al.*[231] indicate nearly complete immiscibility over the entire PC/PET composition range. Minor dependence of T_g on thermal history is also noted. Samples had been cast from two different solvents, HFIP and tetrachloroethane/phenol 40/60 (w/w).

From the observed DSC results, Chen and Birley[232] reported two amorphous regions over a PC/PET composition range of 20/80 to 80/20. Similarly, Suzuki *et al.*[233] reported immiscible blends from both melt-blended and solution-cast samples with PC/PET composition ranged from 10/90 to 90/10. Ahn *et al.*[234] prepared 50/50 (w/w), PC/PET blends by single-screw extrusion, twin-screw extrusion, and in solution precipitation from 1,1',2,2'-tetrachloroethane/phenol solution at 30 and 80 °C into methanol. DSC results on the melt blends and the solution-precipitated sample prepared at 30 °C indicate partial miscibility, whereas, the sample precipitated from the 80 °C solution is completely miscible. Kim and Burns[235] reported partially miscible blends over a wide composition range. The shifts in T_g are similar for both solution-cast and melt-blended samples. Similarly, partial miscibility for PC/PET blends over a composition range from 10/90 to 90/10 was reported by Wang *et al.*[236]

Blend composition also affects polyester crystallization behavior. The melting point (T_m) decreases with decreasing PBT content (~ 5 °C), and dual melting peaks are noted in PC/PBT blends.[237] The size of the PBT spherulites has been shown to decrease following the addition of PC.[225b] The %crystallinity in molded samples,[238] adjusted for blend composition, also decreases from 24 to 7% as PC content increases from 0 to 90%. However, after DSC, the percent crystallinity of PBT ranges from 20 to 28%, with no apparent correlation to PC concentration. The data indicates that crystallization kinetics are affected by blend composition. Indeed, the rate of crystallization decreases with increasing PC content.[239] It was also found by Halder that the Avrami exponent for PBT in a PC/PBT 50/50 blend is decreased to 1.4, indicating the loss of three-dimensional spherulite growth and corresponding to a morphology that is expected to be co-continuous. In PC/PET blends, a decrease in T_m is observed with decreasing PET content, and blends containing less than 20% PET do not crystallize even after annealing for 30 minutes at 167 °C.[229]

The morphology of PC/polyester blends has been investigated by a variety of techniques, including phase-contrast microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). TEM combined with selective staining has revealed the most detailed information about the morphological structure. The morphology of PC/PBT blends as a function of composition has been examined by Delimoy *et al.*[225c] At a PC/PBT ratio of 80/20, a continuous PC phase with included PBT particles is found and at 60/40, a co-continuous morphology is observed. At blend compositions of 40/60 and 20/80, a continuous PBT phase with included PC particles occurs. Excessive staining of the sample reveals amorphous PC incorporated into the interlamellar regions of PBT spherulites. Hobbs *et al.*[225b] also report that PC is located in the interlamellar regions of PBT spherulites. Both authors indicate this as an evidence for partial miscibility in the melt, with PC being forced into the interlamellar regions during PBT crystallization.

PBT/PC blends containing a core-shell impact modifier (IM) have also been examined, where staining with OsO_4 is used to enhance the contrast of the IM, followed by staining with RuO_4 to enhance the PC phase.[225b]

SEM studies on PC/PET blends[235] showed included PET in a continuous PC phase at a composition ratio of 80/20. At ratios of 30/70 and 10/90, the phase behavior is inverted, with included PC particles in a continuous PET matrix. At a 60/40 composition, it is difficult to conclude from the SEM whether a discrete PET phase or a co-continuous morphology is present.

1.9.2 Properties of poly(ether-carbonate)s:

Aromatic-aliphatic poly(carbonate) containing ether linkage can be termed as soft poly(carbonate) having a high tensile elongation, excellent low temperature characteristics as well as transparency has assumed interest in recent years. In this soft poly(carbonate) aromatic part is having crystallinity whereas the aliphatic part is having rubbery properties. These modified poly(carbonate) resins have an increased tensile elongation as a mechanical property as compared to general PC resins, which have reduced strength only to provide moldings of low strength. The properties of poly(oxyethylene) glycol-bisphenol A poly(carbonate)[219] are given in **Table 1.12.**

Table 1.12 : Properties of poly(oxyethylene) glycol bisphenol A poly(carbonate)

Carbowax	Wt	Mol	[η]	Soft. Temp.	Wt. Loss (200^{0}C, 24 h)	Tensile properties[a]					Orientation	Elastic recovery	
	%	%	(dL/g)	(^{0}C)	%	Y, psi	U, psi	E, %	TE, ft-lb/in^2	Temp. (^{0}C)	%	IER	IER$_0$
1000 CBX	50	18.5	0.70	-	21.5	830	2360	565	630	25	-	94	97
						-	5430	320	700	25	64	-	-
						-	290	60	10	120	-	-	-
4000 CBX	50	5.4	1.08	-	41.4	460	7030	460	870	25	-	96	99
						480	10740	280	1010	25	55	-	-
						285	2020	655	460	120	-	-	-
6000 CBX	50	3.7	0.89	-	41.9	980	7080	570	1200	25	-	90	97
						725	10730	305	1180	25	68	-	-
						470	1600	660	425	120	-	-	-
20000 CBX	50	1.1	Insol. gel	170-195	29.0	-	-	-	-	-	-	-	-
20000 CBX	30	0.4	>1.6, some gel	185-200	-	4860	6350	195	-	25	-	-	-

[a] *Y = yield, U = ultimate strength, E = elongation, TE = tensile strength*

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CHAPTER II

SCOPE AND OBJECTIVES OF THE PRESENT STUDY

2.1 INTRODUCTION:

Cyclic carbonates, such as, ethylene carbonate is readily available, have desirable physical properties and are prepared from carbon dioxide and ethylene oxide.[1] Reaction of hydroxy compounds with ethylene carbonate have been well known in the literature. Sakai *et al.*[2] have reported the carbonylation of butylstannyl alkoxide with ethylene carbonate under nitrogen atmosphere to give the corresponding dialkyl carbonate of 27-73% yield. The higher alkyl carbonates were synthesized by the carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compound. Literature predominantly reveals the use of basic inorganic compounds,[3-5] organic base,[6] phase transfer catalysts.[7] Carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compounds were also catalyzed by the organometallic catalysts.[8-11] All the reactions were conducted under homogeneous condition with or without the use of solvent. Basic ion exchange resin[12] containing quarternary ammonium group has been described for the synthesis of dialkyl carbonate from ethylene carbonate and aliphatic hydroxy compounds. Few zeolites were also found to be active for the synthesis of aliphatic carbonates. However, the yield was not high (~60%).[13,14] The advantage of solid base catalyst is that it can be easily separated from the reaction medium.

Therefore, an objective of the present study is to examine the reaction of ethylene carbonate with alcohol using metal exchanged basic zeolite catalyst and compare the results with the conventional organotitanium catalyst.

Carbonate interchange reaction of ethylene carbonate with aromatic hydroxy compound is far less studied and is complicated by the competing decarboxylation reaction.[15] There exists only one report which describes the synthesis of diphenyl carbonate from ethylene carbonate using organotin catalyst.[16] The reaction of ethylene carbonate with aromatic hydroxy compound can either lead to an aromatic carbonate or a decarboxylated product depending on the nature of ring opening reaction. Therefore, another objective of the present study is to examine critically the model reaction of ethylene carbonate with phenol using different catalysts to understand the effect of reaction conditions on the nature of the reaction. It is also proposed to examine the reaction of bisphenol A with a fully aliphatic poly(carbonate) to see if exchange reaction can be promoted. This is because aliphatic carbonate can be more easily prepared from aliphatic diol and dialkyl carbonate and is free of thermodynamic limitation.

Poly(aryl carbonate)s based on bisphenol A have gained importance as an engineering thermoplastic owing to its unusual combination of properties, such as, glass like transparency, high impact strength and high heat distortion temperature.[17] Poly(aryl carbonate)s are prepared by either a phosgene route or by a melt phase carbonate interchange reaction of BPA with diphenyl carbonate in presence of a catalyst above 180 ^{0}C.

With increasing global concern[18] over the use of toxic chemicals, such as, phosgene and environmentally unfriendly chlorohydrocarbons, renewed interest has been focused on a viable nonphosgene route to poly(aryl carbonate)s.

One of the drawbacks of the melt phase carbonate interchange reaction is that the melt viscosities increase dramatically with increase in molecular weight, leading to problems in agitation and heat transfer. This, in turn, adversely impacts on product quality. Specialized equipments capable of providing efficient heat/mass transfer at high melt viscosities (upto 13,000 poise at 300 ^{0}C) are needed to conduct melt phase carbonate interchange reaction, especially for the synthesis of poly(aryl carbonate)s with $[\eta] > 0.45$ dL/g.

Solid state polymerization (SSP) has been well studied[19] in case of crystalline thermoplastics, such as, poly(ethylene terephthalate). However, its applicability to amorphous thermoplastics, such as, poly(aryl carbonate)s[20,21] is of more recent origin. Low molecular weight poly(aryl carbonate)s could be chain extended in the solid state under defined conditions to high molecular weight polymers ($\bar{M}_v > 60{,}000$). This technique removes the limitations of the melt phase process for producing poly(aryl carbonate)s with a wide range of molecular weights. The influence of various reaction parameters, such as, the nature of the reactor, time, temperature, catalyst, initial crystallinity, initial molecular weight and end group concentration have profound effect on the rate of solid state polymerization. However little is known in the literature about the effect of these parameters on the solid state polymerization of oligopoly(aryl carbonate). Bisphenol A poly(carbonate)s are known to undergo crystallization under special conditions. For instance, they can be crystallized from melt, when they are held at 180 ^{0}C for a week.[22,23] They are known to undergo rapid crystallization, when exposed to solvent vapors or when dissolved in a suitable solvent,[24] in presence of a plasticizer[25] or a nucleating agent.[26] It has reported that during the solid state polymerization of poly(aryl carbonate) chain extension is accompanied by increase in the crystallinity of the polymer.[20]

Hence, a second objective of the present study is to investigate the influence of various experimental parameters on solid state polymerization reaction to evaluate its kinetics and examine the influence of SSP on polymer properties, such as, crystallinity and melting behavior.

Another objective of the present study is to extend the capabilities of SSP for generating new polymer structures.

Branched poly(aryl carbonate)s[27] are generally synthesized by the interfacial polymerization process. Branched poly(carbonate)s are difficult to synthesize using melt phase chemistry. Therefore, the third objective of the present study is to examine the feasibility of solid state polymerization for the synthesis of branched poly(aryl carbonate).

Poly(ester-carbonate)s[28-31] are generally synthesized by the interfacial or melt polymerization reaction. Interfacial polymerization is environmentally unfriendly and melt phase polymerization requires higher temperature (~280 °C) where, polymer degradation, side reaction and gel formation can take place. On the other hand, SSP operates under milder condition. Therefore, the fourth objective of the present study is to examine the feasibility of SSP for the synthesis of poly(ester-carbonate)s.

Aromatic-aliphatic block poly(carbonate)s containing ether linkages have attracted attention in view of their desirable properties such as high tensile elongation, excellent low temperature characteristics as well as transparency. They are generally synthesized by copolymerizing bisphenol A polycarbonate block with a polyether block containing appropriate reactive end-groups.[32-34] In the course of a program work to explore the reaction of phenols with ethylene carbonate, it was found that bis(hydroxyethyl ether) of bisphenols could be efficiently synthesized. Hence, the fifth objective of the present study is to synthesize poly(ether-carbonate)s derived from bis(hydroxyethyl ether) of bisphenols and bisphenol A. Controlled introduction of a flexible ether group may render the processability of polycarbonate derived from rigid bisphenols easier.

In summary, the objectives of the present investigations are

2.1.1 Examine the use of ethylene carbonate as a precursor for polycarbonates

2.1.1.1 To examine the effect of solid base catalyst for the synthesis of dialkyl carbonate by the carbonate exchange reaction of alcohols with ethylene carbonate.

2.1.1.2 To examine the effect of catalyst on the nature of reaction between phenols and ethylene carbonate.

2.1.2 Synthesis of high molecular weight poly(aryl carbonate)s using solid state polymerization

2.1.2.1 To examine the effect of reaction parameters on the preparation of linear high molecular weight poly(aryl carbonate)s *via* SSP and to evaluate the kinetic parameters of the reaction.

2.1.2.2 To examine the feasibility of synthesis of branched poly(aryl carbonate)s

2.1.3 Synthesis and characterization of poly(ester-carbonate)s using solid state polymerization

2.1.3.1 Synthesis and characterization of copoly(arylester-carbonate)s

2.1.3.2 Synthesis and characterization of copoly(alkylester-carbonate)s

2.1.4 Synthesis and characterization of copoly(ether-carbonate)s, derived from bis(hydroxyethyl ether) of bisphenols as monomer

2.1.4.1 Synthesis and characterization of bis(hydroxyethyl ether) of bisphenols

2.1.4.2 Synthesis and characterization of copoly(ether-carbonate)s

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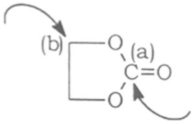
CHAPTER III

ETHYLENE CARBONATE AS A PRECURSOR OF DIALKYL CARBONATES AND POLYCARBONATES

3.1 INTRODUCTION:

Cyclic carbonates, such as, ethylene carbonate is readily available, have desirable physical properties and are prepared from carbon dioxide and ethylene oxide.[1] The structure of ethylene carbonate is given below:



The attack of a nucleophile is possible either on the carbonyl carbon (a) or the methylene carbon (b). The reaction of ethylene carbonate with hydroxy compounds can either lead to an organic carbonate or a decarboxylated product depending on the nature of ring opening reaction.

Reactions of hydroxy compounds with ethylene carbonate have been well known in the literature[2]. Sakai *et al.*[3] have reported the carbonylation of butylstannyl alkoxide with ethylene carbonate under nitrogen atmosphere to give the corresponding dialkyl carbonate of 27-73% yield. The higher alkyl carbonates were synthesized by the carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compound. Literature predominantly reveals the use of basic inorganic compounds,[4-6] organic base[7] or phase transfer catalysts.[8] Carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compounds were also catalyzed by organometallic catalysts.[9-12] All the reactions were conducted under homogeneous condition with or without the use of a solvent. Basic ion exchange resin[13] containing quarternary ammonium group has been described for the synthesis of dialkyl carbonate from ethylene carbonate and aliphatic hydroxy compounds. Few zeolites were also found to be active for the synthesis of aliphatic carbonates. However, the yield was not high (~60%).[14,15] The advantage of solid base catalyst is that it can be easily separated from the reaction medium.

Carbonate interchange reaction of ethylene carbonate with aromatic hydroxy compound is far less studied and is complicated by the competing decarboxylation reaction.[16] There exists only one study which reports the synthesis of diphenyl carbonate from ethylene carbonate using organotin catalyst.[17]

Ethylene carbonate has also been used for the synthesis of aliphatic polycarbonate.[18]

Therefore, the synthesis of poly(aryl carbonate)s using ethylene carbonate as a carbonate precursor is a desirable goal. If feasible, this will result in the use of carbon dioxide as a precursor for carbonate linkage in polycarbonates

This chapter discusses the reaction of ethylene carbonate with alcohol using metal exchanged basic zeolite catalyst and a comparison of the results with the conventional organotitanium catalyst. The model reaction of ethylene carbonate with phenol using different catalysts has been examined with a view to understand the effect of reaction conditions on the nature of the ring opening reaction.

3.2 EXPERIMENTAL:

3.2.1 Materials:

Bisphenol A (Aldrich Chemicals, USA) was recrystallized from toluene (mp = 158 ^{0}C, lit.[19] mp = 158 ^{0}C), ethylene carbonate (EC) (Fluka A.G., Switzerland) was vacuum distilled (bp = 114 ^{0}C at 10 mm of Hg, lit.[19] bp = 243 ^{0}C) and phenol (s.d. fine Chemical, Bombay, India) was vacuum distilled (bp = 67-70 ^{0}C at 10 mm of Hg, lit.[19] bp 180 ^{0}C at atmospheric pressure). DMC (Aldrich Chemicals, USA) was used after distillation. *n*-Butanol, tert-butanol, allyl alcohol and methanol (s.d. fine Chemical, Bombay, India) were used after distillation. All other solvents were purified according to the literature procedure.[19] Maleic acid (s.d. fine Chemical, Bombay, India) was recrystallized according to the literature procedure (mp = 137-139 ^{0}C, lit.[19] mp = 136-141 ^{0}C). Tetramethyl ammonium hydroxide (25% methanol) (Sisco Laboratory, Bombay, India) and dibutyltin oxide (Fascat M & T Chemicals, USA) were used as received.

3.2.2 Preparation of the catalyst:

3.2.2a Synthesis of tetrabutyl-1,3-diphenoxy distannoxane:[20]

Phenol (0.98 g, 0.01 mol) was added to a stirred suspension of dibutyltin oxide (2.45 g, 0.01 mol) in 50 mL benzene in a 100 mL three necked flask equipped with Dean-Stark apparatus, a reflux condenser and a nitrogen inlet. After 2 h reflux, the hazy solution was filtered and benzene was removed by vacuum distillation. The product obtained was recrystallized from hexane.

Yield = 83% and mp = 137-138 °C (lit. mp = 137-139 °C)

3.2.2b Synthesis of tetramethyl ammonium maleate:

Maleic acid (1.16 g, 0.01 mol) was taken in 50 mL conical flask and to it tetramethyl ammonium hydroxide (19.6 mL, 0.51 N) was added. The solution was stirred till the solution became clear. After 15 min stirring, CH_2Cl_2 (25 mL) was added to the solution. The resulting solution was dried over anhydrous magnesium sulfate, filtered and stripped free of solvent. Residual solid was recrystallized from minimum volume of methanol.

Yield : 6.9 g (87%) mp. 188-189 °C)

^{1}H NMR ($CDCl_3$, δ):

3.05 [$N(CH_3)_4$, 12H, s], 6.1 (-C=CH-, 2H, s)

^{13}C NMR ($CDCl_3$, ppm):

55.71 [$N(CH_3)_4$], 136.96 (-C=CH-), 169.07 [-O-C(=O)-O-]

3.2.3 Synthesis of diallyl carbonate (DAC):

To a stirred solution of triphosgene (8.9 g, 0.03 mol) in CH_2Cl_2 (20 mL) at -70 °C was added pyridine (20 mL) and allyl alcohol (3.48 g, 0.06 mol) in CH_2Cl_2 (20 mL). Once addition was complete, the reaction mixture was allowed to warm to room temperature. The resultant homogeneous solution was quenched with saturated NH_4Cl and washed 2-3 times with HCl solution (0.1 N), $CuSO_4$ solution and saturated $NaHCO_3$ solution and dried over Na_2SO_4. The organic layer was filtered, removed in rotavapor and dried under vacuum. Finally, the product was distilled out. bp = 163-165 °C. Yield = 3.45 g (40 mol%).

^{1}H NMR ($CDCl_3$, δ):

4.65 ($-OCH_2$, 4H, m), 5.2-5.45 ($=CH_2$, 4H, m) and 5.8-6.1 (-CH=, 2H, m)

Di-*n*-butyl carbonate (DBC) was also prepared using the same procedure.

bp = 201-205 °C

3.2.4 Synthesis of hydroxyethyl ether of phenol (HEEP):

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Phenol

(1.959 g, 0.0208 mol), EC (1.83 g, 2.02 x 10^{-3} mol) and tetrabutyl-1,3-diphenoxydistannoxane (2.87 x 10^{-3} g, 2.08 x 10^{-5} mol) were taken in the flask and heated at 160 ^{0}C for 3 h under nitrogen. The reaction mixture was cooled to room temperature under nitrogen. The product formed was separated by column chromatography over an adsorbent bed of silica gel (60-120 mesh) using petroleum ether and ethyl acetate mixture as eluent. Yield = 1.97 g (68 mol%)

^{1}H NMR ($CDCl_3$, δ):

2.1 (-OH, 1H, s), 3.95 ($-OCH_2-C\underline{H}_2-OH$, 2H, t), 4.1 ($-OC\underline{H}_2-CH_2-OH$, 4H, t), 6.8-7.6 (Ar-H, 5H)

^{13}C NMR ($CDCl_3$, ppm):

61.18 ($-OCH_2-\underline{C}H_2-OH$), 69.19 ($-O\underline{C}H_2-CH_2-OH$), 114.61 (Ar-C, corresponding to *m* carbons), 121.03 (corresponding to *o* carbons) 129.50 (corresponding to *p* carbon) 158.68 (Ar-C, corresponding to quarternary carbon).

3.2.5 Reaction of *n*-butanol with ethylene carbonate (EC):

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. *n*-Butanol (5.7 g, 0.025 mol) and EC (11.0 g, 0.07 mol) were added followed by zeolite KL (1 wt% of EC) under a stream of nitrogen. The mixture was refluxed for 10 h and an aliquot was taken out after 2 h intervals for GC analysis.

Other reactions of *n*-butanol with ethylene carbonate were also carried out using the same procedure except by varying the ratio of phenol to ethylene carbonate or type of catalyst.

3.2.6 Reaction of *tert*-butanol with EC:

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. *tert*-Butanol (16.8 g, 0.2 mol) and EC (1.76 g, 0.02 mol) were added followed by zeolite KL (1 wt% of EC) under a stream of nitrogen. The mixture was refluxed for 2 h and an aliquot was taken out for GC analysis.

3.2.7 Reaction of methanol with EC:

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Methanol (6.4 g, 0.2 mol) and EC (1.76 g, 0.02 mol) were added followed by KL (1 wt% of EC) under a stream of nitrogen. The mixture was refluxed for 2 h and an aliquot was taken out for GC analysis.

3.2.8 Reaction of allyl alcohol with ethylene carbonate:

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Allyl alcohol (5.7 g, 0.4 mol) and EC (3.524 g, 0.04 mol) were added followed by KL (1 wt% of EC) under a stream of nitrogen. The mixture was refluxed for 4 h and an aliquot was taken out after 2 h intervals for GC analysis.

3.2.9 Reaction of phenol with EC:

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Phenol (4.7 g, 0.5 mol), tetrabutyl-1,3-diphenoxy distannoxane (4.403×10^{-3} g, 1 wt% of EC) were taken in the flask and heated at 180 ^{0}C for 30 min under nitrogen. The reaction mixture was cooled to room temperature under nitrogen and to this EC (0.4403 g, 0.05 mol) was added. The reaction mixture was heated at 180 ^{0}C for 4 h and the product was analyzed by GC using diphenyl ether as an internal standard.

Reactions of phenol with EC using other catalyst were also carried out using the same procedure.

3.2.10 Model reaction of bisphenol A with poly(1,4-butylene carbonate):

Bisphenol A (0.98 g, 4.298×10^{-3} mol), poly(1,4-butylene carbonate) (0.5 g, 0.98 mol, η_{inh} = 0.56 dL/g) and tetrabutyl-1,3-diphenoxy distannoxane (0.1 mol% of BPA) were taken in a 50 mL 3 neck flask equipped with a nitrogen inlet and a thermowell. The reaction mixture was then heated to 180 ^{0}C in 30 min and maintained at that temperature for 90 min. Thereafter, the reaction temperature was increased to 200 ^{0}C and maintained for 135 min while reducing the pressure from 760 to 1 mm of Hg. Furthermore, the reaction was continued at 230 ^{0}C for 30 min, 250 ^{0}C for 30 min and finally at 270 ^{0}C for 15 min. The polymer thus formed was dissolved in 10 mL chloroform and the solution was poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 ^{0}C for 24 h.

Yield : 0.918 g and η_{inh} = 0.64 dL/g in $CHCl_3$ at 30 ^{0}C.

3.2.11 Melt phase reaction of bisphenol A and EC:

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Bisphenol A (5.7 g, 0.025 mol) and ethylene carbonate (11.0 g, 0.07 mol) were added followed by catalyst (0.1 mol% of BPA) under a stream of nitrogen. The mixture was heated from room temperature to 200 ^{0}C over a period of 1 h. Finally, the reaction was carried out at 200 ^{0}C for 8 h. The product formed was separated by column chromatography over an adsorbent bed of silica gel (60-120 mesh) using petroleum ether and ethyl acetate mixture as eluent. The product obtained was characterized by ^{1}H NMR ^{13}C NMR and FT-IR spectra.

Yield = 5.9 g (47 wt%)

Fraction-A:

Yield = 1.49 g (12 wt%)

^{1}H NMR ($CDCl_3$, δ):

1.65 [$C(CH_3)_2$, 6H,s], 3.9 ($-CH_2-CH_2-OH$, 4H,t),4.15 ($-CH_2-CH_2-OH$, 4H, t), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d)

^{13}C NMR (DMSO-d_6, ppm):

31.25 [$C(CH_3)_2$], 41.64 [$C(CH_3)_2$], 60.24 ($-OCH_2-\underline{C}H_2-OH$), 69.93 ($-O\underline{C}H_2-CH_2-OH$), 114.37 and 127.89 (Ar-C, corresponding to *o* and *m* carbons), 143.07 and 156.98 (Ar-C, corresponding to quarternary carbons).

Fraction-B:

Yield = 4.49 g (35 wt%)

^{1}H NMR ($CDCl_3$, δ):

1.65 [$C(CH_3)_2$, 6H, s], 3.7 to 4.5 (a set of peaks corresponding to $-CH_2$), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d).

^{13}C NMR ($CDCl_3$, ppm):

30.95 [C($\underline{C}H_3)_2$], 41.55 [$\underline{C}(CH_3)_2$], 60.93 to 72.50 (a set of peaks corresponding to -CH_2), 113.89 and 127.61 (Ar-C, corresponding to *o* and *m* carbons), 143.54, 143.24, 156.04 and 156.43 (Ar-C, corresponding to quarternary carbons), 154.973 (corresponding to -O-$\underline{C}$(=O)-O- carbons)

3.2.12 Measurements:

Melting points were measured with a Thermonix melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker WH-90FT-NMR and Bruker AC-200 NMR spectrometer. FT-IR spectra were recorded using a Perkin-Elmer model 16PC FT-IR spectrometer. The gas chromatographic analysis of phenol, EC, DMC, DBC, DAC and HEEP were performed using Perkin Elmer Model 1022, using a flame ionization detector and a nonpolar column (BP-1) and N_2 as carrier gas.

3.2.12.1 Saponification of the viscous product (Fraction B):

About 0.6169 g of the viscous oil (**Fraction B**) was taken in a 50 mL round bottom flask and to it methanolic KOH (5 mL, 18%) was added. The mixture was kept for 30 min at room temperature. Methanol was removed in rotavapor and the product was dried under vacuum for 2 h. The product was acidified with HCl extracted with ethyl acetate. The TLC of the organic layer showed two spots. Ethyl acetate was removed in the rotavapor. The product was separated by column chromatography over an adsorbent bed of column silica gel (60-120 mesh) using petroleum ether and ethyl acetate mixture as eluent. The product obtained was characterized by ^1H NMR, ^{13}C NMR and FT-IR spectra.

Fraction C:

Yield = 0.358 g (58 wt%)

^1H NMR, ^{13}C NMR, and FT-IR of this fraction is similar to **Fraction A**.

Fraction D:

Yield = 0.191 g (31 wt%)

^1H NMR ($CDCl_3$, δ):

1.65 [$C(CH_3)_2$, 6H, s], 3.7 to 4.2 (a set of peaks corresponding to -CH_2), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d).

^{13}C NMR ($CDCl_3$, ppm):

30.952 [$C(CH_3)_2$], 41.546 [$C(CH_3)_2$], 60.928 to 72.503 (a set of peaks corresponding to -CH_2), 113.896 and 127.606 (Ar-C, corresponding to *o* and *m* carbons), 143.539, 143.219, 156.040 and 156.427 (Ar-C, corresponding to quarternary carbons).

3.2.12.2 Calibration curves of EC, DBC DAC and DMC using DPE as internal standard:

A) Analysis of EC:

EC was estimated using DPE as internal standard under the following condition:

Column = BP1 (length = 12 m, inner diameter = 0.53 mm, outer diameter = 0.68 mm), Nitrogen flow = 40 mL/min, Hydrogen flow = 45 mL/min, Air = 450 mL/min. Oven Program: 50 ^{0}C (for 2 min) and 50-210 ^{0}C (at a heating rate of 10 ^{0}C/min). Injector temperature = 250 ^{0}C, detector temperature = 300 ^{0}C

Figure 3.1 shows the chromatogram of EC and DPE with retention time 7.89 and 15.87 min respectively. In order to estimate accurately the amount of EC, calibration of EC with DPE was carried out as follows:

A stock solution of DPE was prepared by dissolving 0.5475 g DPE in 25 mL chloroform. From that stock solution 1 mL was taken for the preparation of the solution. A stock solution of EC was prepared by dissolving 1.2707 g in 25 mL chloroform. From this stock solution 0.5, 1, 3, 4 and 5 mL solution was taken along with 1 mL DPE solution in a 10 mL volumetric flask and the volume was made upto the mark.

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of EC to DPE was plotted against corresponding mole ratio (**Figure 3.2**). The slope of the curve was 10.4 and was used directly to calculate the exact quantity of EC as follows:

Mole ratio = Area ratio x RF

Therefore, mole of EC = mole of DPE x Area ratio x RF

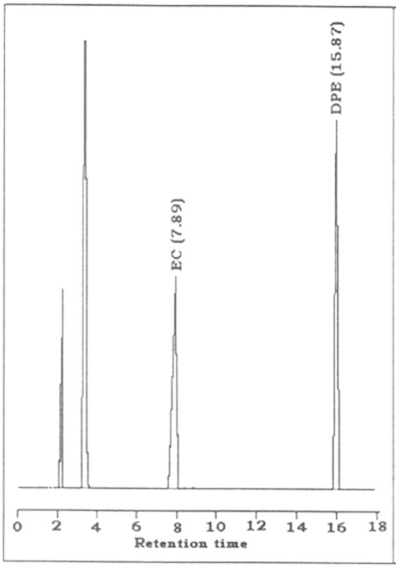


***Figure 3.1:** Gas chromatogram of EC and DPE*

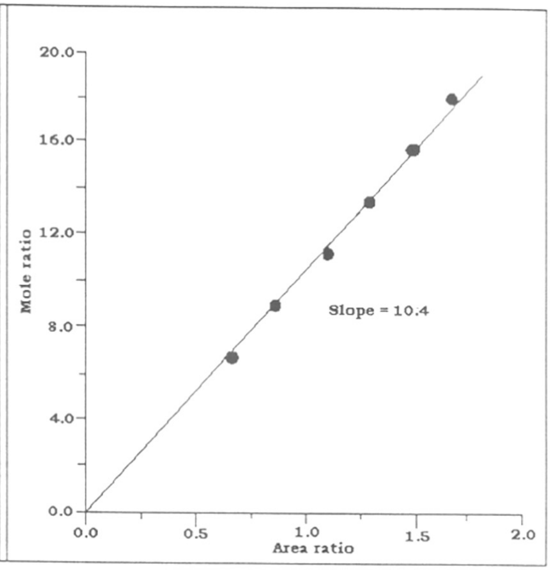


***Figure 3.2 :** Calibration curve of EC using DPE as internal standard*

B) Analysis of di-n-butyl carbonate (DBC):

DBC was estimated using DPE as internal standard under the same conditions as in the case of EC. **Figure 3.3** shows the chromatogram of DBC and DPE with retention time 12.03 and 15.75 min respectively. In order to estimate accurately the amount of DBC, calibration of DBC with DPE was carried out as follows:

A stock solution of DPE was prepared by dissolving 0.5513 g DPE in 25 mL chloroform. From that stock solution 0.5 mL was taken for the preparation of the solution. A stock solution of DBC was prepared by dissolving 0.2835 g in 25 mL chloroform. From this stock solution 1, 2, 3, 5 and 7.5 mL solution was taken along with 0.5 mL DPE solution in a 10 mL volumetric flask and the volume was made upto the mark.

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of DBC to DPE was plotted against corresponding mole ratio (**Figure 3.4**). The exact concentration of DBC was calculated from the slope of the linear plot as described earlier. The slope of the curve was 1.48.

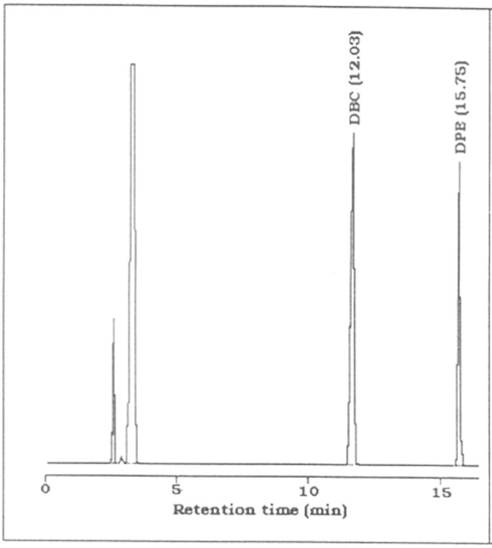


Figure 3.3 *: Gas chromatogram of DBC and DPE*

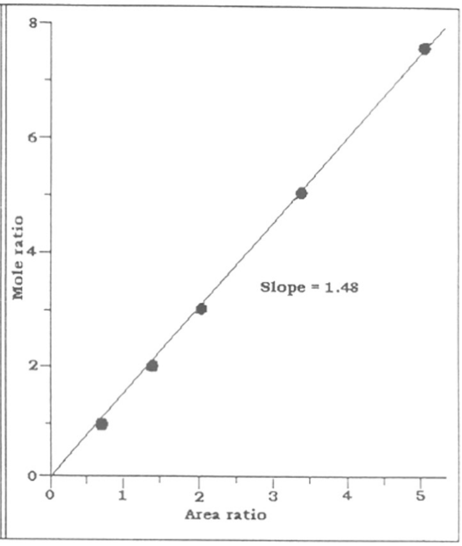


Figure 3.4 *: Calibration curve of DBC using DPE as internal standard*

C) Analysis of diallyl carbonate (DAC):

DAC was estimated using DPE as internal standard under the same conditions as used in case of EC. **Figure 3.5** shows the chromatogram of DAC and DPE with retention time 8.18 and 15.89 min respectively. In order to estimate accurately the amount of DAC, calibration of DAC with DPE was carried out as follows:

A stock solution of DPE was prepared by dissolving 0.5513 g DPE in 25 mL chloroform. From that stock solution 1 mL was taken for the preparation of the solution. A stock solution of DAC was prepared by dissolving 0.5786 g in 25 mL chloroform. From this stock solution 0.5, 1.5, 2.5, 4 and 5 mL solution was taken along with 1 mL DPE solution in a 10 mL volumetric flask and the volume was made upto the mark.

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of DAC to DPE was plotted against corresponding mole ratio (**Figure 3.6**). The exact concentration of DAC was calculated from the slope of the linear plot as described earlier. The slope of the curve was 2.66.

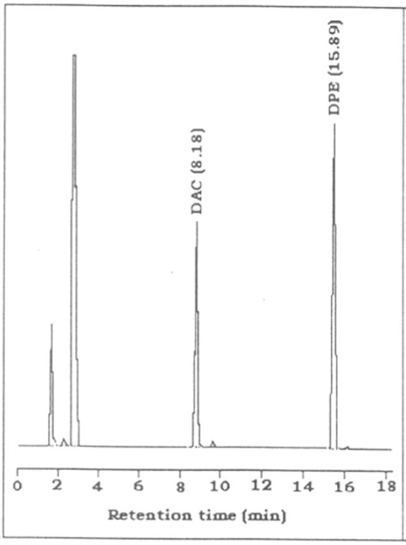


Figure 3.5 : *Gas chromatogram of DAC and DPE*

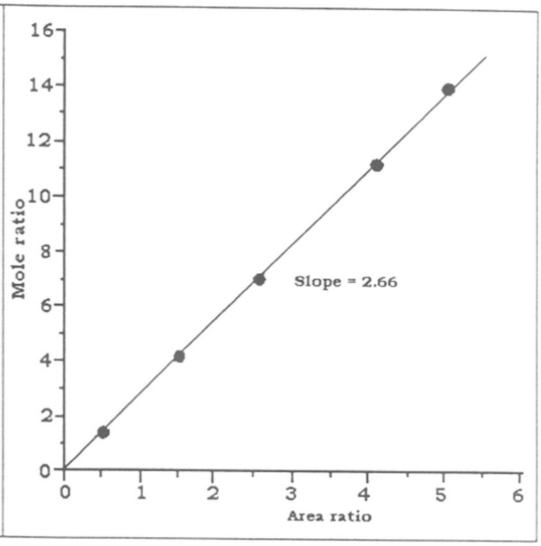


Figure 3.6 : *Calibration curve of DAC using DPE as internal standard*

D) Analysis of dimethyl carbonate (DMC):

DMC was estimated using DPE as internal standard under the same conditions as used in case of EC. **Figure 3.7** shows the chromatogram of DMC and DPE with retention time 3.13 and 15.23 min respectively. In order to estimate accurately the amount of DMC, calibration of DMC with DPE was carried out as follows:

A stock solution of DPE was prepared by dissolving 0.3608 g DPE in 10 mL dichloromethane. From that stock solution 0.1 mL was taken for the preparation of the solution. A stock solution of DMC was prepared by dissolving 0.6706 g in 10 mL methanol. From this stock solution 0.2, 0.4, 0.6 and 0.8 mL solution was taken along with 0.1 mL DPE solution in a 10 mL volumetric flask and the volume was made upto the mark.

