Synthesis and Characterization of Polyamides, Polyimides and Polyesters Containing Flexibilizing Groups

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By
ANJANA SARKAR

Polymer Science and Engineering Division
National Chemical Laboratory
Pune-411008

February 2005

Dedicated To

My

Parents

Form 'A'

Certified that the work incorporated in the thesis entitled **"Synthesis and Characterization of Polyamides, Polyimides and Polyesters Containing Flexibilizing Groups"** submitted by Anjana Sarkar was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

February, 2005	P. P. Wadgaonkar
Pune	(Research Guide)

Abstract

High performance / high temperature polymers such as polyimides, poly(amideimide)s, polyamides, polyesters etc are characterized by their excellent balance of thermal and mechanical properties which makes them useful materials for engineering applications. However, these polymers particularly those with *para*-substituted rings exhibit poor processability and limited solubility in organic solvents. Therefore, many efforts have been made to chemically modify the structure of these polymers with the aim of improving their solubility in organic solvents and / or lowering their transition temperatures to a range which facilitates their processing in the melt.

The main goal of the present research was the synthesis of polyimides, poly(amideimide)s, polyamides and polyesters with improved processability by incorporation of pendent flexible alkoxy chains along the polymer backbone making use of appropriate difunctional monomers. Another objective of the work was to evaluate the applications of selected polymers as alignment layers for liquid crystal display devices and as membrane materials for gas separations.

Thus, our synthetic research effort was directed towards structural modifications designed to disturb regularity and chain packing *via meta*- catenation and internal plasticization thus providing better processability to the polymers. A series of 5-alkoxyisophthalic acids, 5-alkoxyisophthaloyl dichlorides, 5-alkoxy-1,3-phenylene diisocyanates, and 5-alkoxyisophthalic acid dihydrazides were synthesized. Aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages and possessing pendent flexible alkoxy chains were designed and synthesized. By relatively easy and inexpensive chemical routes, these monomers could be prepared that provide the structural characteristics needed for the improvement of properties such as processability, and specifically properties like pretilt angle and gas permeability. The length of pendent side chains

was varied in order to study the effects of chain length on the properties of polymers, such as, solubility, thermal stability, Tg and processabilty.

A series of polyimides and poly(amideimide)s containing pendent flexible alkoxy groups was synthesized from 5-alkoxy-1,3-phenylenediisocyanates, 5-alkoxyisphthalic acid dihydrazides and aromatic diamines containing pre-formed amide linkages by polycondensation with commercially available aromatic dianhydrides. Polyimides and poly(amideimide)s were of moderate to reasonably high molecular weights and could be cast into tough, transparent, and flexible films. The incorporation of pendent flexible alkoxy groups resulted in lowering of glass transition temperature. A large window between glass transition and polymer degradation temperature was observed. This gives an opportunity for these polyimides and poly(amideimide)s to be melt - processed or compression molded. It was demonstrated that improvement in solubility could be achieved by incorporation of pendent alkoxy chains along the backbone of rigid chain polymers and by proper selection of the comonomers (dianhydride). Wide angle X-ray diffraction analysis revealed that layered structures were formed for polyimides and poly(amideimide)s with long pendent alkoxy chains.

The application of organo-soluble polyimide derived from 5-octyloxy-1,3-phenylene diisocyanate and 4, 4'- oxydiphthalic anhydride(ODPA) as alignment layer for liquid crystal display was evaluated in brief. A pretilt angle of 2.97^o was observed which is adequate for display applications. Poly(amideimide)s containing octyloxy and hexadecyloxy side chains exhibited a good rubbing processability and excellent performance in controlling of both the alignment and the pretilt of LC molecules in the LC cell. The pretilt angle of LC molecules was easily achieved in a wide range of $3.8 – 17.5^o$ depending upon the rubbing density as well as the length of the alkoxy chain. These values are in the desirable range for super twisted nematic (STN) LCD devices.

High molecular weight (M_n 101050- 399400, GPC PS Standard) polyesters were synthesized by interfacial polycondensation of 5-alkoxyisophthaloyl dichlorides

with aromatic diols namely BPA and HFBPA. Polyesters could be cast into tough, transparent and flexible films from their solution in chloroform. Thermal degradation kinetics of polyesters revealed that degradation obeyed first order kinetics. The relationship between the chemical structure of polyesters and their thermal degradation behaviour was established.

Polyesters based on 5-alkoxy isophthaloyl dichlorides and BPA showed increase in permeability and decrease in selectivity as length of pendent alkoxy group increases. However, HFBPA- based polyesters behaved differently owing to the presence of bulky hexafluoroisopropylidene group. The permeability behaviour of poly(amideimide) series was similar to that of BPA – polyester series. The marked increase in CO_2 permeability than permeability of other gases tested namely He, O_2 and N_2 indicated potential of these membrane materials for CO_2 – based separation applications.

Polyamides were synthesized from 5-alkoxyisophthalic acids and 4,4’-oxydianiline employing Yamazaki- Higashi reaction conditions. Polyamides containing pendent alkoxy groups were soluble in DMF, DMAc, NMP and pyridine. Tough, transparent, and flexible films could be cast from DMAc solution of polyamides.

Overall, internal plasticization through the incorporation of pendent alkoxy groups was shown to be successful in improving solubility and processability characteristics of polyimides, poly(amideimide)s, polyamides and polyesters with a compromise on thermal stability. Poly(amideimide)s and a polyimide were proved to be suitable as alignment layers for liquid crystal display devices.

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Chapter 1. Introduction and Literature survey

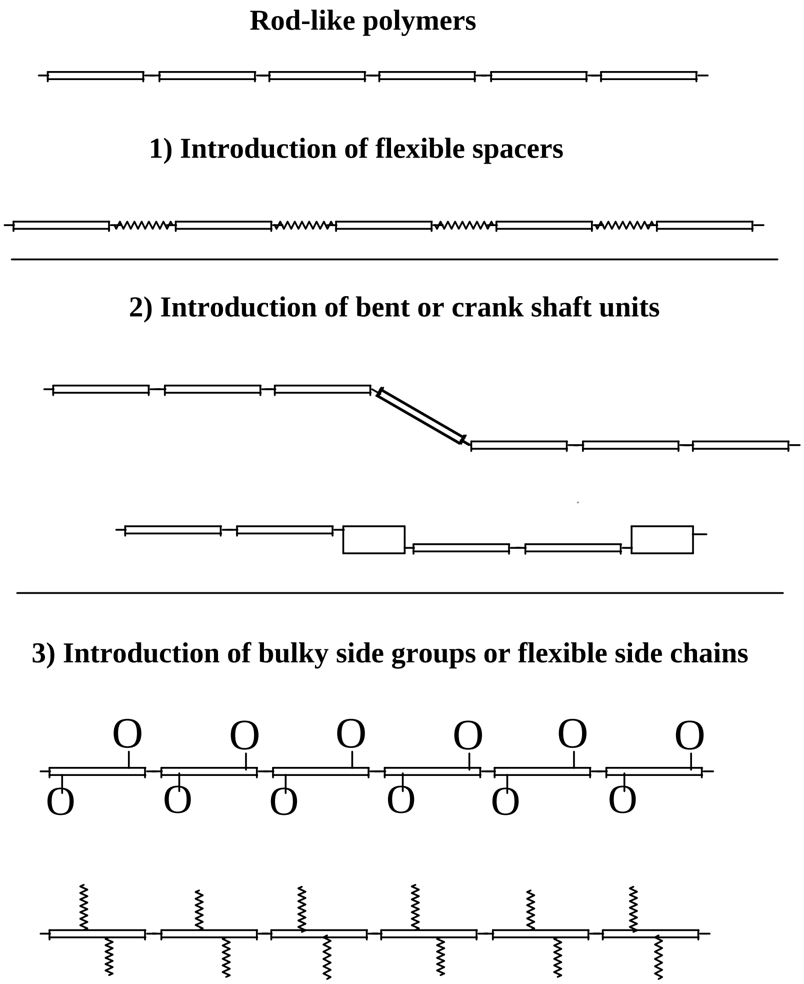
1.1 Introduction

The use of polymers is widespread in modern society, and their applications continue to grow. Many of the important advances in the polymeric material involve imparting desirable properties through the control of polymer structure. In recent years much of the focus has been in the area of high performance polymers (HPPs), in which tailoring polymer structure to give specific set of properties is paramount. It has been observed that high performance, like beauty, is in the eye of the beholder, its definition changing with context. Indeed, although HPPs can be broadly defined as materials that exhibit properties superior to those of state-of-the-art materials, many scientists and technologists prefer more specific definitions. Such definitions may refer to materials, which exhibit not only a unique combination of properties (e.g., high strength, high stiffness and impact resistance, high resistivities, low dielectric constants, chemical and solvent resistance, and low flammability and smoke generation, etc.) superior to those of state-of-the-art materials but also better elevated temperature behavior.

Many of the currently used HPPs have their roots in the research and development work in the 1960s. Then, as now, the aerospace industry was a significant driving force behind the development of new materials for demanding environments and it remains their largest user. The most prolific decade for HPPs was 1960-1970 where most thermally sTable heterocyclic rings were incorporated within polymers. The drive during the early part of this era was directed primarily towards thermal stability; little attention was paid to processability. 1970s saw the commercialization of several HPPs. In the 1980s, work focused on exploring ways to make polymers more processable and on developing more cost-effective routes to convert them into various useful forms.

The research continues in many other areas such as microelectronics (photoresists, interlayer dielectrics), alignment films for liquid crystal display devices, electroactive actuators and devices, optical fiber waveguides, proton exchange membranes for fuel cells, separation/barrier materials, etc.

Polyimides, poly(amideimide)s, aromatic polyesters and polyamides are the important classes of high performance polymers. The high regularity and high rigidity of the backbones of HPPs result in strong chain-chain interactions, high crystallinity, high melting points and low solubility. Thus processing of HPPs is often difficult. In order to increase processability and systematically understand HPPs, a wide variety of modified HPPs have been synthesized. Several approaches have been used to modify HPPs including: (1) the insertion of flexible spacers between the rigid units; (2) the insertion of bent or 'crankshaft' units along the aromatic backbones to form random or alternative copolymers; and (3) the appending of bulky side groups or flexible side chains to the aromatic backbones.



Rod-like polymers

1) Introduction of flexible spacers

2) Introduction of bent or crank shaft units

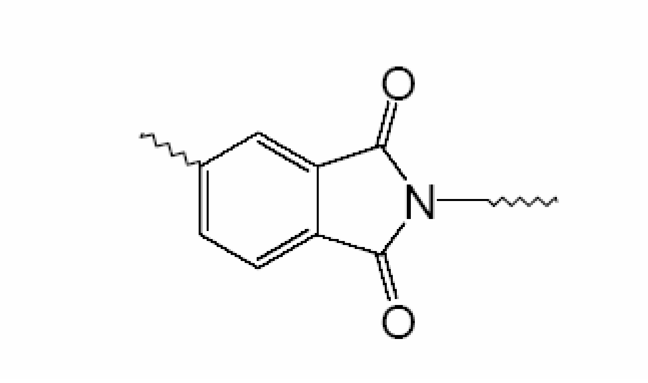
3) Introduction of bulky side groups or flexible side chains

Figure 1.1: Approaches for improving processability of high performance polymers.

This chapter will discuss some topics relevant to this dissertation, including common synthetic chemistry and methods used to prepare polyimides, poly(amideimide)s and polyarylates, important characteristics and their applications.

1.2 Polyimides

Polyimides are a class of polymers containing a heterocyclic imide unit



in the polymer backbone and are derived from the reaction of dianhydrides and diamines.

Historically, the first report concerning polyimides was made by Bogert and Renshaw in 1908.[1] However, only in the early 1960s were polyimides successfully introduced as commercial polymeric materials (Kapton) by DuPont.[2] Since that time, an impressive variety of polyimides have been synthesized and reported in the literature.[3-7]

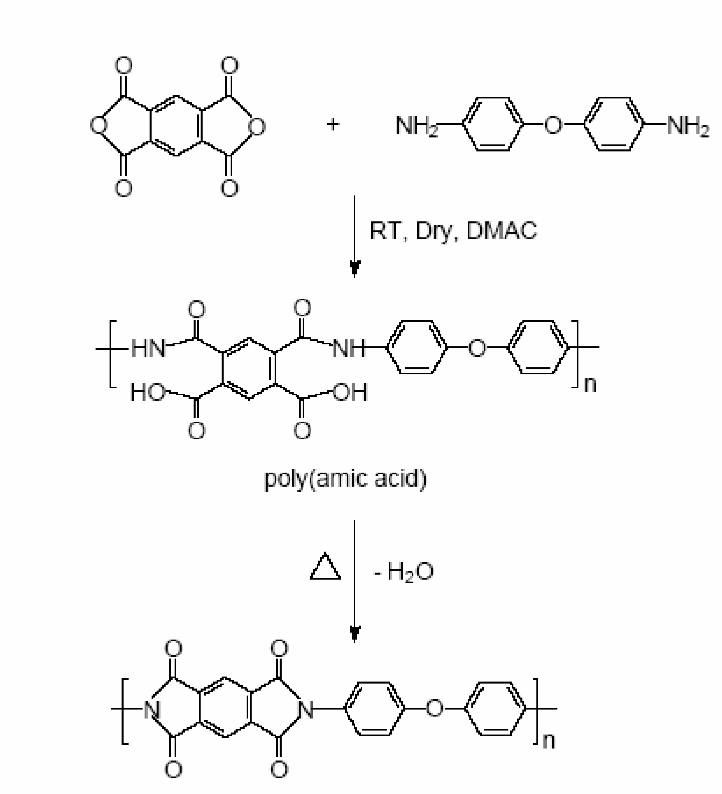
Polyimides are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance. Therefore, in spite of their general difficulty in processing and high cost, polyimides are widely used as matrix resins, adhesives, coatings, printed circuit board and insulators for high performance applications in the aerospace, automotive, electrical, electronics and packaging industries.

1.2.1 Synthesis of polyimides

The design and the synthetic pathway are important constituents in the development of high performance polyimide materials. Polyimides are generally derived from the step or condensation reaction of organic diamines and tetracarboxylic anhydrides. In this Section, the fundamental aspects and some new developments in the chemistry of polyimide synthesis will be discussed.

1.2.1.1 Classical two-step method *via* poly(amic acid)s

The classical synthetic pathway pioneered at DuPont de Nemours and Co. to cope with the infusibility and insolubility of aromatic polyimides is still the most popular technique for the preparation of polyimides. As shown in **Scheme 1.1**, with the example of Kapton synthesis, this preparative approach consists of the formation of soluble, and thus processible, poly(amic acid) (PAA) precursors from diamines and tetracarboxylic anhydrides, followed by the conversion of PAAs acids to the desired polyimide *via* imidization.

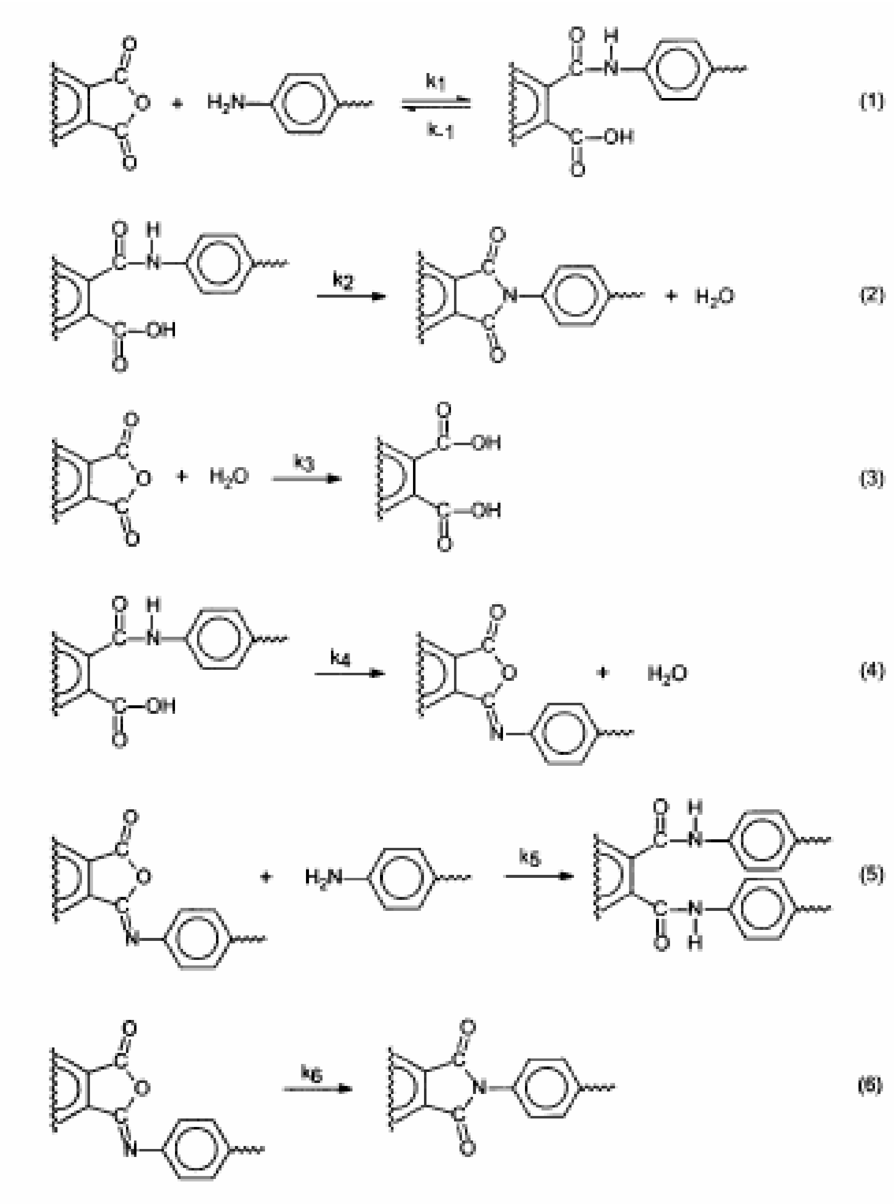


Scheme 1.1: Preparation of Kapton® polyimide.

a) Formation of poly(amic acid)s

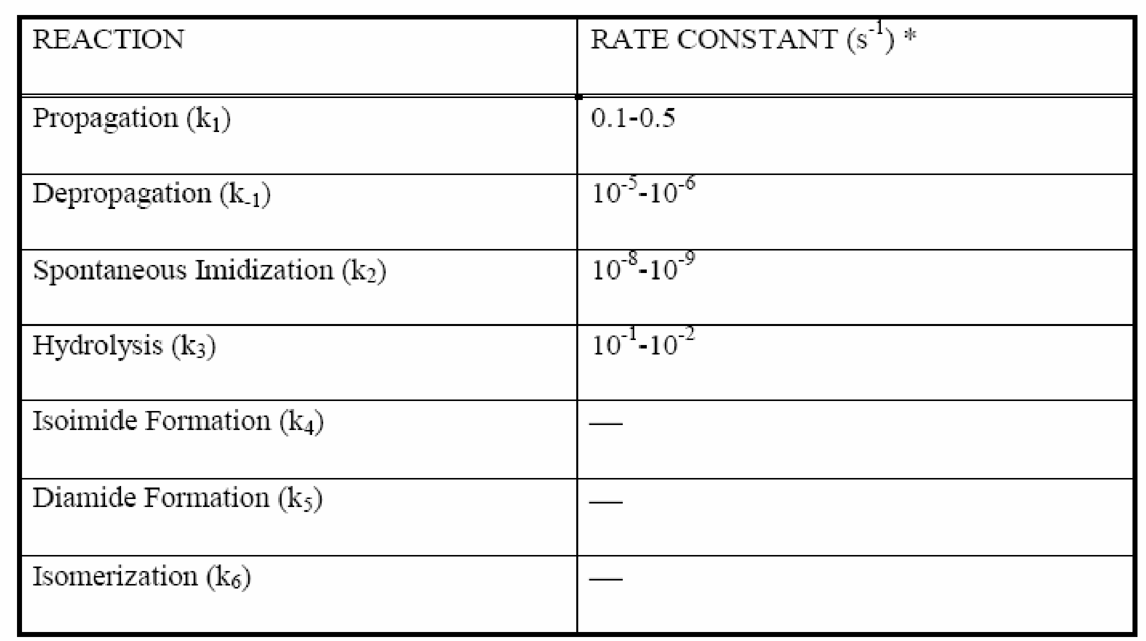
The formation of poly(amic acid)s is achieved *via* the reaction of a dianhydride and a diamine in a dry aprotic solvent at or below room temperature. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride ring to form an amic acid group. In this equilibrium reaction, the forward reaction is often much faster than the reverse reaction. The acylation reaction of amine is an exothermic reaction.[8] The forward reaction in a dipolar solvent is a second-order reaction and the reverse reaction is a first-order reaction. Therefore, the equilibrium is favored at low temperature and high monomer concentration to form high molecular weight poly(amic acid)s.[9] The reactivity of the monomers is an important factor governing the rate of amic acid formation. It is expected that the nucleophilicity of the amino nitrogen atom of the diamine and the electrophilicity of the carbonyl group of the dianhydride are important factors in this process. However, structure of the diamines seems to influence the rate of the acylation reaction more than the variation in dianhydride.[10] The high nucleophilicity of the diamine results in high reactivity. The reactivity of diamines correlates well with their basicities (pK_a) as expressed by Hammett relation.[11] However, very high basic diamines, e.g. aliphatic diamines, have an unfortunate tendency to form ionic salts with the carboxyl group of the formed amic acid linkage, while the protonation of the amine group prevents its reaction with the anhydride. Thus, these diamines are not suited for this preparative pathway. On the other hand, diamines of very low basicity have poor nucleophilic ability and thus do not react well with dianhydrides. It has been suggested that an optimal diamine should have a pK_a of 4.5-6.[12] The effect of the reactivities of anhydrides is manifested by the fact that the reaction rate increases with increasing affinity for the electron by the dianhydride. Earlier investigators[13] quantified electron affinity (E_a) for various dianhydrides by polarographic measurements and demonstrated that the rate of an acylation reaction of 4,4'-diaminodiphenyl ether and a model compound, 4-aminodiphenyl ether, was closely correlated with these E_a values. In addition to the inherent characteristics of the monomers, the properties of the solvent utilized is also critical. For example, the use of polar aprotic solvents that can form strongly hydrogen-bonded complexes with the carboxyl group, plays a major role in driving the equilibrium to amic acid. Dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP) are the solvents most generally used. The rate of poly(amic acid) formation measured for phthalic anhydride and 4-phenoxyaniline increased with solvent in the order of tetrahydrofuran (THF) <acetonitrile < DMAc.[14]

Several minor, but important, reactions also occur during poly(amic acid) formation. These side reactions may become significant under certain conditions, particularly when the acylation reaction of the diamine is relatively slow because of low monomer reactivity or low monomer concentration. In addition to the amic acid propagation route, five additional potential reaction pathways are possible and are illustrated in **Scheme 1.2** Their relative rate constants are listed in **Table 1.1**.[15] The formation of poly(amic acid) is an equilibrium reaction determined by acylation(k_1) and deacylation (k_{-1}) reactions. The latter is also described as an intramolecular acidolysis, forming an anhydride. Poly(amic acid)s are known to undergo hydrolytic degradation even at ambient temperatures. When poly (amic acid)s are in solution, a small amount of the anhydride is always present in an equilibrium concentration. However small, it plays an important role in the hydrolytic degradation of poly(amic acid). In the presence of water, the anhydride group is hydrolyzed to form an *ortho* dicarboxylic group as shown in (3). The reaction is driven by the enhanced nucleophilicity of the water in a dipolar aprotic solvent and by the strong acid-base interaction of the material with the dipolar solvent. The effects of water on the molecular weight of poly(amic acid)s during polymerization, and the effect of added water on the molecular weight of poly(amic acid)s in solution, are well documented.[16] Although water is present from both the solvents and the monomers that contain it as an impurity, it should be noted that water formed *in situ* by the imidization of amic acid, as shown by equation (2), is also important. Even if the rate of imidization, and therefore the formation of water, is relatively low at ambient temperatures, it is still significant enough to cause a gradual decrease in molecular weight over a long period of time. For example, Frost and Kesse[17] studied aging of a 11% DMAc solution of PMDA-4,4’-diaminodiphenyl ether (ODA) poly(amic acid) at 35°C. After 21 days, approximately 20% of the amic acid was converted to the imide, generating the corresponding amount of water, which was equivalent to having 0.19% water in the solvent. When long-term storage is necessary, poly(amic acid) solutions should be kept refrigerated to maintain the properties essential to further processing.



Scheme 1.2: Major reaction pathways involved in poly(amic acid) synthesis.[15]

Table 1.1: Relative rate constants for reactions pathways involved in poly(amic acid) synthesis (Scheme1.2).[15]



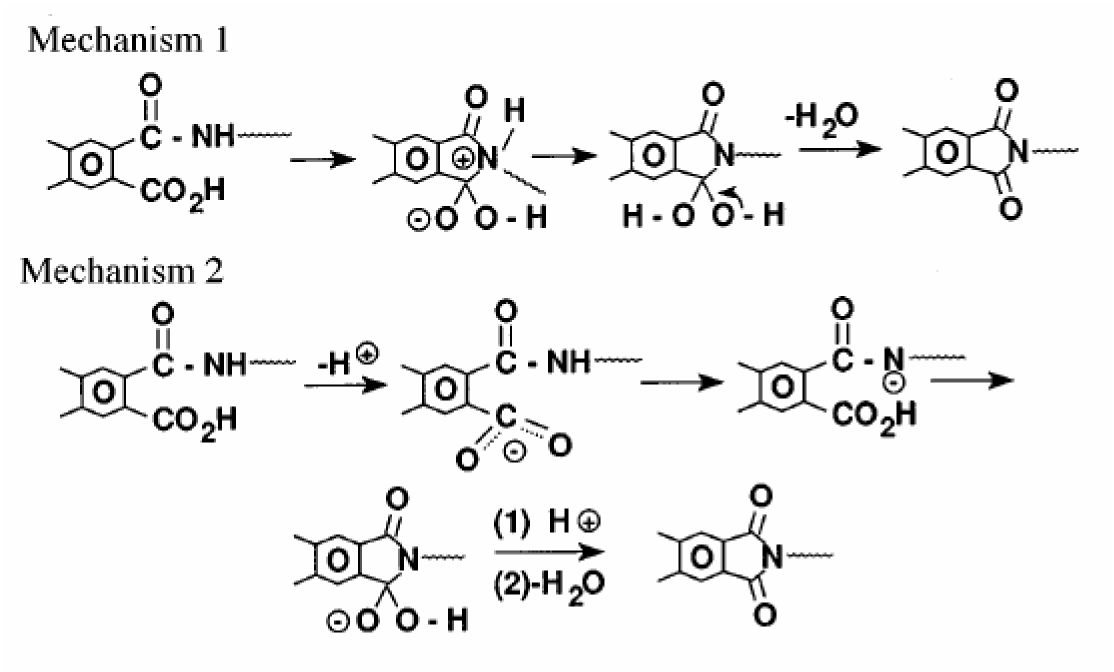
REACTION	RATE CONSTANT (s^{-1}) *
Propagation (k_1)	0.1-0.5
Depropagation (k_{-1})	10^{-5}-10^{-6}
Spontaneous Imidization (k_2)	10^{-8}-10^{-9}
Hydrolysis (k_3)	10^{-1}-10^{-2}
Isoimide Formation (k_4)	—
Diamide Formation (k_5)	—
Isomerization (k_6)	—

*Rate constants are estimated for a typical polymerization at ca. 10 wt.% concentration,i.e. 0.5M.

b) Thermal imidization of poly(amic acid)s

The first pathway for the cyclization of an amic acid moiety into an imide involves gradual heating of the PAA to 250-350°C, depending upon the stability and the glass transition temperature of the polymer. The events occurring during the heating include evolution of solvent and dehydrative cycloimidization. The imidization is accomplished through nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with elimination of water. **Scheme 1.3** shows two amic acid cyclization mechanisms proposed by Harris.[8] The main difference between the two mechanisms is when the loss of the amic acid proton occurs. Harris suggested that mechanism 2 is more likely, since the conjugated base of the amic acid is a more potent nucleophile than the amide. On the other hand, extremely small amide dissociation constants and the demonstrated effectiveness of acid catalyzed reactions[10,18,19] tend to support mechanism-1.