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of DMC to DPE was plotted against corresponding mole ratio (**Figure 3.8**). The exact concentration of DMC was calculated from the slope of the linear plot as described earlier. The slope of the curve was 24.66.

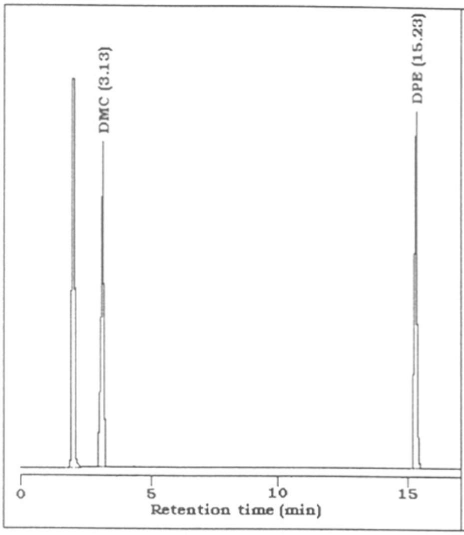


Figure 3.7 : Gas chromatogram of DMC and DPE

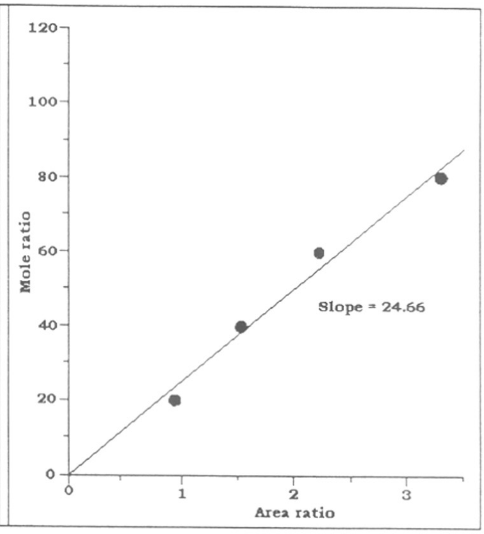


Figure 3.8 : Calibration curve of DMC using DPE as internal standard

E) Analysis of hydroxyethyl ether of phenol (HEEP):

HEEP was estimated using DPE as internal standard under the following conditions:

Column = BP1. Nitrogen flow = 40 mL/min, Hydrogen flow = 45 mL/min, Air = 450 mL/min. Oven Program: 90-240 °C at a heating rate of 10 °C/min and 240 °C for 2 min. Injector temperature = 270 °C, Detector temperature = 300 °C.

Figure 3.9 shows the chromatogram of HEEP and DPE with retention time 7.56 and 10.33 min respectively. In order to estimate accurately the amount of HEEP, calibration of HEEP with DPE was carried out as follows:

A stock solution of DPE was prepared by dissolving 0.5581 g DPE in 25 mL chloroform. From that stock solution 0.1 mL was taken for the preparation of the solution. A stock solution of HEEP was prepared by dissolving 0.1984 g in 10 mL chloroform. From this stock solution 0.2, 0.4, 0.6, and 0.8 mL solution was taken along with 0.1 mL DPE solution in a 10 mL volumetric flask and the volume was made upto the mark.

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of HEEP to DPE was plotted against corresponding mole ratio (**Figure 3.10**). The exact concentration of HEEP was calculated from the slope of the linear plot as described earlier. The slope of the curve was 1.80.

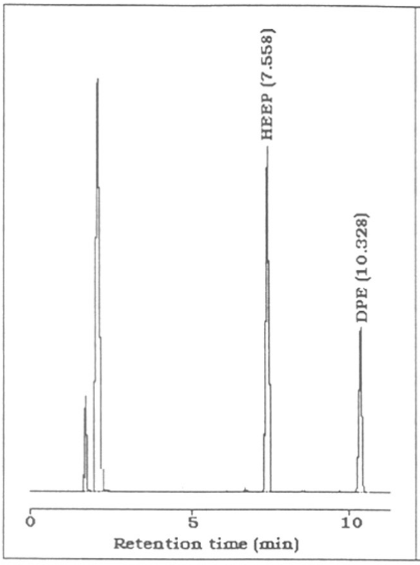


***Figure 3.9** : Gas chromatogram of HEEP and DPE*

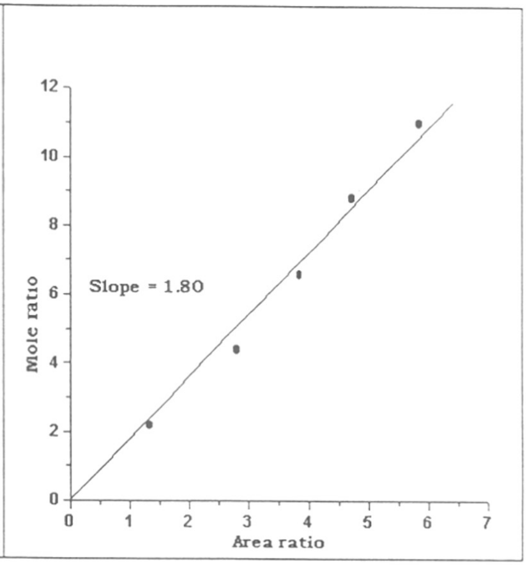


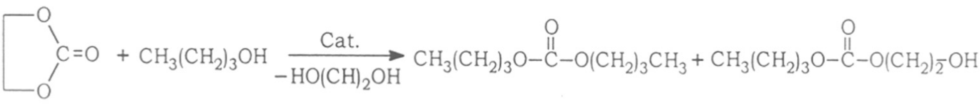
***Figure 3.10** : Calibration curve of HEEP using DPE as internal standard*

3.3 RESULTS AND DISCUSSION:

3.3.1 Reaction of ethylene carbonate with alcohols:

a) Effect of ratio of EC to *n*-butanol:

The reaction was carried out using three different ratios of EC to phenol using titanium butoxide as catalyst (**Scheme 3.1**). The results are given in **Table 3.1**.



Scheme 3.1 : Reaction of EC with n-butanol

The results showed that as the mole ratio of EC to n-butanol increased from 1:2.5 to 1:10 the yield increases from 22 to 50% respectively (**Figure 3.11**). Both DBC and hydroxyethylbutyl carbonate were formed.

Table 3.1 : Effect of ratio on conversion of di-n-butyl carbonate[a]

Time (h)	1 : 2.5[b]		1 : 5[c]		1 : 10[d]	
	%Conv. of EC	%Yield DBC	%Conv. Of EC	%Yield of DBC	%Conv. of EC	%Yield of DBC
0	0	0	0	0	0	0
1	42	12	42	21	-	-
2	42	18	48	23	50	41
3	39	21	50	26	-	-
4	43	22	51	28	62	55

a) $Ti(OBu)_4$ (2 wt%) was used as catalyst. b) Reaction temperature = 122 °C. c) Reaction temperature = 120 °C. d) Reaction temperature = 117 °C.

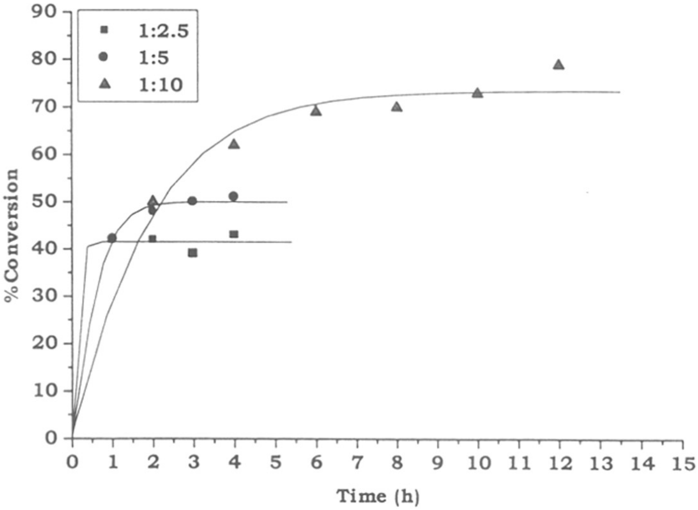


Figure 3.11 *: Effect of ratio of EC : n-butanol on conversion*

b) **Effect of different type of catalyst:**

Dialkyl carbonates are generally synthesized using a basic catalyst.[3-7] However, Tatsumi *et al.*[15] synthesized dimethyl carbonate using a titanosilicate, namely, TS-1 exchanged with potassium ion as catalyst. They showed that the titanium metal present in the zeolite is not responsible for the reaction, but the potassium ion exchanged in the catalyst is responsible for catalysing the reaction.

In the titanosilicate, TS-1 possessing the MFI structure, the Ti^{+4} ions are believed to be present in tetrahedral coordination along with Si^{+4} ions bridged by oxygen linkages.[21] Due to charge equivalence of the ions (Ti^{+4} and Si^{+4}), these molecular sieves can not theoretically possess any Brönsted acid sites. The metal ions which are exchanged in this titanosilicate is due to the defect sites during the synthesis of TS-1 the amount of which is very low. On the other hand ETS-10 is another class of titanosilicate family which has attracted attention for its unique pore structure and charge distribution.[22,23] The crystal structure of ETS-10 reveals that its framework consists of corner-sharing tetrahedrally coordinated silicon and octahedrally coordinated titanium linked through bridging oxygen. Due to octahedrally coordination of Ti^{+4}, each Ti^{+4} ions contain two negative charges in the framework of ETS-10, which is balanced by Na or K. Thus, Si/Ti ratio in ETS-10 is equivalent to the zeolite containing Si/Al =2.5, such as zeolite Y. This makes ETS-10 a potentially interesting material both for cation exchange and catalysis. Again the large cation exchange capacity imparts a basic character to the material when exchanged with alkali metal ions such as Na and K. KL is another type of alumino silicate which possesses unidimentional 12-member rings with 7.1 Å pore diameter. The Linde type L (LTL) structure is based on polyhedral cages formed by five six-membered and six four-membered rings. This arrangement results in the formation of a unidimentional channel system. In the hydrated form of zeolite L, the structure has four cation positions. Only the cations sitting within the 12-member ring channel system will readily exchange. The other three cations are located outside the main channels and occupy sites in close proximity to the framework oxygen atoms. The unit cell composition of all the zeolites and their alkali metal (wt%) content are given in **Table 3.2**.

Table 3.2 : Unit cell composition and wt% of alkali metal content in different zeolite

Sr. No.	Zeolite	Unit cell composition	Alkali metal content (wt%)
1	K-TS-1	-	1.5[a]
2	Na-ETS-10	$\underline{Na}_{29.54}K_{1.96}(Ti_{15.73}\ Si_{80.26}O_{208})65.38H_2O$	8.2
3	K-ETS-10	$Na_{11.23}\underline{K}_{20.27}(Ti_{15.73}\ Si_{80.26}O_{208})65.38H_2O$	9.2
4	Cs-ETS-10	$\underline{Cs}_{12.85}Na_{15.85}K_{2.80}(Ti_{15.73}\ Si_{80.26}O_{208})65.38H_2O$	17.6
5	KL	$\underline{K}_{8.4}[(AlO_2)_{8.4}(SiO_2)_{27.6}]22H_2O$	11.4

a) This value was reported by Tatsumi et al.[15]

In all the above zeolites the content of alkali metal is much higher compared to that of TS-1 exchanged with K ion (entry 1). Therefore, it was of interest to examine the efficiency of KL and ETS-10 exchanged with different alkali metal ions for the carbonate interchange reaction of hydroxyl containing compounds with EC and compare the results with conventional catalyst (titanium-n-butoxide).

The results of the study are summarized in **Table 3.3**. KL zeolite shows the best catalytic performance resulting in 2 h. 90% conversion to di-n-butyl carbonate in 2 h. Na and K exchanged ETS-10 gives 81% and 64% conversion after 2 h. In the case of Cs-ETS-10 the reaction was very slow and 47% conversion was obtained after 2 h. Whereas, in case of titanium butoxide ~50% conversion was obtained after 2 h (**Figure 3.12**). Again, among different type of alkali metal exchanged zeolite it was observed that the conversion was not only dependent on the wt% of the alkali metal exchanged in the zeolite but also the size of the alkali metal. For that reason, Na-ETS-10 (Na content = 8.2%) produced DBC at much faster rate compared to Cs-ETS-10 (Cs content = 17.6%)

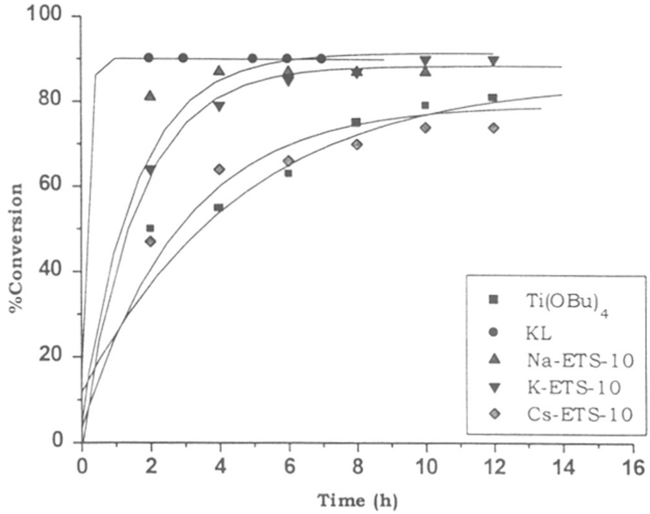


Figure 3.12 : Effect of different zeolite catalysts on conversion of EC to DBC (Table 3.3)

Table 3.3 : Synthesis of di-n-butyl carbonate using different catalyst[a]

Time	Ti (OBu)₄			KL			Na-ETS-10			K-ETS-10			Cs-ETS-10		
(h)	Conv. of EC (%)	DBC (%)	Selectivity (%)	Conv. of EC (%)	DBC (%)	Selectivity (%)	Conv. of EC (%)	DBC (%)	Selectivity (%)	Conv. of EC (%)	DBC (%)	Selectivity (%)	Conv. of EC (%)	DBC (%)	Selectivity (%)
0	0	0	0	0		0	0	0	0	0	0	0	0	0	0
2	50	41	80	90	77	91	81	70	84	64	41	72	47	13	39
3	-	-	-	90	82	92	-	-	-	-	-	-	-	-	-
4	62	55	90	-	-	-	87	81	93	79	67	86	64	32	67
5	-	-	-	90	84	92	-	-	-	-	-	-	-	-	-
6	69	63	92	-	-	-	87	83	94	85	80	92	66	48	84
7	-	-	-	90	82	92	-	-	-	-	-	-	-	-	
8	75	70	94	-	-	92	87	81	94	87	81	92	70	57	84
10	79	73	94	-	-	92	-	-		90	81	92	74	61	84
12	81	79	94	-	-		-	-		90	81	94	74	63	

a) The reaction was performed by refluxing n-butanol. n-BuOH : EC = 1 : 10. Reaction temperature = 117-118 ºC. In case of Ti(OBu)₄ 2 wt% and in other cases 1 wt% catalyst was used.

c) Effect of catalyst concentration:

The reaction was examined using three different concentration of KL zeolite (1, 2.5 and 5 wt%). The results are given in **Table 3.4**. The catalyst concentration has no effect on the conversion.

Table 3.4 : Effect of catalyst concentration on conversion of di-n-butyl carbonate[a]

Time (h)	1 wt%		2.5 wt%		5 wt%	
	%Conv. of EC	%Yield of DBC	%Conv. of EC	%Yield of DBC	%Conv. of EC	%Yield of DBC
0	0	0	0	0	0	0
2	90	77	89	77	90	80
3	90	82	-	-	-	-
4	-	-	89	80	90	80

a) nBuOH : EC = 10 : 1, KL was used as catalyst and reaction temperature =117 °C.

c) Reaction of ethylene carbonate with different alcohols:

The carbonate interchange reaction was examined using four different alcohols and using KL zeolite (1wt%) as catalyst. The results are given in **Table 3.5**. *tert*-Butanol was not converted to corresponding carbonate. The conversion of allyl alcohol was low.

Table 3.5 : Synthesis of dialkyl carbonate using KL zeolite as catalyst

Sr. No.	Alcohol used	Reaction condition	%Yield	%Selectivity
1.	Methanol	66/2	66	-
2.	*n*-butanol	120/2	84	91
3.	t-Butanol	81/2	0	0
4.	Allyl alcohol	96/2	3	15
		96/4	8	50

3.3.2 Reaction of phenol with ethylene carbonate:

a) Effect of catalysts:

The reactions were performed using different catalyst (1 wt%) keeping a fixed ratio of phenol to ethylene carbonate (PhOH : EC = 10 : 1) at 180 °C. The results are given in **Table 3.6**.

The major product in all cases, where reaction proceeded, was hydroxyethyl ether of phenol. This is not surprising in view of the fact that catalyst at Sr. No. 1, 2 and 5 are basic in nature. The Lewis acidic catalysts (Sr. No. 3 and 4) did not promote the reaction. This is, presumably, due to the high thermodynamic stability of five membered cyclic carbonate.

Table 3.6 : Reaction of EC with phenol using different catalyst

(Temp = 180 °C)

Sr. No.	Catalyst	Time	%Yield of ether	%Selectivity
1.	K_2CO_3	4	97	100
2.	TMAM	4	81	100
3.	$Ti(OPr)_4$	4	0	0
		24	0	0
4.	Tetrabutyl-1,3-diphenoxy distannoxane	4	0	0
		24	0	0
5	KL	4	19	100

b) Effect of ratio of phenol to EC:

The reaction of phenol with ethylene carbonate using distannoxane as catalyst was studied using three different ratios of phenol to EC (1:10, 1:2.5 and 2.5:1). The results are given in **Table 3.7**. However, in none of the cases, the reaction was significant.

Table 3.7 : Reaction of ethylene carbonate with phenol using different ratios of phenol to EC^a

Sr. No.	EC : PhOH	%Conversion	%Yield of ether	%Selectivity
1.	1:10	0	0	0
2.	1:2.5	1	0.8	100
3.	2.5:1	3	1.5	100

a) Tetrabutyl-1,3-diphenoxy distannoxane (1 wt% of EC) as catalyst, reaction temperature = 180 °C

3.3.3 Carbonate interchange reaction of bisphenol A with poly(1,4-butylene carbonate):

With a view to examine whether an aromatic hydroxy containing compound will undergo a carbonate interchange reaction with a fully aliphatic PC, the reaction of BPA with poly(1,4-butylene carbonate) (η_{inh} = 0.56 dL/g, in

$CHCl_3$ at 30 °C) was studied. The reaction was carried out at 180 to 270 °C for 5 h under 1 mm of Hg pressure. The product obtained was characterized by ^1H NMR spectrum (**Figure 3.13**) which showed that only 8 mol% BPA was incorporated in the polymer.

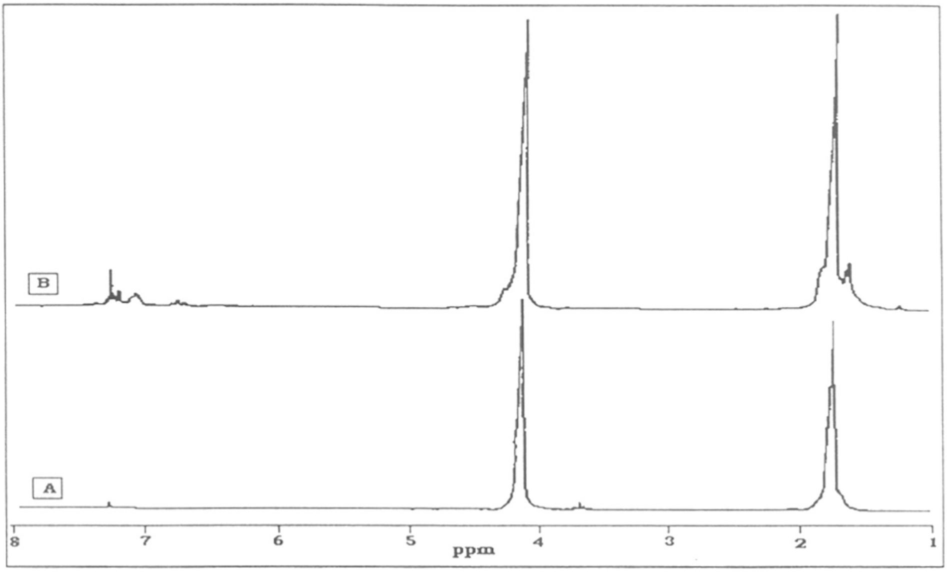


Figure 3.13 : *^1H NMR spectrum of (A) poly(1,4-butylene carbonate) and (B) after reaction with BPA*

3.3.4 Carbonate interchange reaction of bisphenol A with EC:

The reaction of ethylene carbonate with bisphenol A was examined in the presence of tetrabutyl-1,3-diphenoxy distannoxane as catalyst. The product obtained was pale yellow colored and consisted of two fractions which were separated and characterized (**Table 3.8**).

Table 3.8 : Reaction of BPA with EC

BPA : EC (mol%)	Temp (°C)/ Time (h)	Catalyst (0.1 mol% of BPA)	Yield (wt%)	Product (wt%)	
				Fraction A	Fraction B
1 : 5	200/8	Tetrabutyl-1,3-diphenoxy distannoxane	47	12	35

^1H NMR spectrum of **Fraction A** showed two triplet, at δ = 3.9 and 4.15 ppm due to the methylene protons (**Figure 3.14A**). ^{13}C NMR spectrum showed no carbonate in the region of 152-155 ppm (**Figure 3.14B**). FT-IR showed no carbonate peak but bands at 3382 and 3478 cm^{-1} due to -OH stretching vibrations (**Figure 3.15**).

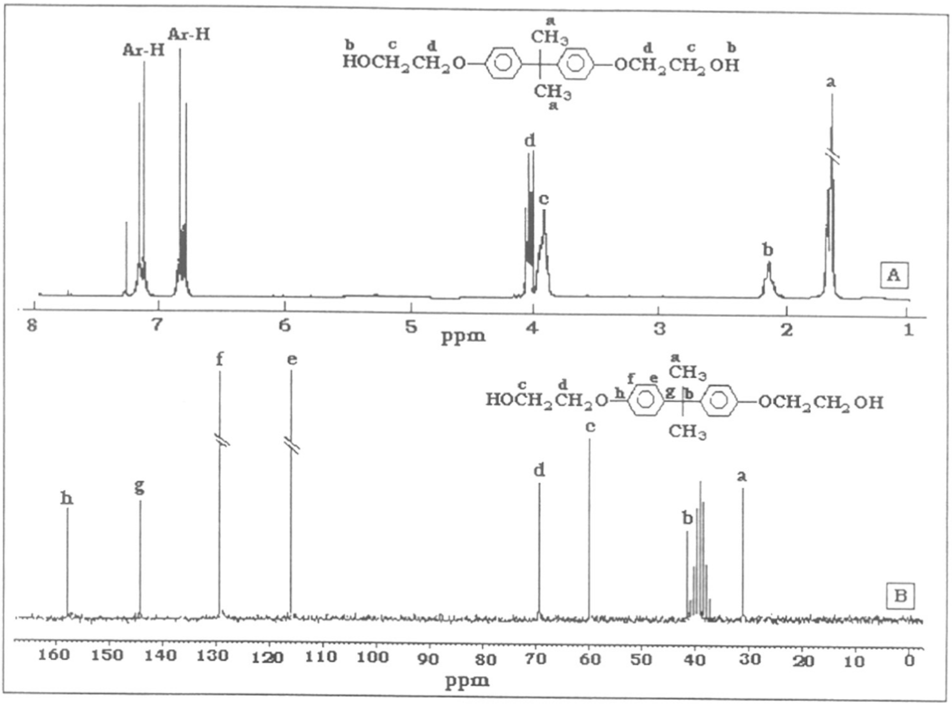


Figure 3.14** : (**A**) ^{1}H NMR and (**B**) ^{13}C NMR spectrum of* ***Fraction A

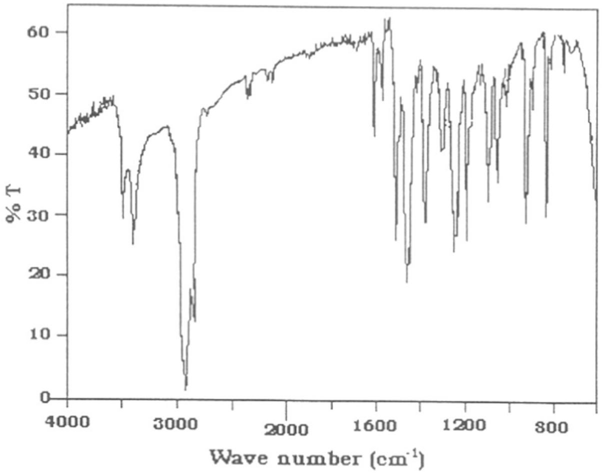


Figure 3.15** : FT-IR spectrum of* ***Fraction A

On the basis of these results **fraction A** was assigned the structure (**V**) shown in (**Scheme 3.2**). The ^{1}H NMR spectrum of **Fraction B** showed a number of signals in the range of 3.7 to 4.5 (**Figure 3.16A**), probably due to ethylene glycol and a set of other complex products. The ^{13}C NMR of **Fraction B** showed a number of signals in the range of 60 to 75 ppm and a aliphatic carbonate peak at 154.97 ppm (**Figure 3.17A**), probably due to ethylene glycol and a set of other complex products. The FT-IR spectrum of **Fraction B** showed strong absorption at 1748 cm^{-1} (corresponding to (-CH_2-O-C(=O)-O-CH_2-) aliphatic carbonate linkage) and at 1248 and 1184 cm^{-1} corresponding to C-O stretching vibration of linear carbonate and ether. The presence of carbonyl frequency at lower value indicates absence of aryl carbonate linkage (**Figure 3.18A**).

To identify the **Fraction B**, it was saponified with methanolic KOH and products were separated by column chromatography. Two products were obtained. One of them is **fraction A** which was characterized by ^{1}H NMR, ^{13}C NMR and FT-IR. The other part, which was not saponified, was characterized by ^{1}H NMR, ^{13}C NMR and FT-IR. ^{1}H NMR of which showed that the peak due to (-$CH_2\underline{C}H_2$-O-(C=O)-O$\underline{C}H_2CH_2$-) was disappeared (**Figure 3.16B**).

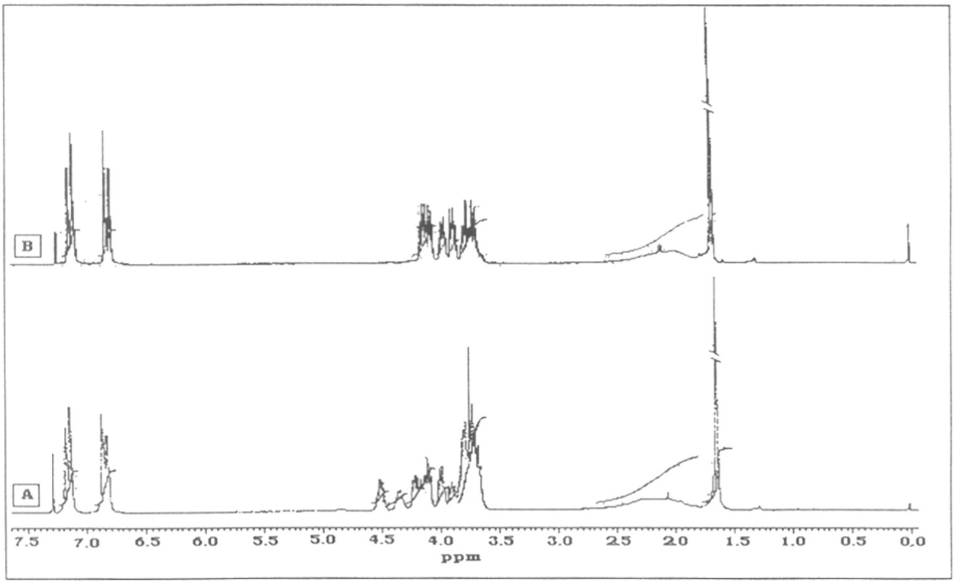


*Figure 3.16 : ^{1}H NMR of (A) **Fraction B** before saponification and (B) **Fraction B** after saponification*

^{13}C NMR of **Fraction B** after saponification showed no carbonate at 154.97 region but singnals due to aromatic carbons and aliphatic carbons are present (**Figure 3.17B**)

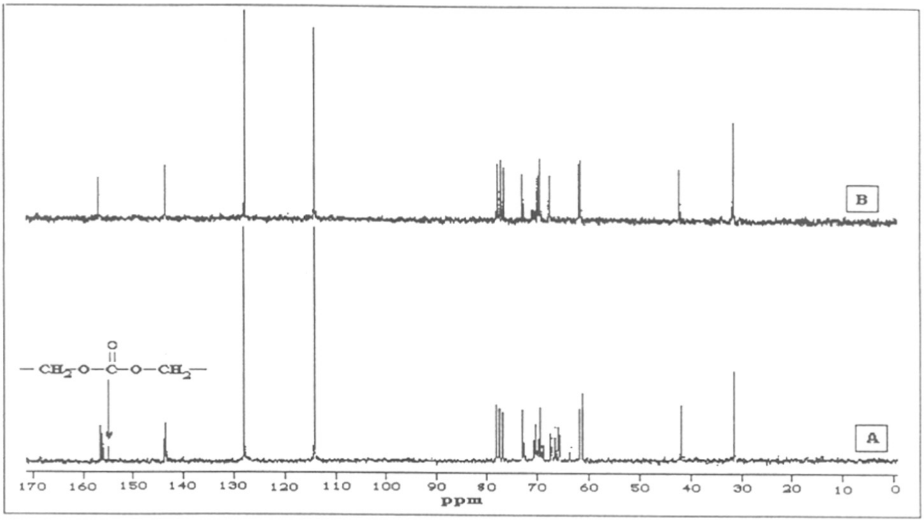


***Figure 3.17** : ^{13}C NMR of **Fraction B** (A) before saponification and (B) after saponification*

FT-IR spectra showed no carbonate linkage but showed ether peaks in the range of 1150-1250 cm^{-1} (**Figure 3.18B**).

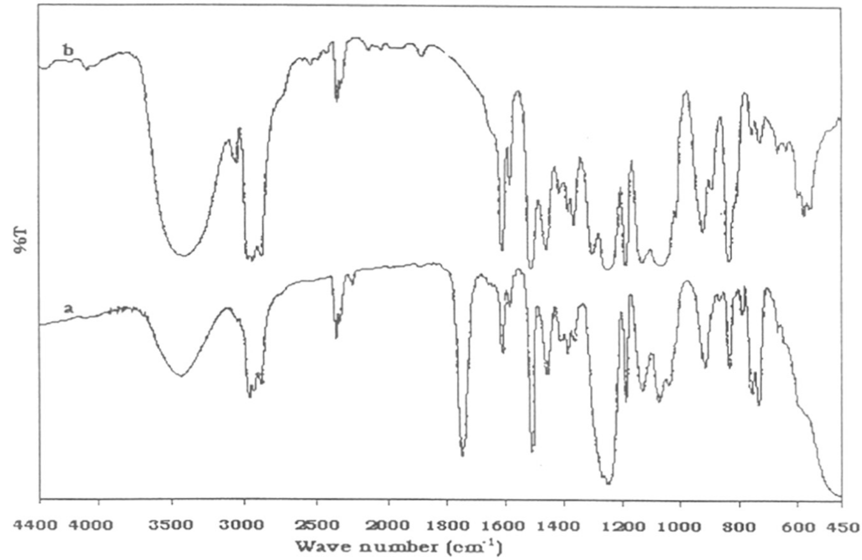
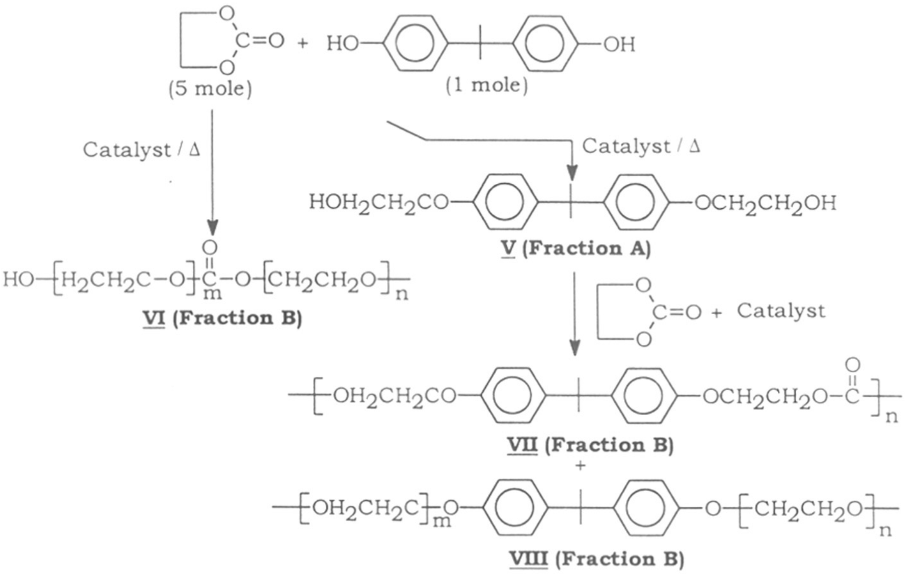


***Figure 3.18 :** FT-IR spectrum of **Fraction B** (a) before saponification and (b) after saponification*

These results are best understood in terms of the **Scheme 3.2**, wherein the product is predominantly a poly(ether-carbonate) and a polyether.



***Scheme 3.2** : Possible product of the reaction of BPA and EC*

3.4 CONCLUSIONS:

1) KL, K-ETS-10 and Na-ETS-10 are much superior catalyst compared to conventional titanium catalyst for the synthesis of dialkyl carbonate. Diphenyl carbonate can not be synthesized from ethylene carbonate using the above catalyst.

2) The reaction of phenol with ethylene carbonate produce only decarboxylated product using basic catalyst.

3) Reaction of BPA with EC leads to products, which contain both ether and carbonate groups.

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CHAPTER IV

SYNTHESIS OF HIGH MOLECULAR WEIGHT POLY(ARYL CARBONATE)S USING SOLID STATE POLYMERIZATION

4.1 INTRODUCTION

4.1.1 Linear poly(aryl carbonate) :

Poly(aryl carbonate) based on bisphenol A is an important engineering thermoplastics due to its unusual combination of properties. World's commercial production of poly(aryl carbonate)s is predominantly based on phosgene and all grades of poly(aryl carbonate)s are accessible by this route. Nevertheless, with the rising global concern over the use of hazardous chemicals like phosgene and environmentally unfriendly chlorohydrocarbon, the melt phase carbonate interchange reaction has acquired renewed interest. Substantial research has been directed towards the development of a viable nonphosgene route for the synthesis of poly(aryl carbonate). The melt phase carbonate interchange reaction[1,2] of diaryl carbonate with bisphenol A has proven to be technically feasible, but is plagued by the high cost of diphenyl carbonate. Another drawback of the melt phase carbonate interchange reaction is that the melt viscosities increase dramatically with increase in molecular weight, causing problems in agitation, heat transfer and consequent impact on product quality. For example, poly(aryl carbonate)s upto an η_{inh} of 0.2 to 0.3 dL/g can be produced in stirred tank reactor with conventional agitators. For producing materials with η_{inh} > 0.4 dL/g (suitable for injection moulding and extrusion applications) further polymerization is conducted in specialized equipments capable of providing efficient heat/mass transfer of high viscosity melts (upto 13,000 poise at 300 °C).

On the contrary, solid state polymerization (SSP) is a commonly practiced technique[3,4] to obtain high molecular weight polyesters and polyamides which are also made by melt polymerization reaction. Solid state polymerization, which proceeds at a lower rate than melt phase reaction, has the advantage that it does not require handling of melts at high temperature. The equipments required are also relatively simple. As polyesters and polyamides are inherently semicrystalline, having high melting points (e.g. 265 °C and 260 °C respectively) they are amenable to solid state polymerization at temperatures greater than 220 °C.

However, the solid state polymerization technique has not been explored in dept with predominantly amorphous polymers, such as, bisphenol A polycarbonate. For predominantly amorphous polymers, a precrystallization step is essential prior to solid state polymerization. The crystallization ensures that at temperatures where SSP rates are appreciable the polymers are non-sticking.

The crystallization of poly(aryl carbonate)s have been well studied in the literature,[5-15] and are aimed at acceleration of crystallization either by solvent/vapor treatment or addition of plasticizers. The melting temperature of poly(aryl carbonate), to a great extent, depends on the nature of crystallization. Solvent induced poly(aryl carbonate) shows a melting temperature in the range of 180 -220 ^{0}C.[5-10] Thermally crystallized poly(aryl carbonate) melts in the range of 220 to 260 ^{0}C.[11-13] Mercier *et al.*[14] developed a process called chemically induced nucleation and obtained poly(aryl carbonate) having melting temperature as high as 310 ^{0}C under these conditions crystallization times are as low as 10 minutes. Jonza and Porter[11] prepared poly(aryl carbonate) that melts at 295 ^{0}C by two step annealing of vapor induced crystalline poly(aryl carbonate) precursor for about 125 h. The imperfect crystals formed during vapor induced crystallization transforms into more perfect lamellae during the two stage annealing process.

In the recent past intense activity is visible in the patent literature on the solid state polymerization of oligopoly(aryl carbonate)s to high molecular weight poly(aryl carbonate)s.[16]

The solid state polymerization rate is dependent on several factors, such as, reaction temperature, reaction time, particle size of the prepolymer, porosity, nature and amount of initial crystallinity, catalysts employed, the molecular weight of the prepolymer and the process used to remove the reaction by-products.[4] Iyer *et al.*[17] have recently demonstrated the solid state polymerization of oligopoly(aryl carbonate)s in the temperature range of 180-250 ^{0}C. Poly(aryl carbonate)s with an inherent viscosity as high as 0.8 dL/g could be synthesized at 210 ^{0}C. On the basis of the results obtained they concluded that during solid state polymerization of poly(aryl carbonate)s chain extension is accompanied by increase in crystallinity. In a separate study[18] the development of structure and morphology of poly(aryl carbonate)s synthesized by solid state polymerization were examined by optical microscopy and wide angle X-ray diffraction. It was observed that poly(aryl carbonate)steric stabilizer obtained after SSP crystallized in orthorhombic configuration

The kinetics of the solid state polymerization reaction in linear polyesters and polyamides has been reported by several investigators.[19-30] The solid state polymerization is either diffusion or chemical reaction control depending on whether the flow rate of the gas or the temperature is rate controlling. It was found that the rate of polymerization could be described by the equation,[31] $rate = kt^n$, indicating a process that is controlled by both chemical reaction and diffusion. Chen and Grisky[25] treated this combined chemical reaction and diffusion in a more fundamental manner. They formulated equations for combined diffusion and chemical reaction in two distinct instances. After fitting the experimental data to various mechanisms, the authors reached the conclusions that chemical reaction is the rate controlling stage for powders of average diameters 0.21 cm of nylon 6.6, PET, for nylon 6.10 and for larger nylon 6.10 particles of average diameter 0.33 cm at temperatures of 160 ^{0}C or higher. Diffusion of by-products through the solid is the rate controlling stage for nylon 6.10 particles of 0.33 cm in diameter or more at temperatures 140 ^{0}C or less.

4.1.2 Branched poly(aryl carbonate):

Branched poly(aryl carbonate)s is an important material which finds wide application in areas, such as, structural sheets and blow moldings.[32] The excellent fit of branched poly(aryl carbonate) in the market place is ascribable to its outstanding property profile, especially glass like transparency, thin section toughness, high heat resistance, and shear sensitivity.[33-35]

The rheological behavior of branched polycarbonate differs from that of linear polycarbonate. The former exhibit pronounced structural viscosity. The non-Newtonian flow makes it possible to obtain polycarbonate with a sufficiently high melt viscosity for extrusion. Melt viscosity decreases to the low range required for injection molding when the shear rate is increased.

Branched poly(aryl carbonate)s are used primarily in the production of twin wall sheets, which is one of the largest growth areas for poly(aryl carbonate)s.[36]

Branched polycarbonates can be synthesized either by phosgene route[37] or melt phase reaction.[38] Typical branching agents used in interfacial phosgenation route are chloroformylisophathalic acid, trimesoyl chloride, cyauric chloride, trimethylol propane tris(chloroformate), 2,2-dihydroxy-5,5-methylene bis(benzoic acid and hydroxy compounds (containing more than 2 hydroxyl groups), whereas, those used in melt phase reaction are triphenyltrimellitate, triglycidyl isocyanurate, hydroxy compounds (containing more than 2 hydroxyl groups). Typically the level of branching is 0.1 to 2 mol%.

In this chapter following aspects of solid state polymerization of oligopoly(aryl carbonate)s are discussed (i) effect of reaction variables on the course of solid state polymerization of poly(aryl carbonate) oligomers, (ii) kinetics of solid state polymerization and (iii) synthesis of branched poly(aryl carbonate) via solid state polymerization reaction

4.2 EXPERIMENTAL

4.2.1 Materials

Bisphenol A (Aldrich Chemical, USA) was recrystallized from toluene, mp 158 °C (lit.[39] mp. 158 °C). Diphenyl carbonate (E. Merck, Bombay/India) was recrystallized from absolute ethanol, mp 78 °C (lit.[39] mp 78 °C). O-Nitrobenzoic acid was recrystallized according to the literature procedure.[39] Lexan 121 was obtained from GE plastics. THPE (Aldrich Chemical, USA) was used as received.

Tetrabutylammonium hydroxide (20% methanol/toluene) and tetramethyl ammonium hydroxide (25% methanol) (Sisco Laboratory, Bombay) were used as received. o-Nitrobenzoic acid p-nitrobenzoic acid and maleic acid were recrystallized according to the literature procedure.[39]

4.2.2 Synthesis of disodium salt of bisphenol A:[40]

Disodium salt of bisphenol A was prepared by adding 8.9 mL of methanolic sodium hydroxide solution (0.98 N) to bisphenol A (1 g, 0.0043 mol). The resulting solution was stirred for one hour, to ensure the complete formation of salt. The methanol was removed, on a rotatory evaporator at 60 °C. Last traces of moisture were removed azeotropically using dry benzene. It was recrystallised from methanol/acetone. The exact strength of disodium salt of bisphenol A solution was estimated by potentiometric titration with sulphuric acid. Yield : 1.06 g (89%).

4.2.3 Preparation of tetramethyl ammonium maleate:

Tetramethyl ammonium maleate was prepared in the same way as described in **Chapter III, Section 3.2.2b**.

Yield : 6.9 g (87%) mp. 188-189 °C

^{1}H NMR (CDCl$_3$, δ):

3.05 [N(CH$_3$)$_4$, 12H, s], 6.1 (-C=CH-, 2H, s)

^{13}C NMR (CDCl$_3$, ppm):

55.71 [N(CH$_3$)$_4$], 136.96 (-C=CH-), 169.07 [-O-C(=O)-O-]

Other tetraalkylammonium hydrogen-bis-carboxylates (**2 and 3**) were prepared by the similar procedure and characterized (**Table 4.1**).

Table 4.1 : Physical characteristics of different bioxyanions.

Sr. No.	Catalyst	Yield %	mp (°C)	Elemental analysis			
					C	H	O
1.	Tetrabutyl ammonium hydrogen-bis-o-nitro-benzoate	89	112-113	Calcd.	62.60	7.83	7.30
				Found.	62.13	8.07	7.26
2.	Tetrabutyl ammonium hydrogen-bis-p-nitro-benzoate	92	109-110	Calcd.	62.60	7.83	7.30
				Found.	62.68	8.82	7.09

4.2.4 Synthesis of poly(aryl carbonate) oligomer:

The poly(aryl carbonate)s prepolymer required for solid state polymerization was synthesized on a 200 g scale in a 2L stainless steel autoclave, (Karl Kurt Jucheim, Germany). Bisphenol A (200 g, 0.88 mol), diphenyl carbonate (197 g, 0.92 mol) and tetrabutyl-ammonium hydrogen-bis-o-nitrobenzoate (1.03×10^{-5} mol) were charged into the reactor under N$_2$ atmosphere. The reaction mixture was then heated to 230 °C in 20 min and maintained at that temperature for 90 min. Thereafter, the temperature was increased to 300 °C in 180 min while reducing the pressure from 760 to 1 mm Hg and maintained under this condition for an additional 120 min. During this period the by-product phenol was continuously distilled and collected. The polymer thus formed was dissolved in 1 L chloroform and the solution poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 °C for 24 h. Yield : 220 g (98%) and η_{inh} = 0.42 dL/g in CHCl$_3$ at 30 °C.

IR (Nujol, cm^{-1}):

1780 (C=O), 1220 (C-O).

^1H NMR ($CDCl_3$, δ):

1.7($C(CH_3)_2$, 6H, s), 7.2 (Ar-H, dd, 4H), 7.4 (Ar-H, dd, 4H).

Poly(aryl carbonate)s having an inherent viscosity of 0.44, 0.33 and 0.17 dL/g were also synthesized by the same procedure by suitable variation of the reaction conditions. The characteristics of the poly(aryl carbonate)s synthesized are given in **Table 4.2.**

Table 4.2 : Properties of different poly(aryl carbonate)s used for solid state polymerization reaction.

Sr. No.	η_{inh} (dL/g) (In $CHCl_3$)	M_n (By VPO)	M_w/M_n (By GPC)	T_g ^{a} (^{0}C) (By DSC)	OH number (By UV)
1	0.44	5096	2.89	137	19.5
2	0.42	5504	2.25	142	7.3
3	0.42	6088	2.52	135	1.4
4	0.33	4775	2.36	144	19.5
5	0.17	2372	2.87	118	18.5

a) 10 ^{0}C/min in N_2

4.2.5 Hydroxyl number determination:

Conventional method of determining the phenolic hydroxyl group by acetylation process cannot be applied to poly(aryl carbonate)s as bases like pyridine employed in acetylation hydrolyze poly(aryl carbonate) at refluxing temperatures of pyridine-acetic anhydride solution. Terminal phenolic hydroxyl groups in bisphenol A polycarbonates are determined colourimetrically[41] by the formation of red orange color complex with $TiCl_4$. However, the method is tedious and involves use of highly moisture sensitive $TiCl_4$. In addition, the manipulations during the determination become difficult owing to stringent purity of chemicals required. We, therefore, estimated the hydroxyl concentration in the polymer by ultraviolet spectroscopy. **Figure 4.1** shows the UV spectrum of bisphenol A polycarbonate in THF. The hydroxyl number was determined using a Hitachi model 220 UV/vis. spectrophotometer and THF as solvent, using the reported[42] ε for bisphenol A and the polymer at 287 nm. The following expression was used.

$$\frac{\text{Hydroxyl Number}}{\text{(mg of KOH required /g sample)}} = \frac{\varepsilon_{BP\text{-}A} \times A_{sample} \times C_{BP\text{-}A} \times 2 \times 56.1 \times 103}{\varepsilon_{polymer} \times A_{BP\text{-}A} \times C_{sample}}$$

Where,

$\varepsilon_{BP\text{-}A}$ = extinction coefficient of bisphenol A (3750 [mole/L x cm]$^{-1}$)

$\varepsilon_{polymer}$ = extinction coefficient of oligomer with two phenolic hydroxyl terminal groups (3450 [mole/L x cm]$^{-1}$)

$A_{BP\text{-}A}$ = absorbance of bisphenol A

A_{sample} = absorbance of sample

$C_{BP\text{-}A}$ = concentration of bisphenol A in mol/L

C_{sample} = concentration of sample in g/L

Hydroxyl number determinations of the polymer were carried out in the absorbance range 0.2-0.8 and accordingly concentrations were suitably prepared.

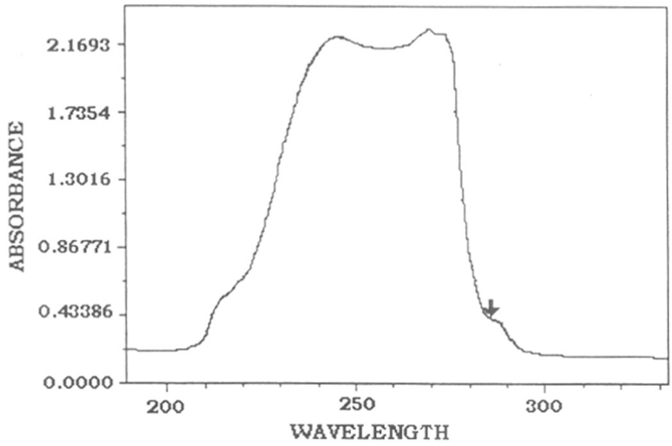


Figure 4.1: *UV spectrum of bisphenol A polycarbonate in THF.*

4.2.6 Solid state polymerization of poly(aryl carbonate):

4.2.6a Crystallization of the prepolymer:

i) Solvent induced crystallization:

About 10 g of the polymer was dissolved in 50 mL chloroform. A methanolic solution (1 mL) of disodium salt of bisphenol A (25 ppm) was added and the mixture stirred for 1 h. Chloroform was evaporated using a rotatory evaporator and the polymer was dried under vacuum at 60 ^{0}C for 4 h. The recovered polymer was then pulverized and particles with a size range of 250–520 μ were used in subsequent reactions.

Approximately 2% crystallinity (in case of totally end capped polymer) was achieved by the rapid evaporation of dichloromethane after dissolving the polymer in dichloromethane.

No crystallinity was achieved by dissolving the polymer in chloroform and precipitated from excess methanol and dried under vacuum at 80 ^{0}C for 24 h.

ii) Nonsolvent induced crystallization:

About 10 g of the prepolymer was taken on a 100 mL round bottom flask to which a methanolic solution (1 mL) of disodium salt of bisphenol A (25 ppm) was added. Acetone (50 mL) was added to the slurry and the mixture was refluxed at 60 ^{0}C for 4 h. Acetone was evaporated using a rotatory evaporator and the polymer was dried under vacuum at 60 ^{0}C for 4 h. The prepolymer was then pulverized and particles with a range of 250-520 μ were used for reaction. Similar method of crystallization was used with methyl ethyl ketone, ethyl acetate and toluene.

iii) Thermal treatment:

About 20 g prepolymer was dissolved in 100 mL chloroform, precipitated from petroleum ether and the polymer was dried under vacuum for 4 h. About 10 g of the precipitated polymer was taken in a 100 mL round bottom flask to which methanolic solution of disodium salt of bisphenol A (25 ppm) along with 50 mL methanol was added. The slurry was well agitated for 15 min. Thereafter, methanol was removed using a rotatory evaporator, dried under vacuum at 60 ^{0}C for 4 h. The crystallinity of the prepolymer as calculated from DSC was 6%. The polymer was heated at 180 ^{0}C for 10 h, upon which the crystallinity increased to 13%. The prepolymer was then pulverized and particles in the size range of 250-520 μ were used for subsequent reaction.

4.2.6b Glass assembly for solid state polymerization:

Solid state polymerizations were carried out using the glass reactor as shown in **Figure 4.2**. Where inert gas is passed through the direction a to b and through the sintered glass above which prepolymer will be taken. The gas will pass through the polymer to keep the prepolymer in fluidized condition. Finally, the gas will pass through the adapter of the reactor where cotton plug was placed so the tiny polymer particles can not go out from the reactor.

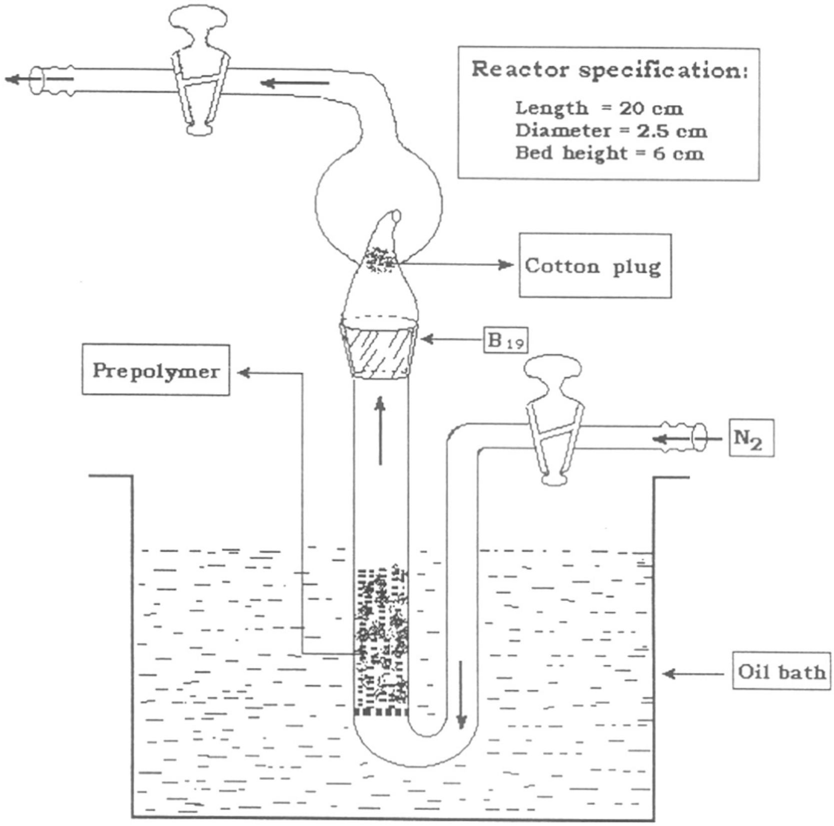


Figure 4.2 *: Glass assembly for solid state polymerization*

4.2.6c Solid state polymerization reaction:

The solid state polymerization reaction was performed in a glass reactor immersed in a thermostated oil bath. The powder was fluidized using nitrogen as a fluidizing medium. Preolymer (3 g) was placed in the reactor and was initially conditioned by slowly heating the reactor from ambient temperature to 180 °C over a period of 1 h. The polymer was held at 180 °C for 1 h and then at 210 °C for 4 h. During this period it was ensured that the powder was in a fluidized state. Thereafter, the temperature was increased to 230 °C. At no point in time was agglomeration or powder sticking observed. Samples were periodically withdrawn and the inherent viscosity, OH number and %crystallinity were determined. In case of samples crystallized thermally and from non-solvent, the prepolymer was heated to 220 ^{0}C directly without prior conditioning and maintained for 10 h.

4.2.7 Solid state polymerization:

4.2.7a Preparation of the sample:

poly(aryl carbonate) (5 g, η_{inh} = 0.17 dL/g) was taken in a 100 mL round bottom flask and dissolved in 50 mL $CHCl_3$. To this solution, a methanolic solution of tetramethyl ammonium maleate (25 ppm) and 0.5-1.5 wt% of THPE were added and the mixture stirred for 1 h. Chloroform was evaporated on a rotatory evaporator and the polymer dried under vacuum at 60 ^{0}C for 4 h. The prepolymer was then pulverized and particles in the range of 250 μ to 520 μ were used for the reaction.

4.2.7b Solid state polymerization:

The solid state polymerization reaction was performed as described before. Polymer sample (3 g) was placed in the reactor and was initially conditioned by slowly heating from room temperature to 180 ^{0}C over a period of 1 h and retaining the sample at 180 ^{0}C for 1 h. The solid state polymerization reaction was performed at 220 ^{0}C for 4 h and at 230 ^{0}C for 4 h. At no point of time agglomeration or powder sticking was observed

4.2.8 Measurements:

Melting points were measured with a Thermonix melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer model 16PC FT-IR spectrometer. ^{1}H NMR spectra were recorded Bruker WH-90FT-NMR and Bruker AC-200 NMR spectrometer. The inherent viscosity of the bisphenol A polycarbonate was measured in chloroform at 30 ^{0}C using a suspended Ubbelohde viscometer. Crystalline poly(aryl carbonate)s which did not dissolve in chloroform even under reflux, could be dissolved in 1:1 (v/v) trifluoroacetic acid/dichloromethane mixture and precipitated into methanol. This causes the destruction of crystallinity. After filtration and drying, 0.5% polymer solution in chloroform was used for viscosity determination. The following relation[43] was used.

$$[\eta] = K \times \bar{M}_n^a \quad \text{where, } K = 12 \times 10^{-5} \text{ dL/g, } a = 0.82$$

The number average molecular weight of the prepolymer was determined using vapor pressure osmometry. Determinations were carried out in Knauer Model II instrument using universal probe and benzil as a standard. Thermal analysis of polymers (T_g and T_m) were measured by differential scanning calorimeter using a Perkin-Elmer thermal analyzer (DSC-7) in a N_2 atmosphere at a heating rate of 10 ^{0}C/min. Powdered X-ray diffraction (XRD) was recorded using Rigaku (Model D/Max IIT VC, Japan), Ni-filtered CuK_α radiation = 1.5404. Alternatively, Phillips diffractometer (PW 1730) was also used. Gel permeation chromatography (GPC)) was performed on Waters GPC) 150C using column set of 10^5,10^4, 10^3, 500 and 100 μ-styragel, at a flow rate of 2 mL/min in THF at 40 ^{0}C and RI detector. Monodisperse polystyrene was used as calibration standard.

4.2.8a Determination of crystallinity:

(1) The percent crystallinity was calculated from differential scanning calorimeter (DSC) from the heat of melting ΔHm; and taking the ΔHm_o of the pure crystal as 26.2 cal/g.[44] The crystallinity (C_i) was determined from the X-ray diffractogram as follows. The area under the main crystalline peaks (Φ_c) and area of the amorphous halo (Φ_a) were measured. These were determined after constructing the curves and reducing the background as shown in **Figure 4.3.** Crystallinity was calculated from the equation (assuming k =1) as $C_i = \Phi_c/(\Phi_a + \Phi_c)$.

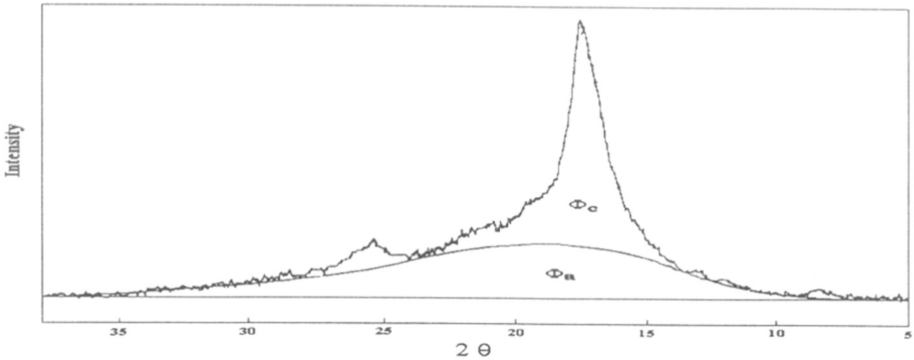


***Figure 4.3** : X-ray diffraction of bispnenol A polycarbonate with amorphous region (ϕ_a) and crystalline region (ϕ_c).*

4.2.8b Characterization of the branched polymer:

The polymer obtained from solid state polymerization reaction was dissolved in chloroform and precipitated from methanol to remove any unreacted THPE. About 0.1 g of the polymer was hydrolyzed with 5 mL of 18 wt% methanolic KOH solution. The wt% of branching agent incorporated was determined by HPLC after degradative hydrolysis of the polymer using a ZORBAX SBC_8 RP column, 2,6-dimethyl naphthalene (DMN) as internal standard and acetonitrile/water solvent, using 30% acetonitrile and 70% water followed by 100% acetonitrile and 0% water to 20% acetonitrile and 80% water in a total time of 45 min. The detector used was a UV multiwavelength detector (Waters 490E) which is set at 280 nm and changed to 264 nm after an elapsed time of 17 min.

Calibration curve of THPE using 2,6-dimethylnaphthalene (DMN) as internal standard:

i) Preparation of sample solution for HPLC :

a) A stock solution of DMN was prepared by dissolving 20.3 mg DMN in 25 mL acetonitrile. From that stock solution 0.5 mL was taken for the preparation of the solution.

b) A stock solution of THPE was prepared by dissolving 50 mg polymer in 25 mL acetonitrile. From this stock solution 0.5, 2.5, 5, 7.5 and 10 mL solution was taken along with 0.5 mL DMN solution in a 10 mL volumetric flask and the volume was made upto the mark (except E)

ii) HPLC analysis for calibration curve:

The calibration curve was drawn by using the value of area ratio and mole ratio from **Table 4.3**

Table 4.3 : Area ratio of different samples obtained from HPLC data.

Sample No.	THPEx10^4 (g)	DMN soln (mL)	Area Ratio (THPE : DMN)	Mole ratio (THPE : DMN)	Slope
A	1	0.5	0.148	0.13	0.81
B	5	0.5	0.773	0.63	
C	10	0.5	1.542	1.26	
D	15	0.5	2.212	1.88	
E	20	0.5	3.194	2.51	

The area ratio was plotted against the mole ratio, which is shown in the **Figure 4.4**

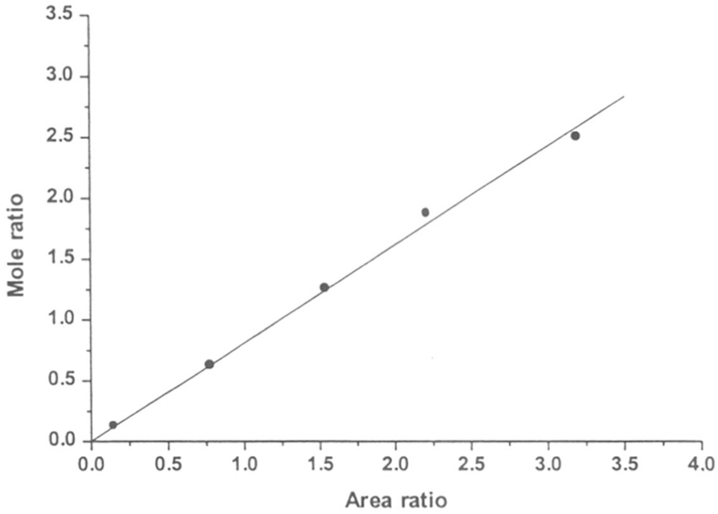


***Figure 4.4**: Calibration curve of THPE using DMN as internal standard.*

Slope of the above plot gives the value of response factor. Slope = 0.81. Therefore, response factor (RF) = 0.81

4.3 RESULTS AND DISCUSSION:

4.3.1 Linear Poly(aryl carbonate) :

The polymers used in the study were prepared by carbonate interchange reaction of bisphenol A with diphenyl carbonate. The properties of the poly(aryl carbonate)s are given in the **Table 4.2**. The prepolymers showed a sharp T_g and no melting endotherms (**Figure 4.5**).

4.3.1a Crystallization of the prepolymer:

In semicrystalline polymers, such as, poly(ethylene terephthalate), nylon 6 etc. which show a well defined crystalline melting temperature, the solid state polymerization is carried out at about 20 ^{0}C below T_m so that the polymer does not fuse or melt during the course of the reaction. Till recently, predominantly amorphous polymers were not considered as suitable candidates for solid state polymerization because they soften and stick when heated above their T_g. In view of this, bisphenol A polycarbonate with a T_g at 149 °C did not attract attention as a potential candidate for solid state polymerization. However, the sticking point of a polymer, which is slightly above the second order transition temperature[45] can be raised close to the melting point, by means of crystallization. The ability of polymers to crystallize depends mainly on chain flexibility. Crystallization in poly(aryl carbonate)s can be induced[46-49] by dissolution in a solvent or exposing the polymer to vapor of a solvent or nonsolvent or by thermal anealing in presence of a nucleating agent or plasticizer. The recognition of the fact that inducing crystallinity in poly(aryl carbonate) may enable it to be heated to temperatures as high as 220-230 °C without sticking or agglomeration, has led to the successful exploitation of the solid state polymerization technique for synthesizing high molecular weight poly(aryl carbonate)s.[17]

The comparative thermal properties of the polymer (η_{inh} = 0.42 dL/g, OH No. 7.3) subsequent to crystallization by different methods is shown in **Figure4.3, Table 4.4** and **Figure 4.6**. The results indicate that the added catalyst has no specific role in determining the extent of crystallization. From the DSC curve it was also observed that the T_m of all cases are not the same (**Figure 4.6**). The difference in T_m may be due to the following reason:

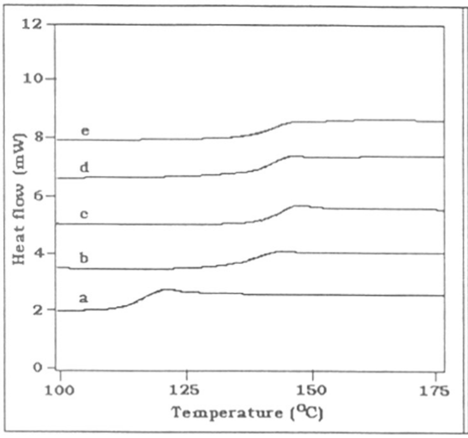
i) When polycarbonate is refluxed in a solvent the T_g of the polymer decreases depending on the reflux temperature and the solubility parameters of the solvent (δ_s).[8] The value of T_m of the polymer after crystallization depends on the difference between T_c and T_g. Higher the difference, higher will be the T_m and for this reason the T_m of polycarbonate crystallized toluene is comparatively higher.

ii) Above a certain crystallization temperature, (which is different for each solvent) the diffusion of the solvent into the polymer takes place with the formation of distinct penetration front. There is evidence to indicate a distinct separation of the diffusion and crystallization front. This difference is due to the ability of different solvents to initiate the crystallization.[10] This also causes a change in T_m depending on the nature of the solvent.

Table 4.4 Crystallization of the prepolymer using different techniques

Entry No.	Process of crystallization	Reflux/heating Time (h)	Tm (^{0}C) (DSC)	%Crystallinity (DSC)
Solvent treatment				
^{a}1	Chloroform	d	236	22
^{b}2	,,	d	238	24
^{c}3	,,	d	237	22
Nonsolvent treatment				
^{a}4	Methyl ethyl ketone	4.5	223	26
^{a}5	Acetone	4.0	218	24
^{a}6	Ethyl acetate	4.0	221	24
^{a}7	Toluene	4.5	242	31
Thermal treatment				
^{a}8	Prepolymer heated at 180 ^{0}C	20	226	10

a) Tetramethyl ammonium maleate (25 ppm) as catalyst
b) Disodium salt of BP-A (25 ppm) as catalyst.
c) No catalyst
d) Dissolve in $CHCl_3$ followed by solvent remove in rotavapor



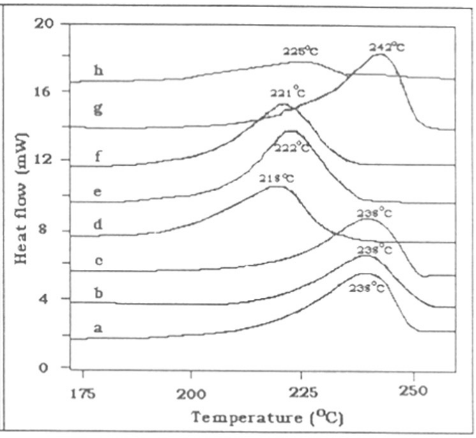


***Figure 4.5** : T_g of poly(aryl carbonate)s (a) η_{inh} = 0.17 dL/g (b) η_{inh} = 0.33 dL/g (c) η_{inh} = 0.42 dL/g (d) Lexan 121R, η_{inh} = 0.42 dL/g and (e) η_{inh} = 0.44 dL/g prepolymer.*

***Figure 4.6** : T_m of poly(aryl carbonate) polymer (η_{inh} = 0.42 dL/g) crystallized from (a) $CHCl_3$, without catalyst, (b) $CHCl_3$, with disodium salt of BPA (25 ppm), (c) $CHCl_3$, with TMAM (25 ppm), (d) Acetone with TMAM (25 ppm), (e) methyl ethyl ketone with TMAM (25 ppm), (f) ethyl acetate with TMAM (25 ppm) (g) Toluene with TMAM (25 ppm) and (h) 180 °C/20 h with TMAM (25 ppm).*

4.3.1b. Effect of solid state polymerization of poly(aryl carbonate)s on the crystallization and melting behavior:

Poly(aryl carbonate)s undergo crystallization concomitant and chain growth during solid state polymerization. **Figure 4.7** shows the variation of crystallinity and melting temperature with SSP time and the inset figure gives the dependence of intrinsic viscosity. All these three parameters show similar behavior, namely, they increase with increase in SSP time. This indicates that solid state polymerization and crystallization proceed simultaneously in the sample. It is also observed that the latter stages of SSP, the crystallization slows down. There no further increase in crystallization beyond 10 h annealing time whereas, η_{inh} shows a linear increase with SSP time.

The crystallization data of the end capped samples having different initial crystallinites are given in **Table 4.4** (entry no 1-3). The samples having lower initial crystallinity shows an increase in crystallinity and reach a value around 20% The sample having an initial crystallinity of 24% does not show an increase in crystallinity but the melting temperature shows a marginal increase from

235 ^{0}C to 243 ^{0}C. The inherent viscosity of the sample remains constant irrespective of the initial crystallinity, indicating the absence of solid state polymerization during crystallization of these samples. The melting temperature also does not show any significant variation.

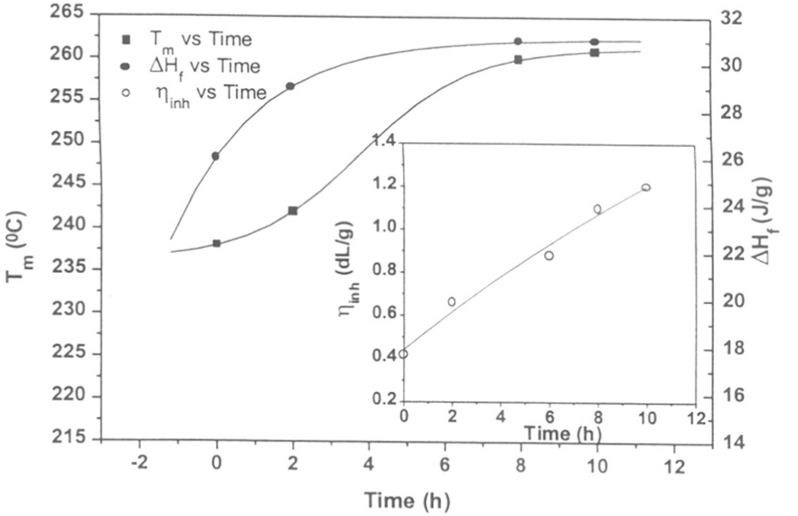


Figure 4.7 : *Variation of melting temperature (■), crystallinity (●) and inherent viscosity (○) with time.*

The results of the samples that have been crystallized and have undergone solid state polymerization simultaneously are presented in **Table 4.5** (entry No. 4-6). When the results in **Table 4.5** (1-3) are compared with (4-6), the most notable differences are the values of inherent viscosity and melting temperature. The η_{inh} increases from 0.42 to 1.06 dL/g in case of sample which show both polymerization and crystallization. This shows that samples have undergone solid state polymerization during crystallization. The melting temperature also shows a significant increase when compared to the values in **Table 4.6**. The melting temperature increases from 236 ^{0}C to 268 ^{0}C for samples that have undergone both crystallization and crystallization. The crystallinity is also higher when compared to the samples that have undergone only crystallization. However, compared to the increase in η_{inh} and T_m, the increase in crystallinity is lower.

In all the above experiments 25 ppm disodium salt of BPA was used as catalyst. Few crystallization experiments were also performed in DSC under identical conditions without the added catalyst to examine the effect, if any, of catalyst on crystallization. As seen from **Table 4.6** the catalyst does not seem to influence the crystallization of poly(aryl carbonate)s. The %crystallinity and T_m are comparable to the samples with added catalyst.

Table 4.5 : Study of crystallization with and without SSP

(Disodium salt of bisphenol A (25 ppm) was used as catalyst)

Sample	Reaction No.	Temp/Time (°C / h)	T_m, (°C) (DSC)	Crystallinity (%) (DSC)	η_{inh} (dL/g)
PC (end capped)	1	Initial (Dissolve in $CHCl_3$ and ppted from methanol)	-	0	0.36
		180/4+200/8	219,229,237	24	0.36
	2	Initial (Dissolve in CH_2Cl_2 and rapid evaporation)	223	2	0.36
		180/4+200/8	233	15	0.35
	3	Initial (Dissolve in $CHCl_3$ and slow evaporation)	235	24	0.36
		180/1+230/10	243	25	0.35
		250/0.5 170/4+200/8	239	17	-
		300/0.5 170/4+200/8	-	0	-
PC (OH No. = 7.3)	4	Initial (Dissolve in $CHCl_3$ and ppted from methanol)	-	0	0.42
		180/4+200/8	237	15	0.55
	5	Initial (Dissolve in $CHCl_3$ and ppted from petroleum ether)	217	6	0.42
		180/4+200/8	243	18	0.82
	6	Initial (Dissolve in $CHCl_3$ and slow evaporation)	236	22	0.42
		180/1+230/10	268	30	1.06

Table 4.6 : Study of crystallization with and without SSP

(No catalyst)

Prepolymer	Temp/Time (°C / h)	T_m (°C) (DSC)	Crystallinity (%) (DSC)
PC (Hydroxyl No. = 7.3)	Initial	-	0
	180/1+200/8	236	20
PC (end capped)	Initial	-	0
	180/4 + 200/8	236	25

Two stage temperature program was used in the above crystallization studies on poly(aryl carbonate). The two stage crystallization process is necessitated because the rate of solid state polymerization decreases if the particle fuse together and fusing of particles is avoided by increasing the crystallinity by annealing the sample at 180 °C, which is very close to the T_c of poly(aryl carbonate)s (190 °C). So the samples can be crystallized at this temperature. This allows crystal imperfections to heal and more uniform and perfect crystallites to form. In the second stage, the temperature is raised to 210 °C or 230 °C where the crystallization rate is lower than at 180 °C but the polymerization rate substantially higher due to the higher mobility of the amorphous phase, since the T between reaction temperature and T_m is of the order of 6-8 °C.

Two aspects are apparent from the above results on thermal crystallization of poly(aryl carbonate)s i) solvent treatment has a significant effect on the rate of thermal crystallization. All the samples having low crystallinity rapidly crystallize within 10 h at an annealing temperature of 200 °C. This rate is very fast compared to the half time of thermal crystallization of poly(aryl carbonate), which is the order of several days, ii) the influence of solid state polymerization on the crystallization behavior. The samples after SSP show consistently higher T_m compared to the samples in which there is only crystallization and no polymerization.