Thermal imidization is particularly effective for the preparation of thin materials such as films, coatings, fibers, and powders because it allows the diffusion of the by product and the solvent without forming bristles and voids. The problem of film cracking as a result of shrinkage stress can be avoided by carefully controlling the curing profile. A typical heating schedule includes a stage below 150°C, followed by a relatively rapid temperature ramp to a second stage above the Tg of the resulting polyimide. The majority of the solvent is slowly driven off in the first stage, while imidization essentially occurs in the second stage, where curing shrinkage stress is releasable.[15] Such a heating cycle allows the conversion of PAA to PI of about 92-99%, and this is considered to be the maximum that can be achieved *via* thermal imidization. Further heating at 300°C or higher does not result in 100% conversion because of the so-called “kinetic interruption” effect.[8] It should be noted that the hydrolytically unsTable residual amic acid units resulting from kinetic interruption are considered as defect sites. Their presence at concentrations of 1-8% in the resulting polyimide can noticeably reduce hydrolytic stability. This is particularly evident for the rigid-rod like polyimides, for which full imidization is considered the most difficult to achieve.[3]



Scheme 1.3: **Possible imide formation mechanisms.**[8]

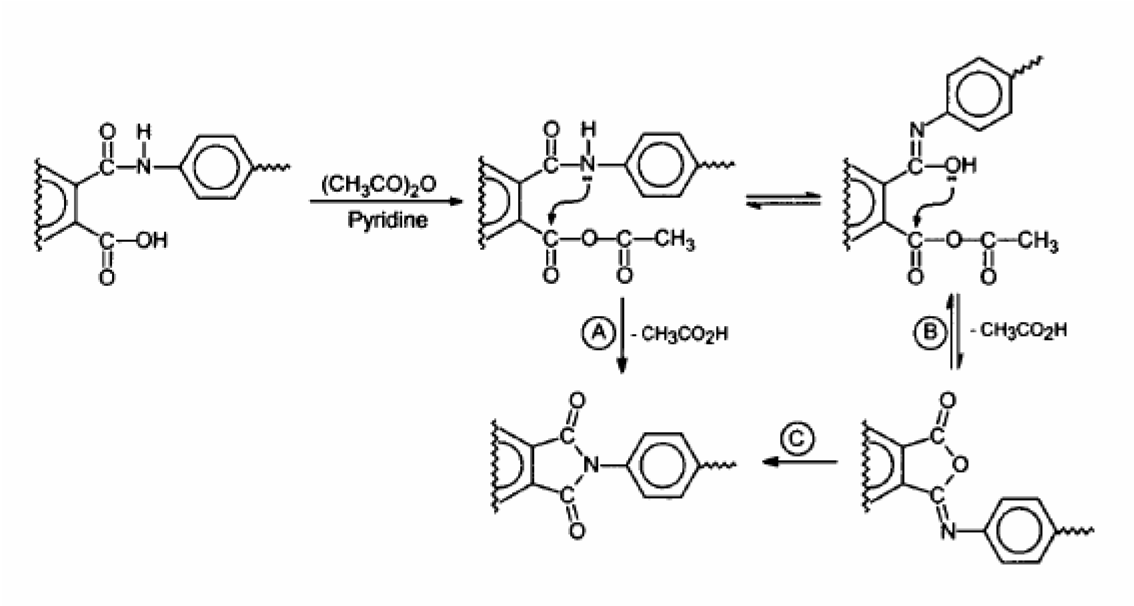
Another important consideration of thermal imidization is the occurrence of side reactions. Compared with polyimides produced from solution imidization, bulk thermal imidization results in polyimides of significantly different properties as a result of these side reactions. A partially reversible decrease in molecular weight in the early stage of imidization was observed as a result of the depolymerization reaction. This effect has been monitored in insoluble PI, by both changes in their mechanical properties during imidization and by the temporary appearance of the anhydride carbonyl absorption band near 1860 cm^{-1} between 100-250°C.[20,21,22] Evidence of this effect was later verified by measuring the molecular weight of the soluble PI at different stages of the thermal imidization.[23] The molecular weight gradually regained at high temperature. The side reactions associated with thermal imidization can also lead to some form of crosslinking.[24] Amine- terminated model imide compounds were monitored by Raman spectroscopy while heating.[25,26] The appearance of Raman absorption at 1665 cm^{-1} (C=N) confirmed that imide-imine conversion was occurring, which was predicted by a proposed crosslink reaction mechanism[27] involving the attack of terminal amino groups to imide carbonyl groups, with the resulting formation of imine. A recent study,[28] however, showed that the imine bond formation is only significant when small amine terminated species were present. The probability of imine formation decreased with the chain length. Side reactions also include isoimide formation, which thermally isomerizes to the normal imide at later stages.

c) Chemical imidization of poly(amic acid)s

The second pathway of cyclodehydration of amic acid to imide involves the use of a chemical dehydrating agent to promote ring closure reactions in temperature ranges of 20-80°C, which is effective for either soluble or insoluble polyimides.[29,30] Commonly used reagents include acid anhydrides in dipolar aprotic solvents or in the presence of tertiary amines. Among the dehydrating agent used were acetic anhydride, propionic anhydride, n-butyric anhydride, benzoic anhydride, as well as others. The amine catalysts used include pyridine, methylpyridine, lutidine, N-methylmorpholine, trialkylamines and others.

The outcome of the reaction can be very different depending on the type of dehydrating agent used, the monomer components of poly(amic acid)s, and the reaction temperature. For example, in the presence of trialkylamines with high pK_a (>10.65), high molecular weight polyimides were obtained. On the other hand, the use of a less basic tertiary amine resulted in the formation of polyimides with lower molecular weight. Different results, however, were obtained for heteroaromatic amines. Despite their lower basicity, high molecular weight polymers were formed when pyridine, 2-methylpyridine and isoquinoline ($5.2 < pK_a < 5.7$) were used as catalysts.[29] The use of acetyl chloride as a dehydrating agent afforded isoimides.[31] The use of N,N-dicyclohexylcarbodiimde (DCC) also resulted in essentially quantitative conversion of amic acid to isoimides.[32] On the other hand, a mixture of imide and isoimide was formed when pyridine was used as the catalyst.[33] However, when the pyridine was replaced with triethylamine, isoimide formation was practically eliminated, which also resulted in a significantly faster reaction rate. In examining the conversion of benzophenone tetracarboxylic dianhydride/9,9-fluorenedianiline based poly(amic acid) to the corresponding soluble polyimide, it was found that the cyclizing agent is most effective when employing 4-9 moles per repeat unit of the poly(amic acid). Increasing the temperature from 20°C to 100°C decreased the reaction time from 15 h to 2 h to achieve complete imidization.[34]

A kinetic study of chemical imidization process has resulted the mechanism shown in **Scheme 1.4**.[15, 35] A mixed anhydride intermediate is formed by the reaction of the amic acid linkage with acetic anhydride, which is promoted by the presence of a base. The mixed anhydride can further tautomerize from the amide to the iminol form. The amide tautomer cyclizes to the imide (pathway A), the thermodynamically favored product, whereas the iminol tautomer yields the kinetically favored isoimide form (pathway B). Although isoimides are known to thermally isomerize to imides (pathway C), in this case, isomerization occurs *via* the back reaction. This back reaction is apparently initiated by the nucleophilic attack of the acetate ion on the isoimide.[36] Such behavior is consistent with the fact that a stronger amine, such as triethylamine, promotes acetate formation, and thus increases the back reaction that results in exclusive imide formation.



Scheme 1.4: Mechanism involved in chemical dehydration of amic acid.[15,35]

In contrast to thermal imidization, the chemical imidization of poly(amic acid)s occurs without the depolymerization reaction, and thus the molecular weight of the polymer remains constant.[37] However, chemical imidization is less attractive for commercial applications because of the expense and process complexity.

d) High temperature solution imidization of poly(amic acid)s

Polyimides resulting from solid state thermal imidization often demonstrate insolubility, infusibility and thus poor processability.[38] To overcome these drawbacks, high temperature solution imidization has been successfully utilized.[10,39,40] Cyclodehydration is conducted by heating a poly(amic acid) solution in a high boiling solvent at temperatures of 160-200°C, in the presence of an azeotropic agent. Compared with bulk thermal imidization,the lower process temperatures and greater mobility in solution ensured the avoidance of degradation and side reactions.

Studies[10,41] were conducted investigating the kinetics and mechanisms of the solution imidization process. Second order kinetics were determined by monitoring amic acid concentrations using non-aqueous titration and an acid-catalyzed imidization mechanism was suggested. It was clearly demonstrated by 2D-^{1}H NMR and intrinsic viscosity that the poly(amic acid) chain cleaved to form anhydride and amine endgroups at the initial stage of the reaction. As the reaction proceeded, the endgroups recombined or the chains "healed" to form polyimides of higher molecular weight.

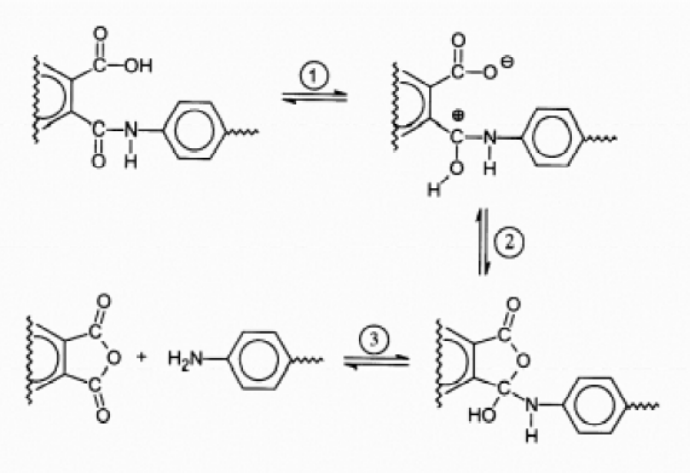
1.2.1.2 One-step high temperature solution synthesis of polyimides

Soluble polyimides can also be prepared *via* a one-step high temperature solution polycondensation of tetracarboxylic acid dianhydrides and diamines. In this process, the dianhydride and diamine monomers are heated in a high boiling solvent, or a mixture of solvents, at temperature in excess of 140°C, which permits the imidization reaction to proceed rapidly. Commonly used solvents are dipolar aprotic amide solvents, nitrobenzene, benzonitrile, α-chloronaphthalene, *o*-dichlorobenzene, trichlorobenzenes, and phenolic solvents such as *meta*-cresol and chlorophenols. Toluene, *o*-dichlorobenzene, 1-cyclohexyl-2-pyrrolidinone (CHP) are often used as cosolvents to remove the water resulting from condensation *via* azeotroping.[42-45] Unlike the methods described earlier, the preparation of a high molecular weight poly(amic acid) is not required for this procedure. Imidization can still proceed *via* an amic acid intermediate. However, the presence of the amic acid group is relatively small during polymerization because it is short-lived at high temperatures and either rapidly imidizes or converts to amine and anhydride. The kinetic profile consists of second-order amic acid formation and first- or second-order imide formation with amic acid formation as the rate-limiting step.[46,47] Under such conditions, steady-state approximation can be applied to the amic acid formation and the entire process can be expected to follow second-order kinetics. However, this predicted behavior is observed only at low conversions (< 30%) and is likely complicated by increased molecular weight at higher conversions. In much of the literature, the reaction was shown to be catalyzed by acid.[48,49] Kreuz et al.,[50] however, observed that thermal imidization of poly (amic acid)s could be catalyzed by tertiary amines. High temperature solution polymerization in *meta*-cresol could be achieved in the presence of high boiling tertiary amines, e.g., using quinoline as the catalyst. Dialkylaminopyridines and other tertiary amines were effective catalysts in neutral solvent such as dichlorobenzene.[51-53] The rate of imidization achieved *via* one-step high temperature solution synthesis was essentially complete, or 100%. No “defect sites,” of either amic acid or isoimide type, were detected in the resulting polymers. This is likely accounts for the differences in the physical properties observed between polyimides produced by solution synthesis and those obtained by the conventional two-step technique.[42,54] Another advantage of the high temperature solution method is that it allows high molecular polyimides to be prepared from monomers with sterically or electronically-hindered groups that would otherwise be hard to successfully polymerize *via* the two-step route. Polyimides whose T_m is $\leq$ 300°C or whose T_g is $\leq$ 250°C can be prepared by one step melt polycondensation using the extrusion molding method.[55]

1.2.1.3 Other synthetic routes to polyimides

1.2.1.3.1 Polyimides *via* derivatized poly(amic acid) precursors

As discussed in Section 1.2.1.1 solutions of poly(amic acid)s are susceptible to hydrolytic degradation. This process breaks down the molecular weight of the amic acid and resulting polyimide.[56] It is believed that hydrolysis occurs through the acid-catalyzed formation of an anhydride, as shown in **Scheme 1.5**,[15] rather than through direct hydrolysis of the amide linkage. To prevent this, efforts have been made to derivatize the amic acid to exclude the proton transfer from the acid group.



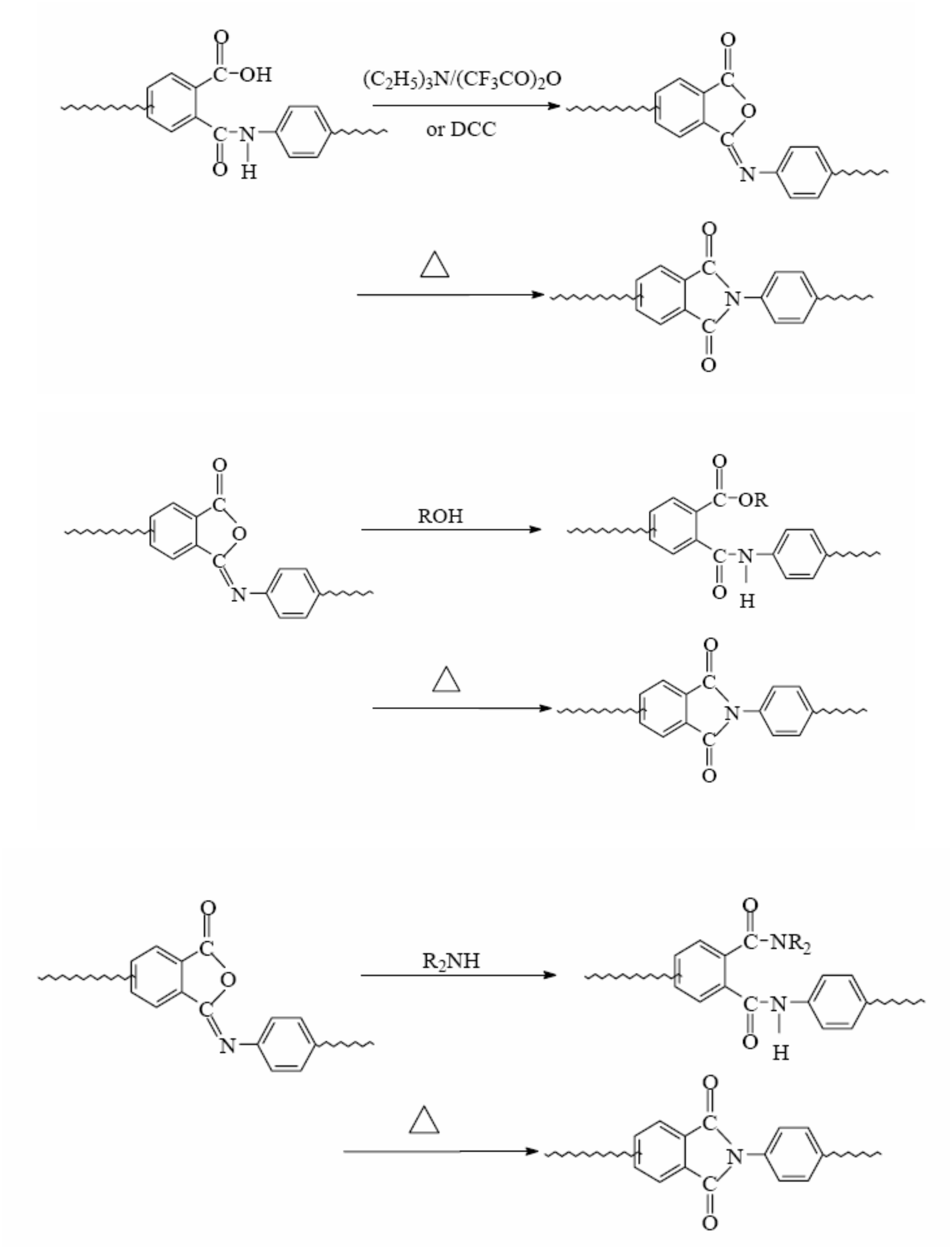
Scheme 1.5: Postulated mechanism for amic acid back reaction to anhydride and amine.

The simplest way to eliminate the proton transfer step is to neutralize the acid group with a base, such as a tertiary or a secondary amine, to form a polymeric salt.[50] However, the viscosity of the solution is very high due to the presence of ionic polymer chains. Alternatively, a more complex approach involves converting the acid group into either an amide or ester moiety. The *ortho*-carboxylic group in poly (amic acid)s can be chemically modified to either an ester or an amide moiety. The ester and amide derivatives of poly(amic acid)s are sTable, unable to form caboxylate anion which prevents the creation of degradation intermediate (reaction 1 in **Scheme 1.5**). Poly(amic ester)s can be isolated by precipitation without degradation and can be stored for an indefinite period at ambient temperatures. Such stability is highly desirable for some applications, such as microelectronics. In the preparation of photosensitive polyimides, the photocurable functionality is usually incorporated through derivatizing the poly(amic acid) to poly(amic ester).

The preparation of derivatized poly(amic acid)s can be achieved by one of two general pathways: 1) Formation of the poly(amic acid) followed by derivatization of the *ortho*-carboxylic acid groups along the polymer backbone; and 2) Derivatization of the monomer and subsequent activation to allow the monomer to enter a polymer forming reaction to yield the desired polymer. Conversion of esters of poly(amic acid) to polyimides readily proceeds thermally but at a slower rate and generally requires a temperature significantly higher than 200°C. The increased imidization temperature regime offers a wider processing window.

1.2.1.3.2 Polyimides *via* polyisoimide precursors

In general, polyisoimides are significantly more soluble and possess lower melt viscosities and lower glass transition temperatures than the corresponding polyimides, mainly because of their lower symmetry and structural irregularity.[57] These features make it possible to prepare rigid rod-like polyimides using soluble and processable polyisoimides.[58] Polyisoimides are formed from the corresponding poly(amic acid), using a dehydrating agent, such as trifluoroacetic anhydride, in conjunction with triethylamine. N, N-Dicyclohexylcarbodiimide (DCC) and acetyl chloride by themselves were reported to form polyisoimides from poly(amic acid)s in high yield.[31,32,59] A polyisoimide can easily be converted to the corresponding polyimide *via* thermal treatment at >250°C. Alternately, polyisoimides have been reacted with alcohol to produce poly(amic ester)s, which could then be thermally converted to polyimides.[60] On treatment with amines, polyisoimides likewise give poly(amic amide)s quantitatively. Poly(amic amide)s were also thermally converted to polyimides.[61] (**Scheme 1.6**).



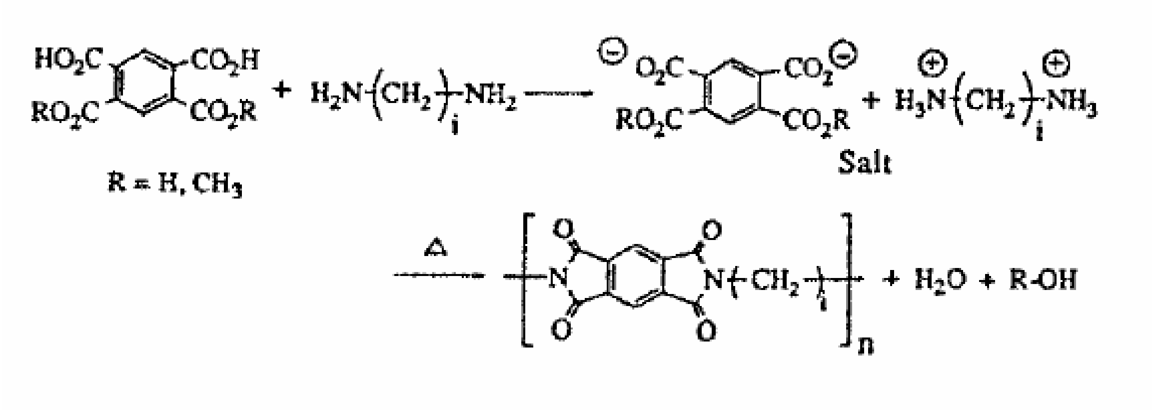
Scheme 1.6 : Polyimides *via* polyisoimide precursors.

1.2.1.3.3 Polyimides from diester-acids and diamines (Ester-acid route)

Synthesizing polyimides *via* the ester-acid route involves derivatizing the anhydrides to ester-acid and subsequently allowing the diamines to react, which yields the desired poly(amic acid) and polyimide. Polyimides are frequently synthesized *via* the ester-acid monomer route because this process is relatively tolerant of water in solvents and reactors.[61,63] In the initial stage of esterification, the dianhydride is simply refluxed in an excess of alcohol. It should be noted that the rate is greatly enhanced by addition of an amine catalyst, e.g., triethylamine, which acts as an acid acceptor. Once the excess alcohol has been evaporated, the resulting diester diacid is then reacted in solution with a suiTable diamine to form a poly(amic acid). A polar, aprotic solvent is needed for the similar reason as for poly(amic acid) route. The polyimide is obtained by thermal or high temperature solution imidization described earlier. Previously, it was thought that that the mechanism of amic acid formation from diester-diacid and diamine proceeds by the nucleophilic attack of ester carbonyl by amine resulting in poly(amic acid) with the elimination of alcohol. However, it was later discovered that the anhydride functional group was formed at elevated temperatures *insitu* from the *ortho* ester-acid.[62-64] The anhydride then reacts with the diamine to yield a poly(amic acid).

1.2.1.3.4 Polyimides from tetracarboxylic acids and diamines

This synthetic route for producing aliphatic-aromatic polyimides with high molecular weight involves combining aromatic tetracarboxylic acids and aliphatic diamines to form salts, similar to the synthesis of nylon *via* nylon salts. The salts are thermally imidized under high pressure at temperatures above 200°C to form polyimides (**Scheme 1.7**). It should be pointed out that the intermediate poly(amic acid)s are not detected during the polycondensation stage. Rather, it appears that the imidization and formation of poly(amic acid)s take place at the same time. This means that the imidization rate is very fast.[65]



Scheme 1.7: Polyimide synthesis from tetracarboxylic acid-amine salt.

In the one-step melt polymerization of polyimides, it is advantageous to use tetracarboxylic acids because high molecular weight poly(amic acid) intermediates of very high melt viscosities are not formed during the initial heating stage. Another advantage of using tetracarboxylic acids is their stability and ease of purification. Many of them can be readily recrystallized from hot water.

1.2.1.3.5 Polyimides from dianhydrides and diisocyanates

It has long been known that phthalic anhydride react with aromatic and aliphatic isocyanates to give n-aryl - and n-alkylphthalimides.[66] respectively. The reaction of aromatic diisocyanates with dianhydrides has been utilized to synthesize polyimides.[67-78] The chemistry developed during the late 1960s, was subsequently investigated to elucidate the reaction mechanism and the effect of conditions on the product yields. It was found that imidization path depended on the reaction conditions.

There has been a lack of consensus over the exact stoichiometry and reaction conditions to obtain high molecular weight polyimides using this route. It has been observed that the reaction of diisocyanates and dianhydrides proceeds at relatively moderate temperatures in dipolar aprotic solvents in the presence of alcohols, water or tertiary amines.

In the case of alcohol it was proposed that a urethane, formed by reaction of alcohol and isocyanate underwent slow reaction with anhydride to form imide.[67] Consequently, regeneration of alcohol and evolution of carbon dioxide occurred as a result.

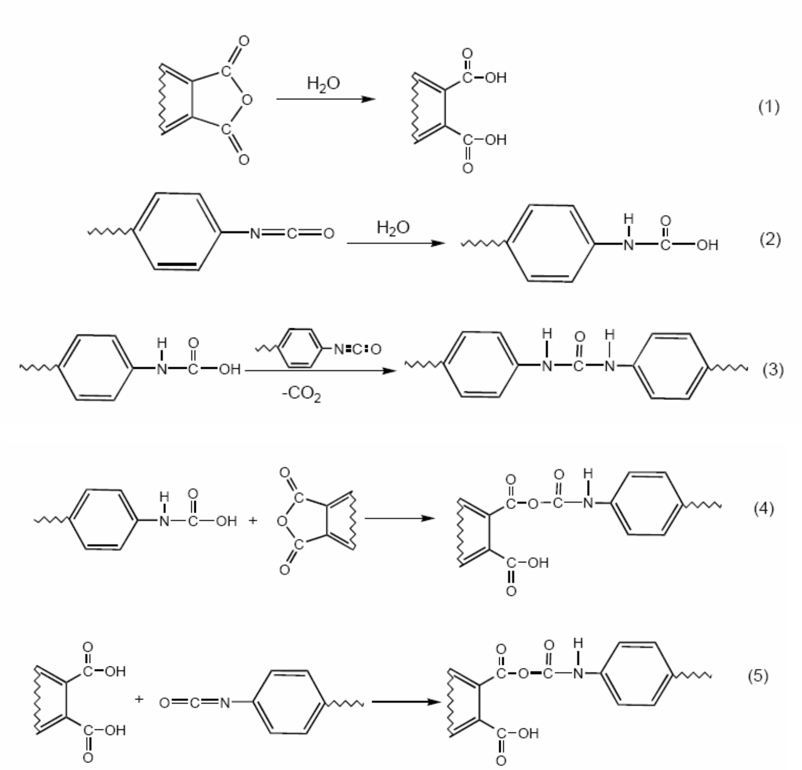
The mechanism with water catalyst has been thought to proceed through the hydrolysis reaction product of isocyanates, carbamic acid, which decomposes to amine and carbon dioxide[68]. In this case, the amine reacts with anhydride to give amic-acid, which subsequently imidizes by releasing water. It may be supposed that the preferential hydrolysis of isocyanate groups by the water of imidization would enhance the rate of cyclization.

It was also reported that high molecular weight polyimides were obtained using mixtures of anhydrides and their corresponding tetracarboxylic acids with diisocyanates in the presence of tertiary amines.[69] The authors could not suggest a mechanistic role for the carboxylic acid groups in the reaction of diisocyanates with dianhydrides. However, since high molecular weights were obtained, it was apparent that the stoichiometry was not upset by the presence of hydrolyzed anhydrides as it would have been in classic polyimide synthesis *via* amic-acids.

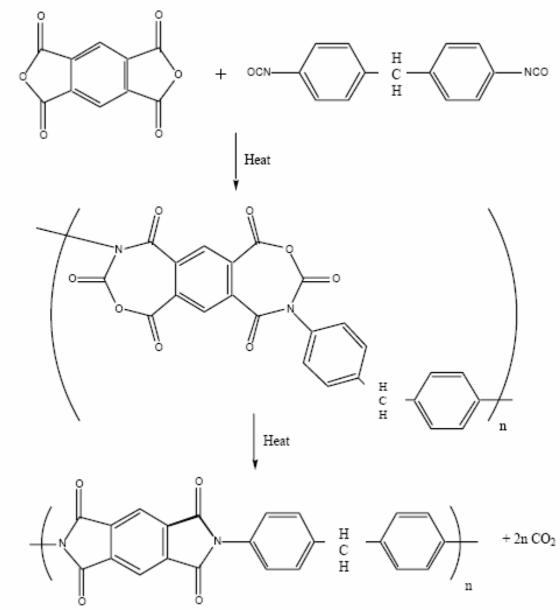
In Volksen's review,[79] a mechanism has been proposed to address the role of the hydrolyzed species (**Scheme1.8**). In the presence of water, the anhydride and isocyanate hydrolyze simultaneously to dicarboxylic and carbamic acids, respectively (reactions 1 and 2). Some of the carbamic acid reacts with isocyanate to form urea (reaction 3). It has been suggested that the urea is capable of reacting slowly with anhydride to form imide,[68] so the presence of urea would not limit molecular weight. Additionally, either product of the hydrolysis, carbamic acid or diacid, is capable of reacting to form a mixed carbamic carboxylic anhydride (Reaction 4 and 5, respectively). Subsequent heating causes the mixed anhydride to cyclize to imide with the loss of carbon dioxide and water.

Recently, a cyclic 7-membered intermediate has been proposed for uncatalyzed reactions in the melt or in anhydrous solutions, which is directly formed by anhydride and isocyanate groups (**Scheme1.9**).[77,79] This intermediate is believed to split off carbon dioxide when heated to form 5-memebered imide rings.

High molecular weight polyimides have been synthesized by reacting blocked isocyanates with anhydrides.[80]



Scheme 1.8: Mechanism of polyimides from dianhydrides and diisocyanates.

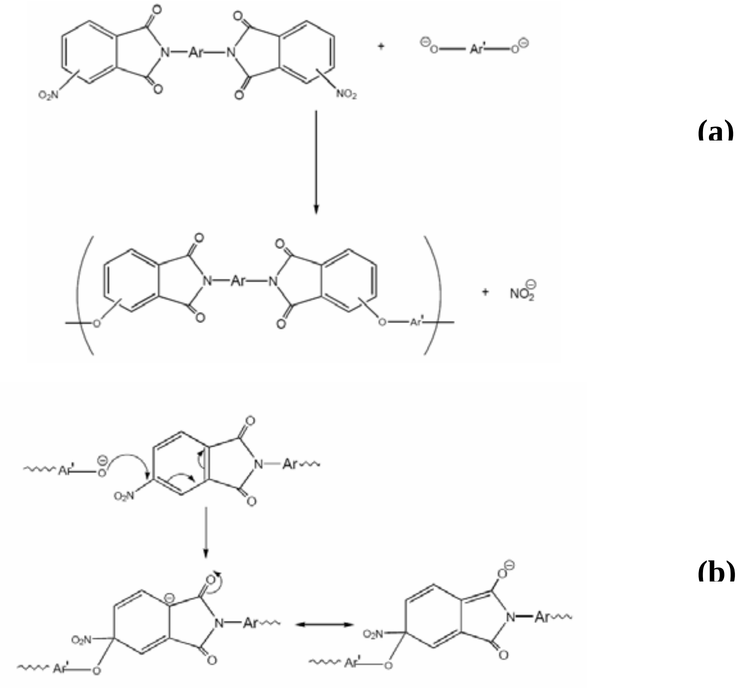


Scheme 1.9: Proposed route to polyimides from dianhydrides and diisocyanates *via* an imide-anhydride seven-membered ring

1.2.1.3.6 Polyetherimides *via* nucleophilic aromatic substitution reactions

Aromatic nucleophilic substitution of bishalo- and bisnitro- substituted aromatic ketones and sulfones with bisphenolates can produce polyetherketones[81] and polyethersulfones,[82] respectively. Aromatic halo- and nitro-groups are also strongly activated by imide groups toward nucleophilic aromatic substitution[83-86] with anhydrous bisphenol salts in polar aprotic solvents. The polymer chain is generated by the formation of successive aromatic ether bonds. A general synthetic pathway is depicted in **Scheme 1.10(a)**. Halo- and nitro-substituted imides are more reactive than the corresponding sulfones and ketones. This is due to the fact that the phthalimide ring is not only activated by the additional carbonyl group, but the two carbonyl groups are locked in a coplanar conformation with the phenyl ring, providing more effective resonance. Because of the favorable carbonyl conformation, the Meisenheimer type transition state is stabilized by the effective delocalization of the negative charge as shown in **Scheme 1.10(b).**[87]

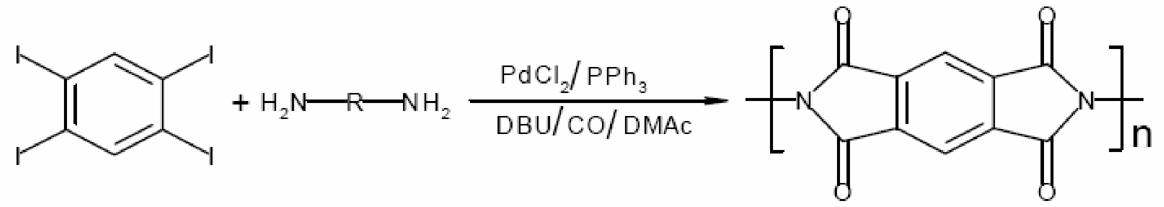
This process is commercially being used by GE, for the production of ULTEM®, a polyether imide.