The time scales used in the above experiments are very short to induce thermal crystallization, since the half time for thermal crystallization of poly (aryl carbonate) is very long. The rapid crystallization that has been observed in the present case may be due to the effect of solvent present in the polymer, which cannot be removed completely by drying. This trace solvent either functions as a plasticizer or maintains the polymer chain in an extended conformation. Upon heating at 180 °C, the last traces of solvents are lost from the polymer, at which time the polymer undergoes rapid crystallization. The crystallinity levels achieved is around 20 to 30% with a T_m of 230 to 240 °C which is typical for solvent induced crystallization. The sample which having been fully crystallized by solvent do not undergo further crystallization on further annealing at 230 °C for 10 h indicating the low levels of structural reorganizations that can occur in these temperatures. These results indicate that the time-temperature program employed in the above experiments just allow the samples to complete the solvent induced crystallization.

The effect of solid state polymerization is to increase the inherent viscosity and the T_m. They increase with increase in polymerization time as well as temperature. The η_{inh} increases from 0.42 to 1.06 dL/g and the T_m increases to 268 °C. A notable feature of the SSP is that the high T_m is achieved under 10 h. The WAXS studies on few selected samples of poly(aryl carbonate)s are shown in **Figure 4.8**.

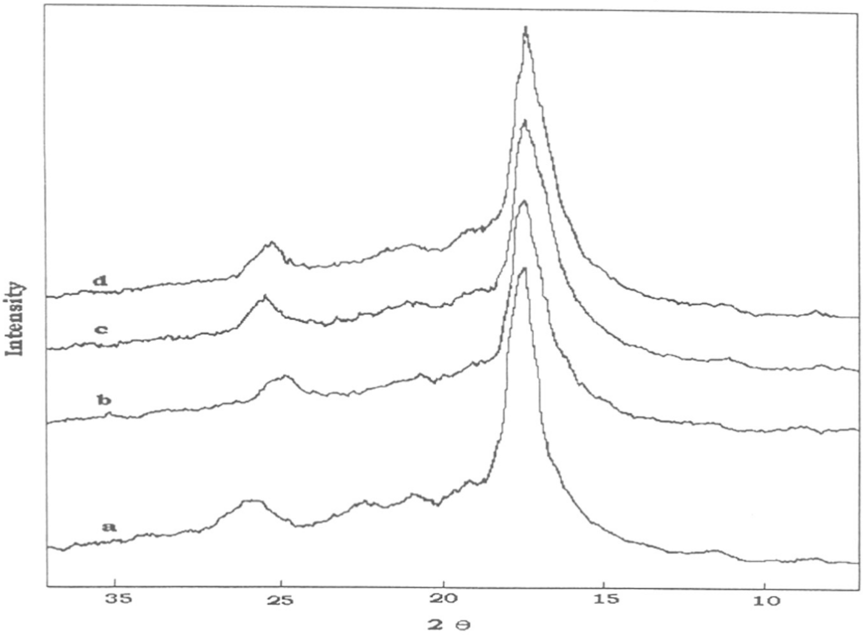


Figure 4.8 : *X-ray diffraction of (a) initial prepolymer (η_{inh} = 0.42 dL/g and OH No. = 7.3) (b) after 230 °C / 2 h (c) after 230 °C / 6 h and (d) after 230 °C / 10 h*

There is no major change in the diffraction patterns indicating there is no improvement in the crystal perfection during the combined crystallization and solid state polymerization process. The DSC curves on few selected samples of poly(aryl carbonate)s are shown in **Figure 4.9**. Which showed that the pattern of DSC curve of initial prepolymer was broad and after progress of the reaction which become sharped with increase in T_m from 238 ^{0}C to 261 ^{0}C.

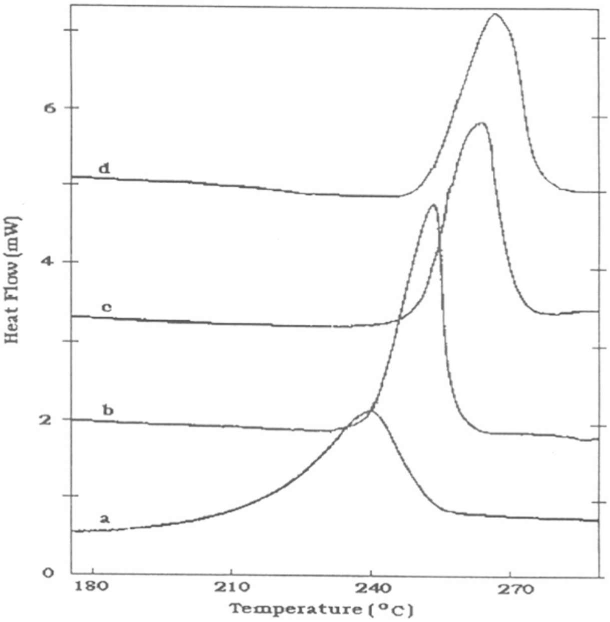


Figure 4.9 : *DSC curve of (a) initial prepolymer (η_{inh} = 0.42 dL/g and OH No. = 7.3) (b) after 230 ^{0}C / 2 h (c) after 230 ^{0}C / 6 h and (d) after 230 ^{0}C / 10 h*

The increase in the T_m is indicative of substantial amount of structural reorganization of the crystallites, during the crystallization, leading to an increase in the lamellar thickness. As reflected in the crystallinity values the rearrangement does not involve much increase in crystallinity. It is interesting to note that in the case of vapor induced crystallized poly(aryl carbonate)[15] required two stage annealing at 180 ^{0}C and 230 ^{0}C for more than 65 h to obtain a melting point above 265 ^{0}C. So it appears the main effect of solid state polymerization is to enhance the structural reorganization to give poly(aryl carbonate) with higher melting temperature which otherwise needs much longer annealing time.[15] The present data shows that solid state polymerization can enhances the crystallization process and can be used to obtain high melting crystalline poly(aryl carbonate) in a short time.

4.3.1c Solid state polymerization reaction: Effect of different parameters.

Using the polymer crystallized as above, the influence of various parameters on the solid state polymerization was studied.

a) Reactor:

The type of reactor used greatly influences the rate of solid state polymerization. **Figure 4.10** shows that solid state polymerization using a fluidized bed reactor gave better results compared to a fixed bed reactor.

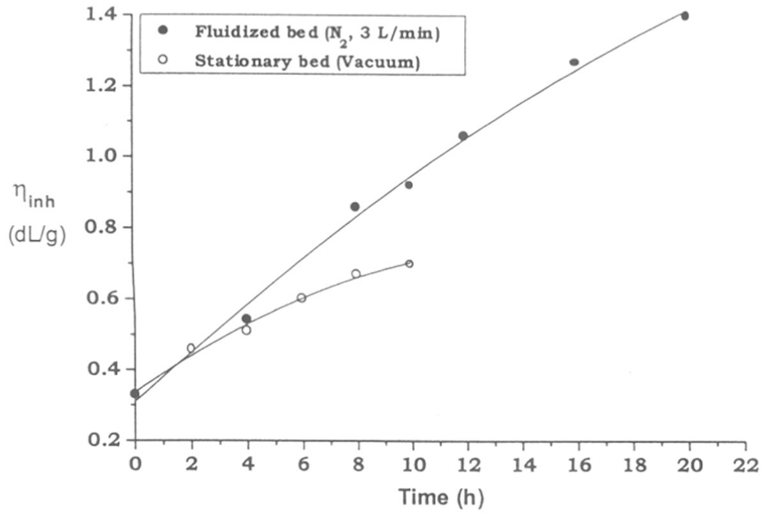


Figure 4.10 *: Effect of reactor on solid state polymerization [in fluidized bed* N_2 *is the carrier gas (flow rate = 3 L/min), and in stationary bed vacuum was used (0.1 mm of Hg). Reaction temperature = 230 °C, catalyst = disodium salt of BPA (25 ppm)]*

In a fluidized bed reactor, the heat is evenly distributed throughout the polymer particles whereas in fixed bed the heat distribution is uneven, therefore, the polymer particles which are nearest to the glass wall are at a higher temperature compared to the polymer particles at the middle of the reactor. Again as the polymer particles are static, there is insufficient driving force for diffusion of the by-product phenol from the reaction mixture compared to the fluidized bed reactor. For these reasons, better results were obtained in a fluidized bed reactor.

b) Flow rate:

Solid state polymerization is greatly influenced by the flow rate of the carrier gas. Li-Chen[50] has reported the effect of gas flow rate on solid state polymerization of PET in a gas chromatograph column. The authors reported that the polymerization rate increased with flow rate and reached an optimum value at 500 mL/min. The SSP of the prepolymer (η_{inh} = 0.33 dL/g) was carried out at three different flow rate 3, 2, and 1 L/min and keeping all other parameters constant. The rate of solid state polymerization was found to be higher when the flow rate was higher (**Table 4.7**) (**Figure 4.11**).

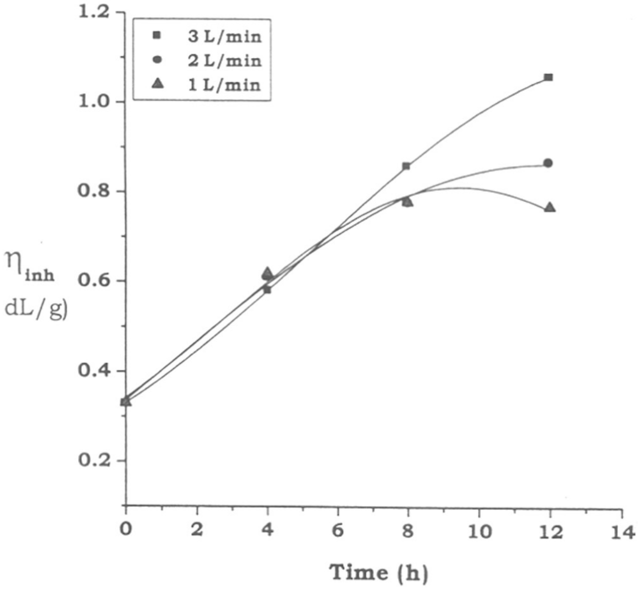


Figure 4.11 *: Effect of flow rate of carrier gas on solid state polymerization [prepolymer η_{inh} = 0.33 dL/g, catalyst = disodium salt of BPA (25 ppm), reaction condition = 230 °C / 2-12 h]*

This clearly indicates that the rate of diffusion of the by-product during solid state polymerization increases with increase in flow rate of the carrier gas. As a result the rate of solid state polymerization also increases. The drop in η_{inh} in case of the experiment using 1 L/min is indicative as reaction reversal at higher temperature.

c) Nature of the catalyst:

The type of catalyst used also influences the solid state polymerization reaction. Any type of catalyst which is efficient in the melt phase carbonate interchange reaction should is also expected to be effective in the solid state polymerization as long as the reaction temperature is high enough to activate terminal hydroxyl groups and those of carbonate linkages nearest to the end of

Table 4.7 : Solid State Polymerization of poly(arylcarbonate)s : Effect of flow rate[a]

(A = 3 L/min, B = 2 L/min and C = 1 L/min)

Sr. No.	Time (h)	η_{inh} (dL/g) (In $CHCl_3$)			OH number (mg of KOH/g) (By UV)			%Crystallinity (By DSC)			T_m (^0C) (By DSC)		
		A	B	C	A	B	C	A	B	C	A	B	C
1	0	0.33	0.33	0.33	19.5	19.5	19.5	21	21	21	227	227	227
2	4	0.58	nd[e]	0.62	12.5	12.3	nd[b]	30	27	23	247	247	250
3	8	0.86	0.78	0.78	10.4	11.8	12.1	34	30	24	261	261	260
4	12	1.06	0.87	0.77	10.1	10.6	11.9	34	31	27	267	267	266
5	16	1.27	0.90	0.67	8.8	9.9	11.4	35	32	27	271	271	274
6	20	1.40	1.05	0.60	8.7	9.5	10.4	36	32	29	274	273	276

a) Flow rate of nitrogen = 3 L/min, reaction condition = 180 ^0C/1 h, 210 ^0C/4 h, 230 ^0C/2-20 h and a disodium salt of BPA (25 ppm) was used as catalyst

b) Not determined

the chains. It has been reported that tetraalkyl ammonium biscarboxylates are useful catalyst for melt phase carbonate interchange reaction.[51] Therefore, the effect of several biscarboxylates were examined on the solid state polymerization. Biscarboxylates are 1 : 1 complex of tetraalkyl ammonium carboxylate and its conjugate acids. A unique feature of these catalysts is that the basicity of these catalysts can be fine tuned by the appropriate choice of carboxylic acid. In addition they are non-metalic, crystalline, shelf-stable and nonhygroscopic. They do not induce any side reactions and leave no metal residues in the polymer. Furthermore, they completely decompose to innocuous products *via* Hoffmann elimination at temperatures >230 °C. The catalyst used were tetramethyl ammonium maleate [TMAM], tetrabutylammonium-bis-4-nitrobenzoate [PBZ(B)] and tetrabutylammonium-bis-2-nitrobenzoate [OBZ(B)]. Of these TMAM and [PBZ(B)] gave better results compared to disodium salt of bisphenol A (DSS) which is shown graphically (**Figure 4.12**).

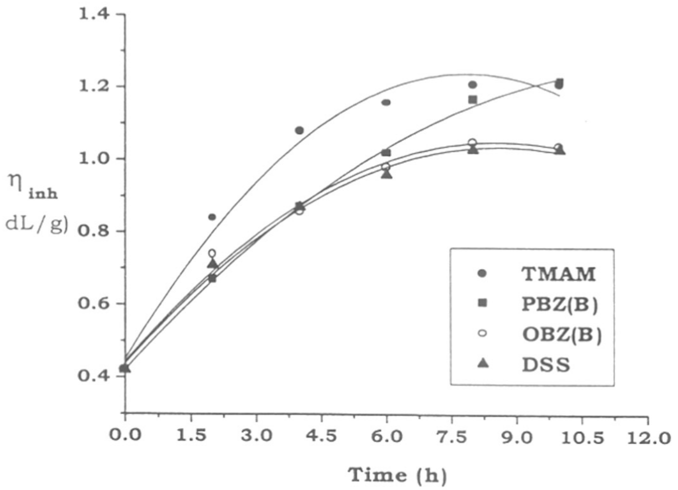


***Figure 4.12** : Effect of alternative catalyst on solid state polymerization [prepolymer η_{inh} = 0.42 dL/g, N_2 flow = 2 L/min, catalyst conc. = 25 ppm, and reaction condition = 230 °C / 2-10 h]*

This shows that bioxyanions are efficient catalyst for solid state polymerization of poly(aryl carbonate)s.

d) Temperature and time :

Temperature is the most important factor due to its interrelation with almost all other aspects of the process. The process can in essence take place between the glass transition temperature and melting temperature.[52] Absolute temperature values need to be sufficiently high enough to ensure the mobility of the reactive end groups or centers. On the other hand reaction time is another factor, which generally tends to act in opposite direction, so that the effect of one may be compensated by the other. For temperature sensitive substances one can operate the reaction at lower temperature for longer time. Generally, a shorter reaction time is always preferable for the industrial polymerization process and for that the reaction temperature should be as close as possible to the melting point of the polymer. The effect of the reaction temperature and time on the solid state polymerization process has already been demonstrated in case of nylon 6.6,[25] nylon 6.10,[25] PET,[25,31,53] nylon 4.6,[27] nylon 6,[54] PBT,[55] where it has been shown that the rate of the reaction depends strongly on the reaction time and temperature. In case of poly(aryl carbonate)s the effect of temperature and time on solid state polymerization were examined. The results are given in **Table 4.8** (**Figure 4.13**), which shows that almost no polymerization occurs at 180 °C or below even after 10 h. The inherent viscosity (η_{inh}) increased rapidly as the reaction temperature increased, indicating that the carbonate interchange reaction rate is significant at higher temperatures.

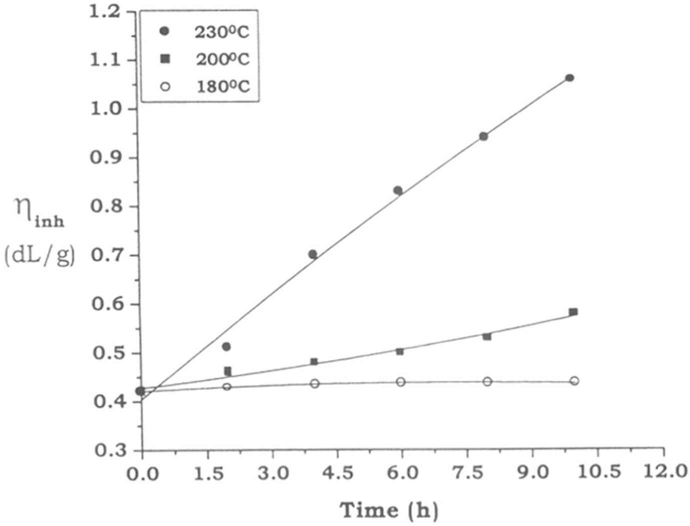


Figure 4.13 *: Effect of temperature on solid state polymerization [prepolymer η_{inh} = 0.42 dL/g, N_2 flow = 2 L/min, catalyst = disodium salt of BPA (25 ppm) and reaction condition = 230 °C / 2-10 h]*

The low hydroxyl number at high inherent viscosity confirmed the occurrence of carbonate interchange reaction. Simultaneous increase in

Table 4.8 : Solid state polymerization of poly(aryl carbonate)s : Effect of temperature[a]

(A = 180 ^{0}C, B = 200 ^{0}C and C = 230 ^{0}C)

Sr. No.	Time (h)	η_{inh} (dL/g) (In $CHCl_3$)			OH number (mg of KOH/g) (By UV)			%Crystallinity (By DSC)			T_m (^{0}C) (By DSC)		
		A	B	C	A	B	C	A	B	C	A	B	C
1	0	0.42	0.42	0.42	7.3	7.3	7.3	22	22	22	236	236	236
2	2	0.43	0.46	0.51	7.4	7.2	6.8	25	27	27	238	239	241
3	4	0.43	0.48	0.70	7.3	7.1	6.5	25	27	28	239	239	245
4	6	0.43	0.50	0.83	7.3	6.7	5.7	25	27	28	239	239	248
5	8	0.44	0.53	0.94	7.3	6.5	4.9	25	nd[b]	30	239	nd[b]	251
6	10	0.44	0.58	1.06	7.2	6.4	4.5	26	29	30	239	240	268

a) Flow rate of nitrogen = 2 L/min, a disodium salt of BP-A (25 ppm) was used as catalyst. B) nd = not determined crystallinity and T_m was also noted from the XRD and DSC thermograms indicating a simultaneous process of crystallization and chain extension. In addition to the chemical process, the diffusion of the reactive end groups to the appropriate site of reaction also plays an important role. The diffusion rate is slower at lower temperature. The effect of higher temperature is to accelerate both the chemical reaction as well as diffusion rates.

d) Initial crystallinity:

It is generally accepted that the solid state polymerization reactions take place in the amorphous regions. For solid state polymerization semicrystalline prepolymers are used due to the two possible effects on the reaction. Firstly, the crystalline phase restricts chain mobility and diffusivity and so reduces the reaction rate. On the other hand, as the chain end groups are concentrated in the amorphous regions, a higher rate may be expected due to the higher local concentration of reagent. A further advantage of the use of a semicrystalline prepolymer as a starting material is that polymer particles do not agglomerate in the reactor. The initial crystallinity of the prepolymer should have a strong effect on the reaction rate. The effect of initial crystallinity on the rate of solid state post-polymerization has been studied by other investigators.[19,28,56] The effect is demonstrated by Chang[28] in his investigation of the kinetics of thermally induced solid state post-polymerization of PET. The process was conducted in a fluidized bed at 230 °C with a PET particle size of 35-48 mesh and a nitrogen flow rate of 43 cm/sec. The effect of initial crystallinity on the reaction rate is fairly evident. Chang attributed it to the influence of crystallinity on diffusivity[57,58] and diffusivity is linearly proportional to the mass fraction of the amorphous region of PET.

Prepolymers having different initial crystallinity 6%, 13% and 22% were used in our study. The effect of initial crystallinity on the solid state polymerization is shown in **Figure 4.14**.

It is evident that the reaction is more facile when initial crystallinity is lower. For instance, the inherent viscosity values obtained after 10 h were 1.06, 0.83 and 0.58 for 6%, 13% and 22% respectively (**Table 4.9**). This is best understood on the premise that chain extension occurs essentially in the amorphous regions of the polymer which requires higher chain mobility, larger

Table 4.9 : Solid state polymerization of poly(arylcarbonate)s : Effect of initial crystallinity[a]

(A = 6%, B = 13% and C = 22%)

Sr. No.	Time (h)	η_{inh} (dL/g) (In $CHCl_3$)			OH number (mg of KOH/g) (By UV)			%Crystallinity (By DSC)			T_m (°C) (By DSC)		
		A	B	C	A	B	C	A	B	C	A	B	C
1	0	0.42	0.42	0.42	7.3	7.3	7.3	6	13	22	217	213	236
2	2	0.45	0.45	0.46	7.1	7.0	7.2	7	15	27	226	221	239
3	4	0.57	0.52	0.48	6.3	6.2	7.1	13	18	27	232	227	239
4	6	0.66	0.64	0.50	5.8	6.0	6.7	14	19	27	237	232	239
5	8	0.82	0.80	0.53	5.0	5.2	6.5	18	21	nd[b]	243	235	nd[b]
6	10	1.06	0.84	0.58	4.4	5.1	6.4	18	22	29	247	239	240

a) Flow rate of nitrogen = 2 L/min, reaction condition = 200 °C/2-10 h and a disodium salt of BP-A (25 ppm) was used as catalyst
b) Not determined

free volume available for diffusion and higher proximity as well as number of available end groups for the reaction.

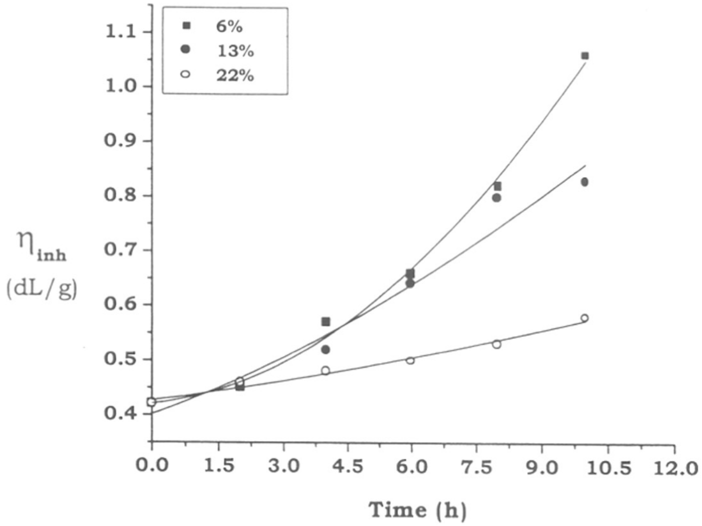


Figure 4.14 *: Effect of initial crystallinity on solid state polymerization [prepolymer* η_{inh} *= 0.42 dL/g,* N_2 *flow = 2 L/min, catalyst = disodium salt of BPA (25 ppm) and reaction condition = 230 °C / 2-10 h]*

e) Initial molecular weight:

It has been reported that higher the initial molecular weight of the polymer, the greater the corresponding molecular weight increase.[16,19] This is understood in terms of changing concentration distribution of the reactive end groups in the solid state on the rate of polymerization. The effect of the initial molecular weight of poly(aryl carbonate)s on the solid state polymerization is shown in **Table 4.10**. Three samples of polymers having the same hydroxyl number but with different initial molecular weight (0.44, 0.33 and 0.17 dL/g respectively) were studied using 25 ppm disodium salt as catalyst. It was also found that the higher initial molecular weight sample produced the polymer of higher molecular weight **(Table 4.10)** (**Figure 4.15**). Thus SSP is applicable to prepolymers with a range of initial molecular weights.

Table 4.10 : Solid State Polymerization of poly(arylcarbonate)s : Effect of initial molecular weight[a]

(A = 0.44 dL/g B = 0.33 dL/g and C = 0.17 dL/g)

Sr. No.	Time (h)	η_{inh} (dL/g) (In $CHCl_3$)			OH number (mg of KOH/g) (By UV)			%Crystallinity (By DSC)			T_m (°C) (By DSC)		
		A	B	C	A	B	C	A	B	C	A	B	C
1	0	0.44	0.33	0.17	19.5	19.5	18.5	21	21	28	232	227	227
2	4	0.90	0.58	0.45	14.5	12.5	10.47	nd[b]	30	36	nd[b]	251	260
3	8	1.05	0.86	0.54	12.9	10.4	8.81	32	34	36	255	263	264
4	10	1.10	0.92	0.57	12.1	10.2	8.62	35	nd[b]	36	259	nd[b]	265

a) Flow rate of nitrogen = 3 L/min, reaction condition = 180 °C/1 h, 210 °C/4 h, 230 °C/2-10 h and a disodium salt of BP-A (25 ppm) was used as catalyst.

b) Not determined.

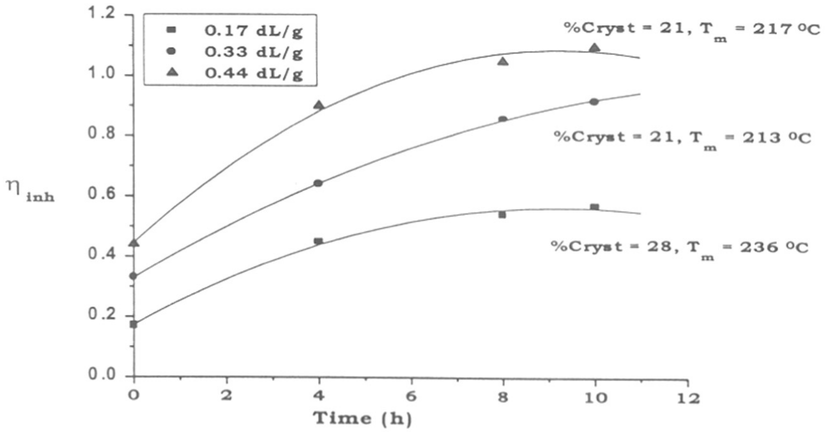


***Figure 4.15** : Effect of initial molecular weight on solid state polymerization [N_2 flow = 2 L/min, catalyst = disodium salt of BPA (25 ppm) and reaction condition = 230 °C / 2-10 h]*

f) Hydroxyl number:

Concentration of end groups influences the solid state polymerization. The influence of concentration of terminal phenolic hydroxyl group is shown in **Table 4.11**. The reaction of the prepolymers, η_{inh} = 0.44 dL/g, OH number = 19.5; η_{inh} = 0.42 dL/g, OH number = 7.3 and Lexan 121R (η_{inh} = 0.42 dL/g), OH number of 1.4, was performed. It was found that the higher the hydroxyl number the faster the rate of solid state polymerization (**Figure 4.16**).

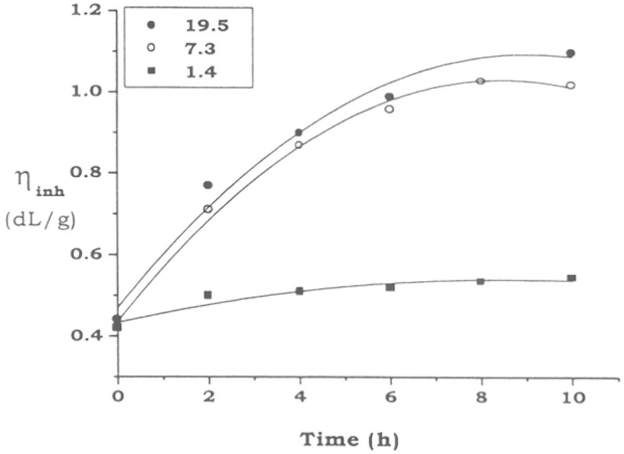


***Figure 4.16** : Effect of initial hydroxyl number on solid state polymerization [prepolymer η_{inh} = 0.42 dL/g, N_2 flow = 2 L/min, catalyst = disodium salt of BPA (25 ppm) and reaction condition = 230 °C / 2-10 h]*

Table 4.11 : Solid State Polymerization of poly(arylcarbonate)s : Effect of initial hydroxyl number[a]

[A = 0.44 dL/g), B = 0.42 dL/g and C = LEXAN 121R (0.42 dL/g)]

Sr. No.	Time (h)	η_{inh} (dL/g) (in $CHCl_3$)			OH number (mg of KOH/g) (By UV)			%Crystallinity (By DSC)			T_m (^{0}C) (By DSC)		
		A	B	C	A	B	C	A	B	C	A	B	C
1	0	0.44	0.42	0.42	19.5	7.3	1.4	21	24	19	232	238	224
2	2	0.77	0.71	0.50	14.8	5.5	nd[b]	23	28	20	250	253	242
3	4	0.90	0.87	0.51	14.5	4.8	1.2	nd[b]	29	nd[b]	nd[b]	259	nd[b]
4	6	0.99	0.96	0.52	13.4	4.5	nd[b]	nd[b]	30	22	nd[b]	260	243
5	8	1.05	1.03	0.54	12.9	4.3	nd[b]	32	31	nd[e]	255	260	nd[b]
6	10	1.10	1.03	0.55	12.1	4.1	1.1	35	31	26	259	261	246

a) Flow rate of nitrogen = 3 L/min, reaction condition = 180 ^{0}C/1 h, 210 ^{0}C/4 h, 230 ^{0}C/2-10 h and a disodium salt of BP-A (25 ppm) was used as catalyst

b) Not determined.

g) Mode of crystallization of the prepolymer:

Crystallization in poly(aryl carbonate)s performed either by exposure to solvent or from melt using additives such as sodium benzoate or phenolates or by thermal annealing the polymer at 140-180 °C for long periods of time. This is because the crystalline state of the polycarbonate can be retained in the solid state even at high temperatures so long as it is below its melting point.

Poly(aryl carbonate)s were crystallized using a solvent as well as thermal annealing. The %crystallinity and T_m obtained are listed in **Table 4.4**. Solid state polymerization reaction was performed with the prepolymer obtained from entry no 1, 4, 7, 8 respectively (**Table 4.4**) and the results are summarized in **Table 4.12**.

Table 4.12 : Solid state polymerization[a] of the prepolymer obtained from Table 4.4

Sr. No.	Time (h)	η_{inh} (dL/g) of the prepolymer crystallized from			
		$CHCl_3$	Methyl ethyl ketone	Toluene	Thermal treatment
1	0	0.42	0.42	0.42	0.42
2	2	0.54	1.11	0.81	0.82
3	4	0.66	1.21	0.95	0.93
4	6	0.74	1.36	1.02	1.11
5	8	0.79	1.42	-	1.18
6	10	0.83	1.52	1.14	1.34

a) Flow rate of nitrogen = 2 L/min. Reaction condition = 220 °C/2-10 h and a tetramethylammonium maleate (25 ppm) as catalyst.

It is seen that the prepolymer obtained from methyl ethyl ketone gave the highest molecular weight whereas, the prepolymer obtained from chloroform gave the lowest molecular weight (**Table 4.12**) (**Figure 4.17**). The rate of solid state polymerization is dependent on the following factors i) the porosity of the crystallized prepolymer, which affects the rate of diffusion of the by-product from the solid, ii) the type of crystallinity. When a polymer is crystallized by dissolving the polymer followed by solvent evaporation there is a likelyhood of a uniform crystallinity throughout the polymer particle whereas, when it is crystallized by refluxing in a solvent in which the polymer is not soluble only the surface of the particle will preferentially crystallize leaving the core to be predominantly amorphous in nature. The rate of SSP can be expected to be faster in the latter case and iii) the reaction temperature at which the SSP is performed. If the reaction is performed at a temperature closer to the T_m of the polymer, the reaction can be expected to be faster.

The rate of SSP in the case of methyl ethyl ketone is faster relative to toluene and chloroform. Crystallization using methyl ethyl ketone produces the lowest T_m (222 °C) which is only 2 °C higher than the reaction temperature (222 °C). Presumably, for this reason, the observed rates are high.

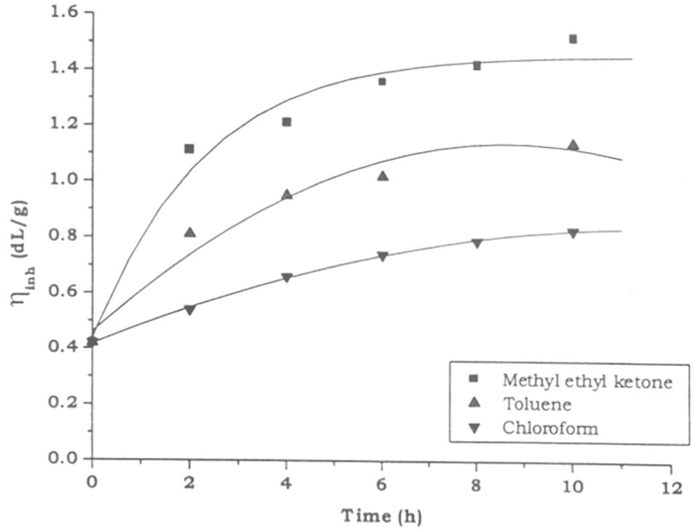


Figure 4.17 : *Effect of mode of crystallization in SSP [Prepolymer* η_{inh} *= 0.42 dL/g,* N_2 *flow = 2 L/min, catalyst = Tetramethyl ammonium maleate (25 ppm) and reaction condition = 220 °C / 2-10 h]*

4.4.1d Kinetic study of SSP:

The kinetics of the solid state polymerization reaction in linear polyesters and polyamides has been reported by several investigators.[19-30] The solid state polymerization is either diffusion or chemical reaction control depending on the flow rate of the carrier gas or the temperature is the rate controlling. It was found that the rate of polymerization could be described by the equation,[31] $rate = kt^n$, indicates a process in the solid material that involves both chemical and diffusion control. Chen and Grisky[25] treated this combined chemical reaction and diffusion in a more fundamental manner. They formulated equations for combined diffusion and chemical reaction in two distinct instances. The first concerned solid state polymerization of polymer chips or flakes, the second dealt with polymer powder. The resulting solutions relate molecular weight to rate functions. Making use of an elaborate technique for deriving the rate functions from the experimental data, they studied solid state polymerization for nylon 66, nylon 6.10 and PET. The experiments were carried out in a fixed bed reactor, with a constant nitrogen flow, at temperatures from 120 to 200 ^{0}C and particle size of 0.095 to 0.21 cm. After fitting the experimental data to various mechanisms, the authors reached the following conclusions: chemical reaction is the rate controlling stage for the powders (average diameters 0.21 cm) nylon 66, PET, for nylon 6.10 and for larger nylon 6.10 particles (average diameter 0.33 cm) at temperatures of 160 ^{0}C or higher. Diffusion of by-products through the solid is the rate controlling stage for nylon 6.10 particles of 0.33 cm in diameter or more at temperatures 140 ^{0}C or less.

In case of poly(aryl carbonate) effect of flow rate and effect of temperature was studied using 250-500 μ particle size, which is lower than the 0.2 cm. From the experimental data (**Table 4.7** and **Table 4.8**) it was observed that the effect of temperature has a more pronounced effect on the solid state polymerization rate compared to the flow rate of the carrier gas. Therefore, it is reasonable to conclude that the solid state polymerization of poly(aryl carbonate) is chemically controlled reaction in the temperature range of 180-230 ^{0}C. Wallas[31] has pointed out that the rate of reaction in solid materials usually varies as some power of the time, t, that is

$$\text{Rate} = kt^n$$

Then we can say that, $$d\,\bar{M}/dt = kt^n$$

If we integrate the eq. 2 by applying the limits

When $t = 0$ then $\bar{M} = \bar{M}_0$ and when $t = t$ then $\bar{M} = \bar{M}$

Where M_0 is the initial molecular weight, we then get

$$\bar{M} - \bar{M}_0 = [k/(n+1)]\, t^{n+1}$$

$$\text{or } \ln(\bar{M} - \bar{M}_0) = \ln(k/n+1) + (n+1)\ln t$$

Thus if one plots ln($\bar{M}$- $\bar{M}_0$) *vs* ln t one should get a straight line with a slope of (n+1). These plots for poly(aryl carbonate)s at 180, 200 and 300 ^{0}C are shown in **Figure 4.18**. From there average n value was obtained as -0.15

Average values of k determined from the intercepts at ln t = 0 are given in **Table 4.13**.

The values of ln k was plotted against the reciprocal of temperature is shown in **Figure 4.19**. The slope of this line yielded an activation energy of 4.08 kcal/g-mole.

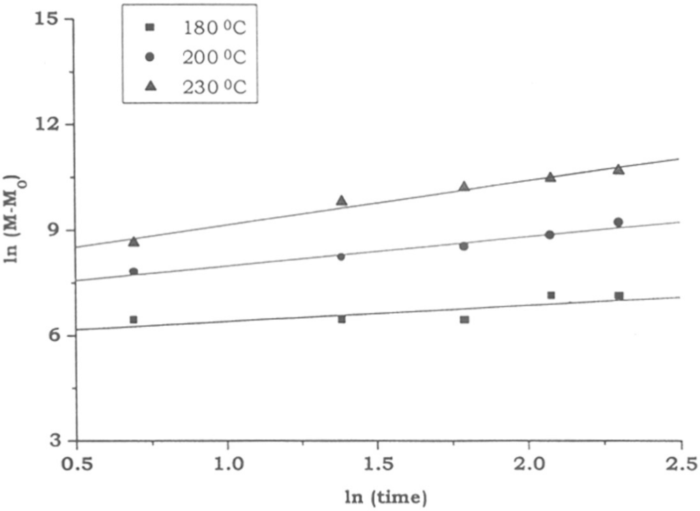


***Figure 4.18** : Plot of ln (M-M$_0$) vs ln (time)*

Table 4.13 : Different values of n and k determined from slope and intercept of ln ($\bar{M}$- $\bar{M}_0$) *vs* ln t at different temperatures.

Sr. No.	Temperature (^{0} C)	Slope (n+1)	n	Average n	Intercept [k/(n+1)]	k ($h^{-1/2}$)
1	180	0.46	-0.54		5.93	3341
2	200	0.84	-0.16	-0.15	7.14	1059
3	230	1.26	0.26		7.88	175

The frequency factor determined from **Figure 4.19** was 1.41X 10^8 h^{-1}

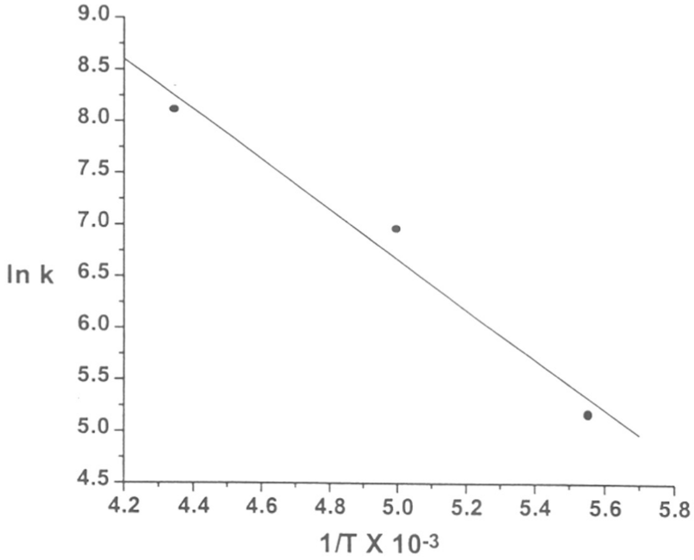


***Figure 4.19** : Plot of ln k vs reciprocal of T*

Table 4.14 : Arrhenius relationship of poly(carbonate) obtained along with the other polymer reported in the literature.

Sr. No.	Polymer	Equation	Temp. range (ºC)
1	Poly(aryl carbonate)	$k = 1.41 \times 10^{8} \exp(-4807/RT)$, h^{-1}	180-230
2.	PET	$k = 6.6 \times 10^{17} \exp(-42{,}500/RT)$, h^{-1}	160-200
3.	Nylon 6-10	$k = 1.68 \times 10^{4} \exp(-13{,}200/RT)$, h^{-1}	120-180
4.	Nylon 66	$k = 1.39 \times 10^{4} \exp(-10500/RT)$, $h^{-1/2}$	120-180

In case of PC the temperature of SSP is much closer to T_m (238 ºC) compared to PET (255 ºC), Nylon 6-10 (220 ºC) and Nylon 66 (260 ºC). This may be the reason for lower observed activation energy

4.3.2 Branched poly(aryl carbonate)s:

The polymers used in this study were prepared by carbonate interchange reaction of bisphenol A with diphenyl carbonate. The starting oligomer used in the present study had inherent viscosity 0.17 and 0.42 dL/g and hydroxyl number 11.3 and 7.3 respectively. Disodium salt of bisphenol A and tetramethyl ammonium maleate were the two catalysts used for the study.

The samples were prepared by dissolving the polymer along with 25 ppm catalyst and THPE (0.5 -1.5 wt%) (in methanol) in chloroform and evaporating the chloroform in the rotavapor. The solid state polymerization reaction was performed by taking 3 g of polymer which was initially conditioned by slowly heating from room temperature to 180 °C over a period of 1 h and retaining the sample at 180 °C for 1 h The solid state polymerization reaction was performed at 220°C for 4 h and at 230 °C for 4 h.

Firstly, the reaction was carried out using an oligomer having η_{inh} = 0.42 dL/g and OH No. = 7.3, disodium salt of bisphenol A as a catalyst and varying the amount of THPE concentration from 0.5-1.5 wt% of the oligomer. The results are given in **Table 4.15**, which shows that at 0.5 wt% THPE and 210 °C/4 h 1.5 wt% gel is formed. In all cases the inherent viscosity increases appreciably.

The study was repeated using η_{inh} = 0.17 dL/g and OH No. = 11.3, oligomer and tetramethyl ammonium maleate as catalyst. The reaction was carried out using 0.5-1.5 wt% THPE and 25 ppm catalyst for 220 °C/4 h. The results are given in **Table 4.16**. In this case gelation was observed only when 1.5 wt% THPE was used. In all cases the inherent viscosity of around 0.3 dL/g was obtained.

Table 4.15 : Synthesis of branched poly(aryl carbonate)s using disodium salt of BPA *via* SSP[a]

Sr. No.	THPE(wt%) taken	Reaction condition (°C/h)	η_{inh}[b] (dL/g)	Gel[d] (wt%)	THPE (wt%) incorporated[c]
1.	0	180/1, 210/4, 230/4	0.87	0	0
2.	0.5	180/1, 210/4	0.58	1.5	0.39
3.	0.5	180/1, 210/4, 230/4	0.85	13.6	0.39
4.	1.0	180/1, 210/4	0.43	4.5	0.76
5.	1.0	180/1, 210/4, 230/4	0.65	17.5	0.87

a) Initial η_{inh} of the oligomer = 0.42 dL/g and OH No. = 7.3, Catalyst concentration = 25 ppm, Flow rate of nitrogen = 2 L/min b) In chloroform at 30 °C c) By HPLC, of the soluble portion d) wt% insoluble in $CHCl_3$

To calculate the gel point, it was assumed that the system contains a mixture of bifunctional monomers A-A and B-B with a multifunctional RA_f (where, A = OH, B = Phenyl carbonate end group of the polymer and R = poly(aryl carbonate)s repeating units). The fraction of A groups belonging to RA_f monomer is ρ. Assuming that all the groups have similar reactivity, the extent of reaction p is equal to the proability that a given group has reacted. Then, the probability of the starting RA_f molecule being part of structure (**1**) is calculated.

$$A_{f-1}-R-A-(B-BA-A)_i-B-B-A-R-A_{f-1}$$

(**1**)

It is clear that the probability of B-B group follows in the chain is ρ; the probability that of A-A group follows is $p(1-\rho)$ and for RA_f is $p\rho$. The overall probability for structure (**1**) is $p[p^2(1-\rho)]^i p\rho$. Therefore, the branching coefficient α is the sum of these probabilities for all possible chain lengths.

$$\alpha = \sum_{i=}^{\alpha} p[p^2(1-\rho)]^i p\rho = p^2\rho/[1-p^2(1-\rho)$$

In the extreme case, when A-A units are absent, then $\rho = 1$ and $\alpha = p^2$. Thus, for the polycondensation of carbonate end groups with THPE (f =3), the gel point should occur when α reaches ½; this corresponds to conversion p = 0.707. In actual experiments, the critical value α_c is found to be higher than the predicted value.

Table 4.16 : Synthesis of branched poly(aryl carbonate)s using tetramethyl ammonium maleate as catalyst *via* SSP[a].

Sr. No.	THPE (wt%) taken	η_{inh}[b] (dL/g)	Gel[c] (%)	THPE (wt%) incorporated[c]
1.	0	0.32	0	0
2.	0.5	0.29	0	0.49
3.	0.75	0.28	0	0.68
4.	1.0	0.27	0	0.96
5.	1.5	0.31	2.5	1.30

a) Initial inherent viscosity of the oligomer = 0.17 dL/g, Flow rate of the carrier gas (N_2) = 2L/min. Catalyst concn. = 25 ppm Reaction condition : 180 °C/1 h and 220 °C/4h b) In chloroform at 30 °C c) By HPLC, of the soluble portion

Characterization of branched polycarbonate has been reported by several methods.[59-61] Dobkowaski and Brzeinski characterized branched polymer using viscometry and GPC technique[59]. They calculated the branching factor using the equation $g_v = M_{vg}^*/M_v^*$ and showed that $g_v = 1$ for linear polycarbonate and $g_v > 1$ for branched polycarbonate. Boden and Krabbenheft[60] characterized branched polycarbonate by measuring the melt index ratio (MIR) and complex melt viscosity (R*), and showed that higher the MIR and R*, higher the shear sensitivity and shear sensitivity is directly related to the branching agent incorporated. In the present study, THPE incorporated in the PC was determined by HPLC after degradative hydrolysis of the polymer using a ZORABAX SBC_8 Rp column, DMN as internal standard and acetonitrile/water solvent system. The retention time of THPE was 13.53 min and that of DMN was 19.59 min (**Figure 4.20**). A calibration curve was drawn using area ratio *vs* mole ratio of THPE to DMN. From the slope of the curve the response factor was determined and was found to be 0.81. Based on known mole% of DMN and the area of THPE to DMN obtained in the sample, the mole% and finally the wt% of THPE was calculated using the response factor. The results are given in **Table 4.15** and **Table 4.16.** Which showed THPE incorporation was found to be quantitative.

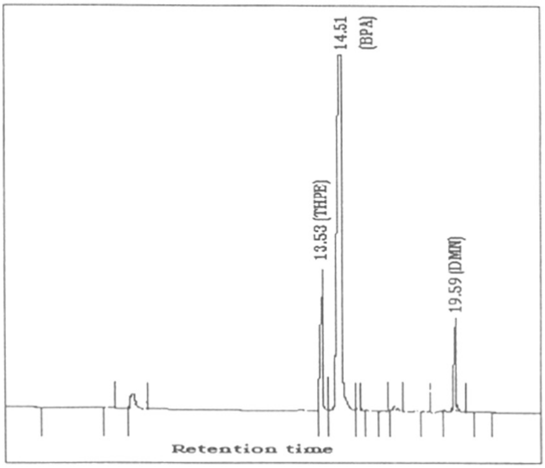
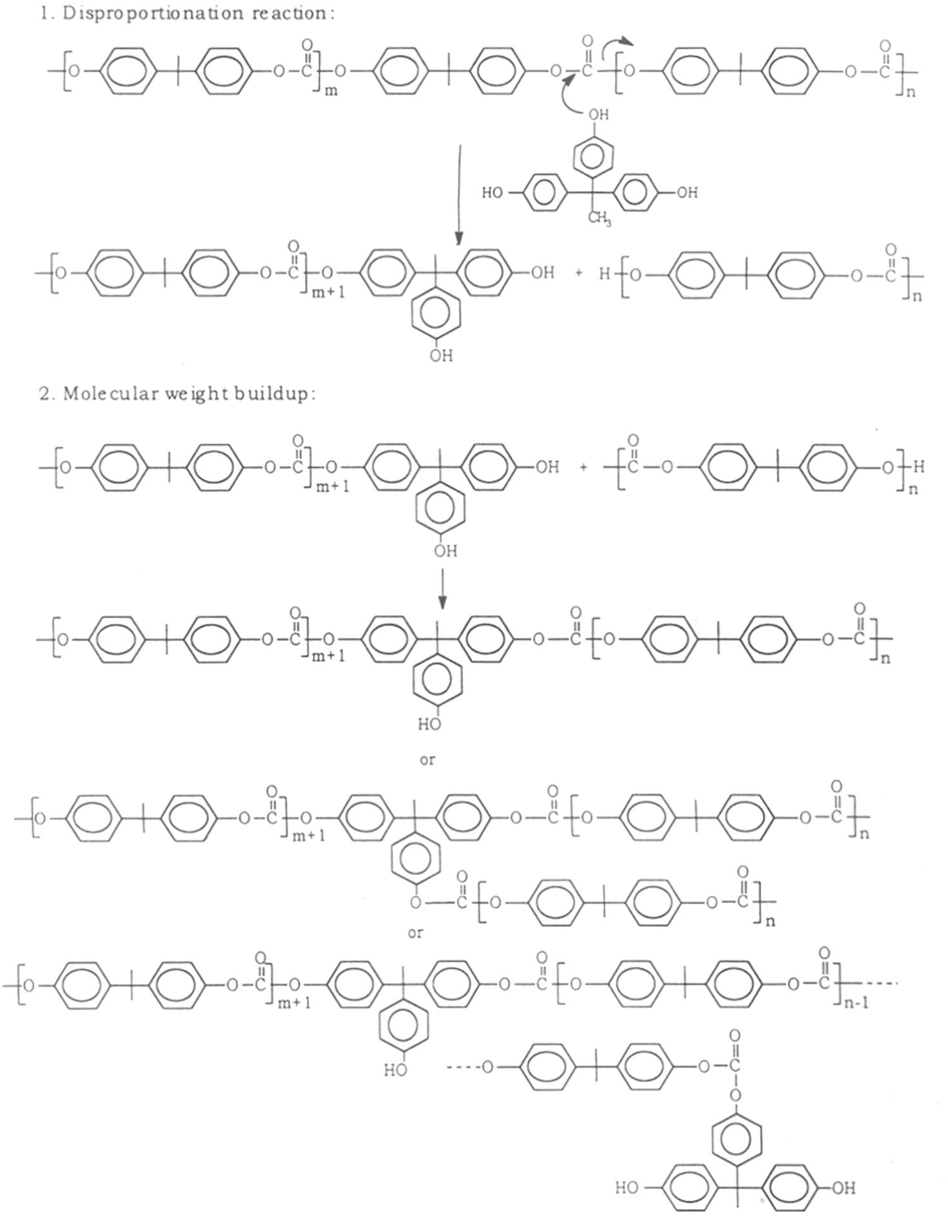


***Figure 4.20** : HPLC spectrum of the saponified branched poly(aryl carbonate)*

Possible reaction scheme:

In the solid state initially disproportionation reaction (**1**) of poly(aryl carbonate) can take place and which the IV of the polymer decreased initially. Finally, the buildup of the molecular weight of the polymer (**2**) will take place as the reaction proceed (**Scheme 4.1**)



Scheme 4.1 : *Possible reactions which can take place during the synthesis of branched polycarbonate in the solid state*

4.4 CONCLUSION:

In conclusion we can say that

1) Rate of solid state polymerization is greatly influenced by temperature, time, nature of catalyst employed, initial crystallinity, end group concentration and molecular weight of the prepolymer.

2) The final crystallinity and T_m are greatly dependent on the solid state polymerization. Solid state polymerization involves chain extension as well as increase in crystallinity and melting point.

3) The manner of crystallization also has profound effect on the rate of solid state polymerization.

4) The kinetic parameters have been evaluated using the kinetic formula

$$d\bar{M}/dt = kt^n$$

Where chemical reaction is the rate controlling step. The Arrhenius equation for the solid state polymerization is found to be

$$K = 1.41\text{x}10^8 \exp(-4807/RT), \text{ unit of } k = (h)^{-1}$$

5) Branched poly(aryl carbonate) can be synthesized using solid state polymerization technique. Degree of branching can be conveniently estimated using HPLC.

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CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF POLY(ESTER-CARBONATE)S USING SOLID STATE POLYMERIZATION

5.1 INTRODUCTION:

Poly(ester-carbonate)s are a class of engineering plastics which are commercially produced and find application as high performance materials. The introduction of carbonate linkage in the matrix of a polyester has the beneficial effect of improving processability, reducing the glass transition temperature and improving impact strength. The ester component of the poly(ester-carbonate)s can be derived either from a poly(aryl ester) or a poly(alkyl ester).

Various methods have been reported for the synthesis of copoly(arylester-carbonate)s. They are interfacial or solution polymerization[1-8] of aromatic dicarboxylic acids or diacid chlorides with bisphenols and phosgene in presence of a base in chlorohydrocarbon solvents or by interchange reaction of dialkyl or diaryl esters of aromatic dicarboxylic acids and diaryl carbonate in the melt phase[9-18] using a suitable polymerization catalyst. Copoly(arylester-carbonate)s can also be obtained by extrusion blending of poly(aryl ester)s and poly(aryl carbonate)s in melt above 300 °C in presence of a catalyst to promote ester-carbonate interchange reaction.[19,20]

Poly(alkylester-carbonate)s are conveniently prepared by a process of reactive blending, in which mixtures of respective homopolymers, namely, poly(ethylene terephthalate) or poly(butylene terephthalate) are melt blended with poly(aryl carbonate) in the barrel of an extruder, in presence of suitable catalysts which can promote an ester-carbonate interchange reaction.[21-35] Such blending is best carried out in a twin screw corotating extruder at 270-280 °C. The product thus obtained are poly(alkylester-carbonate)s. This process has the advantage that it is very flexible, versatile and requires low capital investment.

However, all the forgoing methods suffer from many disadvantages. The interfacial process uses phosgene as well as organic chlorinated solvents both of which are toxic and environmentally polluting. In addition, in the interfacial process large amount of chloride waste as inorganic salt is formed which poses problems in disposal. The melt processes are conducted at high temperatures during which undesirable degradation of the polymer occurs. This leads to poor color and physical properties. Furthermore, the melt processes involve handling of high viscosity melts, which lead to complicate processing equipment. The reactive blending process, although simple, has the disadvantage that the constituent polymers are subjected to a second thermal history. Additionally, presence of catalyst residues in the constituent polymers result in poor control of the ester-carbonate interchange reaction. Such reactive blending processes are always accompanied by the formation of variable quantities of gel (crosslinked polymer), which are undesirable.

On the other hand, solid state polymerization[36] is a process widely practiced to increase the molecular weight of the low molecular weight oligomers of poly(ester)s and poly(aryl carbonate)s. In this process oligomers are subjected to various treatment to induce crystallinity and polymerized in the solid state at a temperature higher than the glass transition temperature of the polymer but below the melting point of the polymer, either in vacuum or in presence of an inert gas flow, whereupon the molecular weight increases in the solid state.

The major advantage of the solid state polymerization process is that it involves relatively low temperatures, is solvent free and produces no effluents. There is no need for special equipments to handle the higher viscosities of the polymer encountered in the melt process. In view of the low temperatures used, there is no undesirable polymer degradation leading to loss of properties. The process is free of gelation or crosslinking.

It was reported that high molecular weight poly(aryl carbonate),[37] poly(aryl ester),[38] poly(ethylene terephthalate)[39-45] can be prepared in the solid state polymerization reaction from their respective lower molecular weight prepolymers.

Reorganization of the copolymer in the solid state has also been reported in the literature.[46] Lenz *et al.* reported the conversion of a random into a block copolymer[47] and *cis-trans* isomerization,[48] where irreversible crystallization of repeating units was observed after isomerization from *cis* to *trans* structure.

This chapter describes the preparation of high molecular weight poly(ester-carbonate)s *via* the solid state copolymerization of a mixture of low molecular weight oligomers derived from poly(aryl carbonate)s, poly(aryl ester)s and poly(alkyl ester)s.

5.2 EXPERIMENTAL:

5.2.1 Materials:

Bisphenol A (Aldrich Chemical, USA) was recrystallized from toluene, mp 158 °C (lit.[49] mp 158 °C). Diphenyl carbonate (E. Merck, Bombay/India) was recrystallized from absolute ethanol, mp 78 °C (lit.[49] mp 78 °C). *o*-Nitrobenzoic acid was recrystallized according to the literature procedure.[49]

Isophthalic acid, terephthalic acid (Aldrich Chemical, USA), dibutyl tin oxide (Fascat M & T Chemicals, USA) and dibutyltin dilaurate (DBTL) (Wilson Laboratory, Bombay, India), antimony trioxide (Aldrich Chemical, USA) and PET (0.65 dL/g) (EniChem S.p.A., Italy) were used as received. Bioxyanion of *o*-nitrobenzoic acid was prepared according to the method of Dicker *et al.*[50]

5.2.2 Measurements:

Melting points were measured with a Thermonix melting point apparatus and were uncorrected. FT-IR spectra were recorded on a Perkin-Elmer model 16PC FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker WH-90 FT-NMR and Bruker AC-200 NMR spectrometer. $\overline{M}_n$ was determined using Knauer vapour pressure osmometer in $CHCl_3$ at 35 ^{0}C. Inherent viscosity was determined in an automated Schott Gerate AVS 24 viscometer using Ubbelohde suspended level viscometer in $CHCl_3$ at 30 ^{0}C (polymer concentration of 0.5% w/v) and in phenol/1,1′,2,2′-tetrachloroethane (60:40, w/w) for PET (polymer concentration of 0.5% w/v). The hydroxyl number was determined using a Hewlett Packard 8452A Diode Array UV/vis. spectrophotometer and THF as solvent, using the reported ε for bisphenol A and the polymer at 287 nm.[51] The analysis carried out in the absorbance range of 0.2-0.8, using suitable concentrations of polymer solutions. T_m and T_g were measured by DSC using Perkin-Elmer thermal analyzer (DSC-7) in N_2 atmosphere at a heating rate of 10 ^{0}C/min and 20 ^{0}C/min respectively. Generally, T_g was determined from the second heating curve, whereas, T_m from the first heating curve.

5.2.3 Synthesis of poly(aryl carbonate)s:

Bisphenol A (200 g, 0.88 mol), diphenyl carbonate (197 g, 0.92 mol) and tetrabutylammonium hydrogen-bis-*o*-nitrobenzoate (1.03×10^{-5} mol) were charged into the reactor (Karl Kurt Jucheim, Germany) under N_2 atmosphere. The polymerization reaction was carried out as described in **Chapter IV, Section 4.2.4**, except heating at 300 ^{0}C for 20 min.

The polymer thus formed was dissolved in 1 L chloroform and the solution poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 ^{0}C for 24 h. Yield of polymer : 200 g (89%). η_{inh} = 0.17 dL/g.

IR (Nujol, cm^{-1}):

3500 (O-H), 1780 (C=O), 1220 (C-O);

^{1}H NMR ($CDCl_3$, δ):

1.7(s, CH_3), 7.2(dd, 4H), 7.4(dd,4H).

5.2.4 Synthesis of poly(aryl ester)s:

The poly(aryl ester)s required for solid state polymerization was synthesized in 50 g scale in a 2L stainless steel autoclave, (Karl Kurt Jucheim, Germany). Bisphenol A (45.70 g, 0.2 mol), dimethyl terephthalate (19.40 g, 0.1 mol), dimethyl isophthalate (19.40 g, 0.1 mol), dibutyltin oxide (0.25 g 0.5 mol% of BPA) and diphenyl ether (120 mL) were charged into the reactor under N_2 atmosphere. The reaction mixture was then heated to 260 ^{0}C in 30 min and maintained at that temperature for 12 h keeping the N_2 flow rate 300 mL/min. During this period the by-product methanol was continuously distilled and collected. Finally, diphenyl ether was removed completely under vacuum (0.5 mm of Hg) at 160 ^{0}C. Then the reactor was cooled to ambient temperature. The polymer was dissolved in chloroform and precipitated from methanol and dried under vacuum at 60 ^{0}C for 6 h, yield = 37 g (54 wt%) and η_{inh} = 0.09 dL/g. 5 g of the above oligomer and 0.5 wt% dibutyltin dilaurate were charged in a thick wall glass reactor under N_2 atmosphere. The reaction mixture was then heated to 300 ^{0}C in 30 min under 0.2 mm of Hg and maintained at that temperature and pressure for 3 h. Then the reaction mixture was cooled to room temperature. The product obtained was dissolved in chloroform and poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 ^{0}C for 6 h. Yield of polymer : 4.3 g (86%). η_{inh} = 0.19 dL/g.

IR (Nujol, cm^{-1}):

3500 (O-H), 1740 (C=O);

^{1}H NMR ($CDCl_3$, δ):

1.55(s, CH_3), 4.0 (s, OCH_3), 7.1(dd, 4H), 7.4(dd,4H), 7.75(t, 1H), 8.3(s, 4H), 8.45(d, 2H), 9.0(s, 1H).

5.2.5 Synthesis of poly(ethylene terephthalate) oligomer:

10 g of PET was taken in a 250 mL round bottom flask and dissolved in 150 mL phenol/1,1′,2,2′-tetrachloroethane (60 : 40, w/w). To this was added 15 mL 0.1N methanolic NaOH solution and heated to 160 ^{0}C for 10 min, the polymer was precipitated from acidified (HCl) methanol, filtered and washed 4-5

times with methanol. The product was dried under vacuum at 60 ^{0}C for 6 h. Weight of the product = 7 g and η_{inh} = 0.14 dL/g in phenol/1,1′,2,2′-tetrachloroethane (60 : 40, w/w) at 30 ^{0}C at a polymer concentration of 0.5%, w/v.

5.2.6 Synthesis of copoly(arylester-carbonate)s:

i) Preparation of the sample:

The oligomer of poly(aryl carbonate) (2 g) and poly(aryl ester) (2 g) were placed in a 100 mL round bottom flask and dissolved in 15 mL $CHCl_3$. To this solution 30 mL methanol was added to precipitate the oligomers. The solvent mixture was removed in a rotavapor. The product was dried under vacuum at 60 ^{0}C for 4 h.

ii) Crystallization of the oligomer:

The mixture of oligomers (3.5 g) prepared as above was placed in a 100 mL round bottom flask. An ethyl acetate solution containing 100 ppm DBTL (50 mL) was added. The slurry was refluxed for 4 h. Ethyl acetate was evaporated on a rotatory evaporator and the oligomer dried under vacuum at 60 ^{0}C for 4 h. The oligomer was pulverized, sieved and particles in the range of 250 to 520 μ were used for further reaction.

iii) Solid state polymerization:

The solid state polymerization was performed in a glass reactor, immersed in an oil bath maintained at a constant temperature. The crystallized oligomer mixture (3 g) was placed in the reactor and was heated slowly from room temperature to 180 ^{0}C over a period of 1 h. The sample was then retained at 180 ^{0}C for 1 h. Further, the reaction was performed at 200 ^{0}C for 1 h, at 210 ^{0}C for 4 h, at 220 ^{0}C for 4 h and finally at 230 ^{0}C for 2 h. Samples were periodically withdrawn and inherent viscosity, T_g and T_m were determined.

5.2.7 Synthesis of copoly(alkylester-carbonate)s:

I) Preparation of the sample:

Poly(aryl carbonate) (6 g) and poly(ethylene terephthalate) (6 g) were taken in a 100 mL round bottom flask and dissolved in 50 mL phenol/1,1′,2,2′-tetrachloroethane (60 : 40 w/w). The polymer mixture was precipitated from methanol and dried under vacuum at 60 ^{0}C for 4 h.

ii) Crystallization of the prepolymer:

In a 100 mL round bottom flask, 10 g of the prepolymer mixture was taken to which acetone (50 mL) and antimony trioxide (1000 ppm) was added and the mixture was refluxed for 4 h. Acetone was evaporated on a rotatory evaporator and the polymer was dried under vacuum at 60 ^{0}C for 4 h. The prepolymer was then pulverized and particles with a range of 250 to 520 μ was used for reaction.

iii) Solid state polymerization reaction:

The solid state polymerization reaction was performed in a glass reactor as described earlier. 6 g of prepolymer mixture was placed in the reactor and was initially conditioned by slowly heating from room temperature to 180 ^{0}C over a period of 1 h and retaining the sample at 180 ^{0}C for 1 h. Further, the reaction was carried out at 200 ^{0}C for 3 h, at 220 ^{0}C for 4 h, and at 230 ^{0}C for 7 h. At no point of time agglomeration or powder sticking was observed. Samples were periodically withdrawn and the inherent viscosity, T_g and T_m were determined.

5.3 RESULTS AND DISCUSSION:

5.3.1 Poly(arylester-carbonate)s:

The poly(aryl carbonate) and poly(aryl ester) oligomers used in the study were prepared by an interchange reaction of bisphenol A with diphenyl carbonate and with 50:50 wt% dimethyl esters of terephthalic and isophthalic acids in melt phase reaction.[38,52,53] The poly(aryl carbonate) oligomer had an η_{inh} = 0.17 dL/g, $\bar{M}_n$ (VPO) = 3265 and hydroxyl number = 11.3 (mg of KOH/g). The poly(aryl ester) oligomer had an η_{inh} = 0.19 dL/g and $\bar{M}_n$ (VPO) = 2930. The physical mixture (1:1) of the two prepolymers had an η_{inh} = 0.18 dL/g and $\bar{M}_n$ (VPO) = 2810.

In semicrystalline polymers, such as, poly(ethylene terephthalate), nylon 6 etc. which show a well defined crystalline melting temperature, the solid state polymerization is carried out at about 20 ^{0}C below T_m so that the polymer does not fuse or stick during the course of the reaction. Poly(aryl carbonate)s and poly(aryl ester)s are predominantly amorphous in nature and hence were not considered as suitable candidates for solid state polymerization since they soften and stick when heated above their T_g. However, the sticking point of a polymer, which is slightly above the second order transition temperature[43] can be raised close to the melting point, by means of crystallization. Amorphous polymers such as poly(aryl carbonate)s and poly(aryl ester)s are difficult to crystallize thermally. However, partial swelling in a non-solvent is known to be an efficient method for inducing crystallinity rapidly in polycarbonates.[54,55] Accordingly, crystallization was induced in the oligomers by refluxing in ethyl acetate for 4 h. The physical mixture of the polymers showed two T_g's at 115 °C for poly(aryl carbonate) and 147 °C for poly(aryl ester) (**Figure 5.1a**). However, when the oligomer mixture was dissolved in chloroform and precipitated from methanol it showed a single T_g at 128 °C and no T_m (**Figure 5.1b**).

Nishi *et al.*[19c] have reported two T_g's in blends of poly(aryl carbonate) and poly(aryl ester). However, upon rapid evaporation of the solvent from the blend a single T_g was observed. The observed single T_g in the present case could be due to the low molecular weight nature of the oligomer, which forms a miscible blend with a single phase. Subsequent to refluxing in ethyl acetate, the DSC endotherm of the mixture of oligomers showed a broad endotherm with a T_m of about 210 °C (**Figure 5.2a**), indicating presence of a low degree of crystallinity.

The solid state polymerization of the oligomer was performed at 200 °C for 2 h, 210 °C for 2 h, 210 °C for 4 h, 220 °C for 4 h and 230 °C for 2 h under reduced pressure (>0.1 mm Hg). The results are shown in **Table 5.1**.

Table 5.1 : Synthesis of copoly(arylester-carbonate)s[a]

Sr. No.	Reaction condition (Temp,°C/Time, h)	η_{inh} (dL\g)	T_g [c] (°C)	T_m [d] (°C)	ΔH_f [d] (J/g)
1.	Initial prepolymer (physical mixture)	0.18	115, 147	-	0
2.	Initial prepolymer (after crystallization)	0.18	128	210	24
2.	180/1, 200/1	0.24	138	215	19
3.	180/1, 200/1, 210/4	0.35	149	228	15
4.	180/1, 200/1, 210/4, 220/4	0.43	159	233	10
5.	180/1, 200/1, 210/4, 220/4, 230/2	0.52	163	236	2

a) *A total of 3.5 g prepolymer (average particle size 520-250 μ) was heated under vacuum (>0.1 mm of Hg) using dibutyltin dilaurate (100 ppm) as catalyst. b) In $CHCl_3$ at 30 °C, at a polymer concentration of 0.5% w/v. c) By DSC at a heating rate of 20 °C/min. e) By DSC at a heating rate of 10 °C/min.*

It is evident that the polymerization reaction proceeds in the solid state with an appreciable increase in molecular weight. During the course of polymerization both the T_g and the T_m increased progressively with an increase in η_{inh} from 0.18 to 0.52 dL/g (**Figure 5.3**). The final value of T_g = 163 °C is comparable to that obtained for copoly(arylester-carbonate)s of a similar composition, synthesized in the melt process.[1,18]

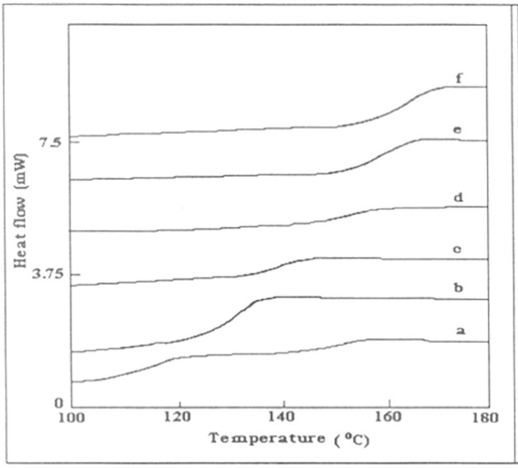


Figure 5.1 *: T_g of (a) physical mixture of poly(aryl carbonate) and poly(aryl ester) (b) after crystallization (c) after 180 °C/1 h + 200 °C/1 h (d) after 210 °C/4 h (e) after 220 °C/4 h and (f) after 230 °C/2 h*

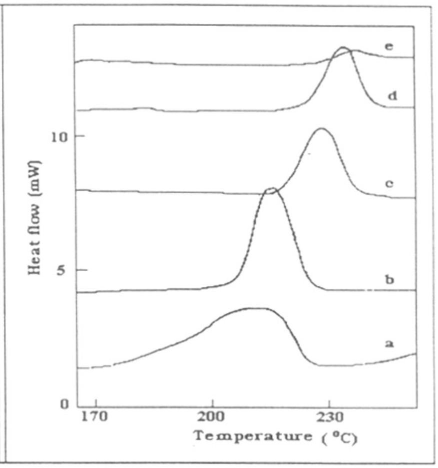


Figure 5.2 : T_m of *(a) prepolymer mixture after ethyl acetate treatment (b) after 180 °C/1 h + 200 °C/1 h (c) after 210 °C/4 h (d) after 220 °C/4 h and (e) after 230 °C/2 h*

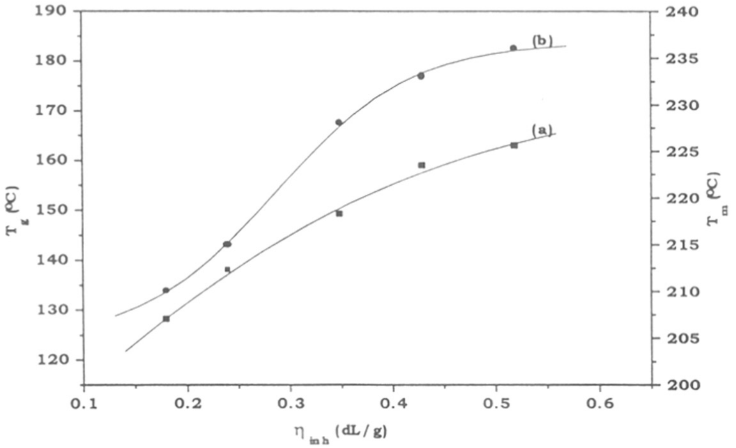


Figure 5.3 *: Variation of (a) T_g and (b) T_m with η_{inh} of copoly(arylester-carbonate)s*

Interestingly, whereas, T_m increased with an increase in molecular weight, the crystallinity of the polymer decreased as evidenced by the decrease in ΔH_f values (**Figure 5.4**).

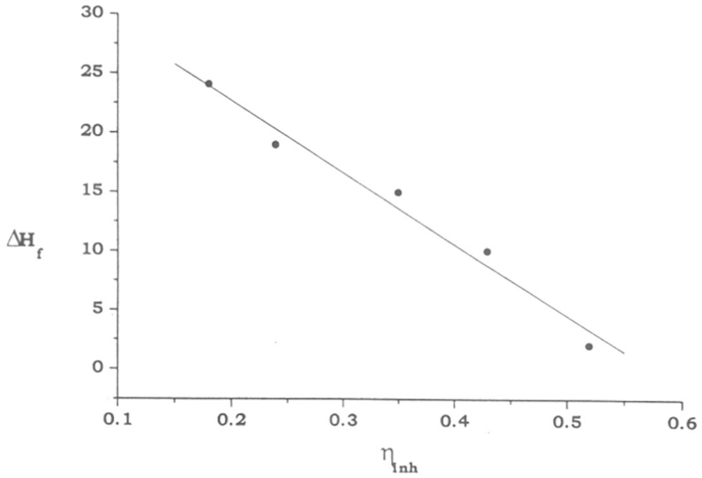


Figure 5.4 *: Variation of ΔH_f with η_{inh} of copoly(arylester-carbonate)s*

This is presumably due to the progressive inclusion of the poly(aryl ester) in the copolymer chain, resulting in the inability of the chains to pack themselves efficiently in the crystalline structure.

5.3.2 Poly(alkylester-carbonate)s:

The poly(aryl carbonate) oligomer was prepared by melt phase carbonate interchange reaction of bisphenol A with diphenyl carbonate. The oligomer had an η_{inh} = 0.17 dL/g (in chloroform at 30 °C) and hydroxyl number = 11.3 (mg of KOH/g). PET oligomer was obtained by methanolysis of the commercially available PET. The oligomer had an η_{inh} = 0.14 dL/g (in phenol/1,1′,2,2′-tetrachloroethane 60:40, w/w, at 30 °C). The physical mixture (1:1) had an η_{inh} = 0.15 dL/g (in phenol/ 1,1′,2,2′-tetrachloroethane 60:40, w/w, at 30 °C).

Poly(ethylene terephthalate) is a semicrystalline polymer which shows a well defined crystalline melting temperature whereas poly(aryl carbonate) is amorphous in nature. Therefore, to induce sufficient crystallinity for solid state polymerization the oligomer mixture was refluxed in acetone for 4 h.

The solid state polymerization of PC-PET oligomer mixture was performed at atmospheric pressure under a flow of nitrogen between the temperature range of 180-230 ^{0}C for 15 h (**Table 5.2**). It is evident that the polymerization reaction proceeds in the solid state with a significant increase in molecular weight.