Scheme 1.10: Synthesis of polyetherimides by nucleophilic aromatic substitution (a) and delocalization of negative charge in Meisenheimer transition state in imide system (b).[87]

1.2.1.3.7 Other routes to polyimide formation

Many other polyimide preparation methods have been reported in addition to the aforementioned routes. Due to the improved stability and solubility of derivatized PAAs, a number of techniques have been developed to form alkyl esters,[88-92] silyl esters,[93,94] and ammonium salts[95,96] of PAAs, all of which can be thermally cyclized to form polyimides. The alkyl esters are formed from the reaction of an ester-acid chloride and the silylated esters are formed in the reaction of N,N'-bis(trialkylsilyl) diamines with various dianhydrides. The ammonium salts of PAA's can be formed by reaction with a secondary or tertiary amine. The resulting polyelectrolyte can then be dispersed in an aqueous medium and used to fabricate carbon fiber composites.[96] Polyimides can also be prepared by Diels-Alder[97-100] and Michael[101,102] cycloaddition reactions. Palladium[103-107] (**Scheme 1.11**) and Nickel[108,109] catalyzed carbon-carbon coupling reactions have also been reported in the literature.



Scheme 1.11: Synthesis of polyimides by Pd-catalyzed carbon-carbon coupling reaction.[103]

1.2.2 Structure-property relationship in aromatic polyimides

The properties of polyimides, as for polymers in general, are governed by three fundamental characteristics: chemical structure, average molecular weight and molecular weight distribution.[110] The chemical structure relates to the chemical composition of the repeat unit and the end groups. It also encompasses the composition of any branches, crosslinks or defects in the structural sequence. The average molecular weight describes the average polymer chain size. The moleculat weight distribution relates to the degree of regularity in the molecular size.

Extensive literature has been published describing alterations in the structure and the size of the polyimide backbone and how these changes affect the physical and mechanical properties.[111-113] In the following Sections, a sampling of this literature will be reviewed with particular emphasis on the properties applicable to the scope of this thesis. A brief introduction of liquid crystal displays (LCDs) and alignment layers for LCDs is provided followed by summary of literature on use polyimides for this application.

1.2.2.1 Liquid crystal displays

Liquid crystals displays (LCDs) are a passive display technology. This means they do not emit light; instead, they use the ambient light in the environment. By manipulating this light, they display images using very little power. This has made LCDs the preferred technology whenever lower power consumption and compact size are critical. Few of the LCDs applications involve, laptop computers, camcorders, porTable TVs, etc.

Liquid crystal (LC) is an organic substance that has both a liquid and a crystal molecular structure. In this liquid, the rod-shaped molecules are normally in a parallel array, and an electric field can be used to control the molecules. Most LCDs today use type of liquid crystal called Twisted Nematic (TN). A Liquid Crystal Display (LCD) consists of two substrates that form a “flat bottle” that contains liquid crystal mixture. The inside surfaces of the bottle or cell are coated with a polymer that is rubbed in one direction to align the molecules of liquid crystals, which is called as an alignment layer. The LC molecules align on the surface in the direction of buffing. For TN devices, the two surfaces are buffed orthogonal to one another, forming a 90° twist from one surface to the other (**Figure 1.2**).

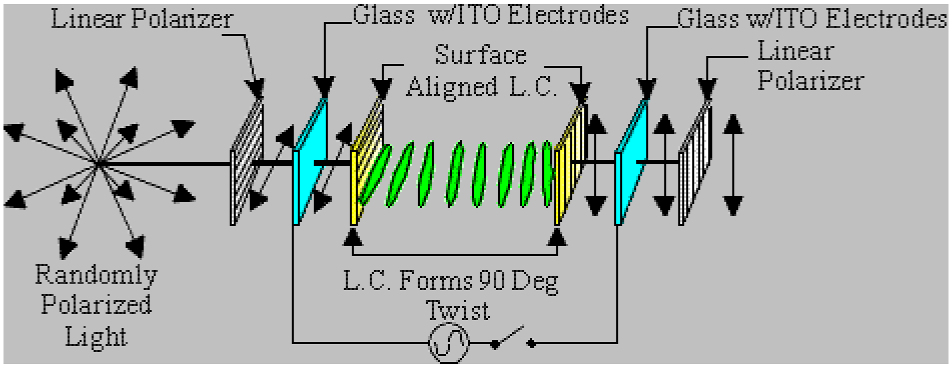


Figure 1.2: Structure of twisted nematic display in normally white mode (off-state).

This helical structure has the ability to control light. A polarizer is applied to the front and an analyzer/reflector is applied to the back of the cell. When randomly polarized light passes through the front polarizer it becomes linearly polarized. It then passes through the front glass and is rotated by the liquid crystal molecules and passes through the rear glass. If the analyzer is rotated 90° to the polarizer, the light will pass through the analyzer and be reflected back through the cell. The observer will see the background of the display, which in this case is the silver gray of the reflector.

The LCD glass has transparent electrical conductors plated onto each side of the glass in contact with the liquid crystal fluid and they are used as electrodes. These electrodes are made of Indium-Tin Oxide (ITO). When an appropriate drive signal is applied to the cell electrodes, an electric field is set up across the cell. The liquid crystal molecules will rotate in the direction of the electric field. The incoming linearly polarized light passes through the cell unaffected and is absorbed by the rear analyzer. The observer sees a black character on a sliver gray background (**Figure 1.3**). When the electric field is turned off, the molecules relax back to their 90° twist structure. This is referred to as a positive image, reflective viewing mode. Carrying this basic technology further, an LCD having multiple selecTable electrodes and selectively applying voltage to the electrodes, a variety of patterns can be achieved.[114]

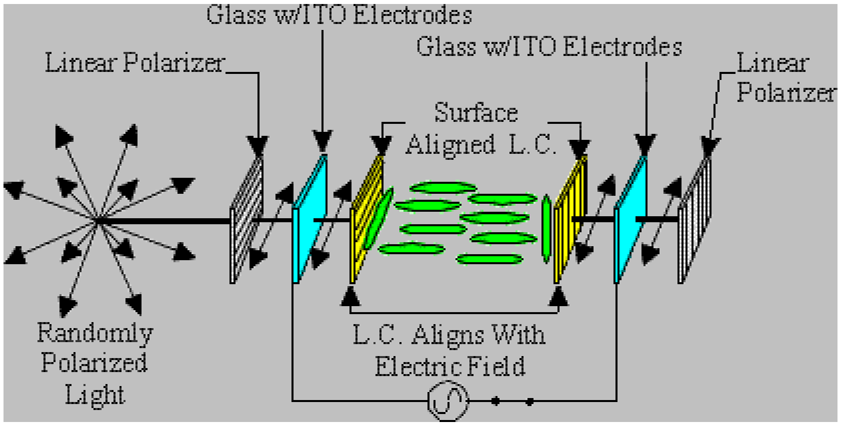


Figure 1.3: Structure of twisted nematic display in normally white mode (on-state).

The alignment layers not only align the liquid crystal molecules unidirectionally, but they also generate a slight tilt to the molecues (**Figure 1.4**). Either end of liquid crystal molecules may rise when the voltage is applied if the molecules lie flat on the surface. The slight tilt, thus, results in a fast responce to the applied voltage. The angle between the axis of the liquid crystal molecules and the alignment layer is called pretilt angle.

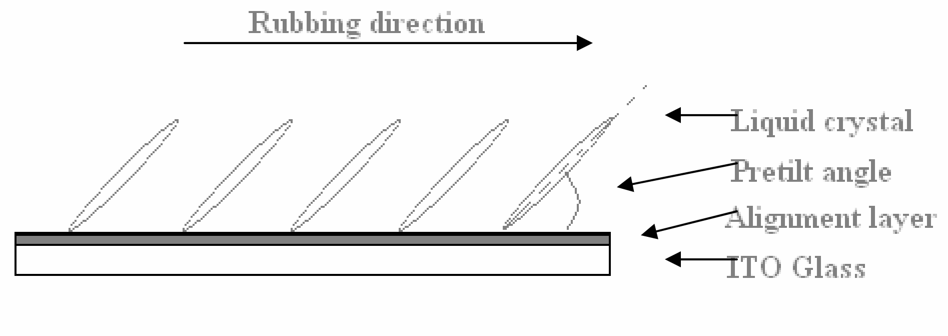


Figure 1.4: Alignment and pretilt of liquid crystal molecules.

1.2.2.2 Polyimides for LCD application

Rubbed polymer films are used in flat-panel displays to control the alignment of liquid crystals in contact with the polymer, a phenomenon first discovered by Maugin in 1911.[115] Polyimide and coployimide (poly(amideimide)) films have been used as alignment layers in LCDs because of their good adhesive properties, insulation ability and orientational ability. A solution of polyamic acid is first spin coated on to a ITO glass plate. The resulting film is cured at 150 to 250°C to form a thin polyimide layer. With soluble polyimides, a thin film is spin coated onto a ITO glass plate and baked to evaporate solvent at relatively low temperature. The polyimide surface is then repeatedly rubbed in the same direction with a cotton, silk or velvet cloth. When liquid crystal molecules are placed on this layer, they will align in the same direction as the rubbing direction. The actual tilt angle obtained is a function of polymer ordering on the surface, the resulting surface energy, the nature of the cloth used to buff the surface and the amount of buffing work. In addition to these variables, each of the hundreds of commercial liquid crystal formulations interact differently with a given surface. In general, however, the single most important factor determining the value range of the tilt angle is the intrinsic character of the polymer used to control this angle. Berreman proposed that liquid crystal molecules are oriented and a pretilt induced by small mechanical grooves.[116] Uchida proposed that the alignment of polyimide chains induced the pretilt.[117]

The pretilt angle is critically important to the manufacture of LCDs. For most standard twisted nematic (TN) LCDs (off = white) a small pretilt angle of 2-3° is enough, which can be generated by simply rubbing several commercial polyimide films. For more sophisticated supertwisted nematic (STN) LCDs higher tilt angles of greater than 5° are required because of the higher twist angles in the liquid crystal molecules.[118] There are, however, other LCD applications which require lower tilt angles of less than 2° while maintaining good and stable alignment properties. For example, normally black LCDs (off = black) require tilt angles lower than that achieved using conventional polyimides.[119]

The effect of several alignment layer chemical structures on pretilt angles generated were determined by Nozaki and coworkers.[120] High pretilt angles were obtained with 1) high level of imidization, 2) rigid tetracaroxylic acid moiety and 3) uneven distribution of fluorine atoms in polymer film. It has been also found that the orientation of polyimide film on thin layer surface played an important role in aligning liquid crystal molecules on the surface.

Liu et al[121] in their study of molecular design of liquid crystal alignment polyimide layer (LCAL) showed that LCAL should have flexible moieties in the polymer backbone and some long-chain alkyl groups should be introduced into the main chain or the side chain so as to raise the LC pretilt angle. Polyimides derived from aliphatic diamines with different lengths and BPDA, displayed and odd even effect. The higher pretilt angle in the reange of 3-6° were obtained with polymers containing even-numbered aliphatic segments. However, lower pretilt angles of 0.5° were obtained with polyimides containing odd-numbered segments (**Figure 1.5**).[122]

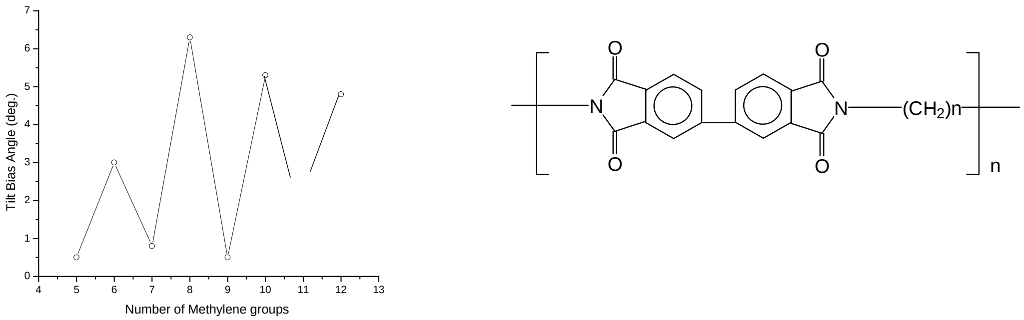


Figure 1.5: Effect of alkylene chain length on pretilt angle.

It has been observed that polyimides with long alkyl and fluorinated alkyl side branches generate high pretilt angle of LCs by rubbing.[123-126] Thus, they have suggested that the high pretilt angles are attributed to steric interactions between LCs and neatly aligned branched chains.

Recently, series of polyimides with side chains containing the mesogens has been prepared.[127-128] In this case the mesogen is supposed to act together with LC in their alignment.

The thermal requirements in the case of LCDs are not stringent and therefore the use of polyimides derived from alicyclic monomers[129-130] and monomers with alkyl groups have gained importance.

Representative examples of polyimides used as alignment layers for LCDs are presented in **Table 1.2.**

Table 1.2: Representative examples of polyimides used as alignment layers for LCDs.

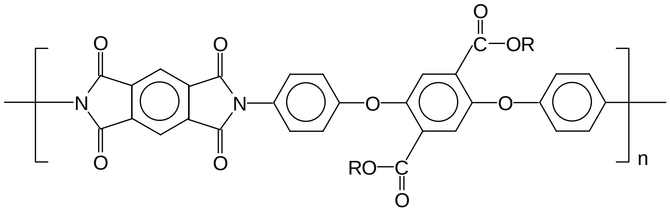
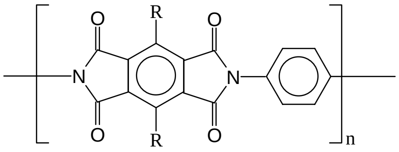
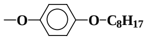
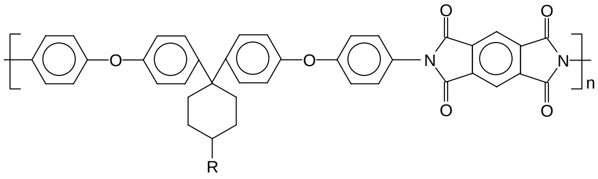
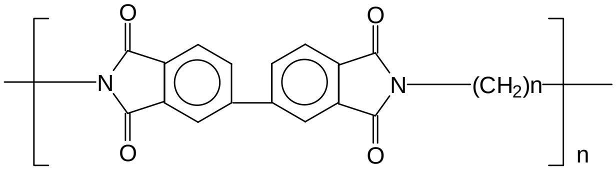
No	Polyimide	Pretilt angle, °	Reference
1	 R = CH_3, C_4H_9, C_8H_{17}, $C_{12}H_{25}$	8.3-10.2	131
2	 R = 	25 - 87	132
3	 R = C_nH_{2n+1} (n = 0-5)	7.3-14	133
4	 n = 5-12	3-6	122

Table 1.2: Representative examples of polyimides used as alignment layers for LCDs…Continued.

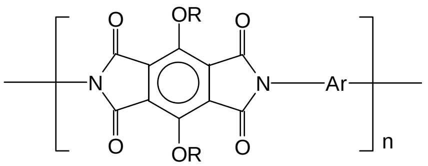
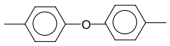
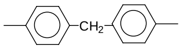
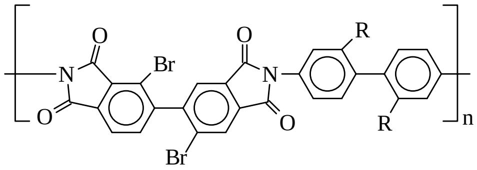
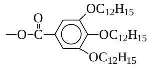
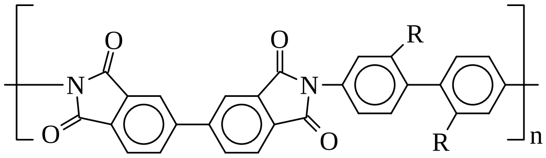
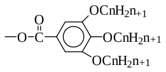
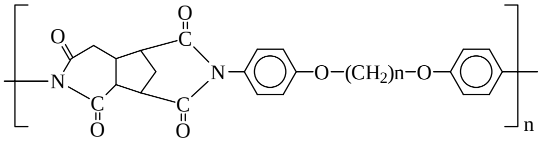
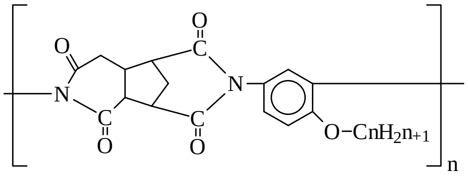
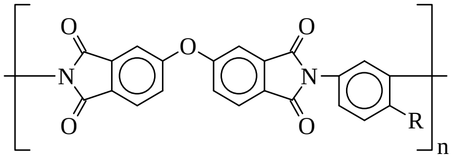
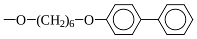
No	Polyimide	Pretilt angle, °	Reference
5	 R = C_8H_{17}, $C_{12}H_{25}$ Ar  	8.0,14.5 5.0,16.4	134
6	 R = 	6	118
7	 R =  n = 14, 16	90	118

Table 1.2: Representative examples of polyimides used as alignment layers for LCDs…Continued.

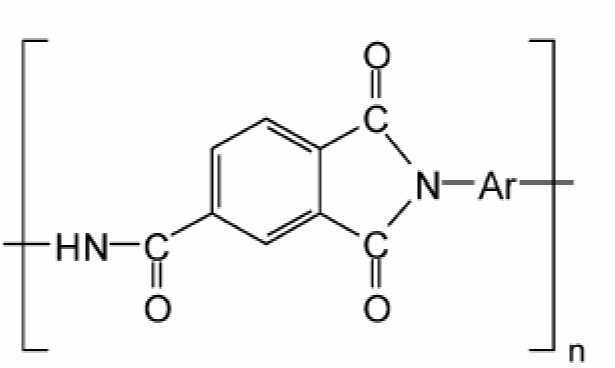
No	Polyimide	Pretilt angle, °	Reference
8	 n = 4,6,8,10,12	1.9-5.4	129
9	 n = 6, 8, 10, 12, 14, 16	4.0-10	130
10	 R = 	11.8	127

1.2.3 Applications of polyimides

The list of polyimide applications is unending and it still keeps growing with the increasing demands of growing technologies. Applications of polyimides as alignment layers in LCD technology have already been described in **Section 1.2.2**. Aerospace industry has been and still continues to be major user of polyimides in various forms, such as, adhesives, coatings, matrix for composites, etc. Polyimides are used in the electronics field in the areas such as wafer fabrication, adhesion, chip packaging and assembly.[135-142] They can be used as optical waveguides in optoelectronic devices.[143]

1.3 Poly(amideimide)s

Poly(amideimide)s are a class of polymers containing, amide and heterocyclic imide unit in the polymer backbone.



Historically, the first report concerning aromatic poly(amideimide) was made by DuPont in 1945. However, only in 1972 poly(amideimide) was successfully introduced as commercial polymeric materials (Torlon) by Amoco.[144] Since that time, an impressive variety of poly(amideimide)s have been synthesized and reported in the literature.

Poly(amideimide)s are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance. Poly(amideimide)s are known to have the advantages of polyamides and polyimides.

1.3.1 Synthesis of poly(amideimide)s

Poly(amideimide)s can be synthesized by methods similar to those of polyimides (**Section 1.2**) and polyamides (**Section 1.4**). They are usually synthesized through three main routes

1. Amide-imide forming reaction[145-153]
2. Imide forming reaction using amide containing monomers[154,155]
3. Amide forming reaction using imide containing monomers[156-166]

Apart from above mentioned routes, poly(amideimide)s can also be prepared by acid hydrazide route.[167-169]

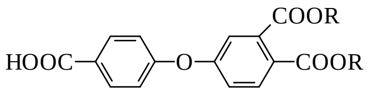
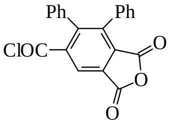
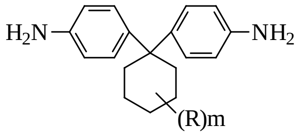
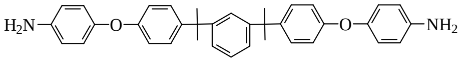
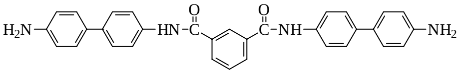
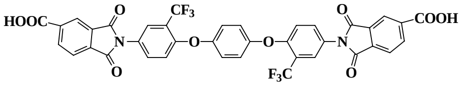
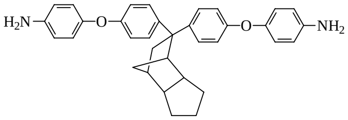
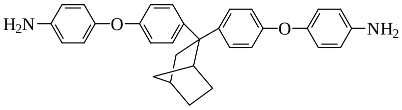
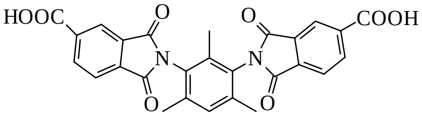
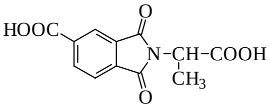
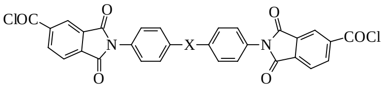
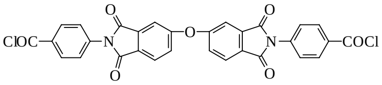
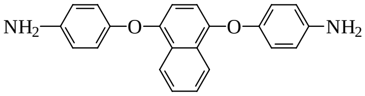
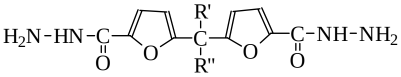
1.3.2 Structure property relationship in poly(amideimide)s

Representative monomers which have been used for synthesis of organosoluble poly(amideimide)s are collected in **Table 1.3**.

1.3.3 Applications of poly(amideimide)s

Poly(amideimides)s has been investigated for various applications. For example poly(amideimides)s have been applied to finger mounted tactile sensors,[171] cold valves for superfluid helium,[172] membranes for separation and purification of fluid mixtures,[173] alignment surfaces for liquid crystals,[174] and as an organic host for inorganic materials,[175] Poly(amideimide)s have a chemical structure similar to polyimide polymers, which have found common use in integrated optic[176] and microelectromechanical[177] devices. However, the inherent stability and mechanical robustness of poly(amideimide)s may make it superior for certain microdevice applications.

Table 1.3: Representative monomers for synthesis of organo-soluble poly(amideimide)s.

No.	Monomer	Ref	No	Monomer	Ref
1		146	2		147
3		148	4		149
5		153	6		156
7		157	8		158
9		159	10		160
11		161	12		162
13		166	14		167

1.4 Polyamides

Polyamides are polymers with recurring amide groups (-CO-NH-) as an integral part of the main polymer chain. Polyamides occupy a prominent position among the synthetic high polymers. The first synthetic polyamide, polybenzamide was obtained by Harbordt in 1862.[178] The first commercially produced aromatic polyamide was poly (m-phenyleneisophthalamide) (Nomex, Du Pont, 1967).[179,181] Some years later, development of the preparation of poly(p-phenyleneterephthalamide) led to the commercialization of the *para* product Kevlar (DuPont) in the early seventies.[180,181]

Although these products have become of great commercial importance, the fabrication of unsubstituted aromatic polyamides has in general proved to be difficult because they show tendency to decompose during, or even before melting and are insoluble in most common organic solvents.[182]

There has been therefore an increased interest in the preparation of polyamides with different substituents or structural irregularities in order to improve their processability.

1.4.1 Synthetic methods for the preparation of aromatic polyamides

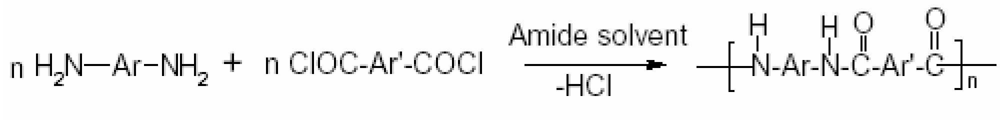
Aromatic polyamides have been prepared by several methods.[183]

1.4.1.1 Low temperature polycondensation of diamines and diacid chlorides

Low temperature polycondensation (<100°C) of diamines and diacid chlorides has been used experimentally and commercially for the preparation of high molecular weight polyamides. This method was developed by Du Pont and can be carried out in solution or at the interface of two solvents. Solution polycondensation involves a diamine and diacid chloride reacting in an amide solvent such as NMP, hexamethylphosphoramide (HMPA), or DMAC.[184,185]

1.4.1.2 (a) Solution polycondensation of diamine and diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide solvent such as NMP, HMPA, DMAc or tetramethylurea (TMU) (**Scheme 1.12**).



Scheme 1.12: Solution polycondensation of a diamine and a diacid chloride.

The amide solvent serves also as an acid acceptor for the hydrogen chloride produced in the reaction. Other polar aprotic solvents such as dimethylformamide and dimethylsulfoxide cannot be used because they react significantly with acid chlorides. The solvent should allow maximum solubility (swellablity) of the polymer formed at the early stage of polycondensation, and the solvation properties of amide solvents can usually be increased by the addition of salts such as LiCl or $CaCl_2$.[186,87]

1.4.1.3 (b) Interfacial polycondensation of diamine and diacid chloride

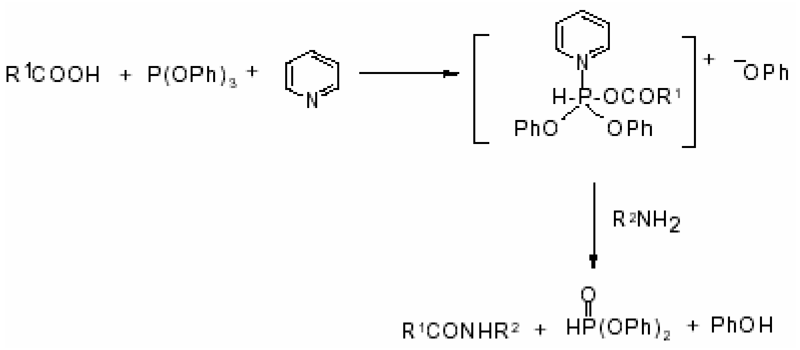
As described above, in low temperature solution methods, the monomers are dissolved and reacted in a single solvent phase. Monomers can also be brought to react at the interface of two phases. The so-called interfacial polycondensation method is an adaptation of the well known Schotten-Baumann reaction. In this method, two fast reacting intermediates are dissolved in a pair of immiscible liquids, one of which is preferably water. The water phase generally contains the diamine and usually an inorganic base to neutralize the byproduct acid. The other phase contains the acid chloride in an organic solvent such as dichloromethane, toluene or hexane (**Scheme 1.13**).

Scheme 1.13: Interfacial polycondensation of diamine and diacid chloride.

The two-phase system is stirred vigorously to obtain high molecular weight polymers. The difference between conventional step polymerization and interfacial polymerization is that in the interfacial polymerization the monomer diffusing to the interface reacts only with the end of the polymer chain resulting in high molecular weight polymer. The key factors that influence this type of polycondensation have been studied in detail by Morgan.[188] Since the temperatures needed are low, the side reactions are minimized and also the polymers, which are unstable at high temperatures, can be synthesized.

1.4.1.4 High temperature solution polycondensation of dicarboxylic acids and diamines

In the beginning of 1970's two Japanese groups Ogata and co-workers[189,190] and Yamazaki and Higashi[191,192] published a series of papers on the successful use of phosphorus compounds as condensing agent for the direct polycondensation of dicarboxylic acids and diamines to form polyamides. This reaction involves the formation of a complex of the acid with triphenylphosphite in NMP and pyridine, which further reacts with diamine to give the product (**Scheme 1.14**).

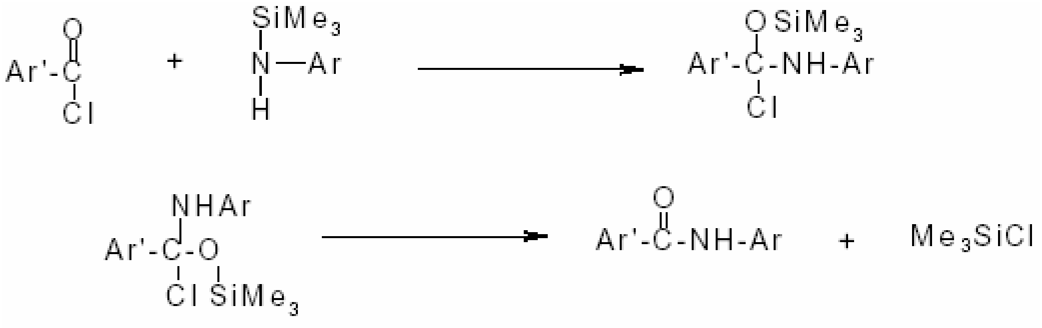


Scheme 1.14: Condensation reaction involving acid and amine to form amide in the presence of triphenylphosphite.

$CaCl_2$ and LiCl were used along with NMP to improve the molecular weight of polymers. The role of $CaCl_2$ and LiCl is quite complicated. They can form complexes with pyridine and are more soluble than the salts alone, and NMP with a higher content of metal salt can solubilize polyamide formed in the reaction medium more effectively, leading to high molecular weight products.

1.4.1.5 Polycondensation of N-silylated diamines and diacid chlorides

While most of the efforts in the synthesis of high molecular weight polyamides have been oriented towards the activation of the diacids, there are some reports on the activation of diamine component by reacting it with trimethylsilyl chloride. Indeed, high molecular weight polyamides have been synthesized by low temperature polycondensation of an N-silylated aromatic diamine with an aromatic diacid chloride.[193-195] The following nucleophilic addition-elimination two-step mechanism has been proposed for the acyl substitution of an acid chloride with an N-silylated amine (**Scheme 1.15**).



Scheme 1.15: Condensation reaction of N-silylated amine and acid chloride.