Table 5.2 : Reaction of PC and PET oligomer in the solid state

Sr. No.	Reaction condition	η_{inh} [a] (dL/g)	T_g [b,c] (^{0}C)	T_g [b,d] (^{0}C)	T_m [b] (^{0}C)	ΔH_f [b] (J/g)	Crystallinity[e] (%)
1.	PC + PET oligomer (after crystallization)	0.15	f	71	215, 247	51	47
2.	180/1+200/3	-	93	85	230, 241	36	38
3.	180/1+200/3+220/4	0.32	102	92	242	23	27
4.	180/1+200/3+220/4 +230/4	0.71	101	93	245	15	20
6.	180/1+200/3+220/4 +230/7	0.84	102	95	248	11	15

a) *In phenol/1,1′,2,2′-tetrachloroethane (60 : 40, w/w) at 30 ^{0}C at a polymer concentration 0.5% w/v.*
b) *By DSC at a heating rate of 10 ^{0}C/min.*
c) *T_g from the first heating run.*
d) *T_g from the second heating run.*
e) *By XRD.*
f) *In the first heating run no T_g was observed.*

The temporal change of T_g for the initial mixture and the polymerized product is shown in **Figure 5.5**. The oligomer mixture after crystallization did not show a T_g in the first run. However, after the second heating run a sharp T_g appeared at 71 ^{0}C. When PET and PC are melt blended, two T_g's are initially observed, which coalesce to a single T_g after sufficient time of mixing.[30,33] Ignatov *et al.*[34] reported that the appearance of two T_g's or single T_g depends on the amount of catalyst used. They showed that when neat PC-PET was extruded two distinct T_g's were observed in the final blend, whereas, when Sm(acac)$_3$ was used as catalyst (≥ 0.045 wt%) the resulting product was transparent with a single T_g.

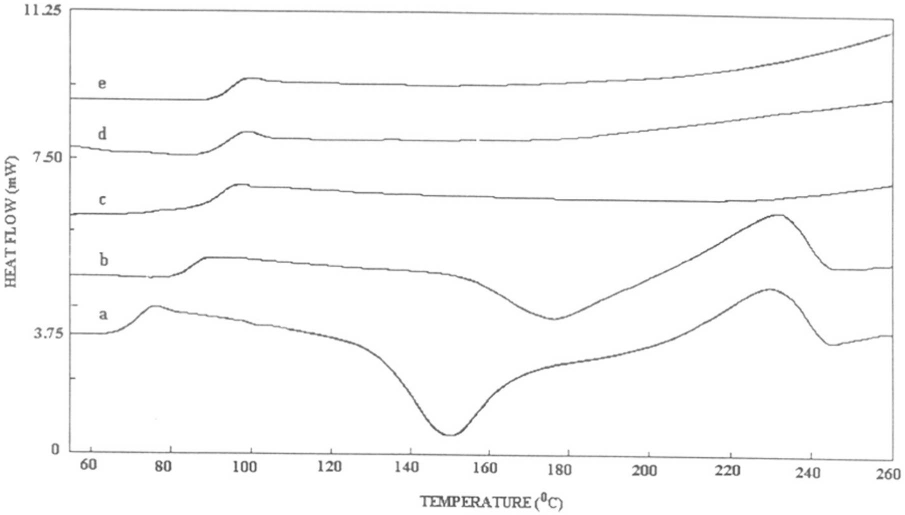


Figure 5.5 *: T_g of (a) physical mixture of oligomers (PC and PET) after crystallization (b) after 180 ⁰C/ 1 h + 200 ⁰C/ 3 h (c) after 180 ⁰C/ 1 h + 200 ⁰C/ 3 h + 220 ⁰C/ 4 h (d) after 180 ⁰C/ 1 h + 200 ⁰C/ 3 h + 220 ⁰C/ 4 h + 230 ⁰C/ 4 h and (e) after 180 ⁰C/ 1 h + 200 ⁰C/ 3 h + 220 ⁰C/ 4 h + 230 ⁰C/ 7 h*

In the present study, when PC and PET (50:50, w/w) oligomers were dissolved in phenol/1,1′,2,2′-tetrachloroethane (60:40, w/w) at 30 ⁰C and precipitated in methanol, only a single T_g was observed in the first heating run. Upon polymerizing in the solid state, the T_g increased to 102 ⁰C. A large difference in the T_g of the first and the second heating run was observed (**Table 5.2**) which indicate that initially a blocky copolymer is formed by the reaction of the two oligomers which upon heating to 280 ⁰C, in the DSC chamber undergoes a rearrangement in the melt phase to a random copolymer. However, in the case of poly(ester-carbonate) produced by melt blending, no difference in T_g is observed between first and the second heating run, since randomization is essentially complete during melt processing.[30]

Peaks corresponding to T_c and T_m were also observed along with T_g upon solution blending the oligomer mixtures (**Figure 5.5**). While T_c increases from 150 to 175 ⁰C, no change in T_m was observed upon heating to 180 ⁰C for 1 h and 200 ⁰C for 3 h. Heating beyond 200 ⁰C for 3 h resulted in the disappearance of T_c and T_m during the second heating run. These observations suggest the occurrence of ester-carbonate interchange reaction in the solid state.

Two T_m's were observed at 215 ^{0}C and 247 ^{0}C after solvent induced crystallization of the oligomer mixtures. With the progress of solid state polymerization, the two values coalesced to a single T_m. This was accompanied by decrease in ΔH_f value from 52 to 11 J/g (**Figure 5.6**).

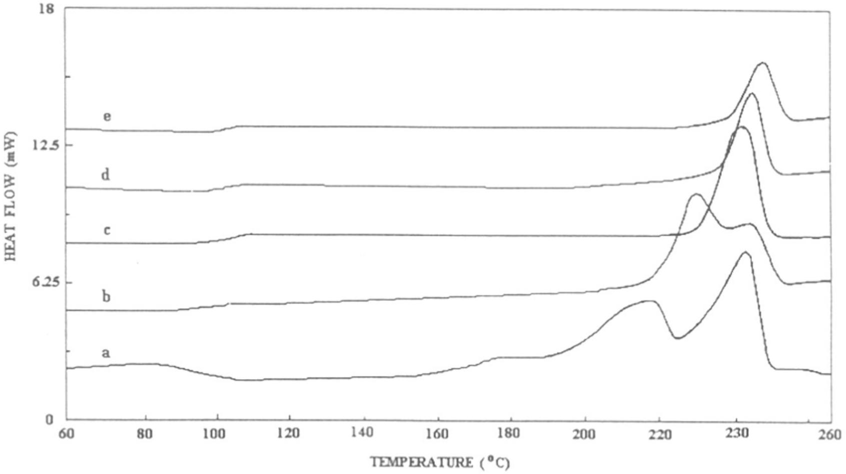


Figure 5.6 *: T_m of (a) physical mixture of the oligomers (PC and PET) after crystallization (b) after 180 ^{0}C/ 1 h + 200 ^{0}C/ 3 h (c) after 180 ^{0}C/ 1 h + 200 ^{0}C/ 3 h + 220 ^{0}C/ 4 h (d) after 180 ^{0}C/ 1 h + 200 ^{0}C/ 3 h + 220 ^{0}C/ 4 h + 230 ^{0}C/ 4 h and (e) after 180 ^{0}C/ 1 h + 200 ^{0}C/ 3 h + 220 ^{0}C/ 4 h + 230 ^{0}C/ 7 h*

Fakirov *et al.*[33] reported that on thermal treatment of a mixture of poly(ethylene terephthalate) and poly(aryl carbonate) (50 : 50, w/w) homopolymers at 280 ^{0}C for 265 min produced a copolymer which exhibited no T_m and crystallinity. Additional annealing at 235 ^{0}C for 360 min and 245 ^{0}C for 180 min caused the reappearance of the melting endotherm at 223 ^{0}C with a crystallinity of 38%. In this case, when the homopolymer was annealed at 280 ^{0}C totally random copolymer was formed which reorganized to a blocky structure upon annealing at 235 ^{0}C and 245 ^{0}C. Contrary to this, in the present study, a block copolymer with long block lengths was initially formed due to ester-carbonate interchange reaction which rearranges to a copolymer with a shorter sequence length of the ester and carbonate units as the polymerization proceeds in the solid state. The appearance of a single T_m and a reduction in crystallinity from 47% to 15% with increasing molecular weight of the copolymer is in agreement with this hypothesis. The final copoly(ester-carbonate) formed had an η_{inh} = 0.84 dL/g. The product was free of any gel as evidenced by total solubility in chloroform-trifluoroacetic acid (4:1, v/v). Additionally, the product was found to be ~92% soluble in chloroform. It is worth noting that poly(ester-carbonate)s obtained by melt blending is always accompanied by the formation of variable quantities of gels.[27]

XRD analysis of the sample also showed that the crystallinity slowly decreases from 47% to 15% (**Table 5.2, Figure 5.7**), which supports the results obtained from DSC.

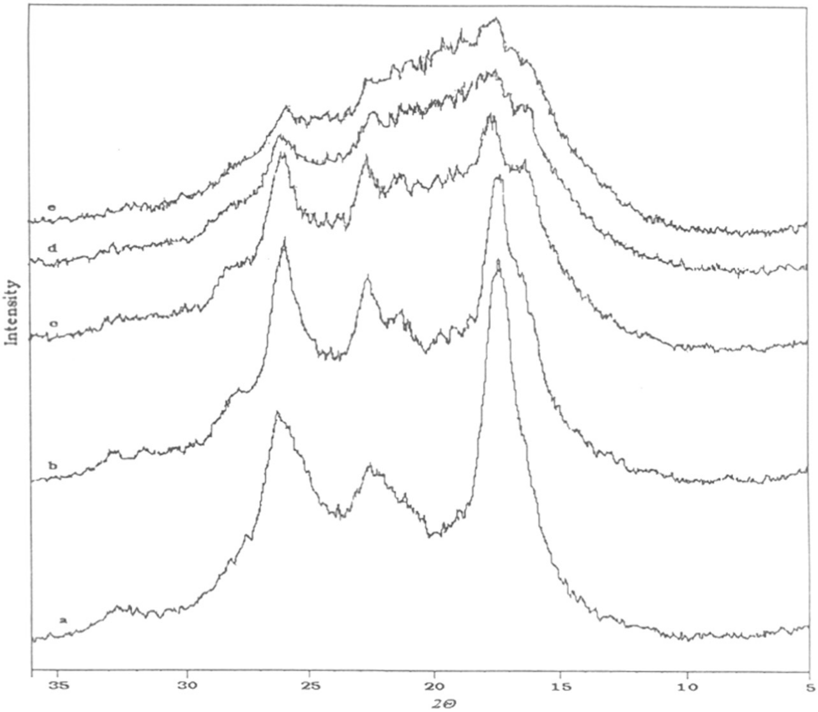


Figure 5.7 *: XRD spectra of (a) physical mixture of the oligomers (PC and PET) after crystallization (b) after 180 °C/1 h + 200 °C/3 h (c) after 180 °C/1 h + 200 °C/3 h + 220 °C/4 h (d) after 180 °C/1 h + 200 °C/3 h + 220 °C/4 h + 230 °C/4 h and (e) after 180 °C/1 h + 200 °C/3 h + 220 °C/4 h + 230 °C/7 h*

^{1}H NMR of the oligomer mixtures was compared with the final polymer (before and after extraction in chloroform) (**Figure 5.8**). In the spectrum (**a**) the four protons of the terephthalic acid residue give a signal at 8.02 ppm. The peak does not reveal a fine structure, because these protons are magnetically indistinguishable. The signals in the 7.00-7.20 ppm region correspond to the aromatic protons of bisphenol A in PC. Significant differences were observed in the spectra of the oligomer mixture (**a**), final polymer before soxhlet extraction (**b**) and after soxhlet extraction (**c**). The multiplet in the 6.40-7.20 ppm region, due to the protons from bisphenol A, is deformed and displays a disturbed fine structure. The formation of the new peak at 8.20 ppm is due to the terephthalic protons of the sequence ~B_2-A_1-B_2~ and at 8.30 ppm is due to the same protons of the B_1-A_1-B_2~ sequence, where A_1 stands for the terephthalic unit (-OC(=O)-C_6H_4-C(=O)O-), B_1 is an ethylene unit (-CH_2CH_2-) and B_2 is a unit of the structure -C_6H_4-C(CH_3)$_2$-C_6H_4-, derived from bisphenol A. NMR thus provides clear evidence that a chemical reaction has occurred between the carbonate and the ester group. Similar NMR observations have been reported in the literature in case of poly(ester-carbonate)s obtained by melt blending.[31,33]

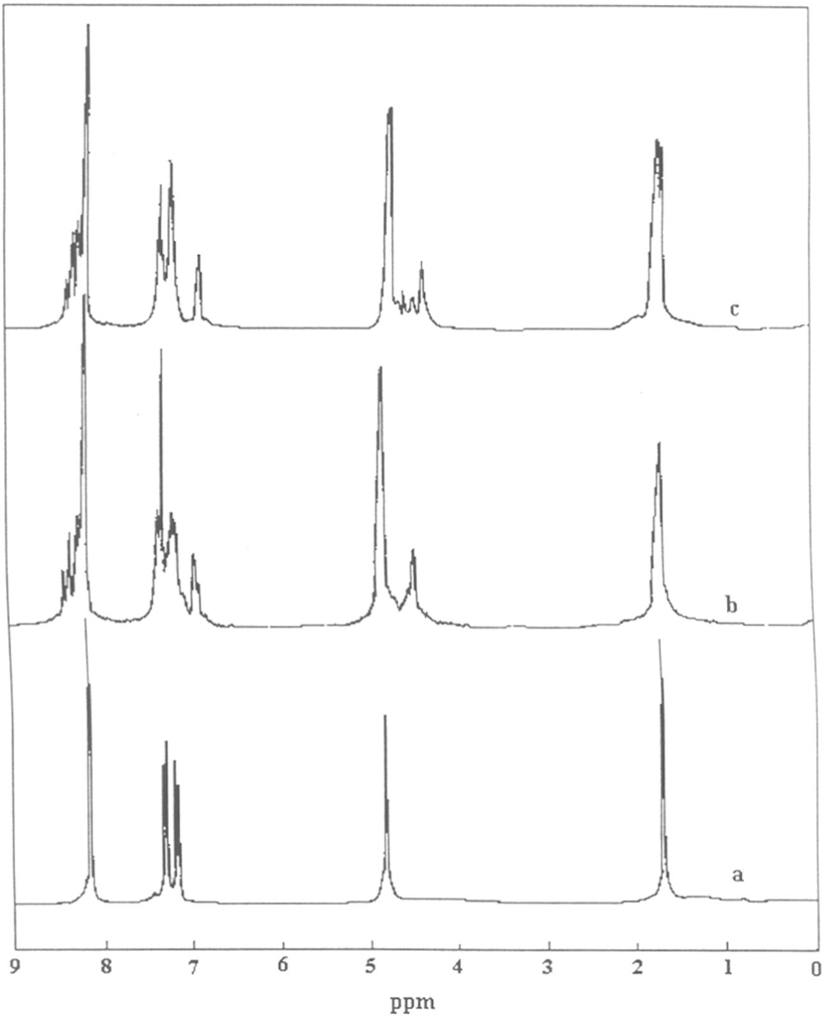


Figure 5.8 : *^{1}H NMR spectra (in $CDCl_3$/TFA, 1:1, v/v) of (a) prepolymer mixture (PC and PET) (b) final copolymer before soxhlet extraction and (c) final copolymer after soxhlet extraction*

The appearance of the peaks at ∂ = 6.7 to 6.9 and ∂ = 4.3 to 4.4 indicates two competitive side reactions: the formation of cyclic ethylene carbonate and the formation of aromatic-aliphatic ether linkages *via* the decarboxylation of the aromatic-aliphatic carbonate moieties formed by the direct ester-exchange reaction.[31]

The FT-IR spectra of PC, PET, PC/PET mixture and the final copolymer is shown in **Figure 5.9**.

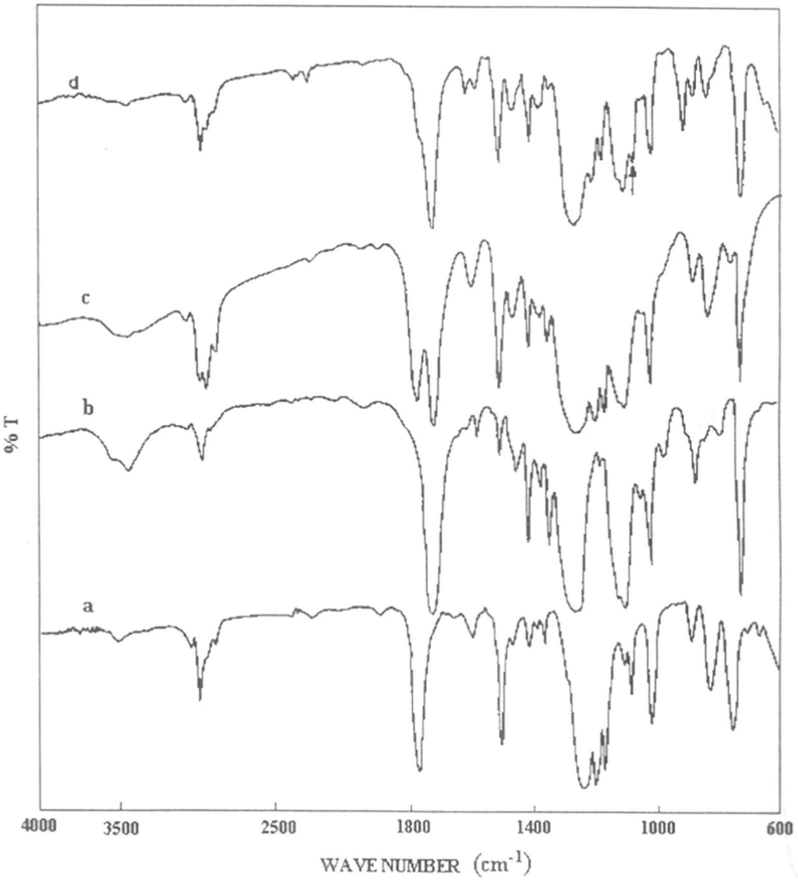


***Figure 5.9** : FT-IR spectra (in KBr) of (a) PC (b) PET (c) PC/PET (50:50, w/w) physical mixture and (d) final copolymer after solid state polymerization. Arrow indicates 1370 cm^{-1} band peak*

The progressive appearance of a well-defined band at 1070 cm^{-1} is observed with the progress of solid state polymerization. This band is attributed to the complex vibration of the aromatic ester structure of the type -Ar-O-C(=O)-Ar-. The occurrence of this structure, bearing evidence to a ester-carbonate interchange reaction, is accompanied by the appearance of a new C=O stretching band, distinct from the ester carbonyl band of PET at 1330 cm^{-1}. However, the effect of the carbonate group is far more pronounced than expected. The intensity of the aromatic carbonate band at 1780 cm^{-1} slowly decreases presumably due to the formation of ethylene carbonate. [11,27]

To further understand the structure of the polymer, the PC blocks in the copolymer were degraded selectively according to the procedure reported by Pilati and coworkers.[2] It was found that after degradation, 27 wt% of the polymer was insoluble in dichloromethane (**fraction I**), whereas, 50 wt% was soluble in dichloromethane, but insoluble in methanol (**fraction II**). The weight loss was 23 wt%. The loss in weight is attributed to the segment containing carbonate linkages, which would completely hydrolyze under the conditions employed. The **fraction I** (η_{inh} = 0.23 dL/g) was identified as pure PET segment from its ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **fraction II** (η_{inh} = 0.17 dL/g) is shown in **Figure 5.10** and consists of both the ethylene terephthalate and bisphenol A moieties. Furthermore, the IR spectrum (**Figure 5.11**) shows only a single carbonyl group, indicating that **fraction II** is a product of exchange reaction in which both an alkyl ester (A) and an aryl ester groups (B) are present.

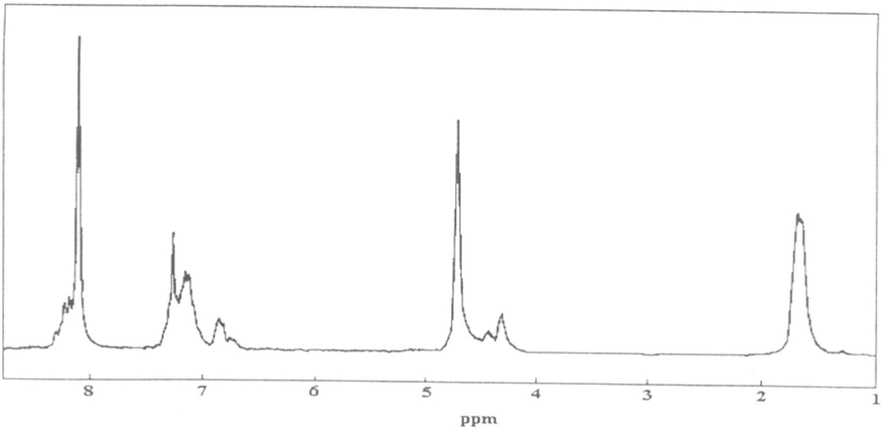


Figure 5.10 : *^{1}H NMR spectra (in $CDCl_3$) of* ***fraction II*** *after selective degradation using piperidine*

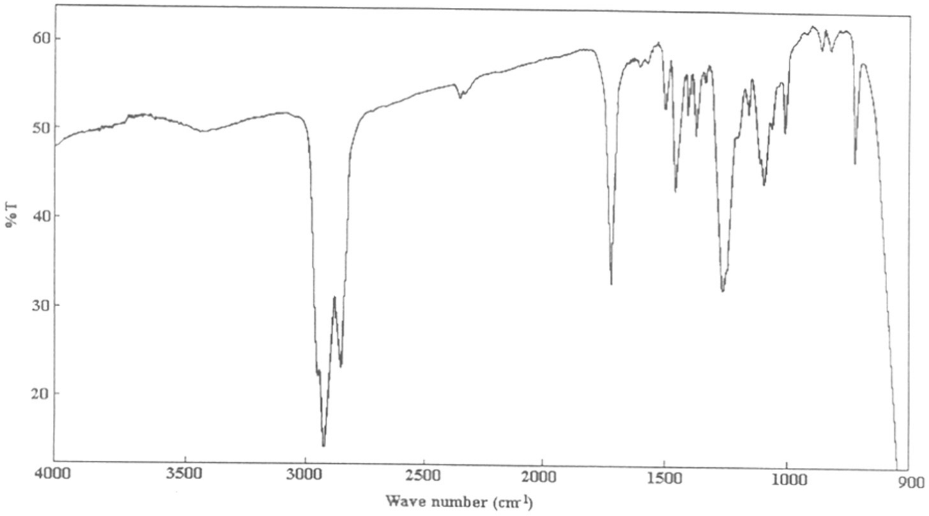
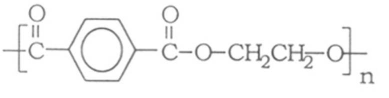
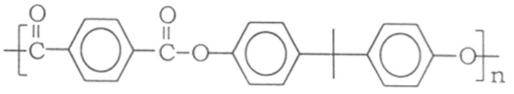


***Figure 5.11** : FT-IR spectra (in nujol) of **fraction II** after selective degradation using piperidine*

From the ^{1}H NMR the relative percentage of these groups can be estimated to be 52% and 48% respectively. The ^{1}H NMR also provides evidence for occurrence of decarboxylation reaction, leading to formation of ether groups.

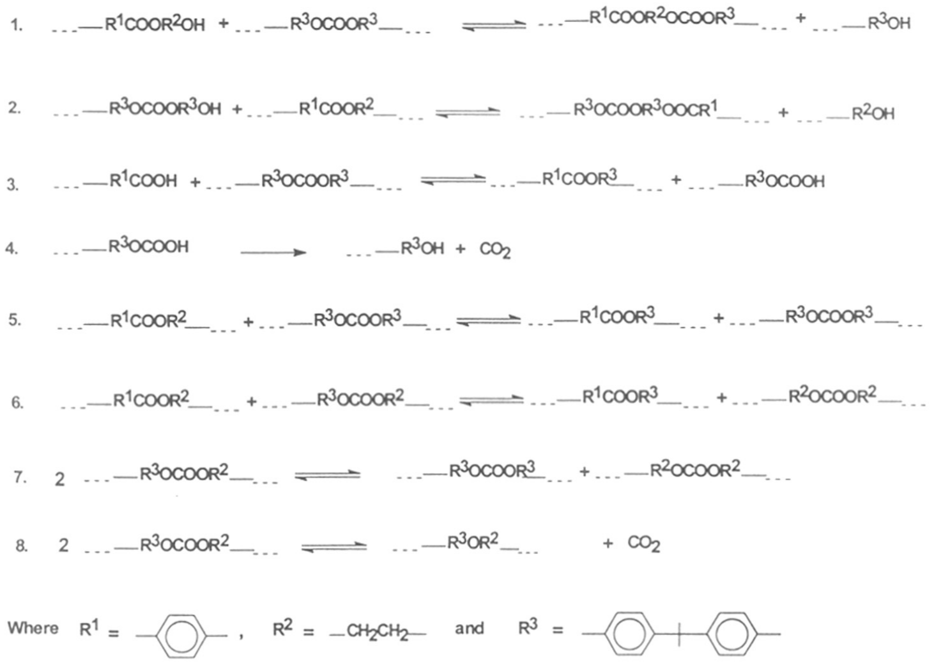


A



B

It is well known that several exchange reactions can take place *via* (intra or intermolecular reactions) during melt mixing of PC and PET.[26,27,31] The results of the present study show that many of the exchange reactions previously reported during the melt blending of PET and PC also occur in the solid state at temperatures below 240 ^{0}C. The most important reactions which occur are shown in **Scheme 1**. Reaction **5-7**, occurs at a relatively higher rate in the melt mixing compared to the others. In solid state as the hydroxyl groups are the active species, therefore reaction **1** and **2** are the most probable reaction along with reaction **5-7**. Reaction **3** and **4** can not take place as it was reported[54] that with the increment of carboxyl group concentration the rate of solid state reaction decreases. From the ^{1}H NMR the formation of ether confirms that reaction **8** also occurs during the reaction.



Scheme 5.1 *: The most important reactions which can occur during the solid state polymerization*

5.4 CONCLUSIONS:

These results indicate that carbonate-ester interchange reactions can occur even in the solid state at temperatures as low as 230 ^{0}C, leading to copolymer formation.

Using this technique poly(arylester-carbonate) and poly(ethylene terephthalate-co-bisphenol A carbonate) can be synthesized. As the ester-carbonate interchange reaction proceeds, the T_g of the copolymer slowly increases and reaches a maximum value of 163 ^{0}C [for poly(arylester-carbonate)] and of 102 ^{0}C [for poly(ethylene terephthalate-co-bisphenol A carbonate)]. In case of poly(arylester-carbonate) T_m slowly increases with the progress of the reaction and crystallization of the polymer is strongly suppressed by the change of the chemical structure. In case of poly(ethylene terephthalate-co-bisphenol A carbonate) the two T_m's of the oligomer mixtures merge as the reaction progresses. The T_m, also slowly increases with the progress of the reaction. Crystallization of the polymer is strongly suppressed by the change of the chemical structure.

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CHAPTER VI

SYNTHESIS OF BIS(HYDROXYETHYL ETHER) OF AROMATIC DIHYDROXY COMPOUNDS AND POLY(ETHER-CARBONATE)S WITH BISPHENOL A

6.1 INTRODUCTION:

Aromatic-aliphatic block poly(carbonate)s containing ether linkages have attracted attention in view of their desirable properties such as high tensile elongation, excellent low temperature characteristics as well as transparency. They are generally synthesized by copolymerizing a bisphenol A polycarbonate block with a polyether block containing appropriate reactive end group. Watanabe and Sato described a soft polycarbonate composition, which consist of a bisphenol A polycarbonate block of $\bar{M}_n$ in the range of 840-1320 and a polyether block derived from poly(tetramethylene)glycol and poly(3-methyltetramethylene)glycol (**Figure 6.1**).[1] These block copolymers exhibit, T_g's in the range of –60 to -67 ^{0}C, high breaking strength (600-700 kg/cm^2) and high elongation at break (400-450 kg/cm^2).

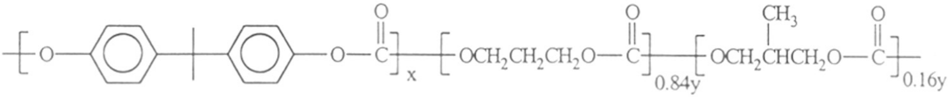
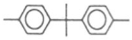


***Figure. 6.1** : Block copoly(ether-carbonate)*

Merrill[2] reported the synthesis of a poly(ether-carbonate) block copolymer using an interfacial technique by reacting bisphenol A polycarbonate with phenolic end group in aqueous alkaline solution with bischloroformate of poly(ethyleneoxy)glycol or poly(tetramethylene)glycol in methylene chloride solution. The introduction of the flexible aliphatic polyether blocks into the chain increases the mobility of the polycarbonate blocks which crystallize during a short curing period at about 60 ^{0}C. The effect was reflected in considerably lowered T_g. Poly(tetramethylene glycol-bisphenol A polycarbonate) shows elastomeric properties (tensile strength at break 100 kg /cm^2; elongation at break 600%; recovery 95%).

Goldberg[3] synthesized elastomeric block copolycarbonate by reacting bisphenol A-poly(oxyethylene) glycol mixture in pyridine with phosgene at 30 ^{0}C. Structure-property relationship in copoly(carbonate)s derived from poly(oxyethylene) glycols (Carbowaxes) have been studied as a function of glycol molecular weight (1000-20,000) and copolymer composition (5-70 wt% or 0.3 to 10 mol% of a 4000 molecular weight glycol). High strength (>700 kg/cm^2) and snappy elasticity (>90% immediate recovery) were found with a copolymer containing poly(oxyethylene) block concentration greater than 3 mol%. These thermoplastic elastomers also exhibit high softening temperatures (>180 °C) and tensile elongation about 700%. Both softening temperature and T_g varied linearly with the poly(oxyethylene) mole ratio over the composition ratio studied.

Rokicki et al.[4] synthesized poly(ether-carbonate) in the melt phase using the reaction of α,ω-diphenolates, cyclic carbonates and dihalocompounds in presence of 18-crown-6. The carbonate content in the polymer was strongly dependent on the reaction temperature. In the temperature range of 100-120 °C the reaction with a participation of a cyclic carbonate predominate due to the facile attack of phenolate anion on the 1,3-dioxolan-2-one ring which results in the formation of relatively high content of carbonate linkages in the product. Beyond 150 °C, only a polyether was obtained due to extensive decarboxylation.

Aliphatic-aromatic polycarbonate of the type $H\text{-}[\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(C{=}O)\text{-}]_n\text{-}$, R =  have been synthesized by phosgenation reaction of bis(hydroxy alkyl ether)s of aromatic dihydroxy compound in presence of pyridine or by the polycondensation reaction of bisaryl or bis(alkyl carbonate) with bis(hydroxyalkyl ether)s of aromatic dihydroxy compounds.[6-8] However, little is known about the properties of these polymers. In the course of a program of work to explore the reaction of phenols with ethylene carbonate, it was found that bis(hydroxyethyl ether) of bisphenol A (**I**) could be conveniently synthesized. Hence, a study was undertaken to synthesize poly(ether-carbonate)s derived from (**I**) and bisphenol A. Controlled introduction of a flexible ether group may be desirable to improve the processability of otherwise difficult to process polycarbonates.

This chapter reports the results of this study.

6.2 EXPERIMENTAL:

6.2.1 Materials:

Bisphenol A (BPA) (**1**) (Aldrich Chemicals, USA) was recrystallized from toluene (mp 158 °C, lit.[9] mp 158 °C). Resorcinol, hydroquinone (Loba Chemicals, Bombay, India) and 4,4'-sulfonyl diphenol (Aldrich Chemical, USA) were recrystallized from suitable solvents as reported in the literature.[9] 1,1-bis(4-hydroxyphenyl) cyclohexane was prepared according to the literature procedure.[10] Ethylene carbonate (Fluka A.G., Switzerland) was vacuum distilled (bp 114 °C at 10 mm of Hg, lit.[9] bp 243 °C at atmospheric pressure). Diphenyl carbonate (E. Merck, Switzerland) was recrystallized from absolute ethanol (mp 78 °C, lit.[9] mp 78 °C). All solvents were purified according to the literature procedure.[10] Dibutyltin oxide (Fascat M & T Chemicals, USA) was used as received. Potassium carbonate (Glaxo Laboratories Ltd. India) was used as received. Tetrabutyl-1,3-diphenoxydistannoxane (mp 137 °C, lit.[11] mp 137 °C) was prepared according to the literature procedure.

6.2.2 Measurements:

Melting points were measured with a Thermonix melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer model 16PC FT-IR spectrometer. ^{1}HNMR and ^{13}C NMR spectra were recorded on Bruker WH-90FT-NMR and Bruker AC-200 NMR spectrometer. Inherent viscosity was determined in an automated Schott Gerate AVS24 using Ubbelohde suspended level viscometer in $CHCl_3$ at 30 °C. T_m and T_g were measured using a Perkin-Elmer thermal analyzer (DSC-7) in N_2 atmosphere at a heating rate of 10 °C/min. Thermal stability of the copolymers were performed on Perkin Elmer Thermal Analyzer (TGA-7), by heating the samples in nitrogen flow at a heating rate of 10 °C/min. The HPLC analysis of the samples were performed in ZORBAX SBC_8 Rp column (7 μm particle size, 250 mm length and 4.6 internal diameter), 2,6-dimethyl naphthalene (DMN) as internal standard and acetonitrile/water solvent, using 60% acetonitrile and 40% water. The detector used is an UV multiwavelength detector (Waters 490E) which is set at 254 nm which was initially changed to 280 nm after an elapsed time of 3 min and finally changed to 264 nm after an elapsed time of 7 min.

6.2.3 Synthesis of bis(hydroxyethyl ether)s of bisphenols:

6.2.3a Synthesis of bis(hydroxyethyl ether)s of bisphenol A (6):

The reaction was carried out in a 50 mL three neck round bottom flask equipped with a nitrogen inlet, a thermowell and a reflux condenser. Bisphenol A (**1**) (5.7 g, 0.025 mol) and ethylene carbonate (4.513 g, 0.05125 mol) were added followed by K_2CO_3 (0.1 mol% of BPA) under a stream of nitrogen. The mixture was heated from room temperature to 160 °C over a period of 1 h. Finally the reaction was carried out at 160 °C for 4.5 h. The product (**6**) formed was separated by column chromatography over an adsorbent bed of column silica gel (60-120 mesh) using petroleum ether and ethyl acetate mixture. The product obtained was characterized by ^{1}H NMR, ^{13}C NMR and FT-IR spectra.

^{1}H NMR (CDCl$_3$, δ):

1.65 [$\mathrm{C(CH_3)_2}$, 6H, s], 3.9 ($\mathrm{-O\text{-}CH_2\text{-}\underline{C}H_2\text{-}OH}$, 4H, t), 4.15 ($\mathrm{-O\text{-}\underline{C}H_2\text{-}CH_2\text{-}OH}$, 4H, t), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d)

^{13}C NMR (DMSO-d$_6$, ppm):

31.2489 [$\mathrm{C(\underline{C}H_3)_2}$], 41.6356 [$\mathrm{\underline{C}(CH_3)_2}$], 60.2429 ($\mathrm{-O\text{-}CH_2\text{-}\underline{C}H_2\text{-}OH}$), 69.9334 ($\mathrm{-O\text{-}\underline{C}H_2\text{-}CH_2\text{-}OH}$), 114.3710 &127.8906 (Ar-C, corresponding to o and m carbons), 143.0683 and 156.9858 (Ar-C, corresponding to quaternary carbons).

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

3478 and 3382 (OH) 1240 and 1186 (C-O-C)

Bis(hydroxyethyl ether)s of other bisphenols (**7-10**) were synthesized using the same procedure. The results are shown in **Table 6.1** and **Table 6.2**.

6.2.4 Synthesis of poly(ether-carbonate) (11) from bis(hydroxyethyl ether) of BPA with diphenyl carbonate:

The reaction was carried out in a glass reactor with a nitrogen inlet. Bis(hydroxyethyl ether) of bisphenol A (**6**) (1.58 g, 5 x 10^{-3} mol) and DPC (1.1235 g, 5.25 x 10^{-3} mol) were added followed by tetrabutyl-1,3-diphenoxy distannoxane (6.68 g, 0.1 mol% of diether) under a stream of nitrogen. The reaction mixture was then heated to 180 ^{0}C in 45 min and maintained at that temperature for 120 min. Thereafter, the temperature was increased to 230 ^{0}C in 15 min and maintained at the same temperature for 30 min. Thereafter, the pressure was reduced from 760 to 1 mm of Hg and maintained under this condition for an additional 120 min. Finally the temperature was increased from 230 ^{0}C to 270 ^{0}C in 30 min and maintained at that temperature for an additional 60 min. During this period the by-product phenol was continuously distilled off and collected. The polymer (**11**) thus formed was dissolved in 50 mL chloroform and the solution poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 ^{0}C for 4 h. Yield : 1.62 g (96%) and η_{inh} = 0.48 dL/g in CHCl$_3$ at 30 ^{0}C.