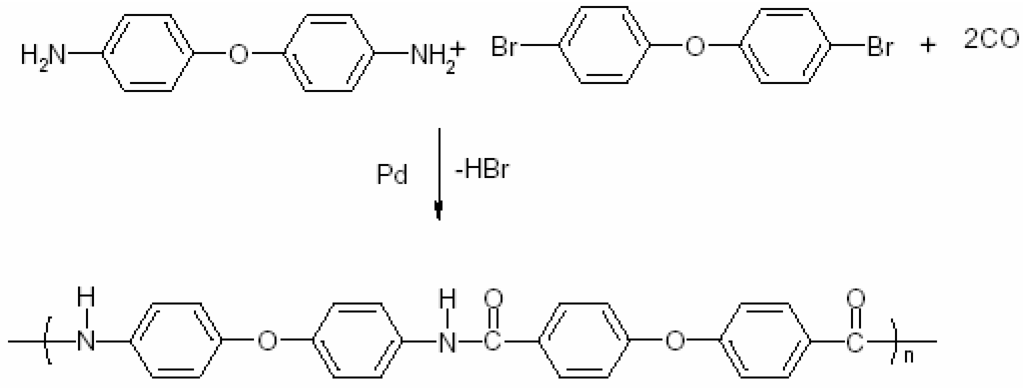
Lozano et. al have reported the formation of silylated diamines *in situ* by adding trimethylchlorosilane to the diamine solution that, on addition of diacid chloride gives polyamides.[196] This method is especially useful for the preparation of polyamides from aromatic diamines having low reactivity.

1.4.1.6 Polycondensation of diisocyanates and dicarboxylic acids

Another promising route for the preparation of aromatic-aliphatic copolyamides has been developed by Simioneseu et al[197] and Onder et al[198,199] from a combination of aromatic diisocyanates and dicarboxylic acids. This route leads to the direct formation of polyamides with the elimination of CO_2 without the use of any condensing agents. Several polyamides and copolyamides have been prepared by this method.[200-201] A commercial scale preparation of aromatic polyamides from 1,3-phenylene diisocyanate and isophthalic acid in the presence of a catalyst has been reported.[202] Polyamides have also been prepared by the reaction of aromatic diisocyanates with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst.[203-204]

1.4.1.7 Transition metal-catalyzed polycondensation of aromatic diamines, dihalides and carbon monoxide

Polyamides can also be synthesized by palladium-catalyzed carbonylative coupling of diamines and dihalides (**Scheme 1.5**).[205-210]



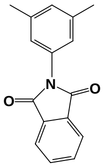
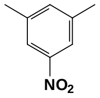
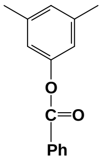
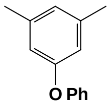
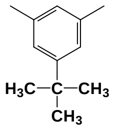
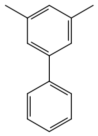
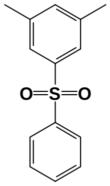
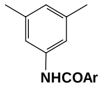
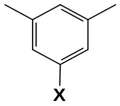
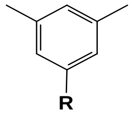
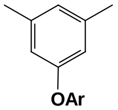
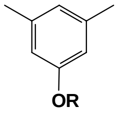
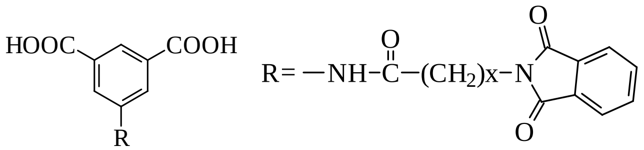
Scheme 1.16: Transition metal catalyzed carbonylative coupling of aromatic diamines and dihalides.

1.4.2 Structure-property relationship in aromatic polyamides

Recently, there has been an increasing requirement for new processable engineering plastics having a moderately high softening temperature and solubility in organic solvents. To alleviate this problem a number of strategies were adopted to synthesize soluble/processable polyamides without significantly affecting the thermo-mechanical properties. Attempts have been made to increase the solubility of polyamides by introducing flexible bonds in the polymer backbone or bulky pendant groups along the main chain. Substituted isophthalic acid has been a center of focus for long time because of the *meta*-catenation, one of the aspects of improvement in processability and ease of synthesis. The representative examples of substituted isophthalic acids are listed in **Table1.4**

It has been observed that incorporation of pendant phenyl groups improved solubility, retaining thermal stability. The incorporation of halogen atoms showed increase in Tg and it had a direct dependence on the size of the halogen.[213] Kajiyama et al[215] studied the effect of perfluoro alkyl group on the properties of polyisophthalamides. There was a decrease in Tg with increase in carbon chain length. The effects of pendant alkoxy groups on polyisophthalamides have not yet been systematically studied.

Table1.4: Representative examples of substituted isophthalic acid monomers.

No	Diacid	Ref	No	Diacid	
1		211	2		212
3		211	4		211
5		214	6		211
7		211	8	 Ar = Ph, PhNHCOPh, Pyridine	211
9	 X = F, Cl, Br, I	213	10	 R = C_4F_9, C_8F_{17}	215
11	 Ar = $PhCF_3$, $Ph(CF_3)_2$	216	12	 R = $C_{11}H_{23}$-$C_{18}H_{37}$	217
13					218

1.4.3 Applications of polyamides

Aromatic polyamides are resistant to alkali and have good hydrolytic stability as compared to nylons and polyesters. Aramids have good permselective properties and are used as hollow-fiber permeation separation membranes to purify sea and brackish water or for the evaporation of numerous types of salts from water.[219] Many polyamides having pendant alkyl groups have been synthesized to improve the selectivity and permeability of the resulting membranes.[220-221] Polyamides are well known for reverse osmosis membranes but less for gas separation.[222] Aromatic polyamides also offer excellent thermal and mechanical properties, show good chemical resistance and are easily spun into hollow fibers for high performance gas separation modules. Polyamides have also been used as liquid crystal alignment layers. But only a few reports are available in this area and most of them are regarding the polyamides having pendant alkyl groups.

1.5 Polyesters

Polyesters are polymers with recurring ester groups (-CO-O-) as an integral part of the main polymer chain.

The reaction of aromatic dicarboxylic acids and diphenols were first noted by Conix[223] in 1957. The literature on polyarylates based on aromatic dicarboxylic acids is extensive. Before the Production of first commercial aromatic polyester, U-polymer (a polyarylate based on bisphenol A and tere/iso phthalates) by Unitica, in 1974, 140 different chemical compositions of polyarylates were listed.[224]

Polyarylates have found applications in wide variety of areas by virtue of their attractive electrical and mechanical properties. However, polyarylates are generally difficult to process because of their limited solubility in organic solvents and high glass transition and melting temperatures. The melt viscosity of BPA-based polyesters is noted to be high and thus it's injection mouldability is considered to be a limitation. Therefore a great deal of effort has been expended to try to improve processability of polyarylates.

1.5.1 Synthesis of Polyesters

High molecular weight aromatic polyesters are prepared by two chemical routes.

1. Acid chloride route
2. Transesterification route

1.5.1.1 Acid chloride route

This route is generally applicable and mostly used for the synthesis of polyarylates. The diacids are converted in diacid chlorides followed by condensation with diphenols. The reaction can be performed by three different processes

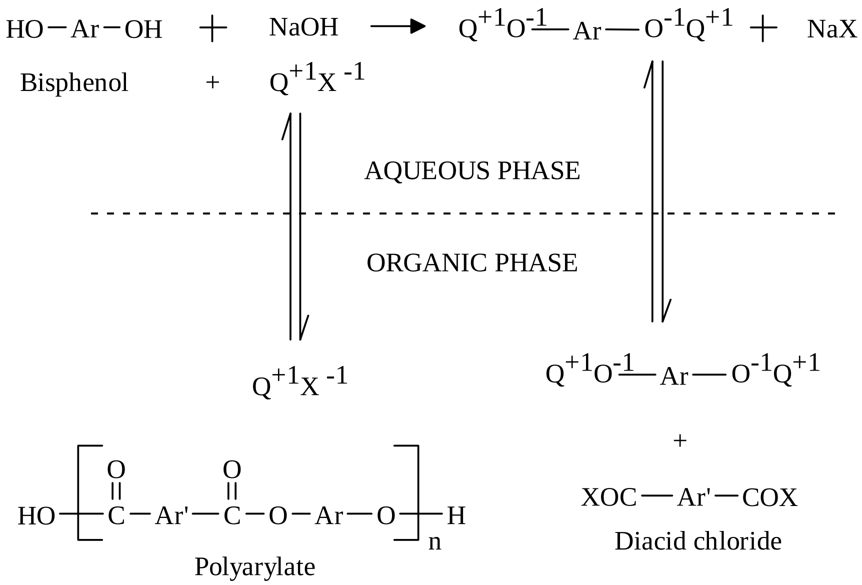
1.5.1.1.1 Interfacial polycondensation

The interfacial process for the preparation of polyarylates was first described by Eareckson[225] and Conix.[223] Basically, the interfacial polymerization involves the reaction of an aqueous solution of the dialkali metal salt of a diphenol with a solution of the acid chloride(s) in a water immiscible solvent which is inert under the reaction condition. The water immiscible solvents used for the interfacial polycondensation are methylene chloride, chloroform, 1,2-dichloroethane, chlorobenzene, nitrobenzene, cyclohexane, etc.

As the two starting immiscible solutions are brought into contact, the polymerization occurs at the interface where a film of the polymer is formed. Diffusion through this film, affected by the extent to which the solvent can swell or dissolve the polyarylate, is an important factor to achieve high molecular weight polyesters.

The two phase reaction can be accelerated by the use of small amount of phase transfer catalyst (PTC) such as tertiary amines as well as quaternary ammonium or phosphonium salts or crown ethers.

A typical phase -transfer catalyzed interfacial polycondensation is shown in **Scheme 1.17.**



Scheme 1.17: Schematic of interfacial polycondensation.

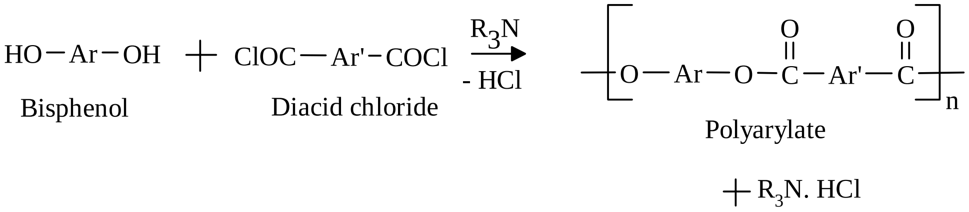
The basic function of PTC is to transfer the anions of the reacting salt into the organic medium in the form of ion pairs. These ion pairs react with chloride ions in the organic phase producing the desired product. The regenerated PTC is transferred back into the aqueous medium.[226,227] The most commonly used PTC's are benzyltriethyl-ammonium chloride (BTEAC), tetraethylammonium chloride (TEAC), tetramethylammonium chloride (TMAC), benzyltriphenyl phosphonium chloride (BTPPC), 15-crown-5 (15-C-15), and 18-crown-6 (18-C-6).

The choice of organic solvent is very important in interfacial polycondensation. It is advantageous that the polyarylate formed during the polymerization should remain in the solution form to obtain the high molecular weight polymers. The precipitation of polymer lowers the reaction rates, hence, low molecular weight polymers are obtained.

An interfacial synthesis of polyarylates using acid chlorides that were prepared *via* the chlorination of the corresponding dimethyl esters was described.[228] The process reportedly yields materials having excellent color, as well as improved thermal and hydrolytic stability.

1.4.1.1.2 Low temperature solution polycondensation

Low temperature solution polycondensations are generally run at room temperature or between -10^{0}C to +30^{0}C. Polyarylates are synthesized by the reaction of equivalent amounts of a diacid chloride and a dihydroxy compound in an inert solvent in the presence of an acid acceptor. The reaction is typically conducted in solvents such as dichloromethane, in the presence of acid acceptor such as pyridine or triethylamine (**Scheme1.18**).



Scheme 1.18: Solution polycondensation of bisphenol and diacid chloride.

High molecular weight polyarylates are successfully synthesized in pyridine alone or in combination with a tertiary amine in an inert organic solvent.[223,225,229-231]

1.5.1.1.3 High temperature solution polycondensation

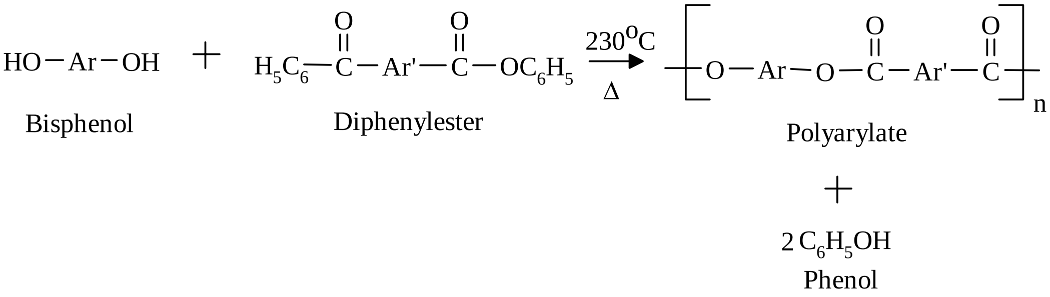
The polycondensation of a diacid chloride with a bisphenol without an acid acceptor is slow at room temperature. The rate of polycondensation increases with increasing temperature. The high temperature solution polycondensation is carried out at elevated temperatures (~200^0C) in an inert high boiling solvent. The high boiling solvents used are nitrobenzene and o-dichlorobenzene.[232] The o-dichlorobenzene and pyridine system is the most effective one to produce the polymer with high molecular weight.[233] Polyarylates are also prepared in good yields at 215-220^0C in dichloroethylbenzene.[234,235] No acid acceptor is needed because the evolved hydrogen chloride is continuously removed from the system with the aid of an inert gas. A wide variety of other solvents are useful and include chlorinated benzenes (tetrachlorobenzene), chlorinated biphenyls or diphenylethers, chlorinated naphthalenes, as well as non-chlorinated aromatics such as terphenyl, benzophenones, dibenzylbenzenes,and the like.

1.5.1.2 Transesterification route

Transesterification reactions are carried out by three different routes.

1.5.1.2.1 Phenyl ester route

The reaction between a diarylester of an aromatic dicarboxylic acids and an aromatic diphenols results in high molecular weight polyesters (**Scheme 1.19**). This method was successfully employed for the first time by Blaschke and Ludwing[236] for the synthesis of polyarylates. The diphenylesters are less reactive as compared to the corresponding acid chlorides, hence, higher reaction temperatures and longer reaction times are necessary to obtain high molecular weight polyarylates.



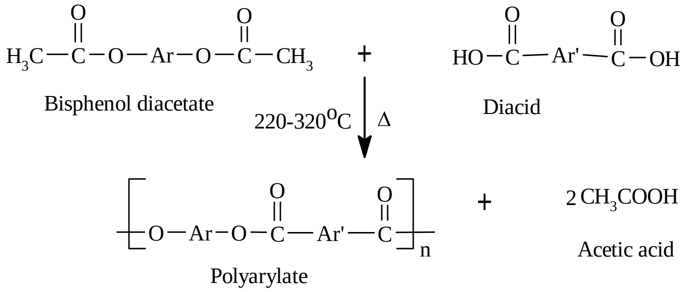
Scheme 1.19: Polyester synthesis *via* diphenylester route.

In this process the ester interchange reaction proceeds without catalysts, but the rate enhancement can be achieved in the presence of catalyst.[237-240] Lithium phenoxide, sodium phenoxide and potassium borophenoxide are the preferred catalysts. This is a reversible reaction, hence, removal of phenol, a by-product from the reaction system is essential to obtain high molecular weight polyarylates. This route compares favorably with the diacetate route.

1.5.1.2.2 Phenol acetate route

In this process, polyarylates are synthesized by the reaction of stoichiometric amounts of an aromatic dicarboxylic acid and the diacetate derivative of an aromatic diphenol at high temperature under inert atmosphere (**Scheme 1.20**).

Phenol acetate route, first described by Conix[223] and Levine and Temin[241] is essentially a reversible melt process which requires continuous removal of acetic acid-a by-product in order to achieve high molecular weight polyesters. It was postulated that the aromatic ester formation occurs by the reaction of a phenol end group and mixed anhydride with elimination of acetic acid. [242]



Scheme 1.20: Polyester synthesis *via* phenol acetate route.

Generally, the polycondensation is carried out in the melt or solid state at a temperature ranging from 200-350^{0}C under nitrogen atmosphere with or without catalyst.[243] The color and the thermal stability of polyarylate is affected by the presence of residual quantity of catalyst in the product, hence, polycondensation reaction without a catalyst is preferred. Catalyst most often cited for the phenol acetate route are based on antimony, titanium, magnesium, manganese and zinc. The choice and use of catalyst is such that there should not be deleterious effects on the color and hydrolytic stability of the polyarylates.

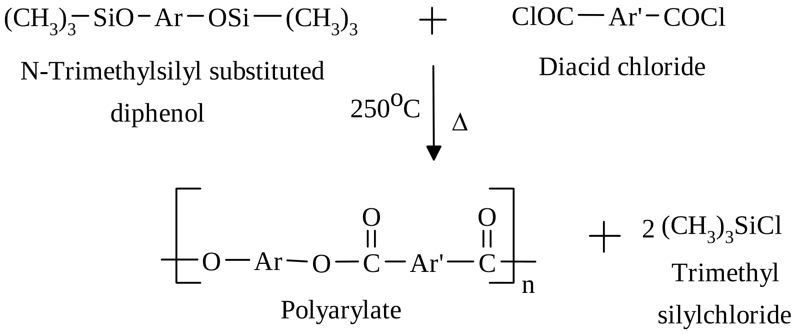
1.5.1.2.3 Phenyl ester and phenol acetate route

One variation of the diacetate route involves the reaction of bisphenol-A diacetate with dimethyl ester of aromatic dicarboxylic acids i.e. dimethyl tere/ isophthalates. In this sequence, condensation would occur with the liberation of methylacetate; however, the reactions proceeds only to very low molecular weights (catalyzed or uncatalyzed).[244] German group around 1990 has claimed that high molecular weight polyarylates can be prepared from bisphenol-A diacetate, dimethylterephthalate, and dimethylisophthalate.[245] An improved process for preparation of aromatic polyesters using simple alkylester of aromatic dicarboxylic acids and dihydric phenols by melt polycondensation has been reported.[246]

1.5.1.3 Other routes for polyester synthesis

1.5.1.3.1 Phenol silyl ether route

Phenol silyl ether route for the synthesis of polyarylates was first demonstrated by Kricheldorf[247] in 1979. The condensation of bisphenol disilylethers with dicarboxylic acid chlorides at elevated temperature yields high molecular weight polyarylates (**Scheme 1.21**). Various polyarylates with high molecular weight have been produced by this method.[248-250]

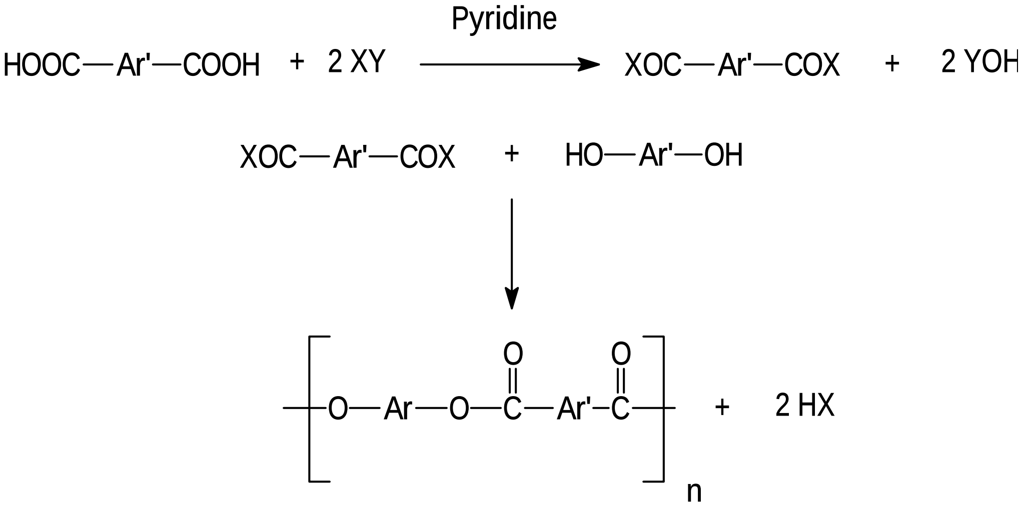


Scheme 1.21: Polyester synthesis *via* phenyl silyl ether route.

There are several advantages of this method. Silylated monomers are obtained in pure form by simple distillation. The volatile halosilanes obtained as a byproduct during the polycondensation are less harmful compared with hydrogen fluoride and hydrogen chloride which are generated in the absence of silyl groups.

1.5.1.3.2 Direct esterification route

Polyesterification of an aromatic dicarboxylic acid and an aromatic diol is very sluggish even at high temperature because of low reactivity of monomers. However, polyarylates have been synthesized by direct polycondensation of a dicarboxylic acid and a diphenol in the presence of a condensing agent, The condensing agent acts as an activating agent for dicarboxylic acid. The activated diacid intermediate formed condenses with bisphenol to form polyarylates (**Scheme 1.22**).



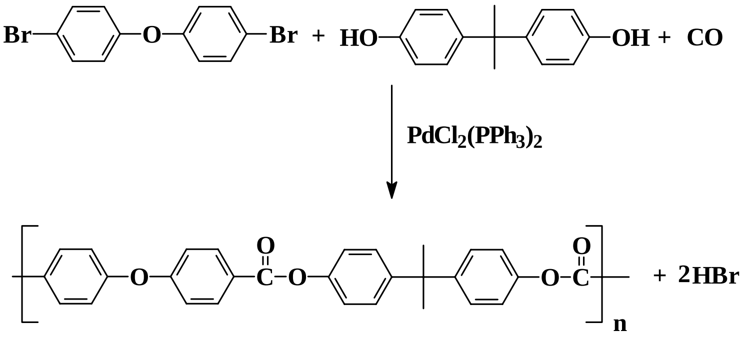
Scheme 1.22: Polyester synthesis *via* activated polycondensation.

This method has been extensively studied by Higashi.[251] A dicarboxylic acid is reacted with a condensing agent in a solvent such as pyridine. The resulting activated diacid intermediate is then condensed with bisphenol in the solution under relatively mild conditions. Mixed polymerization solvent was used to obtain high molecular weight polyarylates.[252] The effective condensing agents investigated so far for the preparation of polyarylates are triphenylphosphine chloride,[253] aryl sulfonyl chloride,[254] diphenyl chlorophosphate with metal salts,[255,256] phosphorous oxychloride with metal salts,[257] thionyl chloride[258] and p-toluenesulfonyl chloride with dimethylformamide.[252,259,260] The condensing agents afford highly reactive diacid derivatives such as acyloxyphosphonium salts or mixed anhydrides by the *insitu* reaction with dicarboxylic acids.

Direct polycondensation reactions are sensitive to reaction medium, aging conditions and reaction temperature. The direct polyesterification method is useful for the laboratory scale preparation of polyarylates.

1.5.1.3.3 Palladium-catalyzed carbonylation of aromatic dibromides and bisphenols

Heck[261]and Stille[262] reported the palladium-catalyzed carbonylation of aromatic dibromides with dihydroxyl compounds. However, the resulting polyesters were low molecular weight polymers. This ester forming reaction was extended by Imai et al[263] for the synthesis of polyesters based on aromatic dibromide, bisphenol-A and carbon monoxide using $PdCl_2(PPh_3)_2$ and 1,8- diazabicyclo[5,4,0]-7-undecene (DBU) in chlorobenzene at 115°C (**Scheme 1.23**).



Scheme 1.23: Polyester synthesis *via* metal catalyzed reaction

The effects of reaction variables, such as type and amount of base, catalyst, reaction medium and reaction temperature have been studied in detail. Synthesis of high molecular weight polyarylates were reported using diiodide monomers such as p-diiodbenzene and 2,5-diiodo-p-dodecyloxybenzene.[264]

1.5.2 Structure-property relationship in polyesters

Effect of monomer structure on the polyester properties has already been reviewed.[244] Structure-property relationship in view of gas separation will be discussed in this Section.

1.5.2.1 Gas separation

Gas separation using polymeric membranes was first reported by Mitchell in a study with hydrogen and carbon dioxide mixture in 1831.[265] Thomas Graham in 1866, made next important step in understanding the permeation process. He postulated that permeation is a three step process: the solution of the gas flows onto the upstream (high-pressure) surface of the membrane, gas diffuses through the membrane and finally, gas evaporates from the downstream (low-pressure) surface of the membrane.[266] This early description of gaseous transport is considered to be the basis for today's "solution-diffusion model", which is used to explain many membrane separations.

The separation of oxygen and nitrogen from air and hydrogen from carbon monoxide, methane or nitrogen are large consumers of energy in the chemical processing industry. In general, purified gases are more valuable than arbitrary mixtures of two or more components since pure components provide the option of formulating an optimum mixture for particular applications.

Energy-intensive compression of feed system is often needed to provide the driving force for permeation in membrane based separations. In their simplest ideal forms, membranes appear to act as molecular scale filters that take a mixture of two gases, A and B, into the feed port of the module and produce a pure permeate containing pure A and a nonpermeate containing pure B (**Figure 1.6**). Real membranes can approach the simplicity and separation efficiency of such idealized devices, but more usually, complex recycling of some of the permeate or nonpermeate stream may be needed because perfect selection of A and B molecules cannot be achieved in a single pass.

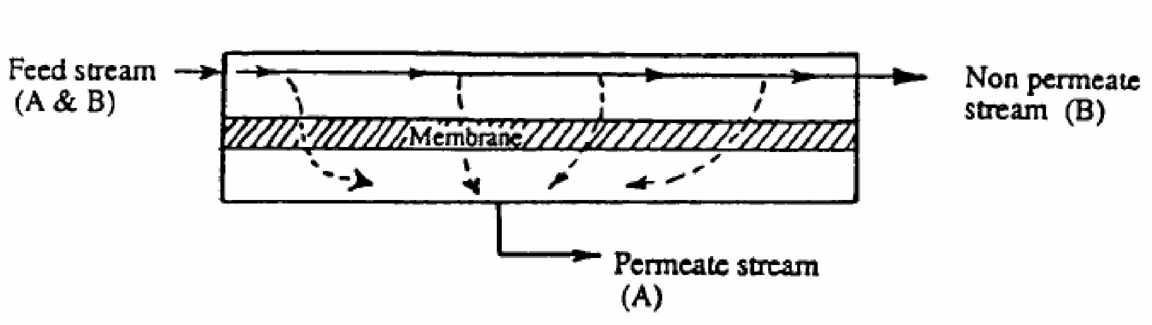


Figure 1.6: Generalized representation of an ideal membrane separation process.

Solution-diffusion membranes rely on the thermally agitated motion of chain segments comprising the polymer matrix to generate transient penetrant-scale gaps that allows diffusion from upstream to the downstream face of the membrane. By varying the chemical nature of the polymer one can change the size distribution of the randomly occurring gaps to retard the movement of one species while allowing the movement of the other. If one could perfectly control this distribution, a true molecular sieving process would occur and infinite selectivity would be achieved. The essential impossibility of such a situation is suggested by kinetic diameter data of various important penetrants (**Table 1.5**). The ability to regulate the distribution of transient-gap sizes in solution diffusion membrane is achieved by the use of molecules with highly hindered segmental motions and packing. Typically these materials are amorphous and are referred to as glassy polymers.

Table 1.5: Minimum kinetic diameter of various penetrants.[267]

Penetrant	He	H_2	NO	CO_2	O_2	N_2	CO	CH_4	C_2H_4	Xe	C_3H_8
Kinetic Diameter (Å)	2.6	2.89	3.17	3.3	3.46	3.64	3.76	3.8	3.9	3.96	4.3

Permeation is a function of two parameters: the solubility constant, S, and the diffusion coefficient, D. The solubility constant is a thermodynamic term based on specific polymer-penetrant interactions and condensability of the penetrant. The diffusion coefficient is a kinetic term referring to the movement of gas molecules inside the polymer matrix.[268] The diffusion coefficient determines "how frequently, on a time-averaged basis, a hole of sufficient volume appears next to the gas penetrant, enabling it to jump further through the membrane".[269]

The permeability of penetrant A (P_A) can be expressed in terms of mean diffusion coefficient (D_A) and the solubility coefficient (S_A) by equation 1.

$$P_A = D_A \times S_A \text{ …………………..(1)}$$

The experimental determination of permeability, P is based on equation 2

$$P = (\text{Steady state flux})/[\Delta p/l] \text{ …………………. (2)}$$

Where, Δp is the partial pressure difference of the penetrant across the membrane of effective thickness l.

The average solubility coefficient is obtained by the secant slope of the sorption isotherm at the upstream condition (penetrant concentration in the polymer/penetrant partial pressure).[270,271]

The ability of a membrane to selectively separate two gases A and B, is given by the separation factor $\alpha_{A/B}$, and is ratio of permeability coefficients of both penetrant gases. When the downstream pressure is negligible relative to the upstream pressure and when strong interactions between the polymer and both the penetrant molecules are not observed, $\alpha_{A/B}$ is almost equal to the "ideal" separation factor, $\alpha^*_{A/B}$. This ideal separation factor can be decomposed into contributions of solubility and diffusivity selectivities as indicated by equation 3.

$$\alpha^*_{A/B} = P_A/P_B = (D_A/D_B)\ (S_A/S_B)……………(3)$$

The diffusivity selectivity measures the ability of the polymer to select between gaseous molecules based on their sizes and shapes and depends on the mobility and packing of the polymer molecules. The solubility selectivity depends primarily on the condensability differences of the penetrants and their interactions with the polymer.

Usually the behavior of gas transport properties is analyzed and correlated to the polymer chemical structure and environment by the determination of physical and thermal properties such as, glass transition temperature (T_g), d-spacing and fractional free volume.

1.5.2.2 Polyarylates for gas separation

A major objective in macromolecular science is to properly design and optimize the polymeric repeat unit, since this allows one to selectively tailor certain material properties. Gas permeation science investigates inter- and intra-chain interactions of the polymer with respect to penetration by gas molecules, and on the microscopic level it is a sensitive probe to slight modifications in molecular structure.

There is a general relationship reported in the literature that as the permeability of gas A increases, its selectivity decreases.[272] This behavior is easily understood if the matrix is capable of tightly packing since the free volume, or unoccupied space, is reduced thereby decreasing its ability to transport permeants. Concurrently, the same material shows an improved “sieving” or higher selecting ability between gases of different sizes, shapes and electronic environments. While this general trend is true of polyesters, as well as most other polymers, there is a continuing goal to synthesize materials which can simultaneously achieve both higher permeability and higher selectivity, or which can attain higher permeability with only a slight reduction in selectivity.

Several researchers have reported on the differences observed by the varying the monomer linkages from *meta* to *para*.[273-276] It has been found that *meta* catenation tends to decrease permeability and increase selectivity due to impeded intra- and inter-segmental motion. The gas permeabilitis of various polyarylates have been studied by several researchers. The representative examples of polyesters based on isophthalic acid monomers are given in **Table 1.6**.

In all above mentioned examples the permselectivities of isophthalic acid -based polyarylates are higher than terephthalic acid based ones. However, the effect of pendant aliphatic chain on gas permeation properties of polyarylates has not yet been systematically studied.[283]

1.5.3 Applications of polyarylates

Polyarylates are excellent in their UV stability and suggests utility in exterior glazing, solar energy collectors, transparent signs, automotive lenses, lighting housing, safety lamp housings, transparent lamp diffusers, traffic lights, etc. They find applications in the field of electronics as electrical connectors and capacitors. Additional suggested applications include bearings, bushings, heater element holders, high temperature valves, and ball joint seals in automotive industry.

Table 1.6: Representative examples of polyesters based on isophthalic acid monomers.

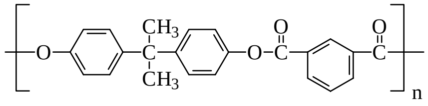
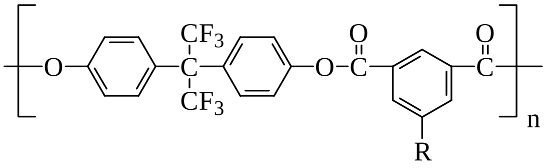
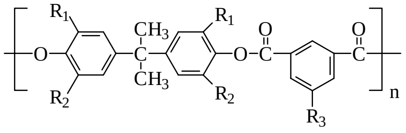
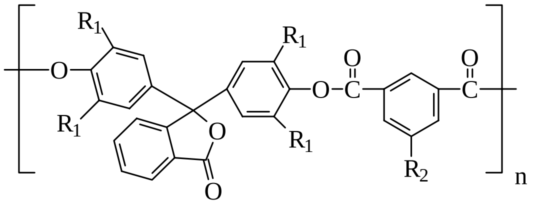
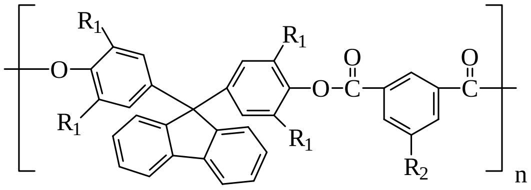
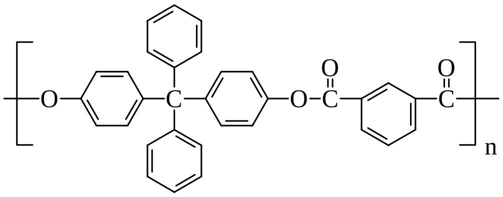
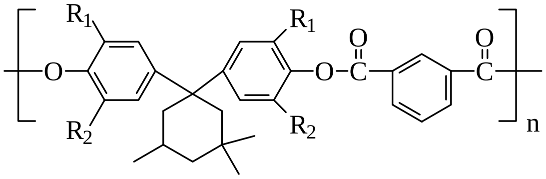
No	Polyester	Reference
1		277
2	 $R = H/C(CH_3)_3$	278
3	 **$R_1 = CH_3, R_2 = H$** **$R_1 = R_2 = CH_3$** **$R_1 = CH(CH_3)_2, R_2 = H$** **$R_3 = H/C(CH_3)_3$** **$R_1 = CH_3, R_2 = Br$** **$R_1 = Br, R_2 = Br$**	280
4	 $R_1 = H/Br, R_2 = H/C(CH_3)_3$	278,279

Table 1.6: Representative examples of polyesters based on isophthalic acid monomers…Continued.

No	Polyester	Reference
5	 R_1= H/ Br, R_2 = H/ C$(CH_3)_3$	278,279
6		281
7	 R_1=R_2 = H R_1=CH_3, R_2 = H R_1=R_2 = CH_3 R_1 =R_2 = Br R_1 =R_2 = Cl R_1=CH_3, R_2 =Br	282

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Chapter 2. Scope and objectives

High performance / high temperature polymers such as polyimides, poly(amideimide)s, polyamides, polyesters, etc. are of considerable interest because of their excellent mechanical and high-temperature properties.[1-8] However, they usually exhibit very low solubilities and melting points far above their thermal decomposition temperatures which limits their widespread applications. There are several reports describing approaches to improve the processability of polymers by making use of structurally modified monomers.[9-20] These include (1) introduction of flexible segments or groups into the polymer backbone which reduces chain stiffness, (2) introduction of bulky side groups which help in the separation of polymer chains and hinder the molecular packing and crystallization, (3) use of enlarged monomers containing angular bonds which suppress coplanar structures, (4) use of 1,3-disubstituted monomers instead of 1,4-disubstituted ones, and / or asymmetric monomers which lower regularity and molecular ordering, and (5) attachment of flexible chains as pendant groups. Several studies have focused on the possibility of improving solubility and processability of polymers, such as, aromatic polyimides, poly(amideimide)s, polyamides, polyesters, etc., by introducing flexible side chains, such as, alkyl or alkoxy groups.[21-24] It is interesting to notice that the peculiar structure of the main chain of such polymers is not altered by the attachment of flexible side chains. It is reported that the use monomers that bear pendent flexible groups greatly reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendent groups not only bring about improved solubility but also help lower the melting and glass transition temperatures.[14,18]

The development of high performance / high temperature polymers either matching different processability requirements or exhibiting new, specific properties is the driving force for the research in new monomers. For structural applications, easy processability, good mechanical properties, and good ageing behaviour are needed but low cost is an important requirement. However, for the functional applications (electronic, liquid crystal devices, membranes for gas separations, fuel cell membranes), the cost factor is not a very important consideration.

In the area of polyimide and poly(amideimide) synthesis, recent efforts have been concentrated on the design and synthesis of processable polymers with the purpose of obtaining certain advantageous properties, such as, adhesion, electrical insulation, transparency, liquid crystal (LC) alignability and gas permeability. The attachment of flexible side chains has drawn particular interest in polyimide and poly(amideimide) synthesis as it is known to increase not only the processability of polymers but also the pretilt angle of LC molecules on rubbed polymer surfaces.[21-23] The pretilt angle is a critical parameter for the excellent performance of liquid crystal display (LCD) devices. Commercial super-twisted nematic LCD devices are currently used in many electronic appliances and require pretilt angles > 5° for optimal performance with wide viewing angles. Some recent reports have pointed out that alkyl side chains along the polymer backbone greatly elevate pretilt angle and that alkyl side chain-containing polyimide and poly(amideimide)s could be highly promising candidates for excellent LC alignment layers.[21-29]

Thus, our synthetic research effort was directed towards structural modifications designed to disturb regularity and chain packing thus providing better processability to the polymers. The goal of the present research was to improve polymer processability *via* internal plasticization. Plasticization normally involves the incorporation of a low molecular weight plasticizer which improves polymer flow and processability. In internal plasticization, the plasticizer is chemically attached to or incorporated in the polymer backbone. The first objective of this research was to develop a synthetic scheme that would allow the introduction of plasticizing groups such as pendant alkoxy groups into the high performance polymers such as polyimides, poly(amideimide)s, polyamides, and polyesters. The approach involved synthesis of a series of alkoxy-substituted isophthalic acids, isophthaloyl dichlorides, *meta*-phenylenediisocyanates and isophthalic acid dihydrazides starting from 5-hydroxyisophthalic acid – a commercially available chemical. The 1,3-disubstitution of the reactive groups in the monomer structure was selected for the following reasons: (i) acid, acid chloride, isocyanate and acid hydrazide groups were placed in the 1 and 3 positions in order to obtain *meta*-catenation in the polymer backbone. Such catenation is known to increase solubility and reduce the Tg of polymers;[14] (ii) the functional groups were located at a sufficient distance from the alkoxy group so that their reaction with comonomers (dianhydrides / diamines / bisphenols) would not be sterically hindered. By relatively easy and inexpensive chemical routes, these monomers could be prepared that provide the structural characteristics needed for the improvement of properties such as processability, and specifically properties like pretilt angle and permeability. The length of pendent side chains was systematically varied in order to study the effects of side chain length on properties of polymers, such as, solubility, thermal stability, Tg and processabilty.

Another series of monomers consisting of alkoxy-substituted aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages was designed and synthesized.

The second objective of this research was to synthesize and characterize polyimides, poly(amideimide)s, polyamides and polyesters containing pendent flexible alkoxy chains. In order to investigate the effect of incorporation of pendent alkoxy groups on the properties of polymers, properties, such as solubility, thermal transitions and heat resistance were evaluated and compared with those of the unsubstituted ones. For this study, four series of polymers such as polyimides, poly(amideimide)s, polyamides, and polyesters, were synthesized and characterized, thus, permitting the establishment of a reliable structure-property relationship. Based on these objectives the following specific problems were chosen for the present work**.**

1. Design and synthesis of difunctional monomers such as alkoxy-substituted isophthalic acids, isophthaloyl dichlorides, *meta*-phenylenediisocyanates and isophthalic acid dihydrazides.
2. Design and synthesis of alkoxy-substituted aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages.
3. Synthesis of polyimides and poly(amideimide)s from these diisocyanates, diacylhydrazides, diamines, and commercially available aromatic dianhydrides and study the effect of incorporation of pendent alkoxy groups on polymer properties.
4. Study the applications of selected polyimides and poly(amideimide)s as alignment layers for liquid crystals and as membrane materials for gas separations.
5. Synthesis of aromatic polyesters from 5-alkoxyisophthaloyl dichlorides and bisphenols and study the effect of incorporation of pendent alkoxy groups on polymer properties.
6. Study the application of selected polyesters as membrane materials for gas separations.
7. Synthesis of polyamides from 5-alkoxyisophthalic acids and commercially available aromatic diamines and study the effect of incorporation of pendent alkoxy groups on polymer properties.

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Chapter 3. Synthesis and Characterization of Difunctional Monomers Containing Pendent Flexible Alkoxy Groups

3.1 Introduction

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

In the area of high performance polymers such as polyimides, poly(amideimide)s, polyamides, polyesters, etc., a large number of difunctional monomers have been synthesized in the past three decades with a view to overcome the traditional processing problems caused by the limited solubility and poor processability of these polymers. Efforts devoted to incorporating the structural features that improve processability have led to an outstanding enrichment of the chemistry of high performance polymers, and have allowed the opening of new investigations and application areas for these polymers.[4, 5]

There are a plethora of monomers with structural variations that have been synthesized to date to be catalogued here. Nevertheless, representative difunctional monomers such as aromatic diamines, dianhydrides, diisocyanates, diacylhydrazides diacids, diacid chlorides, and diphenols containing pendent flexible groups that have bearing on the theme of the thesis are summarized in **Tables 3.1 to 3.6**.

Table 3.1: Aromatic diamines containing pendent flexible groups.

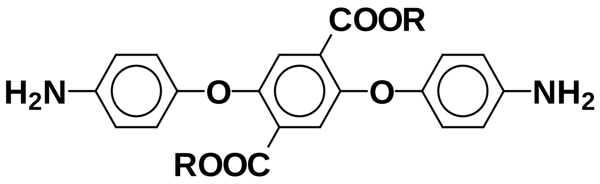
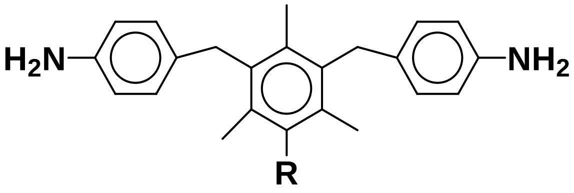
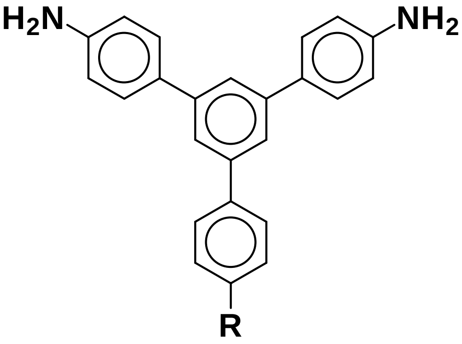
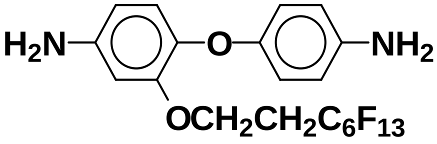
Sr. No	Diamine	Polymers Synthesized	Ref.
1	 $(R = -CH_3, -C_4H_9, -C_8H_{17}, -C_{12}H_{25})$	Polyimides	6
2	 $(R = -C_6H_{13}, -C_8H_{17})$	Polyimides	7
3	 $(R = -O(CH_2)_5CH_3, -O(CH_2)_{11}CH_3)$	Polyimides, Polyamides	8
4		Polyimides	9

Table 3.1: Aromatic diamines containing pendent flexible groups …continued.

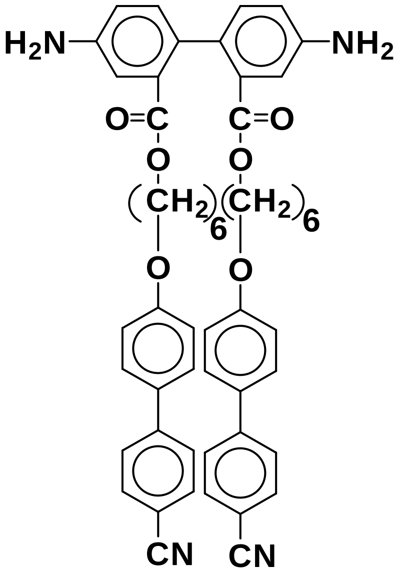
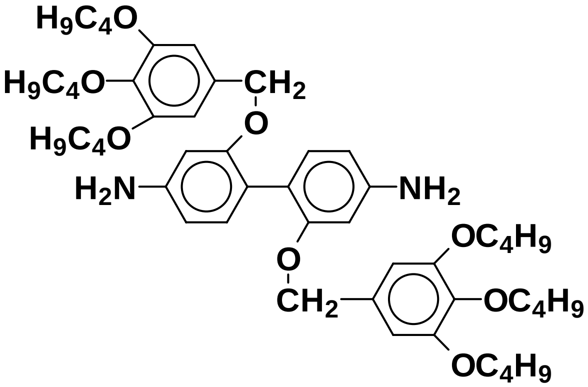
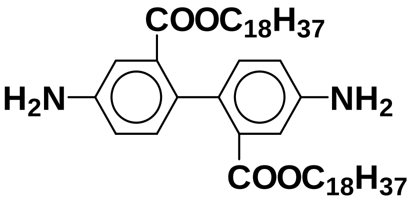
Sr. No	Diamine	Polymers Synthesized	Ref.
5		Polyimides	10
6		Polyimides, Polyamides	11
7		Polyimides	12

Table 3.1: Aromatic diamines containing pendent flexible groups …continued.

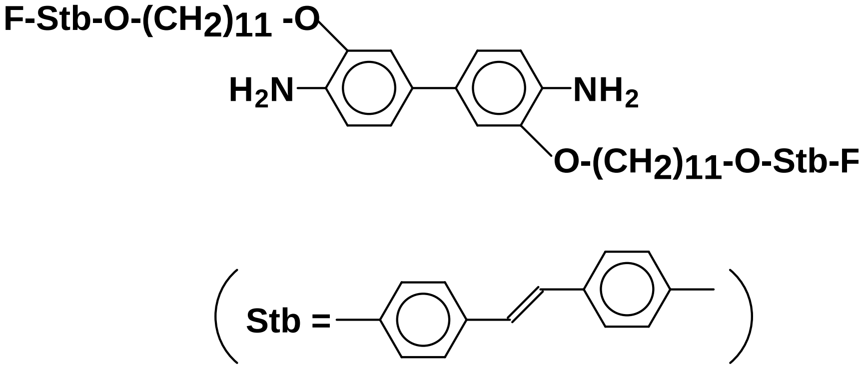
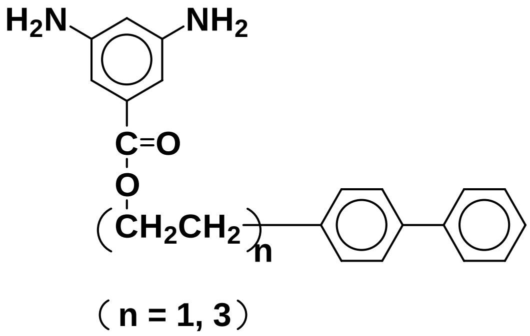
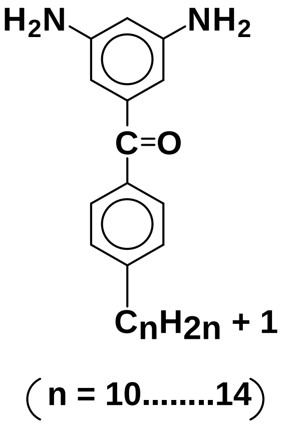
Sr. No	Diamine	Polymers Synthesized	Ref.
8		Polyimides	13
9		Polyimides	14
10		Polyimides	15, 16

Table 3.1: Aromatic diamines containing pendent flexible groups…continued.

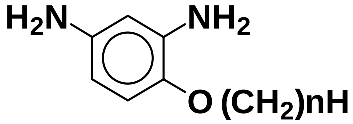
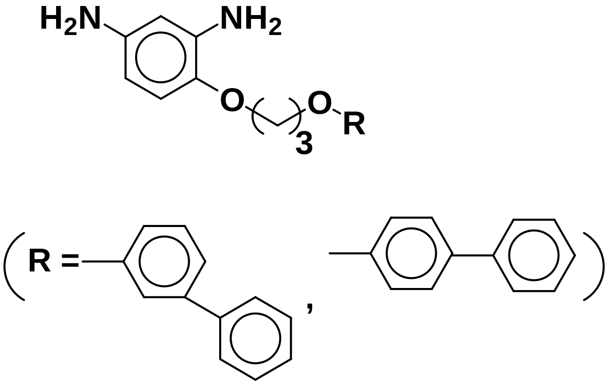
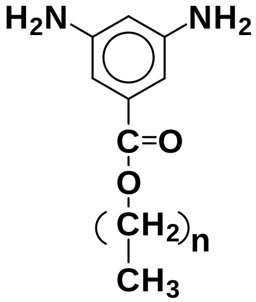
Sr. No	Diamine	Polymers Synthesized	Ref.
11	 (n = 4, 8, 10, 12, 14, 16)	Polyimides	17, 18, 19
12		Polyimides	20
13	 (n = 3, 7, 11, 17)	Polyimides	21

Table 3.1: Aromatic diamines containing pendent flexible groups…continued.

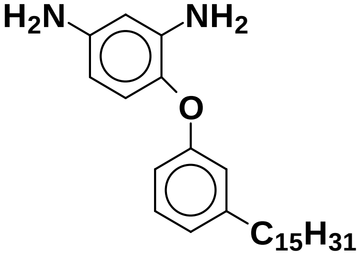
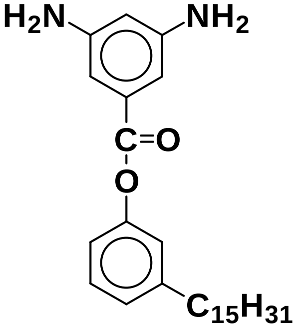
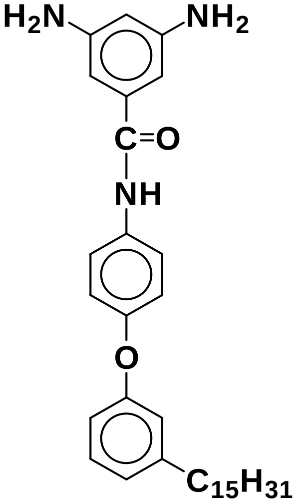
Sr. No	Diamine	Polymers Synthesized	Ref.
14		Polyimides, Polyamides	22
15		Polyimides, polyamides	22
16		Polyimides, Polyamides	22

Table 3.1: Aromatic diamines containing pendent flexible groups…continued.

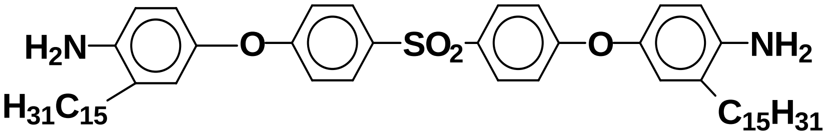
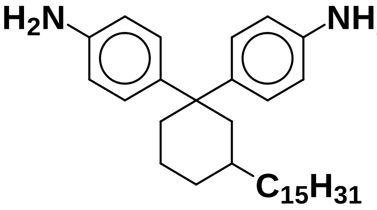
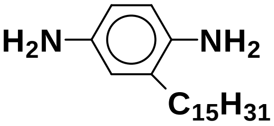
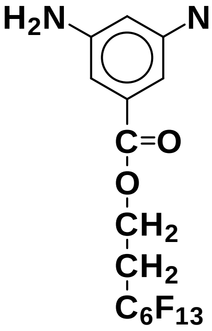
Sr. No	Diamine	Polymers Synthesized	Ref.
17		Polyamides	23
18		Polyimides	24
19		Polyimides	25
20		Polyimides	26

Table 3.1: Aromatic diamines containing pendent flexible groups…continued.

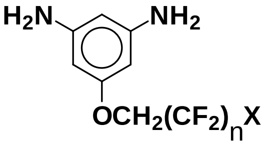
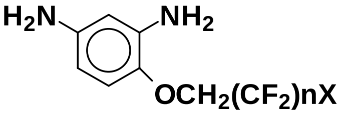
Sr. No	Diamine	Polymers Synthesized	Ref.
21	 X = F , n = 1 X = H , n = 2 X = H , n = 4 X = H , n = 6	Polyimides	27
22	 X = F, n = 3 X = F, n = 6 X = F, n = 7 X = H, n = 10	Polyimides	28

Table 3.2: Aromatic dianhydrides containing pendent flexible groups.

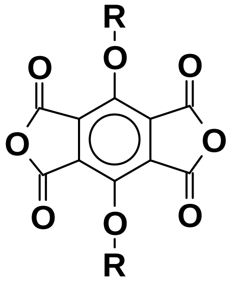
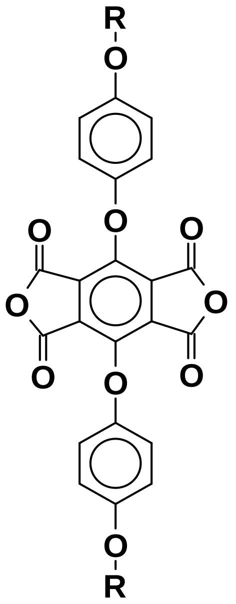
Sr. No.	Dianhydride	Polymers Synthesized	Ref.
1	 ($R = n\text{-}C_8H_{17}, n\text{-}C_{12}H_{25}$)	Polyimides	29
2	 ($R = n\text{-}C_nH_{2n} + 1$ $n = 1, 4, 8, 12$)	Polyimides, Poly(amideimide)s	30-32

Table 3.2: Aromatic dianhydrides containing pendent flexible groups… Continued.

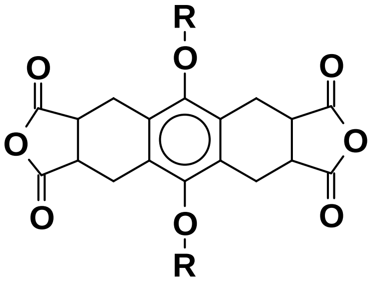
Sr. No.	Dianhydride	Polymers Synthesized	Ref.
3	 R = -C_4H_9, -C_8H_{17}, -$C_{12}H_{25}$	Polyimides	33, 34

Table 3.3: Aromatic diisocyanates containing pendent flexible groups.

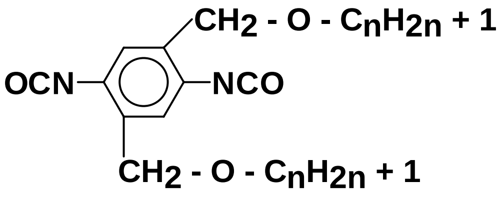
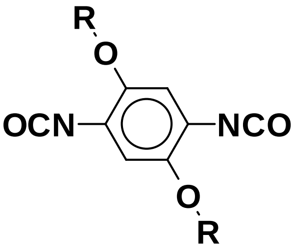
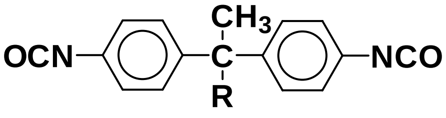
Sr. No.	Diisocyanate	Polymers Synthesized	References
1	 (n = 4, 6, 8)	Polyimides	35 - 37
2	 R = - C_nH_{2n+1} n = 4, 6, 10, 12, 14, 16	Polyimides	38
3	 R = —$CH_2CH_2CH_3$	Polyimides	39

Table 3.4: Aromatic diacyl hydrazides containing pendent flexible groups.

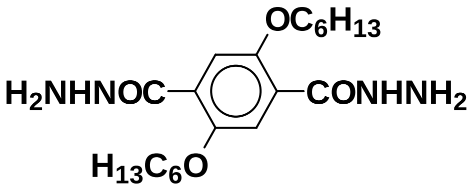
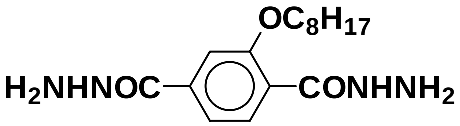
Sr. No	Diacyl hydrazide	Polymers Synthesized	Reference
1		Copolyethers with alternate stilbene derivatives and aromatic 1,3,4-oxadiazoles.	40
2		Poly(1,3,4-oxadiazole)s	41

Table 3.5: Aromatic diacids and aromatic diacid chlorides containing pendent flexible groups.

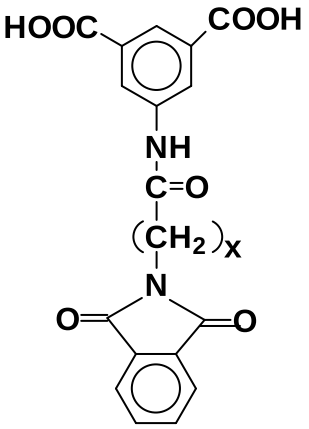
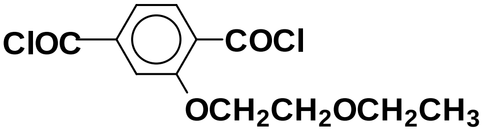
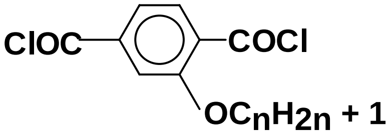
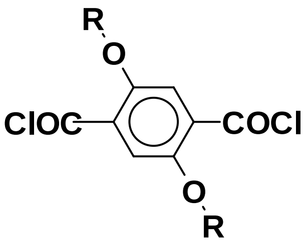
Sr. No	Diacid /Diacid chloride	Polymers synthesized	Ref.
1	 (x = 2, 3, 5, 10)	Polyamides	42
2		Polyesters	43
3	 (n = 2, 5, 8, 10)	Poly(1,3,4-oxadiazoles)s	44
4	 ($R = n\text{-}C_4H_9, n\text{-}C_6H_{13}, n\text{-}C_8H_{17}, n\text{-}C_{10}H_{21}, n\text{-}C_{12}H_{25}$)	Poly(benzobisthiazole)s	45

Table 3.5: Aromatic diacids and aromatic diacid chlorides containing pendent flexible groups…Continued.

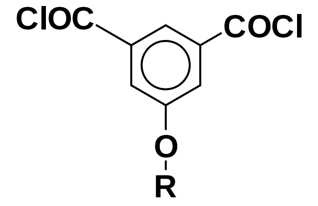
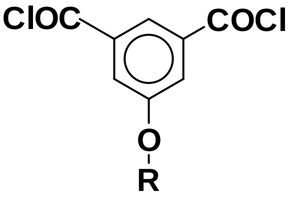
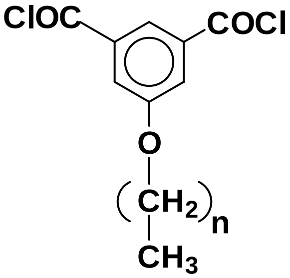
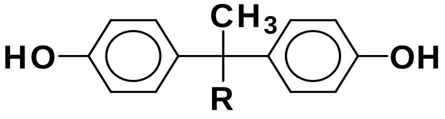
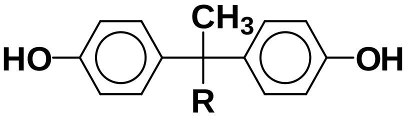
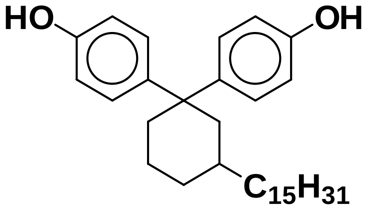
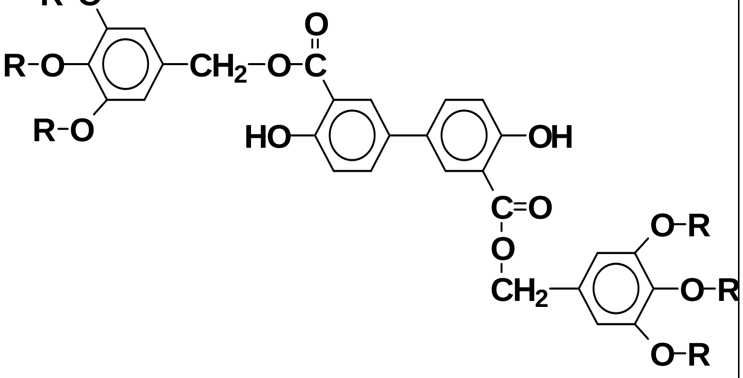
Sr. No	Diacid /Diacid chloride	Polymers synthesized	Ref.
5	 R = -$C_{10}H_{21}$, -$C_{12}H_{25}$	Poly(benzobisthiazole)s	45
6	 R = -C_2H_5, -C_6H_{13}, -$C_{10}H_{21}$	Aromatic Polyketones	46
7	 n = 11..........18	Polyamides	47

Table 3.6: Bisphenols containing pendent flexible groups.