^{1}H NMR (CDCl$_3$, δ):

1.65 [$\mathrm{C(C\underline{H}_3)_2}$, 6H, s), 4.15 [$\mathrm{-C\underline{H}_2\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}O}$], 4H, t), 4.45 ($\mathrm{-CH_2\text{-}C\underline{H_2}\text{-}O\text{-}C(=O)\text{-}O\text{-}}$, 4H, t), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d).

^{13}C NMR spectral data is given in **Table 6.3**.

Table 6.1 : Synthesis of bis(hydroxyethyl ether) of different aromatic diols

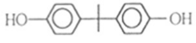
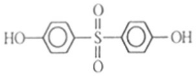
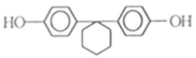
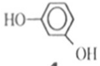
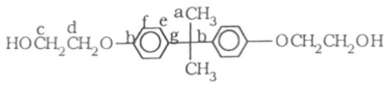
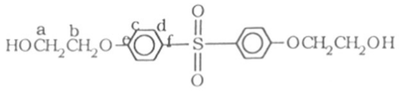
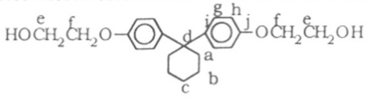
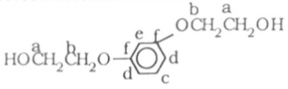
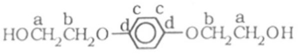
Bis(hydroxyethyl ether) of	Yield (%)	mp (ºC)	Elemental analysis		^{1}H NMR
			Calcd.	obsvd.	(CDCl$_3$, δ, ppm)
 **1**	61	110	-	-	1.65 [C(CH_3)$_2$, 6H, s], 3.9 (-O-CH_2-$\underline{C}H_2$-OH, 4H, t), 4.15 (-O-$\underline{C}H_2$-CH_2-OH, 4H, t), 6.8 (Ar-H, 4H, d), 7.15 (Ar-H, 4H, d)
 **2**	41	179	C = 56.81 H= 5.32 O = 28.40 S = 9.47	C = 56.85 H= 5.08 O = 27.41 S = 10.65	3.85 (-O-CH_2-$\underline{C}H_2$-OH, 4H, t), 4.15 (-O-$\underline{C}H_2$-CH_2-OH, 4H, t), 7.1(Ar-H, 4H, d), 7.85 (Ar-H, 4H, d)
 **3**	56	106	C = 74.14 H= 7.86 O = 18.00	C = 74.49 H= 8.18 O = 17.33	1.55 [-CH_2-, 4H, q], 3.9 (-O-CH_2-$\underline{C}H_2$-OH, 4H, t), 4.15 (-O-$\underline{C}H_2$-CH_2-OH, 4H, t), 6.85 (Ar-H, 4H, d), 7.2 (Ar-H, 4H, d)
 **4**	72	92-93	C = 60.6 H= 7.07 O = 32.33	C = 60.26 H= 7.31 O = 32.43	3.95 (-O-CH_2-$\underline{C}H_2$-OH, 4H, t), 4.1 (-O-$\underline{C}H_2$-CH_2-OH, 4H, t), 6.55 (Ar-H, 3H, d), 7.15 (Ar-H, H, t)
 **5**	63	103	C = 60.4 H= 7.07 O = 32.33	C = 60.64 H= 7.12 O = 32.24	3.65 (-O-CH_2-$\underline{C}H_2$-OH, 4H, t), 3.9 (-O-$\underline{C}H_2$-CH_2-OH, 4H, t), 6.8 (Ar-H, 4H, s)

Table 6.2 : ^{13}C NMR data of bis(hydroxyethyl ether) of bisphenols (6-10)

Compound	a	b	c	d	e	f	g	h	i	j
 **6**	31.25	41.63	60.24	69.93	114.37	127.89	143.07	156.98		
 **7**	59.94	70.69	115.79	129.79	133.94					
 **8**	36.74	22.69	26.02	44.51	59.85	69.49	114.18	127.81	140.68	156.35
 **9**	59.79	69.60	101.45	106.84	130.00	160.04				
 **10**	60.40	70.58	115.96	153.36						

FT-IR ($CHCl_3$, cm^{-1}):

1748 [-O-C(=O)-O-], 1272,1216 and 1194 (C-O-C).

6.2.5 Synthesis of poly(ether-carbonate) (12) from bis(hydroxyethyl ether) of BPA with BPA and diphenyl carbonate:

The reaction was carried out in a glass reactor with a nitrogen inlet. Bis(hydroxyethyl ether) of bisphenol A (**6**) (0.079 g, 2.5 x 10^{-4} mol), bisphenol A (1.083 g, 4.75 x 10^{-3} mol) [bis(hydroxyethyl ether) : bisphenol A = 5 : 95, mol%] and diphenyl carbonate (1.1235 g, 5.25 x 10^{-3} mol) were added followed by tetrabutyl-1,3-diphenoxydistannoxane (6.68 x 10^{-3} g, 0.1 mol% of dihydroxy compound) under a stream of nitrogen. The reaction mixture was then subjected to a programmed increase of temperature and decrease of pressure as described in the previous procedure. The polymer (**12**) thus formed was dissolved in 50 mL chloroform and the solution poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum at 60 ^{0}C for 4 h. Yield : 1.23 g (94%) and η_{inh} = 0.40 dL/g in $CHCl_3$ at 30 ^{0}C.

^{1}H NMR ($CDCl_3$, δ):

1.65 [$C(CH_3)_2$, 12H, s), 4.15 [-$C\underline{H}_2$-CH_2-O-C(=O)-O], 4H, t), 4.45 [-CH_2-$C\underline{H}_2$-O-C(=O)-O-CH_2-, 4H, t), 6.7-7.4 (Ar-H, 16H).

^{13}C NMR spectral data is given in **Table 6.3**.

FT-IR ($CHCl_3$, cm^{-1}):

1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

Other poly(ether-carbonate)s (**13-15**) of bis(hydroxyethyl ether) of bisphenol A (**6**) and bisphenol A (**1**) with diphenyl carbonate were synthesized using the same reaction conditions but by varying the ratio of diether to bisphenol. The results are given in **Table 6.4**.

6.2.6 Synthesis of poly(ether-carbonate) (16) from bis(hydroxyethyl ether) of sulfone diol (7) with BPA and DPC:

Bis(hydroxyethyl ether) of bisphenol S (**7**) (0.338 g, 1 x 10^{-3} mol), bisphenol A (0.912 g, 4 x 10^{-3} mol), diphenyl carbonate (1.1235 g, 5.25 x 10^{-3} mol) and tetrabutyl-1,3-diphenoxy distannoxane (6.68 x 10^{-3} g, 0.1 mol% of dihydroxy compound) were taken in a glass reactor under a stream of nitrogen. The polymerization was carried out as described in **Section 6.2.4.**

Yield = 1.24 g (90%), η_{inh} = 0.49 dL/g (in $CHCl_3$ at 30 ^{0}C)

^{1}H NMR ($CDCl_3$, δ) :

1.7 [C(CH$_3$)$_2$, 6H, s), 4.2 (-O-C$\underline{H}_2$-CH$_2$-O-C(=O)-O-CH$_2$, 4H, t) 4.3 (-O-CH$_2$-C$\underline{H}_2$-O-C(=O)-O-Ar, 4H, t), 4.5 (-O-CH$_2$-C$\underline{H}_2$-O-C(=O)-O-CH$_2$, 4H, t), 4.6 (-O-C$\underline{H}_2$ –CH$_2$-O-C(=O)-O-Ar, 4H, t), 7.8 (Ar-H, 4H, d), 7.15 (Ar-H, 12H, m).

^{13}C NMR spectral data is given in **Table 6.3**.

FT-IR ($CHCl_3$, cm^{-1}):

1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

6.2.7 Synthesis of poly(ether-carbonate) (17) from bis(hydroxyethyl ether) of bisphenol C (8)and BPA with diphenyl carbonate:

Bis(hydroxyethyl ether) of bisphenol C (**8**) (0.178 g, 5 x 10^{-4} mol), bisphenol A (0.456 g, 2 x 10^{-3} mol), diphenyl carbonate (0.562 g, 2.625 x 10^{-3} mol) and tetrabutyl-1,3-diphenoxy distannoxane (3.34 x 10^{-3} g, 0.1 mol% of dihydroxy compound) were taken in a glass reactor under a stream of nitrogen. The polymerization was carried out as described in **Section 6.2.4.**

Yield = 0.68 g (97%), η_{inh} = 0.34 dL/g (in $CHCl_3$ at 30 ^{0}C)

^{1}H NMR ($CDCl_3$, δ):

1.65 [C(CH$_3$)$_2$, 6H, s), 4.15 (-O-C$\underline{H}_2$-CH$_2$-O-C(=O)-O-), 4H, t), 4.45 (-O-CH$_2$-C$\underline{H}_2$-O-C(=O)-O-CH$_2$, 4H, t), 4.55 (-O-$\underline{CH_2}$-CH$_2$-O-C(=O)-O-Ar, 4H, t) 6.8 (Ar-H, 4H, m), 7.2 (Ar-H, 12H, m).

^{13}C NMR spectral data is given in **Table 6.3**.

FT-IR (CH_3Cl, cm^{-1}):

1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

6.2.8 Synthesis of poly(ether-carbonate) (18) from bis(hydroxyethyl ether) of resorcinol (9) with BPA and diphenyl carbonate:

Bis(hydroxyethyl ether) of resorcinol (**9**) (0.198 g, 1 x 10^{-3} mol), bisphenol A (0.912 g, 4 x 10^{-3} mol), diphenyl carbonate (1.1235 g, 5.25 x 10^{-3} mol) and tetrabutyl-1,3-diphenoxy distannoxane (3.34×10^{-3} g, 0.1 mol% of dihydroxy compound) were taken in a glass reactor under a stream of nitrogen. The polymerization was carried out as described in **Section 6.2.4.**

Yield = 1.14 g (92%), η_{inh} = 0.32 dL/g (in $CHCl_3$ at 30 °C)

^{1}H NMR ($CDCl_3$, δ):

1.7 [$C(CH_3)_2$, 6H, s), 4.2 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-CH_2, 4H, t), 4.3 (-O-CH_2-C$\underline{H}_2$-O-C(=O)-O-Ar, 4H, t), 4.5 (-O-CH_2-C$\underline{H}_2$-O-C(=O)-O-CH_2, 4H, t), 4.6 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-Ar, 4H, t), 6.55 (Ar-H, 3H,t) 6.8 (Ar-H, 4H, d), 7.25 (Ar-H, 9H, m).

^{13}C NMR value is given in **Table 6.3**.

FT-IR ($CHCl_3$, cm^{-1}):

1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

6.2.9 Synthesis of poly(ether-carbonate) (19) from bis(hydroxyethyl ether) of BPA, HQ and BPA with DPC:

Bis(hydroxyethyl ether) of bisphenol A (**6**) (0.158 g, 5×10^{-3} mol), hydroquinone (**5**) (0.275 g, 2.5×10^{-3} mol) bisphenol A (**1**) (0.456 g, 2×10^{-3} mol), diphenyl carbonate (0.562 g, 2.625×10^{-3} mol) and tetrabutyl-1,3-diphenoxy distannoxane (3.34×10^{-3} g, 0.1 mol% of dihydroxy compound) were taken in a glass reactor under a stream of nitrogen. The polymerization was carried out as described in **Section 6.2.4.**

Yield = 0.62 g (61%), η_{inh} = 0.28 dL/g (in $CHCl_3$ at 30 °C)

^{1}H NMR ($CDCl_3$, δ):

1.7 [$C(CH_3)_2$, 6H, s), 4.15 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-CH_2, 4H, t), 4.25 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-Ar, 4H, t), 4.5 (-O-CH_2-C$\underline{H}_2$-O-C(=O)-O-CH_2, 4H, t), 4.6 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-Ar, 4H, t), 6.7-7.5 (Ar-H, 22H)

^{13}C NMR spectral data is given in **Table 6.3**.

FT-IR ($CHCl_3$, cm^{-1}):

1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

6.2.10 Synthesis of poly(ether-carbonate) (20) from bis(hydroxyethyl ether) of BPA, HQ and BPA with DPC:

Bis(hydroxyethyl ether) of bisphenol A (**6**) (0.79 g, 2.5 x 10^{-4} mol), hydroquinone (**5**) (0.165 g, 1.5 x 10^{-3} mol) bisphenol A (**1**) (0.741 g, 3.25 x 10^{-3} mol), diphenyl carbonate (1.1235 g, 5.25 x 10^{-3} mol) and tetrabutyl-1,3-diphenoxy distannoxane (6.68 x 10^{-3} g, 0.1 mol% of dihydroxy compound) were taken in a glass reactor under a stream of nitrogen. The polymerization was carried out as described in **Section 6.2.4.**

Yield = 0.1.0253 g (91%), η_{inh} = 0.33 dL/g (in $CHCl_3$ at 30 °C)

^{1}H NMR ($CDCl_3$, δ):

1.7 [$C(CH_3)_2$, 6H, s), 4.15 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-CH_2, 4H, t), 4.25 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-Ar, 4H, t), 4.5 (-O-CH_2-C$\underline{H}_2$-O-C(=O)-O-CH_2, 4H, t), 4.6 (-O-C$\underline{H}_2$-CH_2-O-C(=O)-O-Ar, 4H, t), 6.7-7.5 (Ar-H, 22H)

^{13}C NMR spectral is given in **Table 6.3**.

FT-IR ($CHCl_3$, cm^{-1}):

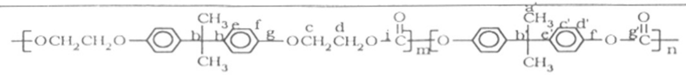
1748 [-O-C(=O)-O-], 1100-1250 (C-O-C).

6.2.11 HPLC analysis of the poly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of BPA with HQ, BPA and DPC:

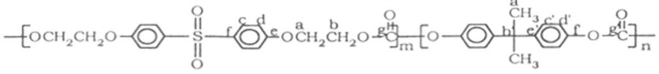
About 0.05 g of the polymer was hydrolyzed with 5 mL 18 wt% methanolic KOH solution. The mol% of HQ incorporated was determined by HPLC after degradative hydrolysis of the polymer using a ZORBAX SBC_8 Rp column, 2,6-dimethyl naphthalene (DMN) as internal standard and acetonitrile/water solvent, using 60% acetonitrile and 40% water. The detector used is an UV multiwavelength detector (Waters 490E) which is set at 254 nm, was initially changed to 280 nm after an elapsed time of 3 min and finally changed to 264 nm after an elapsed time of 7 min.

Table 6.3 : ^{13}C NMR data of copoly(ether-carbonate)s

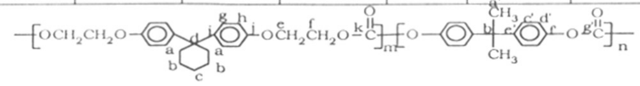
Polymer



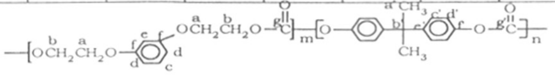
	a	b	c	d	e	f	g	h	i	a′	b′	c′	d′	e′	f′	g′
11	31.23	41.92	65.79	66.52	114.24	127.96	143.85	156.39	155.23							
12	31.04				114.21	128.04				31.04	42.68	120.46	128.04	148.38	149.12	152.25
13	31.08	41.89	65.71	67.00	11424	128.08	143.88	156.36	153.89	31.08	42.69	120.49	128.08	148.22,148.43	149.15	152.30
14	31.23	41.95	65.79	66.54,67.05	114.27	128.02	143.87,143.94	156.40	155.25	31.23	42.74	120.53,120.64	128.02	148.31,148.50	149.23	153.95
15	31.17	41.87	65.74	66.50,67.02	114.21	127.93	143.81	156.33	155.22	31.17	42.65	120.58	127.92	148.28	149.15	153.22



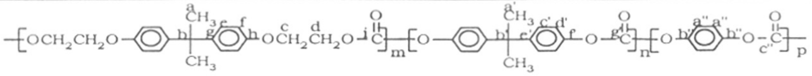
	a	b	c	d	e	f	g	a′	b′	c′	d′	e′	f′	g′
16	66.09	66.43	115.21	129,79	134.65	162.02	153.79	31.08	42.73	120.53	128.10	148.46	149.16	152.33



	a	b	c	d	e	f	g	h	i	j	k	a′	b′	c′	d′	e′	f′	g′
17	45.55	37.72	23.14	26.63	65.63	66.97	114.42	128.29	142.02	156.08	155.91	31.04	42.66	120.46	128.04	14841	149.13	152.28



	a	b	c	d	e	f	g	a′	b′	c′	d′	e′	f′	g′
18	65.84	66.90	102.42	107.69	130.52	159.80	153.87	31.10	42.73	120.51	128.09	148.27,148.46	149.20	152.29



	a	b	c	d	e	f	g	h	i	a′	b′	c′	d′	e′	f′	g′	a″	b″	c″
19	31.14	41.95	65.95	67.45	114.49	128.17	143.92	156.34	155.05	31.14	42.81	120.54	128.07	148.49	149.38	152.07	122.14	148.67	152.90
20	31.03	41.85	6585	66.95	114.22	128.06				31.03	42.68	120.47	128.06	148.40	149.13	152.05	122.09	148.49	152.85

Calibration curve of THPE using DMN as internal standard:

i) Preparation of sample solution for HPLC:

a) A stock solution of DMN was prepared by dissolving 34.6 mg DMN in 25 mL acetonitrile. From that stock solution 0.2 mL was taken for the preparation of the solution.

b) A stock solution of HQ was prepared by dissolving 30.3 mg polymer in 25 mL acetonitrile. From this stock solution 0.5, 1, 3, 4 and 5 mL solution was taken along with 0.2 mL DMN solution in a 10 mL volumetric flask and the volume was made upto the mark.

ii) HPLC analysis for calibration curve:

A minimum three injection was used to confirm the reproducibility in the analysis. Average area and area ratio of HQ to DMN was plotted against corresponding mole ratio (**Figure 6.2**). The slope of the curve was 5.44 and was used directly to calculate the exact quantity of HQ as follows:

Mole ratio = Area ratio x RF

Therefore, mole of HQ = mole of DMN x Area ratio x RF

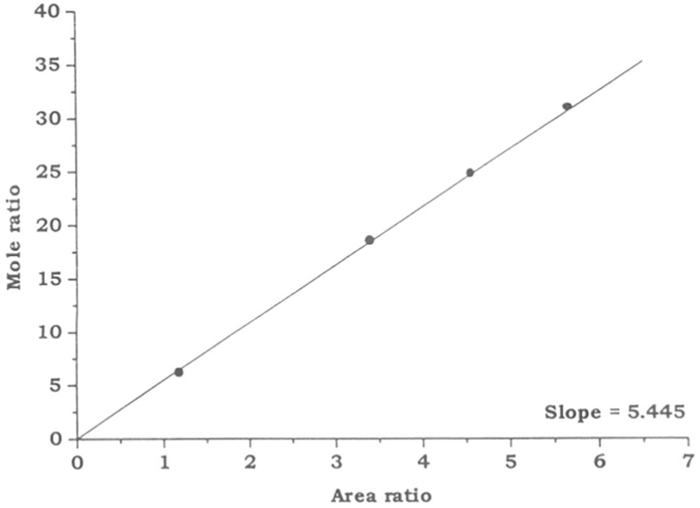


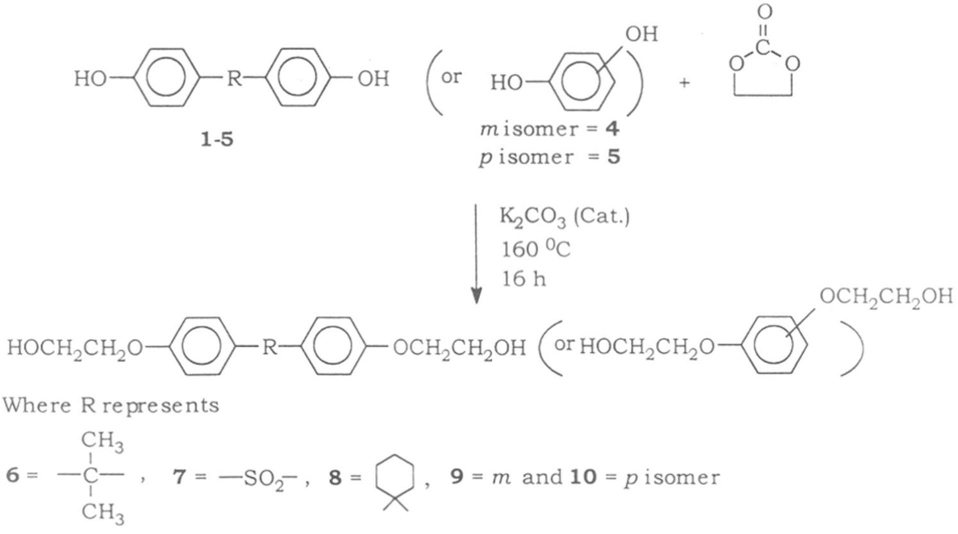
Figure 6.2 : Calibration curve of HQ using DMN as internal standard

6.3 RESULTS AND DISCUSSION:

6.3.1 Synthesis and characterization of bis(hydroxyethyl ether):

Patent literature reports the synthesis of bis(hydroxyethyl ether) of aromatic diols by (a) the reaction of aromatic diols with ethylene carbonate in presence of a basic catalyst,[12] (b) the addition reaction of aromatic diols with an epoxide[13] and (c) disproportionating polycarbonate by reacting with ethylene glycol in presence of a basic catalyst followed by treatment with ethylene carbonate.[14] However, the structure of the product or its purity has not been adequately described in the prior literature.

We have found that the reaction of aromatic diols with ethylene carbonate in presence of potassium carbonate as catalyst is a convenient method for the synthesis of bis(hydroxyethyl ether) of bisphenol A (**6**) with good yields and high purities (**Scheme 6.1**). In general, the obtained yields were lower for bisphenols of lower basicities.



Scheme 6.1** : Synthesis of bis(hydroxyethyl ether) of bisphenols **(6-10)

FT-IR spectrum showed no carbonate peak but bands at 3382 and 3478 cm^{-1} due to -OH stretching vibrations (**Figure 6.3**).

The results are given in **Table 6.1** and **Table 6.2**. ^1H NMR spectrum of bis(hydroxyethyl ether) of bisphenol A (**6**) showed two triplets, at $\delta = 3.9$ and

4.15 ppm due to the methylene protons (**Figure 6.4A**). ^{13}C NMR spectrum showed no carbonate peak in the region of 152-155 ppm (**Figure 6.4B**).

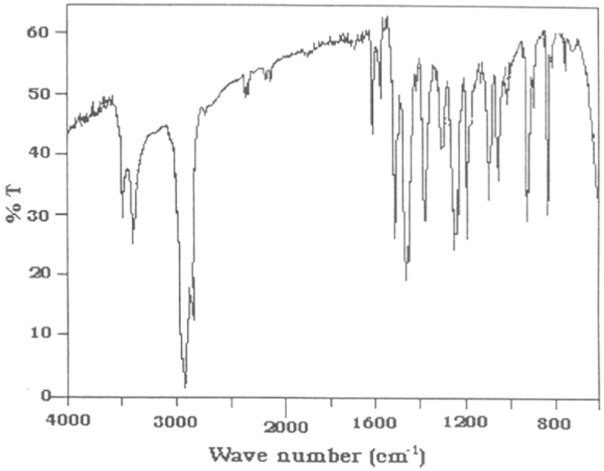


Figure 6.3 *: FT-IR spectrum of bis(hydroxyethyl ether) of bisphenol A (**6**)*

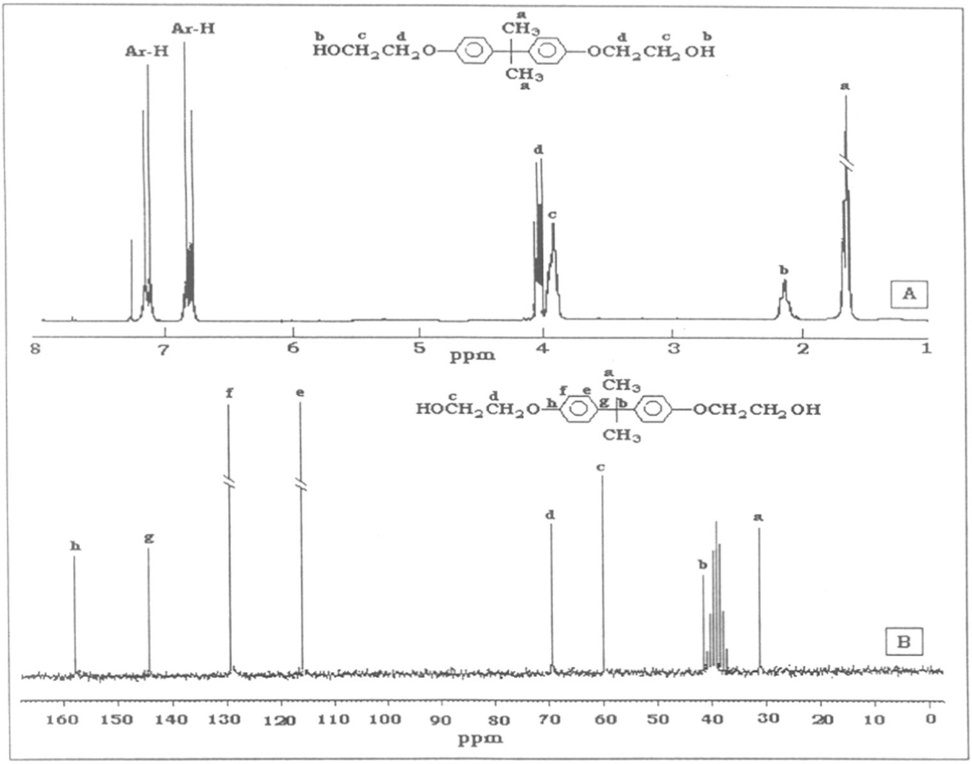
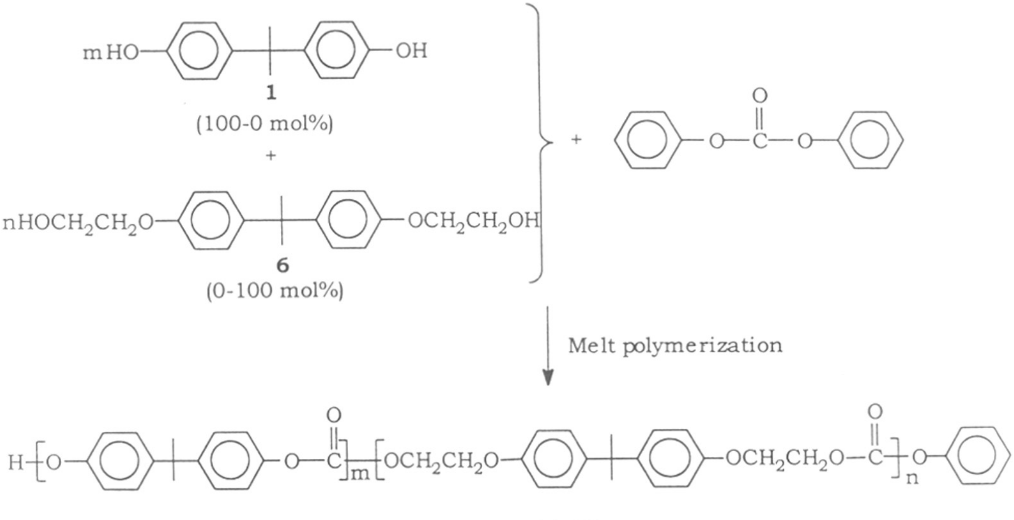


Figure 6.4 *: (**A**) ^{1}H NMR and (**B**) ^{13}C NMR spectrum of bis(hydroxyethyl ether) of BPA (**6**)*

6.3.2 Synthesis of poly(ether carbonate):

6.3.2a Synthesis of poly(ether-carbonate) of bis(hydroxyethyl ether) of bisphenol A with bisphenol A and diphenyl carbonate:

Polymerization reaction was conducted using the bis(hydroxyethyl ether) of bisphenol A with bisphenol A (BPA) and diphenyl carbonate in the melt phase, at 270 °C and under reduced pressure. Tetrabutyl-1,3-diphenoxy distannoxane (0.1 mol%) was used as catalyst. The reaction was carried out using different ratios of bis(hydroxyethyl ether) of BPA and BPA (**Scheme 6 2**).



11-15

Scheme 6.2 *: Synthesis of poly(ether-carbonate)s using different ratios of bis(hydroxyethyl ether) of bisphenol A and bisphenol A*

The results are shown in **Table 6.3** and **Table 6.4**. In all the cases the conversions to polymer were >90%. The inherent viscosity of the copolymer obtained was in the range of 0.3 to 0.5 dL/g, in $CHCl_3$ at 30 °C. The composition of the copolymer was determined by ^1H NMR spectra. In all cases, the incorporation of the ether linkages was near quantitative.

6.3.2b Synthesis of pol(ether-carbonate) of bis(hydroxyethyl ether) of bisphenols (7-9) with bisphenol A and diphenyl carbonate:

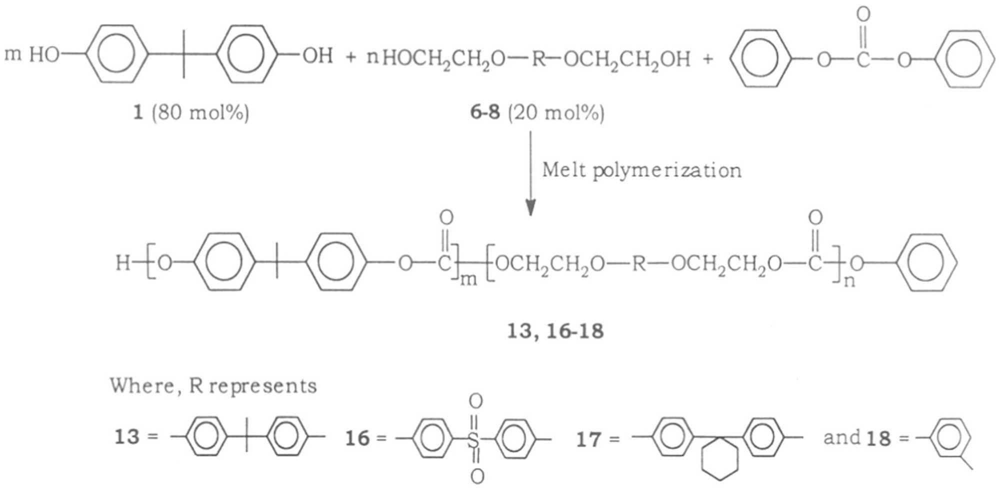
The polymerization reaction was conducted using the bis(hydroxyethyl ether) of bisphenols (**7-9**) and bisphenol A (BPA) with diphenyl carbonate in the melt phase, at 270 °C and under reduced pressure. The reaction was carried out

Table 6.4 : Synthesis of poly(ether-carbonate) by reaction of bis(hydroxyethyl ether) of BPA with BPA and DPC

Sr. No.	Diether in feed (mol%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	IDT[c] (°C)	Diether incorporated[d] (mol%)
1	100	0.46	62	372	100
2	70	0.44	74	377	68
3	50	0.37	82	365	55
4	20	0.33	113	386	18
5	5	0.40	132	382	3

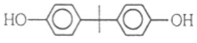
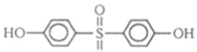
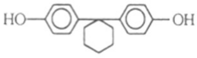
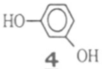
a) In $CHCl_3$ at 30 °C.
b) By DSC at a scaning rate of 10 °C/min under nitrogen.
c) By TGA at a scanning rate of 10 °C/min under nitrogen
d) From ^1H NMR.

using a 20 : 80 mol ratio of bis(hydroxyethyl ether) of bisphenols and BPA (**Scheme 6.3**). The results are shown in **Table 6.3** and **Table 6.5**. The inherent viscosity of the copolymer obtained was in the range of 0.3 to 0.5 dL/g, in $CHCl_3$ at 30 °C. The composition of the copolymer was determined by ^1H NMR spectra. In all cases, the incorporation of the ether linkages was near quantitative.



Scheme 6.3 : Synthesis of poly(ether-carbonate)s of bis(hydroxyethyl ether) of bisphenols with BPA and DPC

Table 6.5 : Synthesis of poly(ether carbonate) by reaction of bis(hydroxyethyl ether) of bisphenols with BPA and DPC

Bishydroxy ethyl ether of	η_{inh} [b] **(dL/g)**	T_g [c] **(°C)**	**IDT** [d] **(°C)**	**Diether incorporated** [e] **(mol%)**
 1	0.33	113	386	18
 2	0.49	136	357	20
 3	0.34	117	368	18
 4	0.32	100	380	26

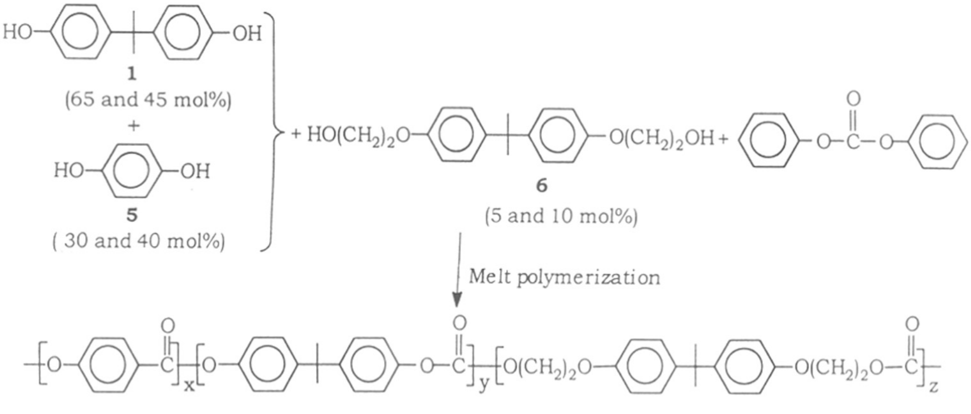
a) *[Bis(hydroxyethyl ether)]:[BP-A] = 20:80*
b) *In $CHCl_3$ at 30 °C*
c) *By DSC at a scaning rate of 10 °C/min under nitrogen.*
d) *By TGA at a scanning rate of 10 °C/min under nitrogen*
e) *From ^1H NMR.*

6.3.2c Synthesis of poly(ether-carbonate) of bis(hydroxyethyl ether) of bisphenol A (1) with hydroquinone, bisphenol A and diphenyl carbonate:

Brunelle et al.[15,16] have reported that solvent resistant polycarbonate can be synthesized from cyclic oligocarbonate of BPA and HQ incorporation. Incorporation of HQ is difficult in polycarbonate structure, since, even small amounts of HQ renders the polycarbonate insoluble and intractable. It was, therefore, reasoned that incorporation of a small amount of bis(hydroxyethyl ether) of bisphenol A (**6**) along with BPA and HQ could enable the synthesis of solvent resistant polycarbonates which are tractable. Hence, the polymerization reaction was conducted using the bis(hydroxyethyl ether) of bisphenol A (**6**) with hydroquinone (**5**), bisphenol A (**1**) (BPA) and diphenyl carbonate in the melt phase, at 270 °C and under reduced pressure. The reaction was carried out using a mole ratio of bis(hydroxyethyl ether) of BPA (**6**) : BPA (**1**) : HQ (**5**) =

10:40:50 (**19**) and 5:65:30 (**20**) (**Scheme 6.4**). The results are given in **Table 6.6**.

In both the cases some insoluble product was obtained. In the case of (**19**) 84% of the product was soluble of which only 61% could be precipitated from methanol with an inherent viscosity 0.28 dL/g whereas, in case of (**20**) 91% of the product was soluble with an inherent viscosity 0.33 dL/g (**Table 6.6**).



19 and 20

***Scheme 6.4** : Synthesis of copoly(ether-carbonate) (**19 and 20**)*

Table 6.6 : Synthesis of poly(ether-carbonate)s from bis(hydroxyethyl ether) of BPA, BPA and HQ

Polymer	**BPA:Diether:HQ (mol%)**	η_{inh}^{a} **(dL/g)**	**T$_g$^{b} (°C)**	**Soluble polymer^c (wt%)**	**HQ incorporated in the copolymer (mol%)**
19	45:10:40	0.28	104	84	12
20	65:5:30	0.33	120	91	14

a) In $CHCl_3$ at 30 °C.
b) By DSC at a scanning rate of 10 °C/min
c) In $CHCl_3$.

6.3.3 Structural Characterization of the polymer:

Structural characterization of the copolymers were carried out using ^1H NMR, ^{13}C NMR and FT-IR spectra.

6.3.3a Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenol A with bisphenol A and diphenyl carbonate:

^{1}H NMR spectrum provides evidence for the formation of the copolymer. The ^{1}H NMR spectra of (**11**) showed that the peak at 3.8 ppm of (**6**) is disappeared and a new signal appeared at 4.45 ppm due to the formation of carbonate linkage (-C$\underline{H}_2$-O-C(=O)-O-C$\underline{H}_2$). The ^{1}H NMR spectra of copolymers (**12-15**) showed the signal at 3.8 ppm due to bis(hydroxyethyl ether) disappeared and new signals appeared at 4.45 ppm due to the methylene protons [-O-CH$_2$-C$\underline{H}_2$-O-C(=O)-O-Ar-] and 4.45 ppm due to [-O-CH$_2$-C$\underline{H}_2$-O-C(=O)-O-CH$_2$-] (**Figure 6.5A**).