Sr. No	Bisphenol	Polymers Synthesized	Ref.
1	 ($R = -(CH_2)_2CH_3,$ $-(CH_2)_6CH_3,$ $-(CH_2)_8CH_3$)	Epoxies	48
2	 $R = -C_{11}H_{23}, -C_{17}H_{35}$	Poly(arylether-ketone)s	49
3		Polycarbonates, Polyesters	50
4	 $R = -C_6H_{13}, -C_{12}H_{25}$	Polyesters	51

In the present work, a series of 5-alkoxyisophthalic acids, 5-alkoxyisophthaloyl dichlorides, 5-alkoxy-1,3-phenylene diisocyanates and 5-alkoxyisophthalic acid dihydrazides were synthesized. Furthermore, alkoxy-substituted aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages were designed and synthesized.

3.2 Experimental

3.2.1 Materials

5-Hydroxyisophthalic acid, 1-bromobutane, 1-bromooctane, 1-bromododecane, 1-bromohexadecane, methyl iodide, isophthaloyl dichloride (Aldrich Chemicals), potassium carbonate, potassium hydroxide, methanol and tetrahydrofuran (THF) (s.d.fine Chemicals) were used as received. p-Nitrophenol (Loba Chemie) was purified by recrystallization from ethanol. Triethylamine, ethylchloroformate, thionyl chloride, N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF) were of reagent grade and were distilled prior to use as per literature procedures.[52] Sodium azide was ‘activated’ by trituration with hydrazine hydrate and left overnight. It was dissolved in a minimum quantity of water and precipitated with acetone, filtered and dried in a vacuum oven at room temperature. p- Nitroaniline (Loba Chemie) was recrystallised from water:ethanol (1:2, v/v) mixture. Pd/C (10%) (Aldrich) and hydrazine hydrate (Loba Chemie) were used as received. Isophthalic acid dihydrazide was prepared by the procedure reported in the literature. [53]

3.2.2 Measurements

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

FT-IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer in nujol mull or in chloroform.

^{1}H-NMR spectra were recorded on a Bruker NMR (200 or 300 MHz) spectrophotometer.

^{13}C NMR spectra were recorded on a Bruker NMR instrument (300 or 500 MHz) spectrophotometer.

Mass spectra were recorded on GC-MS, QP-2010 spectrometer from Shimadzu company. (Column: DP 5; Length: 30 Meters. For DI the temperature programming was: Initial temperature was room temperature and then every 10^{o}C rise per minute till 350^{o}C.and at the maximum temperature the hold time was 10 minutes).

3.3 Preparations

3.3.1 Preparation of dimethyl-5-hydroxyisophthalate

Into a 1 l two-necked round bottom flask fitted with a reflux condenser and an addition funnel were placed 5-hydroxyisophthalic acid (100 g, 0.55 mol) and methanol (500 ml). To the flask was added concentrated sulfuric acid (5 g) dropwise. The reaction mixture was refluxed for 8 h and then the methanol was removed by distillation. The resulting product was dissolved in chloroform (500 ml) and filtered to remove the unreacted acid, if any. The chloroform solution was washed with water (2 x 250 ml), separated, and dried over anhydrous sodium sulfate. The solution was filtered and the chloroform was removed on a rotary evaporator to obtain crude dimethyl-5-hydroxyisophthalate. Crystallization from methanol afforded pure dimethyl-5-hydroxyisophthalate. Yield: 105.0 g (91 %). M.P.159-160^{o}C.

3.3.2 Preparation of dimethyl-5-methoxyisophthalate

Into a 500 ml three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were placed dimethyl-5-hydroxy isophthalate (8.4 g, 40 mmol), potassium carbonate (16.5 g, 0.12 mol) and DMF (100 ml) and stirred at 40°C for 1 h. To the reaction mixture methyl iodide (11.3 g, 0.080 mol) dissolved in DMF (100 ml) was added dropwise and the mixture was stirred at 40°C for 24 h. DMF was removed under reduced pressure and the residue was poured into excess water. The reaction mixture was extracted into dichloromethane (2 x 100 ml). The dichloromethane solution was washed with water (2 x 50 ml), separated, and dried over anhydrous sodium sulfate. The solution was filtered and dichloromethane was removed on a rotary evaporator. The crude product was crystallized from methanol to get pure dimethyl-5-methoxyisophthalate. Yield: 8.5 g (94 %), M.P. 111°C (Lit. M.P. 110 - 112°C)[54]

3.3.3 Preparation of dimethyl-5-alkoxyisophthalates

A representative procedure for the preparation of dimethyl-5-hexadecyloxyisophthalate is described below.

Into a 250 ml three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were placed dimethyl-5-hydroxy isophthalate (18.4 g, 0.087 mol), potassium carbonate (30 g, 0.22 mol) and DMF (100 ml) and stirred at 80°C for 1 h. To the reaction mixture 1-bromo-hexadecane (40 g, 0.13 mol) dissolved in DMF (100 ml) was added dropwise and the mixture was stirred at 80°C for 24 h. DMF was removed under reduced pressure and the residue was poured into excess water. The reaction mixture was extracted into dichloromethane (2 x 100 ml). The dichloromethane solution was washed with water (2 x 50 ml), separated, and dried over anhydrous sodium sulfate. The solution was filtered and dichloromethane was removed on a rotary evaporator. The crude product was crystallized from methanol to get pure dimethyl-5-hexadecyloxyisophthalates. Yield: 35.6 g (94%). M.P. 75°C .

The other dimethyl-5-alkoxyisophthalates were prepared following the procedure described above.

3.3.4 Preparation of 5-alkoxyisophthalic acids

A representative procedure for the preparation of 5-hexadecyloxyisophthalic acid is described below.

Into a 100 ml three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were placed dimethyl-5-hexadecyloxyisophthalate (5 g, 0.12 mol). A solution of potassium hydroxide (6.9 g, 0.12 mol) in a mixture of ethanol and water (2:1, v/v) (24 ml) was added to the reaction flask and the reaction mixture was refluxed under stirring for 12 h. The reaction mixture was concentrated under reduced pressure and was acidified with concentrated hydrochloric acid to pH 2. White precipitate obtained was filtered at pump and washed several times with DI water. The solid was dried in vacuum. The crude product was purified by crystallization from methanol. Yield: 4.3 g (92%). M.P.: 162-165°C (Lit. M.P. 164.4°C.)[55]

The other 5-alkoxyisophthalic acids were prepared following the procedure described above.

3.3.5 Preparation of 5-alkoxyisophthaloyl dichlorides

A representative procedure for the preparation of 5-hexadecyloxyisophthaloyl dichloride is described below.

Into a 250 ml three-necked round bottom flask equipped with a reflux condenser, an addition funnel and a magnetic stirring bar were placed 5-hexadecyloxyisophthalic acid (10 g, 0.024 mol) and DMF (3 drops). Thionyl

chloride (150 ml) was added dropwise over a period of 30 minutes and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 ml). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice. The crude product was purified by distillation under reduced pressure (230°C / 10^{-3} mm Hg). Yield: 10.0 g,
(92 %).

The other 5-alkoxyisophthaloyl dichlorides were prepared following the procedure described above.

3.3.6 Preparation of 5-alkoxyisophthaloyl diazides

A representative procedure for the preparation of 5-hexadecyloxyisophthaloyl diazide is described below.

Into a 100 ml two-necked round bottom flask equipped with an addition funnel, thermowell and a magnetic stirring bar were placed 5-hexadecyloxyisophthalic acid (1 g, 0.0025 mol) and a mixture of THF-water (3:1, v/v) (7 ml). The reaction mixture was cooled to 0°C and a solution of triethylamine (0.74 g, 0.0073 mol) in THF (3 ml) was added dropwise over a period of 15 min. To the clear solution formed was added ethylchloroformate (0.79 g, 7.3 mmol) drop-wise over a period of 10 min. and stirred for 2 h. A solution of ‘activated’ sodium azide (0.63 g, 0.0097 mol) in water (5 ml) was added dropwise over a period of 15 min. and the mixture was stirred at 0°C for 4 h. Cold water (50 ml) was added gradually to the reaction mixture and the solid separated out. The solid was separated by filtration and washed with cold water (2 x 25 ml). The product was dissolved in dichloromethane (25 ml), dried over anhydrous sodium sulfate, filtered and dichloromethane was removed under reduced pressure at room temperature to obtain a white solid. Yield: 1.02 g (91%).

A similar procedure was adapted for the preparation of other 5-alkoxyisophthaloyl diazides.

3.3.7 Preparation of 5-alkoxy-1,3-phenylenediisocyanates

A representative procedure for the preparation of 5-hexadecyloxy-1,3-phenylenediisocyanate is described below.

Into a 100 ml three-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet tube and a reflux condenser were placed 5-hexadecyloxyisophthaloyl diazide (1.0 g, 0.0022 mol) and dry toluene (20 ml). Nitrogen gas was bubbled gently through the reaction mixture. The reaction mixture was heated at 60^{o}C for 24 h. Evaporation of toluene under reduced pressure afforded a crude product. Crystallization of the crude diisocyanate from dry hexane yielded 5-hexadecyloxy-1,3-phenylenediisocyanate in pure form. Yield: 0.72 g (82 %).

A similar procedure was adapted for the preparation of other 5-alkoxy-1,3-phenylenediisocyanates. Purification of the crude diisocyanates was achieved by either distillation under reduced pressure or by crystallization from dry hexane.

3.3.8 Preparation of 5-alkoxyisophthalic acid dihydrazides

Into a 100 ml two-necked round bottom flask equipped with a magnetic stirring bar, an addition funnel and a reflux condenser were placed dimethyl-5-hexadecyloxy-isophthalate (4.34 g, 0.01 mol) and ethanol (50 ml). Hydrazine hydrate (12.8 g, 0.26 mol) was added dropwise to the reaction mixture over a period of 15 min and refluxed for 10 h. The solid that separated out was filtered and dried. It was purified by crystallization from ethanol. Yield: 3.2 g (75%).

A similar procedure was adapted for the preparation of other 5-alkoxyisophthalic acid dihydrazides.

3.3.8 Preparation of 5-alkoxy-N,N'-bis(4-nitrophenyl)isophthalamides

A representative procedure for the preparation of 5-hexadecyloxy-N,N'-bis(4-nitrophenyl)isophthalamide is described below.

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirring bar, an addition funnel and a reflux condenser were placed 5-hexadecyloxyisophthaloyl dichloride (6 g, 0.013 mol) and DMAc (75 ml) and stirred at room temperature to form a solution. Triethylamine (3.15 g, 0.031mol) dissolved in DMAc (5 ml) was added dropwise to the reaction mixture followed by the dropwise addition of a solution of p-nitroaniline (4.28 g, 0.031 mol) in DMAc (10 ml). The reaction mixture was stirred for 24 h at room temperature. DMAc was removed under reduced pressure and the residue was poured into a mixture of methanol : water (1 : 1, v / v) (200 ml). The solid that separated out was filtered at pump and washed with water (2 x 50 ml). The crude product was purified by crystallization from a mixture of methanol : DMF (1 : 2, v / v). Yield: 7.9 g (90%).

A similar procedure was adapted for the preparation of other 5-alkoxy-N,N'-bis(4-nitrophenyl)isophthalamides and N,N'-bis(4-nitrophenyl)isophthalamide.

3.3.9 Preparation of 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides

A representative procedure for the preparation of 5-hexadecyloxy-N,N'-bis(4-aminophenyl)isophthalamide is described below.

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirring bar, an addition funnel and a reflux condenser were placed 5-hexadecyloxy-N,N'-bis(4-nitrophenyl)isophthalamide (6.5 g, 0.010 mol), ethanol (150 ml) and palladium-on-charcoal (10 wt%) (0.19 g, 3 wt % based on dinitro compound). Hydrazine hydrate (15.88 g, 0.32 mol) was added dropwise over a period of 15 min and the reaction mixture was refluxed for 24 h. The reaction mixture was cooled and filtered to remove Pd / C. Ethanol was removed under reduced pressure. The crude product thus obtained was purified by two crystallizations from methanol to get a white crystalline compound. Yield: 4.5 g (76%).

A similar procedure was adapted for the preparation of other 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides and N,N'-bis(4-aminophenyl)isophthalamide.

3.3.11 Preparation of 5-alkoxyisophthalic acid bis(4-nitrophenyl) esters

A representative procedure for the preparation of 5-dodecyloxyisophthalic acid bis(4-nitrophenyl) ester is described below.

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirring bar, an addition funnel and a reflux condenser were placed 5-dodecyloxyisophthaloyl dichloride (6 g, 0.016 mol) and DMF (75 ml) and the reaction mixture stirred at room temperature to form a solution. Triethylamine (3.15 g, 0.031 mol) dissolved in DMF (5 ml) was added dropwise to the reaction mixture followed by the dropwise addition of a solution of p-nitrophenol (4.28 g, 0.031 mol) in DMF (10 ml). The reaction mixture was stirred at room temperature for 24 h. DMF was removed under reduced pressure and the residue was poured into a mixture of methanol : water (1 : 1, v / v) (200 ml). The solid that separated out was filtered at pump and washed with water (2 x 50 ml). The crude product was purified by crystallization from a mixture of methanol : DMF (1 : 2, v / v). Yield: 7.8 g (85%).

A similar procedure was adapted for the preparation of 5-octyloxyisophthalic acid bis(4-nitrophenyl) ester.

3.3.12 Preparation of 5-alkoxyisophthalic acid bis(4-aminophenyl) esters

A representative procedure for the preparation of 5-dodecyloxyisophthalic acid bis(4-aminophenyl) ester is described below.

Into a 300 ml Parr Reactor were placed 5-dodecyloxyisophthalic acid bis(4-nitrophenyl) ester (5 g, 8.4 mmol), DMAc (50 ml) and Pd / C (10%) (0.5 g, 10 wt %

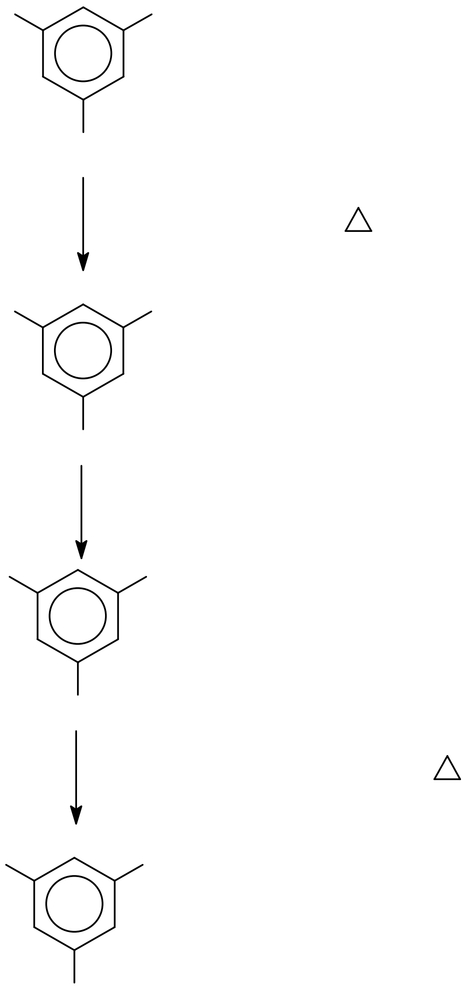
based on dinitro compound). The Parr Reactor was purged first with nitrogen and then with hydrogen. The reactor was pressurized with hydrogen gas (150 psi) and the reaction mixture was stirred at 35^{o}C for 20 h. Hydrogen gas was replenished equivalent to the volume of gas absorbed from time to time. At the end of 20 h, hydrogen gas was released. The DMAc solution was filtered to remove Pd / C and the solvent was evaporated under reduced pressure. The residue was treated with petroleum ether to remove the traces of DMAc. The crude product was crystallized twice from ethanol to obtain yellow colored crystals. Yield: 3.8 g (85%).

A similar procedure was adapted for the preparation of 5-octyloxyisophthalic acid bis(4-aminophenyl) ester.

3.4 Results and Discussion

3.4.1 Synthesis of 5-alkoxyisophthalic acids

Scheme 3.1 depicts route for the synthesis of 5- alkoxyisophthalic acids.



Scheme 3.1: Synthesis of 5-alkoxyisophthalic acids.

The starting material used for the synthesis was commercially available 5-hydroxyisophthalic acid for which several manufacturing processes are available.[56] 5-Hydroxyisophthalic acid was converted into dimethyl-5-hydroxyisophthalate by esterification with methanol in the presence of sulfuric acid catalyst.

In the FTIR spectrum of dimethyl-5-hydroxyisophthalate (**Figure 3.1**) a band at 1760 cm^{-1} was observed which is characteristic of the carbonyl of the ester group. The phenolic hydroxyl group showed absorption at 3350 cm^{-1}**.**

^{1}H-NMR spectrum of dimethyl-5-hydroxyisophthalate is shown in **Figure 3.2**. A singlet observed at 8.03 δ ppm is assignable to proton flanked by electron withdrawing ester groups while a singlet at 7.59 δ ppm corresponds to protons *ortho* to hydroxyl group. A singlet at 3.80 δ ppm is due to the methyl protons of the methyl ester.

^{13}C-NMR spectrum of dimethyl-5-hydroxyisophthalate along with assignments of the carbon atoms is shown in **Figure 3.3.**

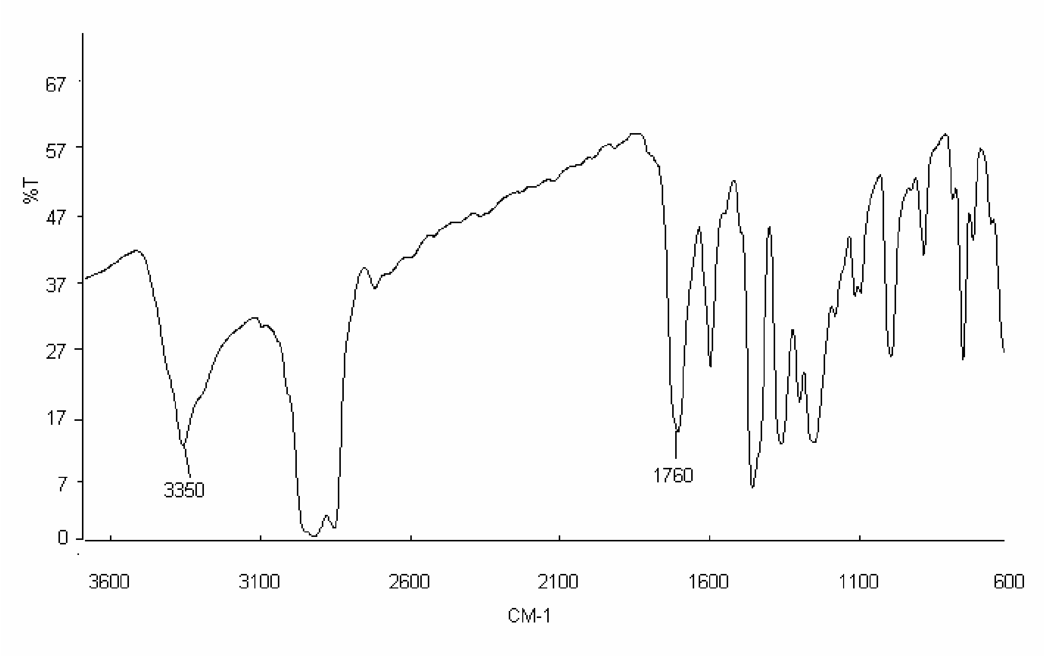


Figure 3.1: IR spectrum of dimethyl-5-hydroxyisophthalate in nujol mull.

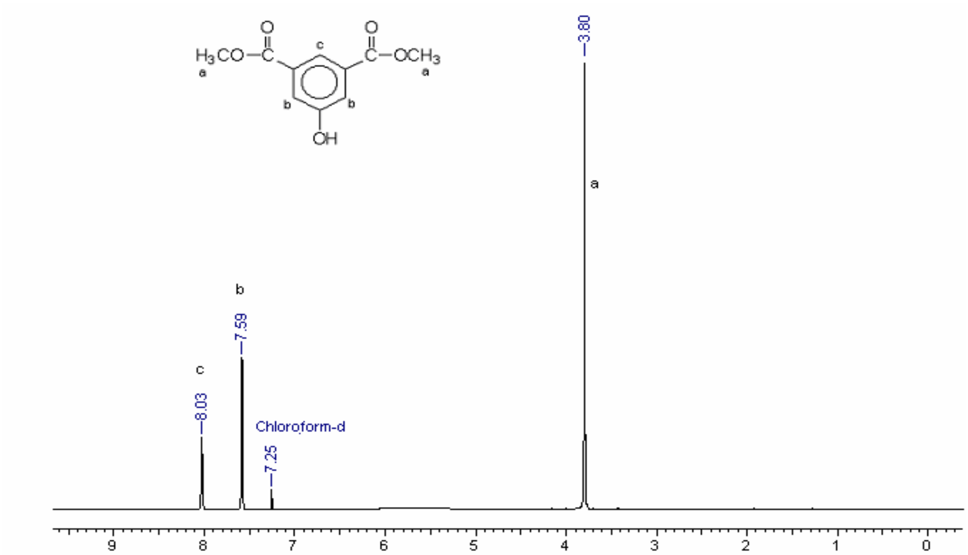


Figure 3.2: ^{1}H-NMR spectrum of dimethyl-5-hydroxyisophthalate in $CDCl_3$.

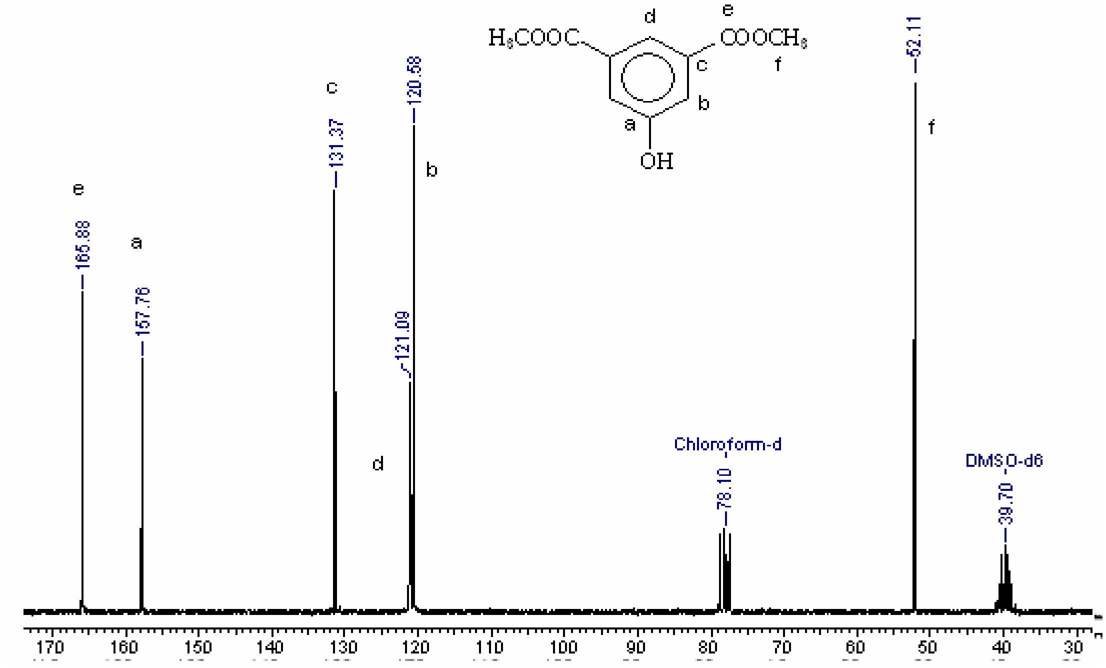


Figure 3.3: ^{13}C-NMR spectrum of dimethyl-5-hydroxyisophthalate in $CDCl_3$+DMSO-d_6

A series of dimethyl-5-alkoxyisophthalates was prepared by Williamson etherification reaction of dimethyl-5-hydroxyisophthalate with alkyl halides in DMF in the presence of potassium carbonate at 80°C.[57 – 60] Dimethyl –5-

methoxyisophthalate was synthesized by reaction of dimethyl-5-hydroxyisophthalate with methyl iodide in DMF at 40°C.

The following five dimethyl-5-alkoxyisophthalates were prepared and their characterization data is summarized in **Table 3.7**.

Dimethyl-5-methoxyisophthalate (DMI)
Dimethyl-5-butyloxyisophthalate (DMBI)
Dimethyl-5-octyloxyisophthalate (DMOI)
Dimethyl-5-dodecyloxyisophthalate (DMDDI)
Dimethyl-5-hexadecyloxyisophthalate (DMHDI)

Table 3.7: Physical and spectral characterization data of dimethyl-5-alkoxy-isophthalates.

No	Diester	Yield (%)	M.P. (^{o}C) (Lit. M.P. ^{o}C)	I.R (cm^{-1})	^{1}H NMR (δ ppm), $CDCl_3$
1	DMI	95	111 (110-112)[54]	1720(-C=O), 1230(Ar-O-C)	3.83(6H,s,-OCH_3), 3.99(3H,s,-OCH_3), 7.70(2H,s, ArH *ortho* to ether), 8.20(1H,s, ArH *ortho* to both –C=O)
2	DMBI	92	54	1720(-C=O), 1230(Ar-O-C)	0.97 (3H,t,-CH_3), 1.40-1.65 (2H,m,-CH_2),1.68-1.85(2H,m,-CH_2), 3.92 (6H,s,-OCH_3), 4.0 (2H,t,-OCH_2), 7.72 (2H,s, ArH *ortho* to ether), 8.20 (1H,s, ArH *ortho* to both –C=O)
3	DMOI	94	50-52	1720(-C=O), 1230(Ar-O-C)	0.87 (3H,t,-CH_3),1.10-1.58(10H,m,-CH_2), 1.60-1.80(2H,m,-CH_2), 3.92 (6H,s,-OCH_3), 4.01(2H,t,-OCH_2), 7.71(2H,s, ArH *ortho* to ether), 8.20(1H,s, ArH *ortho* to both –C=O)
4	DMDDI	96	58-59 (58-59)[45]	1720(-C=O), 1230(Ar-O-C)	0.86(3H,t,-CH_3),1.10-1.57(18H,m,-CH_2), 1.62-1.80 (2H,m,-CH_2), 3.92 (6H,s,-OCH_3), 4.01(2H,t,-OCH_2), 7.72(2H,s, ArH *ortho* to ether), 8.24(1H,s, ArH *ortho* to both –C=O)
5	DMHDI	94	75	1720(-C=O), 1230(Ar-O-C)	0.95(3H,t,-CH_3),1.10-1.60(26H,m,-CH_2), 1.65-1.85(2H,m,-CH_2), 3.92 (6H,s,-OCH_3), 4.01(2H,t,-OCH_2), 7.72(2H,s, ArH *ortho* to ether), 8.25(1H,s, ArH *ortho* to both –C=O).

A representative FTIR spectrum of dimethyl-5-octyloxyisophthalate is shown in **Figure 3.4**. Bands characteristic of ester carbonyl and Ar-O-C were observed at 1720 cm^{-1} and 1230 cm^{-1}, respectively.

^{1}H-NMR spectrum of dimethyl-5-dodecyloxyisophthalate is shown in **Figure 3.5** as an example. Aromatic proton flanked by ester carbonyl groups exhibited a singlet at 8.24 δ ppm while the other two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.72 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.01 δ ppm and a multiplet centered at 1.79 δ ppm, respectively. Methyl protons of methyl ester group appeared as a singlet at 3.92 δ ppm. The other methylene protons displayed a multiplet at 1.10-1.51 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.86 δ ppm. The distortion of the triplet is due to the virtual long range coupling in normal alkyl groups.[19]

^{13}C-NMR spectrum of dimethyl-5-dodecyloxyisophthalate along with the assignments of carbon atoms is shown in **Figure 3.6**.

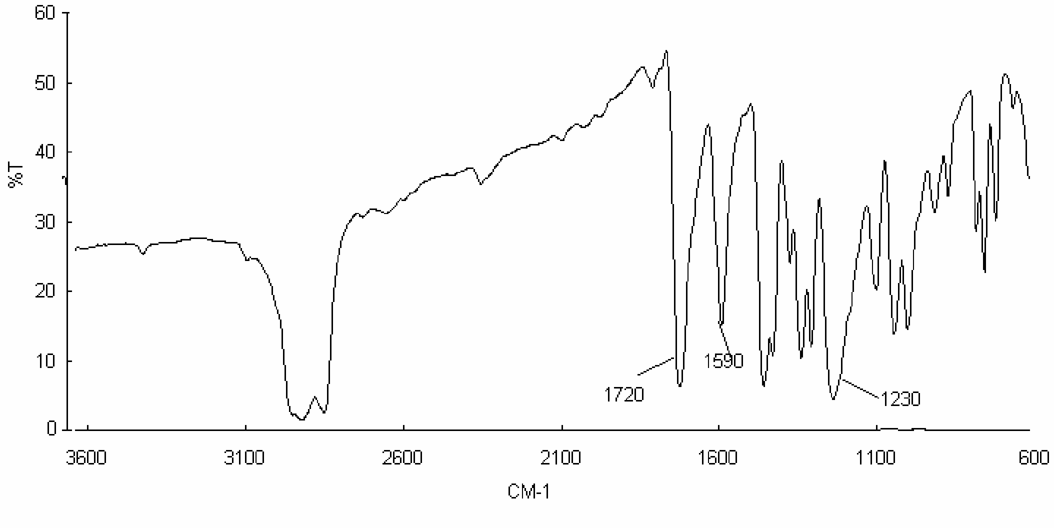


Figure 3.4: IR spectrum of dimethyl-5-octyloxyisophthalate in nujol mull.