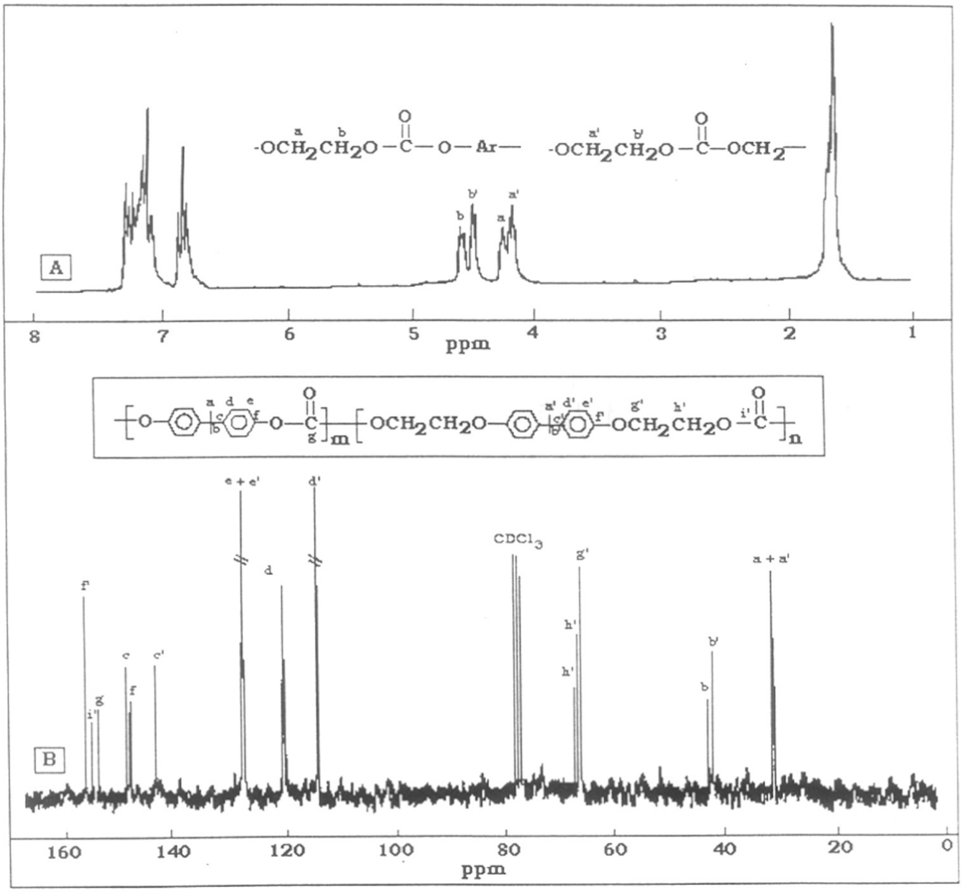


*Figure 6.5 : (**A**) ^{1}H NMR and (**B**) ^{13}C NMR of poly(ether-carbonate) prepared from bis(hydroxyethyl ether) of BPA and BPA (50 : 50, mol ratio) with DPC*

In all cases, the mole ratio of bis(hydroxyethyl ether) of BPA and BPA in the polymer was almost identical to that of the ratio of the monomers in the feed (**Table 6.4**).

The ^{13}*C NMR spectra of* (**11**) showed one carbonate at 155.23 ppm due to aliphatic carbonate group [–CH_2-O-C(=O)-O-CH_2-, **A**] and that of (**12**) showed one carbonate peak at 152.25 ppm due to aromatic carbonate linkage [-Ar-O-C(=O)-O-Ar-, **B**]. The carbonate linkage of (**12**) due to **A** was not detectable by ^{13}C NMR as the amount of (6) incorporated in the polymer is very less (3%). The ^{13}C NMR spectra of the copolymers (**13-15**) showed two carbonate peaks at 153.95 and 155.25 ppm, respectively, which confirm the formation of the copolymer (**Table 6.3**). The ^{13}C NMR spectra of (**14**) is given in **Figure 6.5B**.

FT-IR spectrum of the copolymer (**11**) showed one peak at 1748 cm^{-1} due to aliphatic carbonate. In case of copolymers (**12-15**) a broad peak at 1775 cm^{-1} due to the aromatic carbonate [-Ar–O-C(=O)-O-Ar-, **B**] linkage. The peak at 1748 cm^{-1} due to the aliphatic carbonate linkage (-CH_2-O-C(=O)-O-CH_2-, **A**) was not resolved from the former peak (**Figure 6.6**).

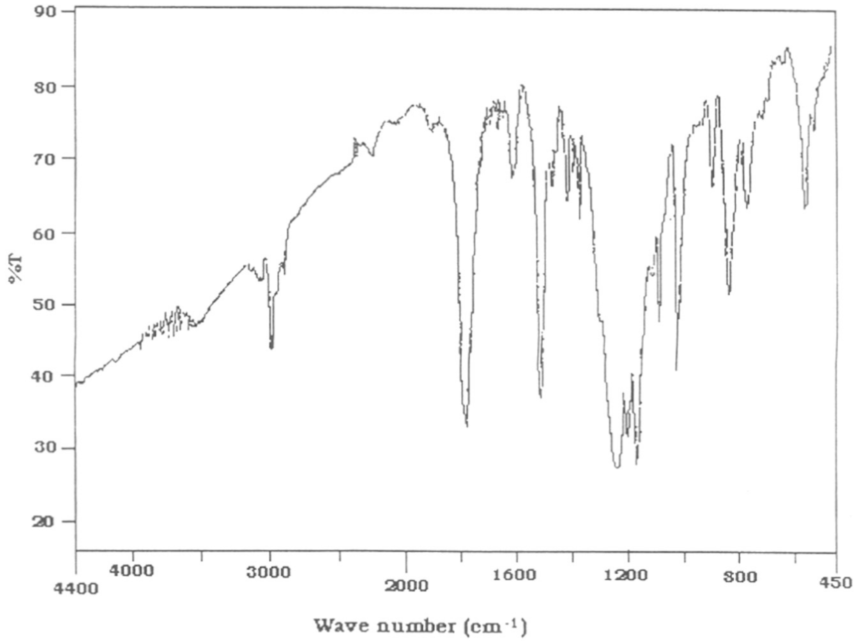


Figure 6.6 : FT-IR spectrum of *poly(ether-carbonate) prepared from bis(hydroxyethyl ether) of BPA and BPA (50 : 50, mol%) with DPC*

6.3.3b Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenols with bisphenol A and diphenyl carbonate

The ^{1}H NMR ^{13}C NMR and FT-IR spectra of copolymers (**16-18**) showed same type of observations as in the case of (**13**).

6.3.3b Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenols with bisphenol A and diphenyl carbonate

From ^{1}H NMR and FT-IR spectra of the copolymers (**19** and **20**) we can not draw any conclusion whether HQ was incorporated in the polymer or not. The ^{13}C NMR spectra (**Table 6.3**) (**Figure 6.7**) of (**19**) showed two carbonate peaks at 152.07 and 152.90 ppm due to the aromatic carbonate linkage [Ar-O-<u>C(=O)</u>-O-Ar] attached with BPA and HQ.

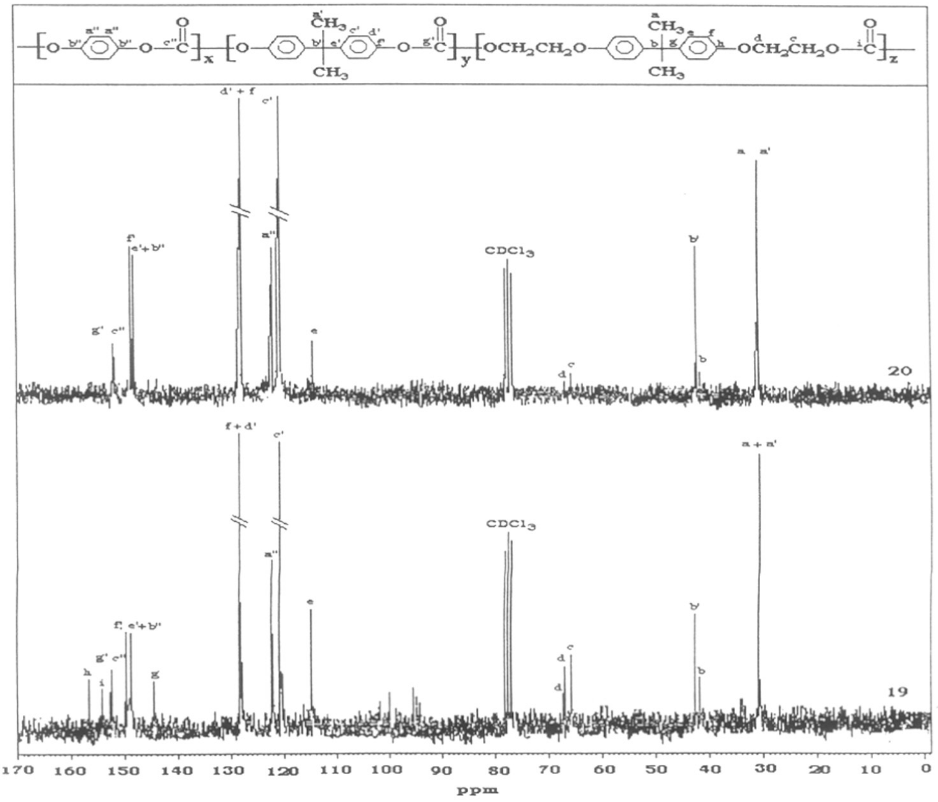


*Figure 6.7 : ^{13}C NMR spectrum of copoly(ether-carbonate) (**19**) and (**20**)*

The carbonate peak at 153.0 ppm appeared due to aliphatic carbonate linkage [CH_2-O-<u>C(=O)</u>-O-CH_2]. Whereas, poly(ether-carbonate) (**20**) showed three carbonate peaks at 152.05 and 152.85 ppm due to aromatic carbonate linkage [-Ar-O-C(=O)-O-Ar-] attached with BPA and HQ and 153.05 ppm due to aliphatic carbonate group [CH_2-O-C(=O)-O-CH_2] was not detected in the ^{13}C NMR spectra as the amount of (**6**) used for the synthesis of (**20**) was very less (**5 mol%**) (**Figure 6.7**).

6.3.4 Thermal characterization of the copolymer:

Thermal characterization of the copolymer was performed by DSC and TGA.

6.3.4a Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenol A with bisphenol A and diphenyl carbonate:

The DSC thermogram of the copolymers (**11-15**) showed that all are amorphous in nature. The T_g of the copolymers (**11-15**) progressively decreases with increasing mol% of bis(hydroxyethyl ether) of bisphenol A (**Figure 6.8**). This is a reflection of the presence of a conformationally more flexible ether groups in the polycarbonate.

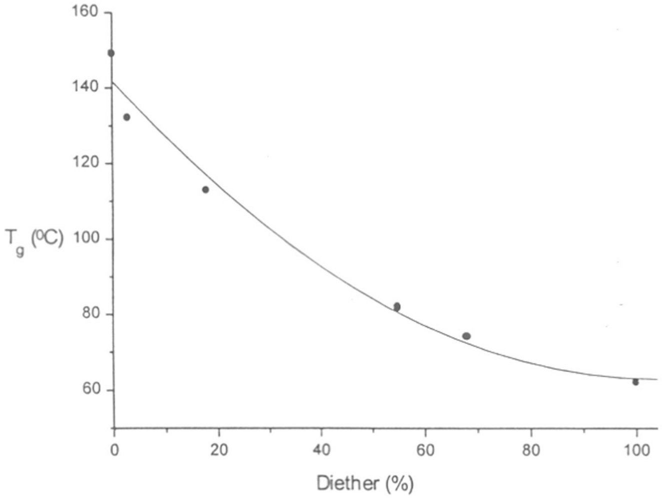


***Figure 6.8** : Change of T_g of poly(ether-carbonate) with the change of %bis(hydroxyethyl ether) of BPA*

The thermogravimetric analysis of the copolymer showed that the copolymers were stable upto 380 °C, which is about 20 °C lower than the decomposition temperature of polycarbonate (**Figure 6.9**). The lower thermal stability attributed to the ether linkages in the copolymer, which undergoes chain scission by elimination of hydrogen β to the oxygen group.

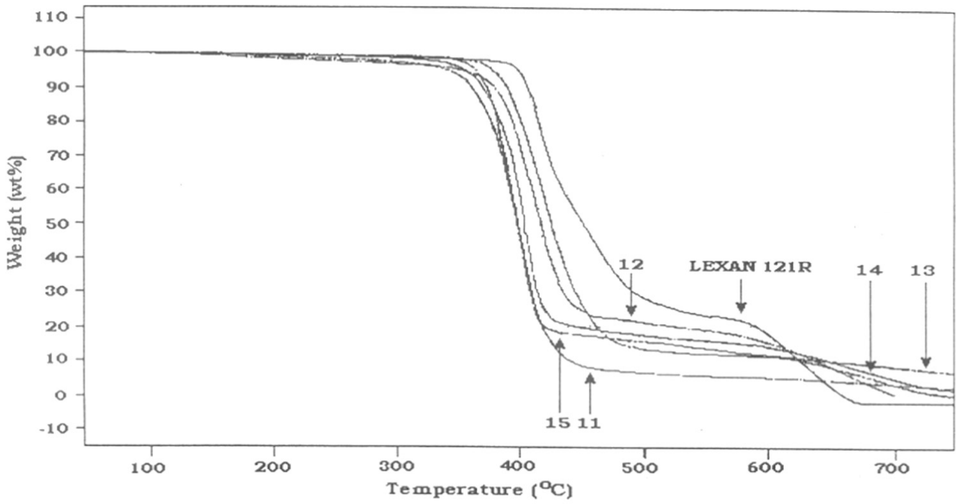


Figure 6.9 : Thermogravimetric analysis of copoly(ether-carbonate)s prepared from bis(hydroxyethyl ether)of BPA with BPA and DPC

6.3.4b Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenols with bisphenol A and diphenyl carbonate:

The T_g of the copolymers (**16-18**) are given in **Table 6.5**, which showed bis(hydroxyethyl ether) of sulfone diol (**7**) gives maximum T_g (136 °C) which is comparable with bisphenol A polycarbonate, whereas, bis(hydroxyethyl ether) of resorcinol (**8**) gives lowest T_g (100 °C).

The thermogravimatric analysis of the copolymers (**16-18**) were compared with (**13**) and LEXAN 121R (**Figure 6.10**). The copolymer (**18**) showed the stability upto 380 °C which is comparable with (**13**). But in case of copolymer (**16** and **17**) the IDT is 357 °C 370 °C respectively. The reason may be due to the rigidness of the bisphenol moiety in this two copolymer.

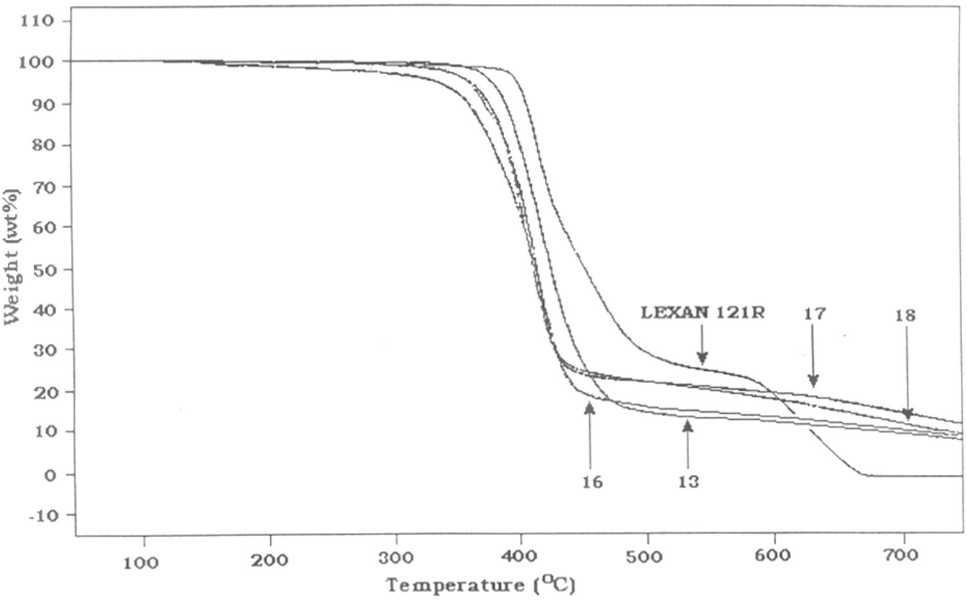


Figure 6.10 : Thermogravimetric analysis of the copoly(ether-carbonate)s of bis(hydroxyethyl ether) of bisphenols with BPA and DPC

6.3.5 Determination of HQ content in the copoly(ether-carbonate) synthesized from bis(hydroxyethyl ether) of BPA with HQ, BPA and DPC:

The mol% of HQ incorporated in the copolymers (**19** and **20**) was determined by HPLC after degradative hydrolysis of the polymer using a ZORABAX SBC$_8$ Rp column, DMN as internal standard and acetonitrile/water solvent system. The retention time of HQ was 2.24 min and that of DMN was 8.58 min (**Figure 6.11**). The calibration curve was drawn using area ratio *vs* mole ratio of HQ to DMN. From the slope of the curve the response factor was determined and was found to be 5.44. Based on known mol% of DMN and the area ratio of HQ to DMN obtained in the sample, the mol% HQ was calculated using the response factor. The results are given in **Table 6.6**, which showed that only 12-14 mol% HQ was incorporated in the copolymer.

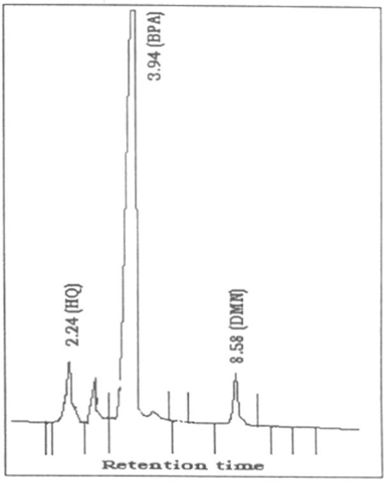


***Figure 6.11** : HPLC spectrum of saponified product of poly(ether -carbonate) (**20**)*

6.4 CONCLUSIONS:

Copoly(ether-carbonate)s with T_g's ranging from 62–140 °C were synthesized by a melt phase polycondensation reaction of bis(hydroxyethyl ether) of bisphenols with bisphenol A and diphenyl carbonate. Using bis(hydroxyethyl ether)s of a variety of bisphenols, a wide range of poly(ether-carbonate)s could be synthesized.

Copolycarbonates of HQ, BPA and bis(hydroxyethyl ether) of BPA were syntheiszed. However, more than 14 mol% HQ could not be incorporated in the copolymer chain *via* melt phase reaction.

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CHAPTER VII

CONCLUSIONS

The results embodied in this thesis is an outcome of the research aimed at synthesizing homo and co-poly(aryl carbonate)s using melt phase chemistry.

Cyclic carbonates, such as, ethylene carbonate is readily available, have desirable physical properties and are prepared from carbon dioxide and ethylene oxide.[1] Reaction of hydroxy compounds with ethylene carbonate have been well known in the literature. The reaction was generally conducted using basic inorganic compounds, organic base, phase transfer catalysts. Carbonate interchange reaction of ethylene carbonate with aliphatic hydroxy compounds were also catalyzed by the organometallic catalysts. All the reactions were conducted under homogeneous condition with or without the use of solvent. Basic ion exchange resin[12] containing quarternary ammonium group has been described for the synthesis of dialkyl carbonate from ethylene carbonate and aliphatic hydroxy compounds. Few zeolites were also found to be active for the synthesis of aliphatic carbonates. However, the yield was not high (~60%). The advantage of solid base catalyst is that it can be easily separated from the reaction medium.

Carbonate interchange reaction of ethylene carbonate with aromatic hydroxy compound is far less studied and is complicated by the competing decarboxylation reaction. There exists only one report, which reports the synthesis of diphenyl carbonate from ethylene carbonate using organotin catalyst. The reaction of ethylene carbonate with aromatic hydroxy compound can either lead to an aromatic carbonate or a decarboxylated product depending on the nature of the ring opening reaction.

Hence, the present study of the reaction of alcohols with ethylene carbonate was undertaken with a view to identify suitable catalysts capable of giving high rate of conversion and easily separable from the reaction media. ETS-10 exchanged with different alkali metal cations (Na, K and Cs) and KL was identified for this reaction. The results obtained with these catalysts were compared with a conventional Lewis acid catalyst, namely, titanium-n-butoxide. The rate of carbonate interchange reaction using a zeolite catalyst was found to be significantly faster compared to the titanium-n-butoxide catalyst. Among the different type of alkali metal exchanged zeolite it was observed that the conversion was not only dependent on the wt% of alkali metal exchanged in the catalyst but also the size on the alkali metal. For this reason Na-ETS-10 (Na content = 8.2 wt%) produced dialkyl carbonates at a much faster rate compared to Cs-ETS-10 (Cs content = 17.6 wt%)

The reaction of phenol with ethylene carbonate was also studied using different catalysts and reaction conditions. It is concluded that with aromatic hydroxy compounds, decarboxylation is the predominant mode of reaction, especially with basic catalyst. The reaction of BPA with ethylene carbonate also produce decarboxylated product in presence of distannoxane as a catalyst. It was also concluded that aromatic poly(carbonate)s can not be prepared from fully aliphatic polycarbonate by a carbonate interchange reaction.

Substantial research has been invested towards the development of a viable nonphosgene route for the synthesis of poly(aryl carbonate)s. The melt phase carbonate reaction was proven to be feasible but one of the drawbacks associated with it is the melt viscosity increases dramatically with increase in molecular weight, leading to problems in agitation and heat transfer. This, in turn, adversely impacts on product quality. Specialized equipments capable of providing efficient heat/mass transfer at high melt viscosities (upto 13,000 poise at 300 ^{0}C) are needed to conduct melt phase carbonate interchange reaction, especially for the synthesis of poly(aryl carbonate)s with $[\eta] > 0.45$ dL/g.

Low molecular weight poly(aryl carbonate) oligomers could be chain extended in the solid state under defined conditions to high molecular weight polymers ($\bar{M}_v > 60{,}000$). This technique removes the limitations of the melt phase process for producing poly(aryl carbonate)s with wide range of molecular weights. Influence of various reaction parameters, such as, type of reactor used, time, temperature, catalyst (metal-free bioxyanions and conventional catalysts), initial crystallinity, initial molecular weight and initial end group concentration on the rate of solid state polymerization were studied in a fluidized bed reactor. The changes in crystallinity and melting temperature of poly(aryl carbonate) synthesized by solid state polymerization were explored. It is proposed that solid state polymerization of poly(aryl carbonate) involves simultaneous occurrence of chain extension as well as increase in crystallinity (increase in T_m). Kinetic parameters for the solid state polymerization reaction were evaluated. Chemical reaction was found to be rate-controlling step in the solid state polymerization. The Arrhenius relationship was found to be $k = 1.41 \times 10^8 \exp(-4807/RT)$, h^{-1}.

Branched poly(aryl carbonate)s were synthesized by solid state polymerization technique. The amount of branching agent incorporated in the polymer was determined quantitatively using HPLC after saponification of the polymer. The branching reactions were found to be quantitative under these conditions.

The synthesis of poly(ester-carbonate)s by melt phase or interfacial routes is beset with several problems. Solid state copolymerization was found to overcome many of these problems. The polymerization was carried out using poly(aryl carbonate)s with poly(aryl ester)s or poly(ethylene terephthalate) oligomers in the presence of a suitable catalyst below 230 ^{0}C. Prior to solid state polymerization, the oligomer mixtures were crystallized using ethyl acetate or acetone and pulverized to 250 to 520 μ size. The products were analyzed by ^{1}H NMR, DSC and viscosity. It is proposed that solid state polymerization of two chemically distinct oligomers involves ester-carbonate interchange reaction with simultaneous chain extension. The results establish that ester-carbonate interchange reaction can occur at appreciable rate at as low a temperature as 240 ^{0}C.

Different bis(hydroxyethyl ether)s were synthesized from bisphenols and ethylene carbonate and were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. Poly(ether-carbonate)s were synthesized using bis(hydroxyethyl ether) of bisphenols and bisphenol A with diphenyl carbonate by the melt phase carbonate interchange reaction. Structure-property relationships were examined in poly(ether carbonate). With increasing content of bis(hydroxyethyl ether) in the copolymer, the T_g of the polymer was found to decrease.

In summary:

Zeolite catalysts could be employed for the synthesis of dialkyl carbonates by carbonate interchange reaction of aliphatic alcohols with ethylene carbonate. More than 90% conversion is obtained in 2 h. The synthesis of branched poly(aryl carbonate)s using solid state polymerization technique was demonstrated. The research has also led to the synthesis of the copoly(ester-carbonate) using solid state polymerization of poly(aryl carbonate)s and poly(arylester)s or poly(alkylester)s oligomer. The occurrence of carbonate-ester interchange reaction at temperatures substantially lower than hiterthofore reported was demonstrated. Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenols and bisphenol A with diphenyl carbonate in the melt phase produced a range of copolymer structures with T_g ranging from 62 to 140 ^{0}C. These are novel soft segment containing copoly(aryl carbonate)s.

Additional thoughts for future work:

The present research has raised a number of new questions that still await answers.

The use of reusable heterogeneous catalyst in the condensation and polycondensation reaction has significant interest in industrial point of view. Zeolites are that kind of catalyst which are very reactive, easily separable and reusable. Further exploration in this area for the synthesis of dialkyl carbonate is required. Use of pressure and high temperature may have potential benefits in the conversion. Fully aliphatic polycarbonate with high molecular weights and free of ether linkages can be synthesized from ethylene carbonate using such catalysts.

The solid state polycondensation technique for poly(aryl carbonate)s too requires further exploration. In the area of branched polycarbonate detailed study is required by using different types of branching agent during SSP which may lead to branched poly(aryl carbonate)s with new properties and applications. Use of difunctional coupling agent in the solid state to improve the efficiency of chain extension may be interesting. Copolymer of different block length can be prepared by proper choice of oligomers with proper molecular weight, catalyst and using appropriate reaction condition. Liquid crystalline block copolycarbonate could be prepared by reacting polycarbonate oligomer with liquid crystalline oligomer with sufficient reactive end groups. There is a wide scope for practical applications of SSP in the area of recycling of poly(aryl carbonate) wastes.

The bis(hydroxy ethyl) ether of bisphenols can be used as monomer along with bisphenol A for the synthesis of copoly(aryl ester) with low T_g *and high impact strength by varying the ratio of bisphenol A to bis(hydroxy ethyl) ether of bisphenols. This type of copolyester may fill the middle ground between poly(aryl ester) and poly(ethylene terephthalate).*

SYNOPSIS OF THE THESIS

The thesis entitled ***"Synthesis and characterization of homo and copoly(aryl carbonate)s via carbonate interchange reaction"*** is divided into seven chapters.

INTRODUCTION:

Poly(aryl carbonate)s based on bisphenol A have gained importance as an engineering thermoplastic owing to its unusual combination of properties, such as, glass like transparency, high impact strength and high heat distortion temperature.[1] Poly(aryl carbonate)s are prepared by phosgene route or by melt phase carbonate interchange reaction.

With increasing global concern[2] over the use of toxic chemicals, such as, phosgene and environmentally unfriendly chlorohydrocarbons, renewed interest has been focused on a viable nonphosgene route to poly(aryl carbonate)s.

The melt phase carbonate interchange reaction of diaryl carbonate with bisphenol A has been known to be technically feasible.[2] However, a non-phosgene route to diphenyl carbonate based on the carbonate interchange reaction of phenol with dimethyl carbonate has been developed only recently.[3] Dimethyl carbonate is available by direct carbonylation of methanol using a copper or palladium catalyst.[4] More recently, a carbonate interchange reaction of methanol with ethylene carbonate has been reported for the synthesis of dimethyl carbonate.[5] Cyclic carbonates, such as, ethylene carbonate is readily available, have desirable physical properties and are prepared from carbon dioxide and ethylene oxide.[6] Therefore, synthesis of poly(aryl carbonate)s using ethylene carbonate as a carbonate precursor is a desirable goal. If feasible, this will result in the use of carbon dioxide as a precursor for carbonate linkage in polycarbonates.

One of the drawbacks of the melt phase carbonate interchange reaction is that the melt viscosities increase dramatically with increase in molecular weight, leading to problems in agitation and heat transfer. This in turn adversely impacts on product quality. Specialized equipments capable of providing efficient heat/mass transfer at high melt viscosities (upto 13,000 poise at 300 ^{0}C) are needed to conduct melt phase carbonate interchange reaction, especially for the synthesis of poly(aryl carbonate)s with $[\eta] > 0.45$ dL/g.

Solid state polymerization is a commonly practiced technique[7] to obtain high molecular weight polyesters and polyamides ($[\eta] > 0.5$ dL/g). Solid state polymerization proceeds at a relatively lower temperature than melt phase reaction and has the advantage that it does not require handling of melts at high temperature. The equipment required for solid state polymerization is also relatively simple. In the case of poly(aryl carbonate)s the application of solid state polymerization process is of recent origin.[8,9] Relatively, little information is available in the literature on the factors that control the course of solid state polymerization of a predominantly amorphous polymer (T_g = 149 ^{0}C), such as, poly(aryl carbonate)s.

The carbonate linkage in organic polymers contributes to desirable physical properties, such as, high impact strength, high heat distortion temperature and good ductility. Therefore, copolymers containing arylcarbonate linkages have assumed importance as useful materials. Poly(ester-carbonate)s, prepared by melt blending of poly(ester)s and poly(aryl carbonate)s have aroused widespread interest in the literature in recent times. Similarly, use of flexible segments such as polyethers in polycarbonates are also of significant interest in extending the scope of applications of poly(aryl carbonate)s.

Objectives of the present investigation:

The objectives of the present investigations are

1. To explore the use of ethylene carbonate for the synthesis of organic compounds and polymers with carbonate functional groups;
2. To examine the synthesis of linear high molecular weight poly(aryl carbonate) *via* solid state polymerization and study the effect of reaction parameters on the course of solid state polymerization; To evaluate the kinetic parameters of solid state polymerization;
3. To examine the feasibility of synthesis of branched poly(aryl carbonate)s and copoly(ester-carbonate) *via* solid state polymerization methods;
4. Synthesis and characterization of copoly(arylether-carbonate)s.

Chapter I

The introductory chapter briefly surveys the various routes to poly(aryl carbonate)s, such as, carbonate interchange reaction, direct and interfacial phosgenation. Relevant literature regarding the use of ethylene carbonate for the synthesis of dialkyl carbonate and polycarbonate are presented elaborately. A general background on the solid state polymerization is provided. Synthetic methods available in the literature for copoly(aryl carbonate)s are discussed.

Chapter II

The objective and scope of the present investigations are described in this chapter.

Chapter III

This chapter deals with the study of the reaction of aromatic hydroxy compounds with ethylene carbonate. The carbonate interchange reaction using ethylene carbonate has not been studied widely, especially using aromatic hydroxy compounds. One of the complicating factor is the competitive decarboxylation reaction occurring during the reaction, especially at higher temperatures. The reactions of ethylene carbonate with phenol and bisphenol A were studied under different reaction conditions and the products were characterized by ^{1}H NMR, ^{13}C NMR and FT-IR. It is observed that at or above 160 ^{0}C, decarboxylation is the main reaction.

Aliphatic carbonates were also synthesized from ethylene carbonate and aliphatic alcohols using zeolites as catalyst. The results were compared with conventional metal-based catalyst systems, used for such reactions. The rate of carbonate interchange reaction using a zeolite catalyst was found to be sigficantly faster compared to the tetra-n-butyltitanate catalyst. With a KL type zeolite, 90% conversion of ethylene carbonate was obtained within 2 h, whereas, in case of titanium catalyst 82% conversion was obtained after 12 h.

Chapter IV

This chapter examines the effect of various reaction parameters on the solid state polymerization of poly(aryl carbonate) oligomers. Solid state polymerization has been well studied[7] in the case of crystalline polymers, such as poly(ethylene terephthalate). However, its applicability to amorphous polymers such as poly(aryl carbonate)s is of recent origin.[8,9] The solid state polymerization was found to be also useful for the synthesis of branched poly(aryl carbonate)s.

Low molecular weight poly(aryl carbonate) oligomers could be chain extended in the solid state under defined conditions to high molecular weight polymers ($\bar{M}_v > 60,000$). This technique removes the limitations of the melt phase process for producing poly(aryl carbonate)s with wide range of molecular weights. Influence of various reaction parameters, such as, type of reactor used, time, temperature, catalyst (metal-free bioxyanions and conventional catalysts), initial crystallinity, initial molecular weight and initial end group concentration on the rate of solid state polymerization were studied in a fluidized bed reactor. The changes in crystallinity and melting temperature of poly(aryl carbonate) synthesized by solid state polymerization were explored. It is proposed that solid state polymerization of poly(aryl carbonate) involves simultaneous occurrence of chain extension as well as increase in crystallinity (increase in T_m). Kinetic parameters for the solid state polymerization reaction were evaluated. Chemical reaction was found to be rate controlling step in the solid state polymerization. The Arrhenius equation was found to be $k = 1.41 \times 10^8 \exp(-4807/RT)$, h^{-1}.

Branched poly(aryl carbonate)s,[10] were synthesized by solid state polymerization technique. The amount of branching agent incorporated in the polymer was determined quantitatively using HPLC after saponification of the polymer. The branching reactions were found to be quantitative under these conditions.

Chapter V

The synthesis of poly(ester-carbonate)s by melt phase[11,12] or interfacial[13,14] routes are beset with several problems. Solid state copolymerization was found to overcome many of these problems. The polymerization was carried out using poly(aryl carbonate)s and poly(aryl ester)s or poly(ethylene terephthalate) oligomers in presence of a suitable catalyst below 230 °C. Prior to solid state polymerization, the oligomer mixtures were crystallized using ethyl acetate or acetone and pulverized to 250 to 520 μ size. The product was analyzed by ^{1}H NMR, DSC and viscosity. It is proposed that solid state polymerization of two chemically distinct oligomers involves ester-carbonate interchange reaction with simultaneous chain extension. The results established that carbonate-ester interchange reaction can occur at appreciable rate at as low a temperature as 240 °C.

Chapter VI

This chapter deals with the synthesis of different bis(hydroxyethyl ether)s[15] from aromatic dihydroxy compound and ethylene carbonate. They were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis.

Poly(ether-carbonate)s were synthesized using bis(hydroxyethyl ether) of aromatic hydroxy compounds and bisphenol A with diphenyl carbonate by the melt phase carbonate interchange reaction. Structure-property relationships were examined in poly(ether carbonate). With increasing content of bis(hydroxyethyl ether) in the copolymer, the T_g of the polymer was found to decrease.

Chapter VII

This chapter summarizes the results and describes the salient conclusions of the study. Additional thoughts for further research are also indicated.

Zeolite catalysts could be employed for the synthesis of dialkyl carbonates by carbonate interchange reaction of aliphatic alcohols with ethylene carbonate. >90% conversion is obtained in 2 h. The synthesis of branched poly(aryl carbonate)s using solid state polymerization technique was demonstrated. The research has also led to the synthesis of the copoly(ester-carbonate) using solid state polymerization of poly(aryl carbonate)s and poly(aryl ester)s or poly(alkyl ester)s oligomer. The occurrence of carbonate-ester interchange reaction at temperatures substantially lower than hithertofore reported was demonstrated. Copoly(ether-carbonate)s synthesized from bis(hydroxyethyl ether) of bisphenols and bisphenol A with diphenyl carbonate in the melt phase produced a range of copolymer structures with T_g ranging from 62 to 140 ^{0}C. These are novel soft segment containing copoly(aryl carbonate)s.

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LIST OF PUBLICATIONS

PAPERS:

1. **S.B. Hait** and S. Sivaram

   Synthesis of coploy(ester-carbonate)s *via* solid state polymerization of poly(aryl carbonate)s with poly(aryl ester)s and poly(ethylene terephthalate)

   Macromolecules, (communicated)

2. **S.B. Hait** and S. Sivaram

   Synthesis of copoly(ether-carbonate)s from bis(hydroxyethyl ether) of different aromatic diol with bisphenol A and diphenyl carbonate.

   J. Polym. Sci. Polym. Chem. Ed., (communicated)

3. **S.B. Hait** and S. Sivaram

   Synthesis of dialkyl carbonates using zeolite catalysts.

   (in preparation)

PATENTS:

1. **S.B. Hait** and S. Sivaram

   Preparation of branched poly(aryl carbonate)s using solid sate polycondensation process.

   Ind. Pat. Appl. 2463/DEL/95 dated December 29, 1995;
   U.S. Pat. Appl. No. 08/653166 dated May 29, 1996;
   Eur. Pat. Appl. No. 96302603.4.

2. G.S. Varadrajan, J. King, B.B. Idage, S. Sivaram, and **S.B. Hait**

   Method for preparing polycarbonate by solid state polymerization.

   US/17.12.96/US 767740
   Eur. Pat. Appl. No. 97302927.5-1270 (23.7.97)

3. **S.B. Hait** and S. Sivaram

   An improved process for the preparation of poly(ester-carbonate)s.

   Ind / US / Eur. Pat. applied for (1997)