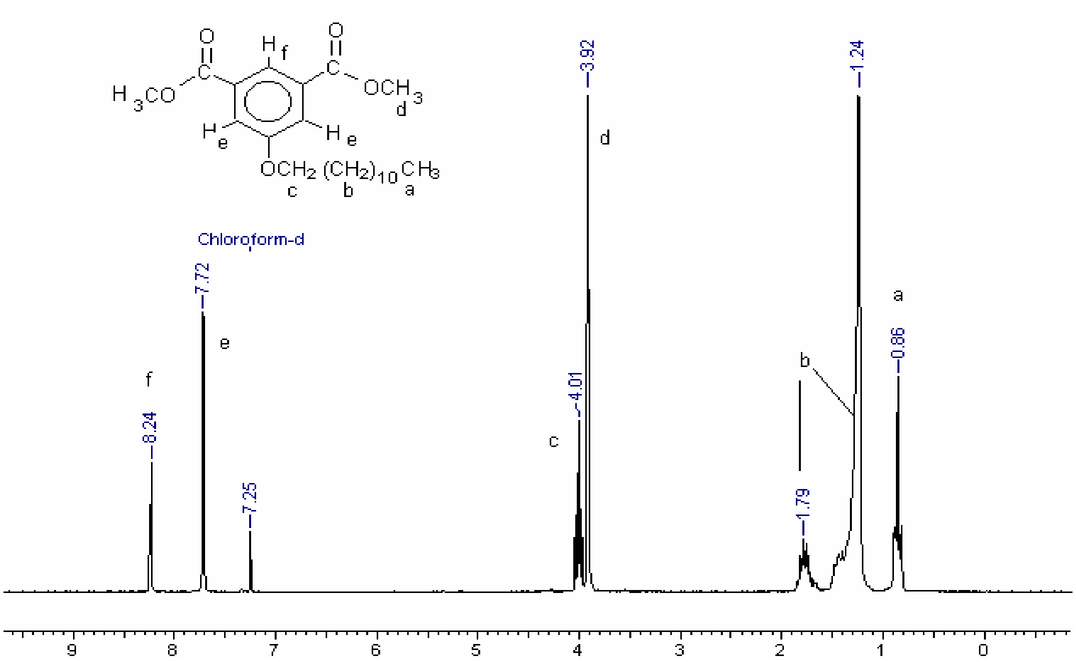


Figure 3.5: ^{1}H-NMR spectrum of dimethyl-5-dodecyloxyisophthalate in CDCl$_3$.

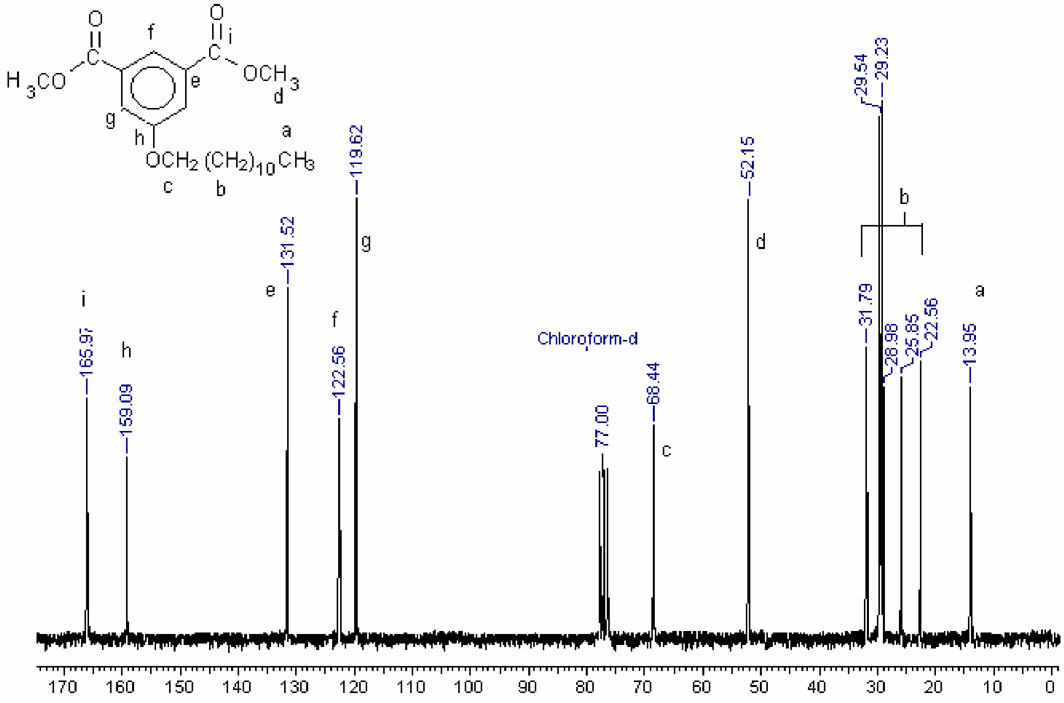


Figure 3.6: ^{13}C-NMR spectrum of dimethyl-5-dodecyloxyisophthalate in CDCl$_3$.

5-Alkoxyisophthalic acids were obtained by the alkaline hydrolysis of the dimethyl-5-alkoxyisophthalates in ethanol / water mixture.

The following five 5-alkoxyisophthalic acids were synthesized and their characterization data is shown in **Table 3.8.**

5-Methoxyisophthalic acid (MIA)
5-Butyloxyisophthalic acid (BIA)
5-Octyloxyisophthalic acid (OIA)
5-Dodecyloxyisophthalic acid (DDIA)
5-Hexadecyloxyisophthalic acid (HDIA)

A SciFinder search indicated that 5-butyloxyisophthalic acid has not been reported in the literature.

Table 3.8: Physical and spectral characterization data of 5-alkoxyisophthalic acids.

No.	Diacid	Yield (%)	M.P. (^{o}C) (Lit M.P. ^{o}C)	I.R (cm^{-1})	^{1}H NMR (δ ppm), DMSO-d$_6$	MS m/z (relative intensity,%)
1	MIA	96	267 (267-268)[61]	1709(-C=O), 1250(Ar-O-C)	3.89(3H,s,-OCH3), 7.60 (2H,s,ArH *ortho* to ether), 8.10(1H,s,ArH *ortho* to both –C=O)	-
2	BIA	92	242-243	1710(-C=O), 1250(Ar-O-C)	0.97(3H,t,-CH$_3$), 1.35-1.65(2H,m,-CH$_2$),1.65-1.90(2H, m,-CH$_2$), 4.02 (2H, t,-OCH$_2$), 7.57 (2H,s,ArH *ortho* to ether), 8.12(1H,s,ArH *ortho* to both –C=O)	238(M$^+$,35) 182 (100)
3	OIA	94	234-235	1707(-C=O), 1250(Ar-O-C)	0.97 (3H,t,-CH$_3$), 1.10-1.55 (10H,m,-CH$_2$), 1.68-1.85 (2H,m,-CH$_2$), 4.0 (2H,t,-OCH$_2$), 7.57 (2H,s,ArH *ortho* to ether), 8.12(1H,s,ArH *ortho* to both –C=O)	294(M$^+$,35) 182 (100)
4	DDIA	96	170-171 (169-170)[45]	1710(-C=O), 1250(Ar-O-C)	0.90 (3H,t,-CH$_3$), 1.10-1.52 (18H,m,-CH$_2$), 1.65-1.83 (2H,m,-CH$_2$), 4.0 (2H,t,-OCH$_2$), 7.57 (2H,s,ArH *ortho* to ether), 8.12(1H,s,ArH *ortho* to both –C=O)	350(M$^+$,30) 182(100)
5	HDIA	92	163-164 (164.4)[55]	1710(-C=O), 1250(Ar-O-C)	0.89 (3H,t,-CH$_3$), 1.10-1.53 (26H,m,-CH$_2$), 1.65-1.82 (2H,m,-CH$_2$), 4.02 (2H,t,-OCH$_2$), 7.57 (2H,s,ArH *ortho* to ether), 8.12(1H,s,ArH *ortho* to both –C=O)	406(M$^+$,25) 182 (100)

A representative FTIR spectrum of 5-dodecyloxyisophthalic acid is shown in **Figure 3.7**. Bands between 2300 to 3250 cm^{-1} are characteristic of the carboxylic acid group. The 1710 cm^{-1} band is assigned to the carbonyl of the carboxylic acid.

^{1}H-NMR spectrum of 5-butyloxyisophthalic acid is shown in **Figure 3.8** as an example. Aromatic proton flanked by acid carbonyl groups exhibited singlet at 8.12 ppm while the other two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.57 δ ppm. The methylene protons attached to oxygen atom appeared as a triplet at 4.02 δ ppm. The methylene protons one and two carbons removed from the ether oxygen exhibited multiplets centered at 1.78 δ ppm and 1.51 ppm, respectively. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.97 δ ppm.

^{13}C-NMR spectrum of 5-butyloxyisophthalic acid along with the assignments of carbon atoms is shown in **Figure 3.9**.

The mass spectrum of 5-butyloxyisophthalic acid (**Figure 3.10**) showed molecular ion peak at 238, indicating the agreement with the expected value.

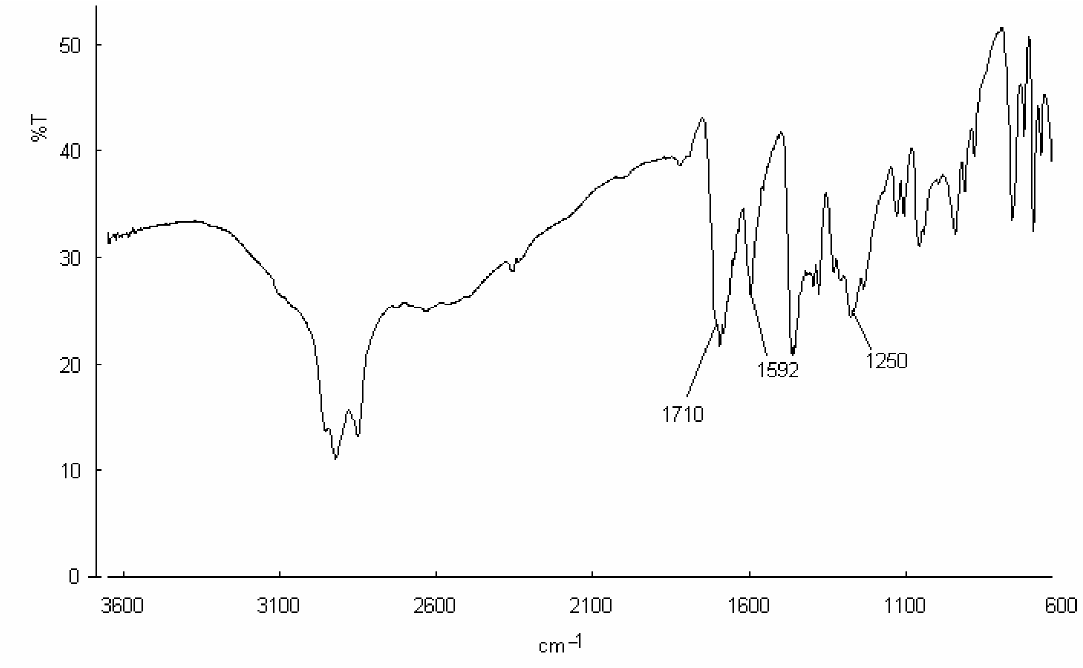


Figure 3.7: IR spectrum of 5-dodecyloxyisophthalic acid in nujol mull.

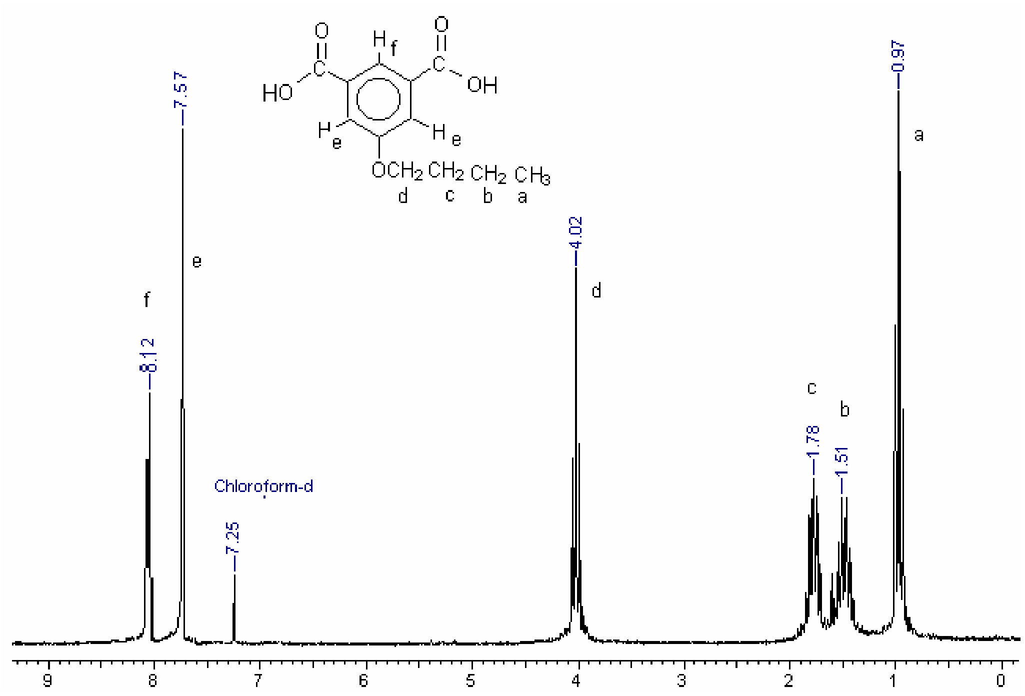


Figure 3.8: ^{1}H-NMR spectrum of 5-butyloxyisophthalic acid in $CDCl_3$+DMSO-d_6

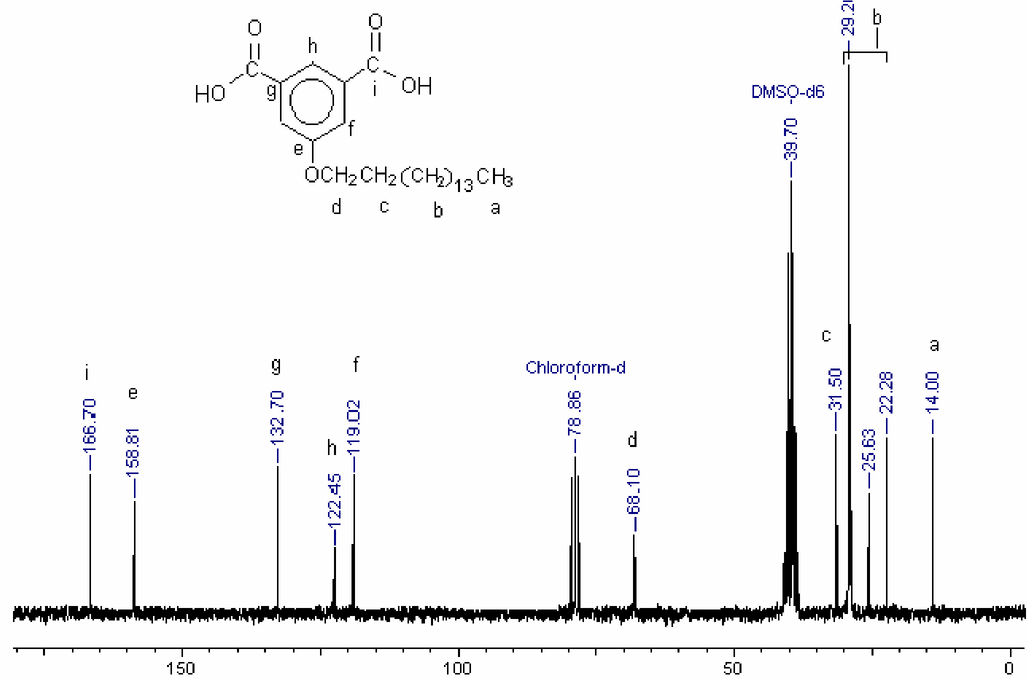


Figure 3.9: ^{13}C-NMR spectrum of 5-butyloxyisophthalic acid in $CDCl_3$ + DMSO-d_6.

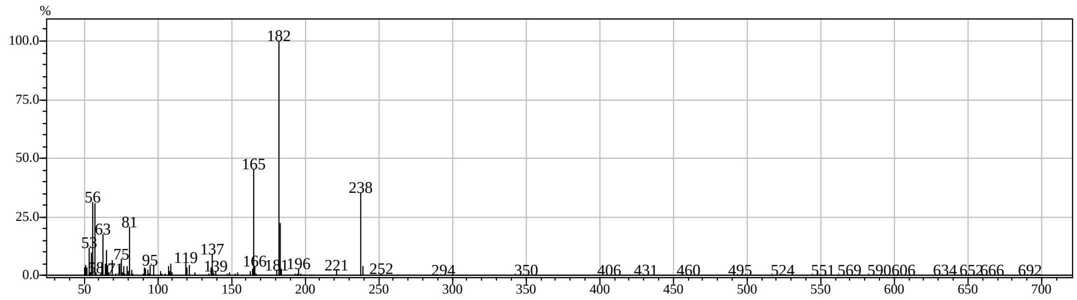
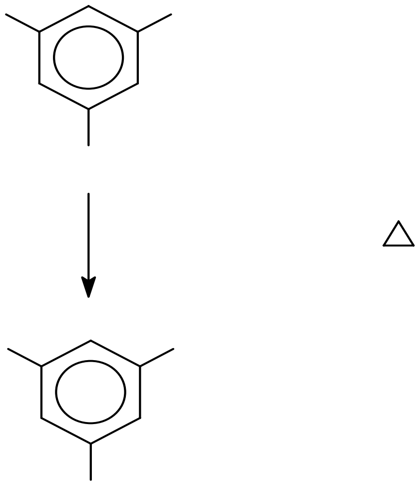


Figure 3.10: Mass spectrum of 5-butyloxyisophthalic acid.

3.4.2: Synthesis of 5-alkoxyisophthaloyl dichlorides

The 5-alkoxyisophthaloyl dichlorides were prepared by reacting the corresponding diacids with excess thionyl chloride in the presence of DMF as a catalyst (**Scheme3.2**). The diacid chlorides were obtained in pure form by distillation under reduced pressure.



Scheme 3.2: Synthesis of 5-alkoxyisophthaloyl dichlorides.

The following five 5-alkoxyisophthaloyl dichlorides were prepared and their characterization data is summarized in **Table 3.9**.

5-Methoxyisophthaloyl dichloride (MIC)
5-Butyloxyisophthaloyl dichloride (BIC)
5-Octyloxyisophthaloyl dichloride (OIC)
5-Dodecyloxyisophthaloyl dichloride (DDIC)
5-Hexadecyloxyisophthaloyl dichloride (HDIC).

5-Butyloxyisophthaloyl dichloride is being reported for the first time.

Table 3.9: Physical and spectral characterization data of 5-alkoxyisophthaloyl dichlorides.

No	**Diacid chloride**	**Yield (%)**	**M.P. (^oC) (lit. M.P. ^oC)**	**I.R., (cm^{-1})**	**^1H NMR (δ ppm), $CDCl_3$**
1	MIC	85	48-49 (48-49)[61]	1764(C=O), 1220(Ar-O-C)	3.94(3H,s,-OCH_3), 7.87(2H,s,ArH *ortho* to ether), 8.44(1H,s, ArH *ortho* to both –C=O)
2	BIC	80	32-33	1762(C=O), 1220(Ar-O-C)	0.97(3H,t,-CH_3), 1.40-1.66(2H, m,-CH_2),1.66-1.90(2H,m,-CH_2), 4.05(2H,t,-OCH_2), 7.87(2H,s, ArH *ortho* to ether), 8.45(1H,s, ArH *ortho* to both –C=O)
3	OIC	82	34-35	1754(C=O), 1220(Ar-O-C)	0.88(3H,t,-CH_3),1.10-1.55(10H,m,-CH_2),1.70-1.90(2H,m,-CH_2),4.07(2H,t,-OCH_2), 7.88(2H,s, ArH *ortho* to ether), 8.45(1H,s, ArH *ortho* to both –C=O)
4	DDIC	78	42-43 (42-43)[45]	1764(C=O), 1220(Ar-O-C)	0.86(3H,t,-CH_3),1.12-1.55(18H,m,-CH_2),1.77-1.90(2H,m,-CH_2),4.07(2H,t,-OCH_2), 7.86(2H,s, ArH *ortho* to ether), 8.40(1H,s, ArH *ortho* to both –C=O)
5	HDIC	91	53-54	1757(C=O), 1220(Ar-O-C)	0.90(3H,t,-CH_3),1.12-1.55(26H,m,-CH_2),1.77-1.90(2H,m,-CH_2), 4.07(2H,t,-OCH_2), 7.60(2H,s, ArH *ortho* to ether), 8.40(1H,s, ArH *ortho* to both –C=O)

A representative FTIR spectrum of 5-octyloxyisophthaloyl dichloride is shown in **Figure 3.11**. Bands characteristic of the carbonyl of acid chloride and Ar-O-C were observed at 1754 cm^{-1} and 1220 cm^{-1}, respectively.

^{1}H-NMR spectrum of 5-octyloxyisophthaloyl dichloride is shown in **Figure 3.12** as an example. Aromatic proton flanked by acid chloride groups exhibited a singlet at 8.45 δ ppm while the other two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.88 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.07 δ ppm and a multiplet centered at 1.80 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.10 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.88 δ ppm.

^{13}C-NMR spectrum of 5-octyloxyisophthaloyl dichloride along with the assignments of carbon atoms is shown in **Figure 3.13**.

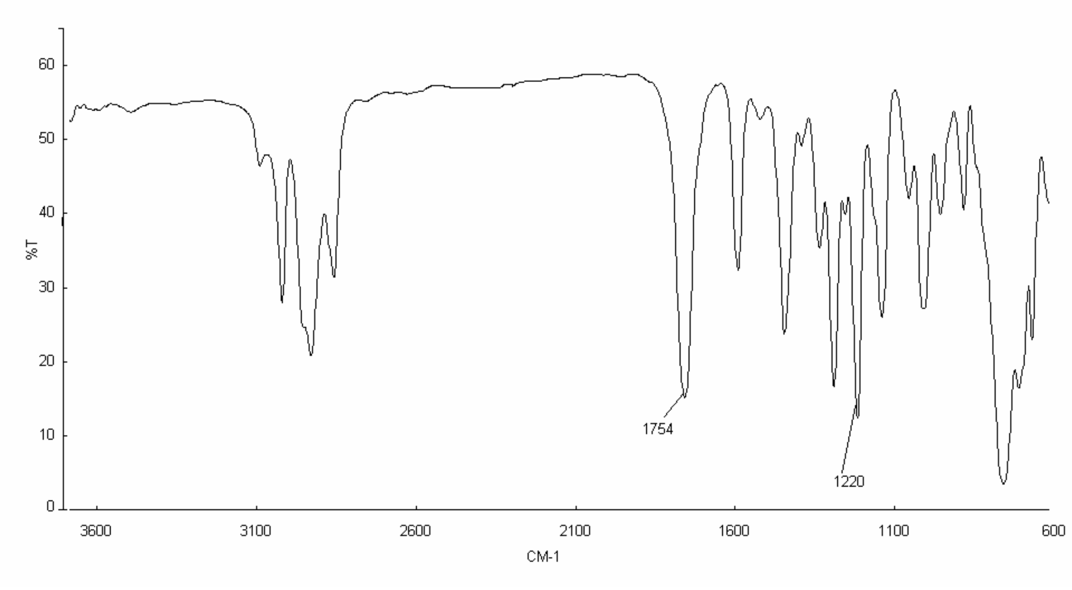


Figure 3.11: IR spectrum of 5-octyloxyisophthaloyl dichloride in chloroform.

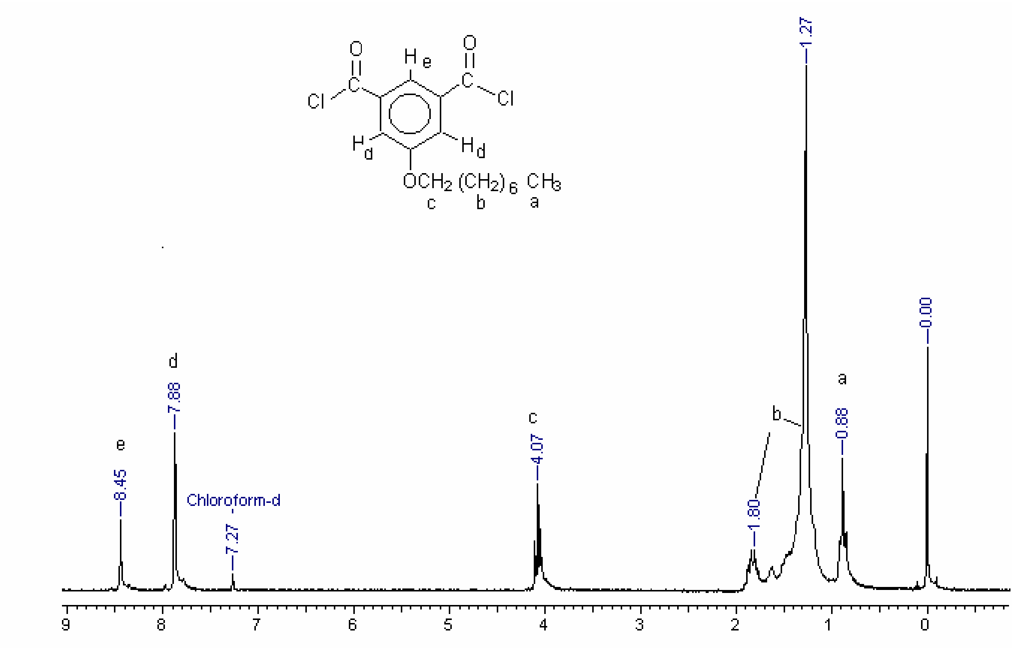


Figure 3.12: ^{1}H-NMR spectrum of 5-octyloxyisophthaloyl dichloride in CDCl$_3$.

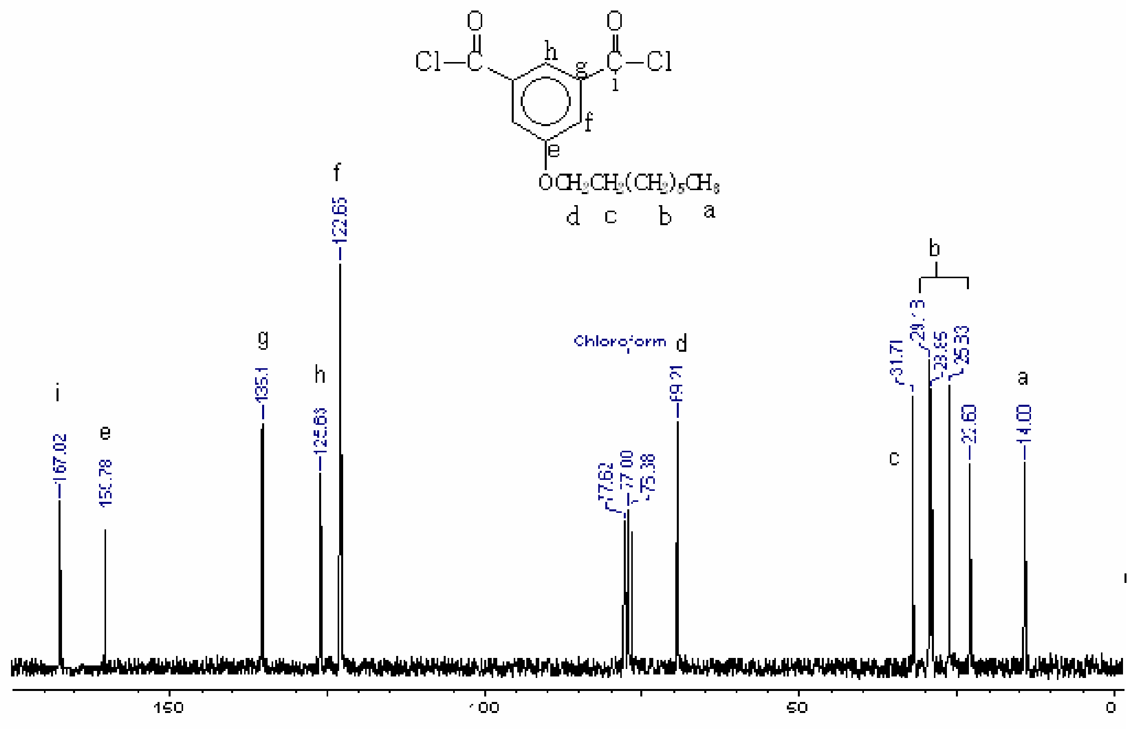
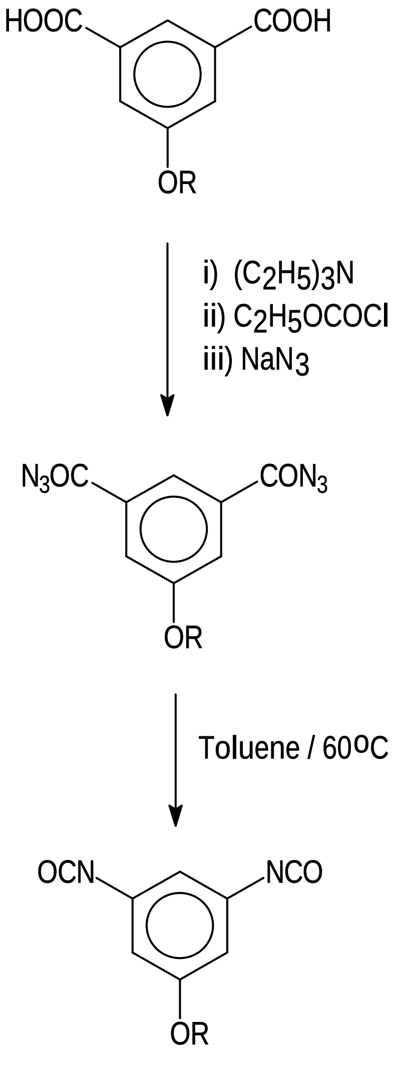


Figure 3.13: ^{13}C-NMR spectrum of 5-octyloxyisophthaloyl dichloride in CDCl$_3$.

3.4.3 Synthesis of 5-alkoxy-1,3-phenylene diisocyanates

Scheme 3.3 illustrates the route followed for the synthesis of 5-alkoxy-1,3-phenylene diisocyanates**.**



R = $-C_4H_9$, $-C_8H_{17}$, $-C_{12}H_{25}$, $-C_{16}H_{33}$

Scheme 3.3: Synthesis of 5-alkoxy-1,3-phenylene diisocyanates.

A series of new *meta*-oriented pendent alkoxy group- containing diisocyanates was synthesized by the non-hazardous, non- phosgenation Curtius rearrangement reaction of the corresponding 5-alkoxy-1,3-phenylene diacylazides as described below.

Acyl azides are usually prepared from acid derivatives such as acid halides and acid hydrazides.[62, 63] The direct conversion of carboxylic acids to acyl azides can be brought about by employing acid activators such as ethyl chloroformate,[64] phenyldichlorophosphate,[65] $SOCl_2$-DMF,[66] NCS- triphenylphosphine,[67] triphosgene,[68] 3,4,5-trifluorobenzeneboronic acid,[69] cyanuric chloride,[70] followed by the reaction with sodium azide.

In the present work, the diacylazides were prepared from 5-alkoxyisophthalic acids by the elegant `one-pot’ Weinstock modification of the Curtius reaction.[71, 72] Diacids were successively treated with triethylamine, ethylchloroformate and sodium azide. The reaction of a diacid with triethylamine produces a salt which on treatment with ethylchloroformate results in the formation of a mixed carboxylic-carbonic anhydride. In the reaction of mixed carboxylic-carbonic anhydride, the azide ion attacks the more electrophilic carbonyl group resulting in the formation of the acylazide. The reaction conditions employed are mild and there are apparently no side products formed in this ‘one-pot’ reaction.

Thus , the following four new 5-alkoxyisophthaloyl diazides were synthesized and their physical and spectral characterization data is presented in **Table 3.10**.

5-Butyloxyisophthaloyl diazide (BIDAz)
5-Octyloxyisophthaloyl diazide (OIDAz)
5-Dodecyloxyisophthaloyl diazide (DDIDAz)
5-Hexadecyloxyisophthaloyl diazide (HDIDAz)

Table 3.10: Physical and spectral characterization data of 5-alkoxyisophthaloyl diazides.

No	Diacyl azide	Yield (%)	M.P. (°C)	IR (cm^{-1})	^{1}H NMR (δ ppm), $CDCl_3$
1	BIDAz	98	42-43	2148(-N_3), 1690(-C=O), 1230(Ar-O-C)	0.97(3H,t,-CH_3),1.40-1.66(2H,m,-CH_2), 1.66-1.90(2H,m,-CH_2), 4.02(2H,t,-OCH2), 7.74 (1H,s, ArH *ortho* to ether), 8.19(2H,s, *ortho* to both –C=O)
2	OIDAz	98	49	2147(-N_3), 1690(-C=O), 1230(Ar-O-C)	0.90(3H,t,-CH_3),1.15-1.58(10H,m,-CH_2),1.73-1.90(2H,m,-CH_2), 4.02(2H,t,-OCH_2), 7.74(1H,s,ArH *ortho* to ether), 8.19(2H,s, *ortho* to both –C=O)
3	DDIDAz	96	57	2148(-N_3), 1690(-C=O), 1230(Ar-O-C)	0.90(3H,t,-CH_3),1.15-1.58(18H,m,-CH_2),1.74-1.90(2H,m,-CH_2), 4.02(2H,t,-OCH_2), 7.75(1H,s,ArH *ortho* to ether), 8.20(2H,s, *ortho* to both –C=O)
4	HDIDAz	91	68	2148(-N_3), 1690(-C=O), 1230(Ar-O-C)	0.89(3H,t,-CH_3),1.14-1.58(26H,m,-CH_2),1.74-1.92(2H,m,-CH_2), 4.02(2H,t,-OCH_2), 7.74(1H,s,ArH *ortho* to ether), 8.19(2H,s, *ortho* to both –C=O)

Representative IR spectrum of 5-hexadecyloxyisophthaloyl diazide is shown in **Figure 3.14.** A strong absorption band was observed at 2148 cm^{-1} which is due to asymmetric stretching vibration of the - N_3 group. A slight splitting of the - N_3

asymmetric band was observed and this may be explained as being due to Fermi interaction with a combination tone involving the - N_3 symmetric or C-N stretching vibration and other low lying frequencies.[73] The carbonyl of the acylazide exhibited a strong absorption band at 1690 cm^{-1}.

^{1}H-NMR spectrum of 5-butyloxyisophthaloyl diazide is shown in **Figure 3.15** as an example. Aromatic proton flanked by acyl azide groups exhibited a singlet at 8.19 δ ppm while the other two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.74 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.02 δ ppm and a multiplet centered at 1.79 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.40 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.97 δ ppm.

^{13}C-NMR spectrum of 5-octyloxyisophthaloyl diazide along with the assignments of the carbon atoms is shown in **Figure 3.16**, as an example.

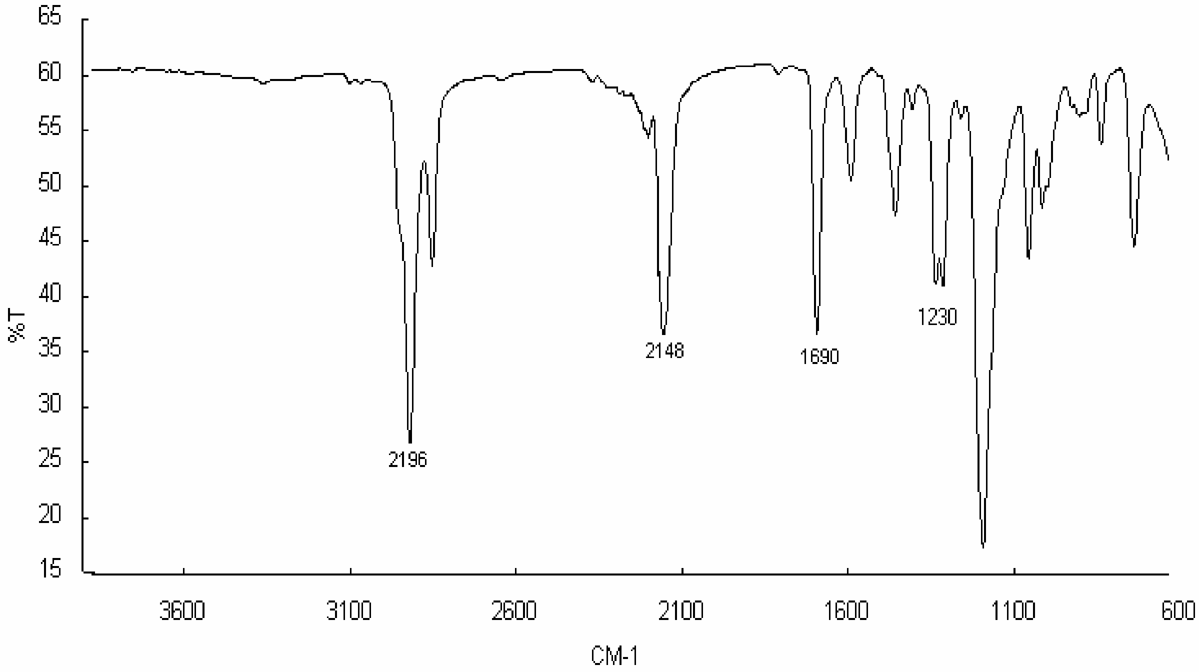


Figure 3.14: FTIR spectrum of 5-hexadecyloxyisophthaloyl diazide in $CHCl_3$.

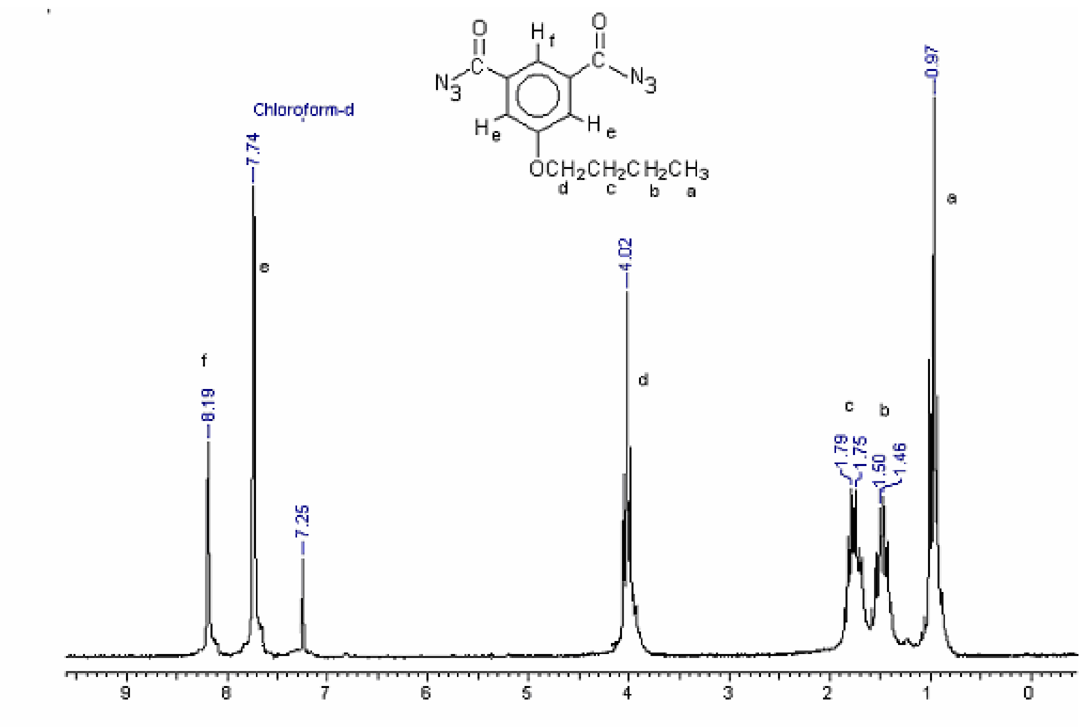


Figure 3.15: ^{1}H-NMR spectrum of 5-butyloxyisophthaloyl diazide in CDCl$_3$.

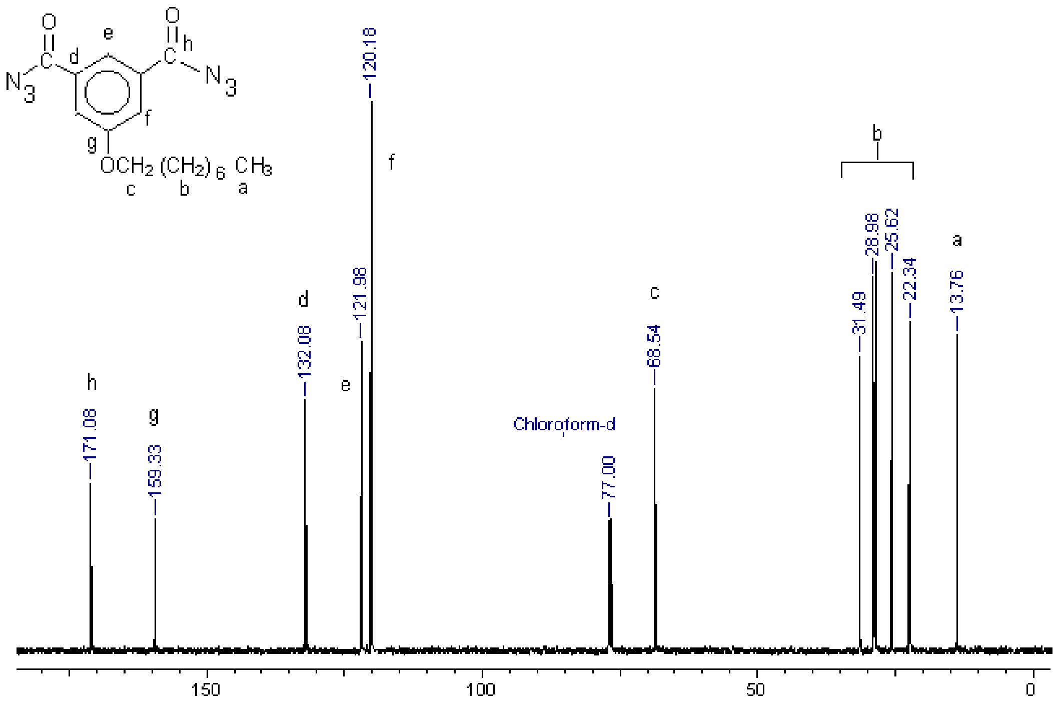


Figure 3.16: ^{13}C-NMR spectrum of 5-octyloxyisophthaloyl diazide in CDCl$_3$.

The thermal Curtius Rearrangement of the diacyl azides in dry toluene was carried out to afford the desired diisocyanates.[74] The diisocyanates were purified by distillation under reduced pressure. The following four new diisocyanates were synthesized and their physical and spectral characterization data is presented in **Table 3.11**.

5-Butyloxy-1,3-phenylenediisocyanate (BPDC)
5-Octyloxy-1,3-phenylenediisocyanate (OPDC)
5-Dodecyloxy-1,3-phenylenediisocyanate (DDPDC)
5-Hexadecyloxy-1,3-phenylenediisocyanate (HDPDC)

Table 3.11: Physical and spectral characterization data of 5-alkoxy-1,3-phenylenediisocyanates

No	Diisocyanate	Yield (%)	M.P. (°C) /B.P (°C), mm Hg	I.R (cm^{-1})	^{1}H NMR (δ ppm), $CDCl_3$
1	BPDC	89	199/10^{-3} mm Hg	2256 (-N=C=O) 1214(Ar-O-C)	0.97(3H,t,-CH_3),1.40-1.60(2H,m,-CH_2), 1.65-1.80(2H,m,-CH_2),3.90 (2H,t,-OCH_2), 6.40 (1H,s, ArH *ortho* to both –C=O), 6.45(2H,s, ArH *ortho* to ether)
2	OPDC	88	210/10^{-3} mm Hg	2256 (-N=C=O) 1216(Ar-O-C)	0.90(3H,t,-CH_3),1.12-1.55 (10H,m,-CH_2),1.65-1.90(2H,m,-CH_2),3.89(2H,t,-OCH_2), 6.41(1H,s, ArH *ortho* to both –C=O), 6.45(2H,s, ArH *ortho* to ether)
3	DDPDC	87	50	2258 (-N=C=O) 1214(Ar-O-C)	0.87(3H,t,-CH_3), 1.12-1.55 (18H,m,-CH_2), 1.65-1.90 (2H,m,-CH_2),3.89(2H,t,-OCH_2), 6.40(1H,s, ArH *ortho* to both –C=O), 6.45(2H,s, ArH *ortho* to ether)
4	HDPDC	82	66-67	2262 (-N=C=O) 1214(Ar-O-C)	0.87(3H,t,-CH_3), 1.12-1.55 (26H,m,-CH_2), 1.67-1.92 (2H,m,-CH_2),3.89(2H,t,-OCH_2), 6.40(1H,s, ArH *ortho* to both –C=O), 6.44(2H,s, ArH *ortho* to ether)

A representative FTIR spectrum of 5-butyloxy-1,3-phenylene diisocyanate is shown in **Figure 3.17**. Strong absorption band at 2256 cm^{-1} characteristic of the asymmetric stretching vibration of the isocyanate group was observed.

^{1}H-NMR spectrum of 5-butyloxy-1,3-phenylene diisocyanate is shown in **Figure 3.18** as an example. Aromatic protons *ortho* to the ether linkage appeared as a singlet at 6.45 δ ppm, while aromatic proton flanked by isocyanate groups exhibited a singlet at 6.40 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 3.90 δ ppm and a multiplet centered at 1.74 δ ppm, respectively. The other methylene protons displayed a multiplet centered at 1.45 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.97 δ ppm.

The upfield chemical shift of the aromatic protons in the diisocyanate is likely to be due to a combination of mesomeric effect of ether oxygen and shielding due to neighboring group anisotropy of the isocyanate group. The dominating effect appears to be the mesomeric effect of the ether linkage.

The aromatic protons in the corresponding diacyl azide appeared downfield in comparison to the aromatic protons of the diisocyanate (**Figure 3.15 and 3.18**). In the case of diacyl azide, the electron donating effect of the ether oxygen and the neighbouring group anisotropy of the carbonyl of acyl azide group would be operative. The downfield chemical shift indicates that the latter dominates over the former.

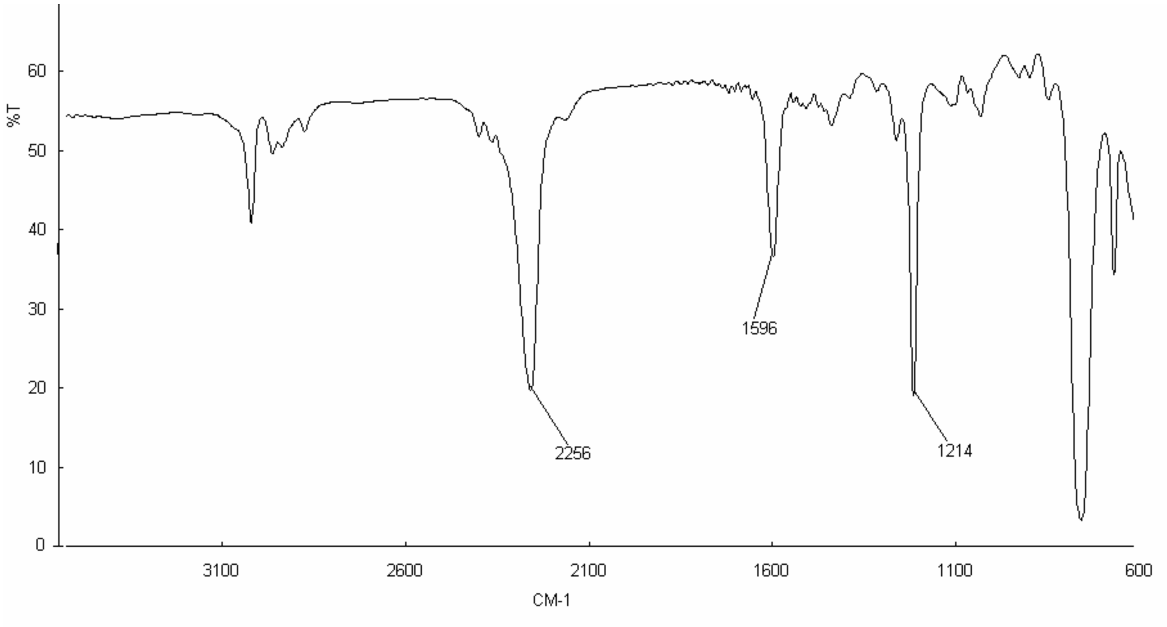


Figure 3.17: IR spectrum of 5-butyloxy-1,3-phenylenediisocyanate in $CHCl_3$.

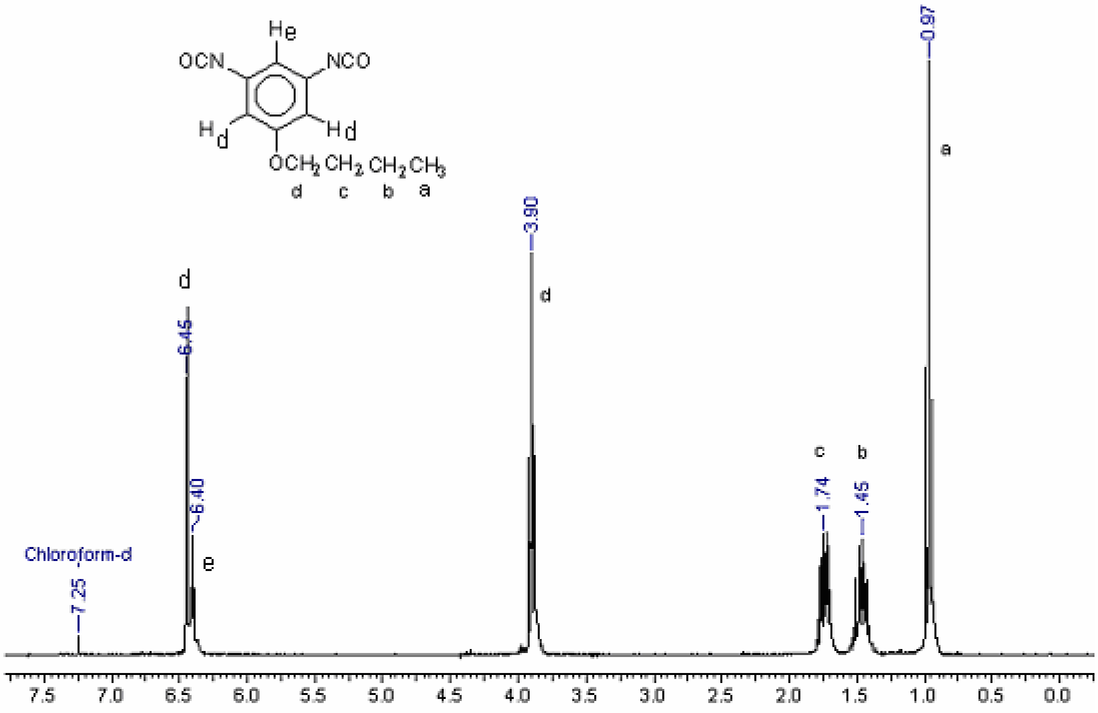


Figure 3.18: ^{1}H-NMR spectrum of 5-butyloxy-1,3-phenylenediisocyanate in $CDCl_3$.

^{13}C-NMR spectrum of 5-butyloxy-1,3-phenylene diisocyanate along with the assignments of the carbon atoms is shown in **Figure 3.19**. In the ^{13}C-NMR spectrum of the diisocyanate the chemical shift at 125.08 ppm was assigned to the carbon atom of the NCO group (based on the assignment of the carbon atom of the NCO group in phenyl isocyanate.[75]

Table 3.12 incorporates the ^{13}C-NMR spectral data of the synthesized diisocyanates.

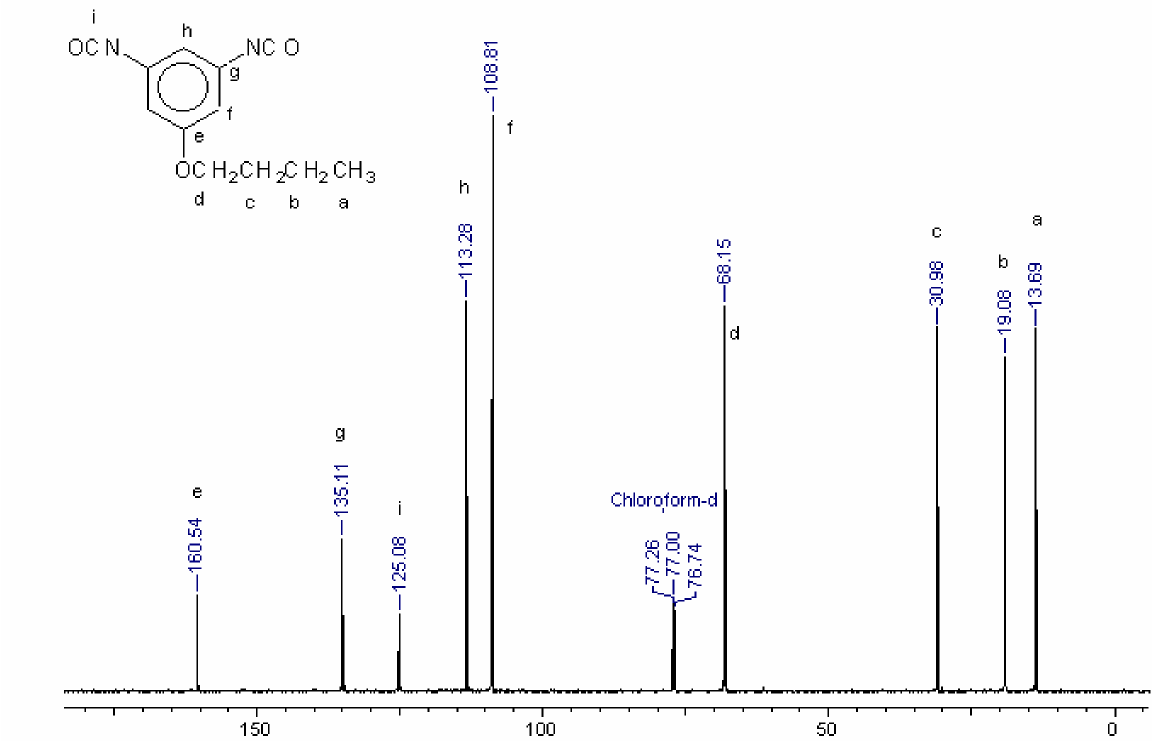
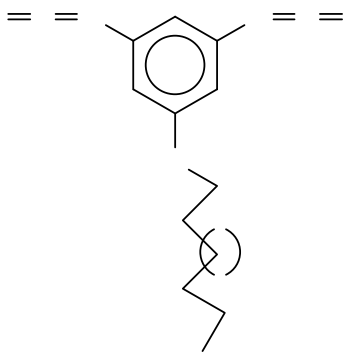


Figure 3.19: ^{13}C-NMR spectrum of 5-butyloxy-1,3-phenylenediisocyanate in $CDCl_3$

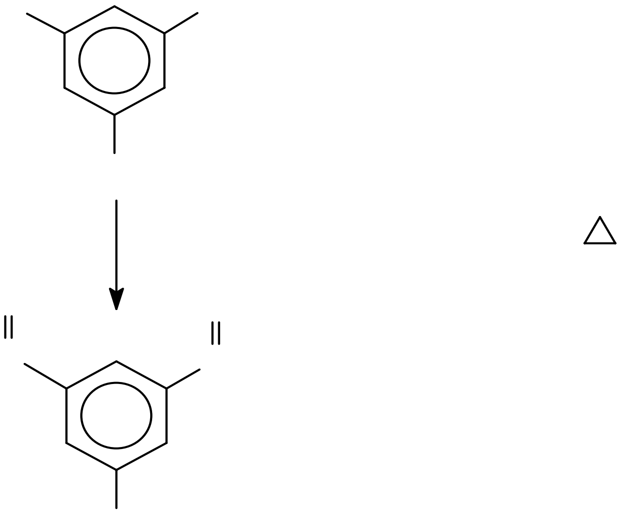
Table 3.12: ^{13}C-NMR spectral data of the 5-alkoxy-1,3-phenylenediisocyanate



C-Atom	OPDC (δ ppm) n=3	DDPDC (δ ppm) n=7	HDPDC (δ ppm) n=11
a	13.75	13.76	13.76
b	22.36	22.38	22.38
c	25.60	25.63	25.63
d	28.71-29.37	28.73-29.39	28.73-29.39
e	31.60	31.63	31.63
f	68.25	68.28	68.28
g	160.35	160.38	160.38
h	108.62	108.60	108.60
i	134.97	134.96	134.96
j	113.0	113.03	113.03
k	124.95	124.92	124.92

3.4.4 Synthesis of 5-alkoxyisophthalic acid dihydrazides

Scheme 3.4 depicts synthetic step for the preparation of 5-alkoxyisophthalic acid dihydrazides. The 5-alkoxyisophthalic acid dihydrazides were synthesized by the hydrazinolysis of the corresponding dimethyl-5-alkoxyisophthalates with hydrazine monohydrate in ethanol under refluxing condition.[76]



Scheme 3.4: Synthesis of 5-alkoxyisophthalicacid dihydrazide

The following four new 5-alkoxyisophthalicacid dihydrazides were synthesized and their physical and spectroscopic characterization data is presented in **Table 3.13.**

5-Butyloxyisophthalic acid dihydrazide (BIADH)

5-Octyloxyisophthalic acid dihydrazide (OIADH)

5-Dodecyloxyisophthalic acid dihydrazide (DDIADH)

5-Hexadecyloxyisophthalic acid dihydrazide (HDIADH)

Table 3.13: Physical and spectral characterization data of 5-alkoxyisophthalic acid dihydrazides

No.	Diacyl hydrazide	Yield (%)	M.P. (^oC)	IR (cm^{-1})	^{1}H-NMR (δppm), DMSO-d_6
1	BIADH	85	160	3312-3228 (-NH_2,-NH) 1662(-C=O)	0.94 (3H,t,-CH_3), 1.40-1.60 (2H, m,-CH_2), 1.66-1.80 (2H, m, -CH_2), 4.04 (3H, t, -OCH_2), 4.51 (4H,br, s, -NH_2), 7.46 (2H, s, ArH *ortho* to ether), 7.85(1H, s, ArH *ortho* to both –C=O), 9.79 (2H,br,-NH)
2	OIADH	78	150	3312-3228 (-NH_2,-NH) 1662(-C=O)	0.85 (3H,t,-CH_3), 1.15-1.55(10H,m,-CH_2), 1.66-1.89 (2H,m, -CH_2), 4.03 (3H,t, -OCH_2), 4.52 (4H, br, s, -NH_2), 7.46 (2H, s, ArH *ortho* to ether), 7.85(1H, s, ArH *ortho* to both –C=O), 9.79 (2H,br,-NH)
3	DDIADH	80	131	3312-3228 (-NH_2,-NH) 1662(-C=O)	0.95 (3H,t,-CH_3), 1.17-1.57 (18H,m,-CH_2), 1.66-1.89 (2H,m, -CH_2), 4.04 (3H,t,-OCH_2), 4.51 (4H, br, s, -NH_2), 7.46 (2H, s, ArH *ortho* to ether), 7.85(1H, s, ArH *ortho* to both –C=O), 9.79 (2H,br,-NH)
4	HDIADH	75	130	3312-3228 (-NH_2,-NH) 1662(-C=O)	0.95 (3H,t,-CH_3), 1.15-1.55 (26H,m,-CH_2), 1.66-1.89 (2H,m,-CH_2), 4.04 (3H,t,-OCH_2), 4.51 (4H, br, s,-NH_2), 7.46 (2H, s, ArH *ortho* to ether), 7.85(1H, s, ArH *ortho* to both –C=O), 9.79 (2H,br,-NH)

A representative IR spectrum of 5-hexadecyloxyisophthalic acid dihydrazide is shown in **Figure 3.20.** Absorption band at 3289 cm^{-1} is assignable to -NH_2 and –NH- functions. Absorption band at 1662 cm^{-1} is attributed to the carbonyl of the acid hydrazide group.

^{1}H-NMR spectrum of 5-butyloxyisophthalic acid dihydrazide is shown in **Figure 3.21** as an example. A singlet at 9.79 δ ppm is due to the –NH- of the acid hydrazide group. The aromatic proton flanked by acid hydrazide groups exhibited a singlet at 7.85 δ ppm while the other two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.46 δ ppm. A broad singlet at 4.51 δ ppm is due to the $–NH_2$ of the acid hydrazide group. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.04 δ ppm and a multiplet centered at 1.70 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.40 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.94 δ ppm.

^{13}C-NMR spectrum of 5-butyloxyisophthalic acid dihydrazide along with the assignments of carbon atoms is shown in **Figure 3.22**, as an example.

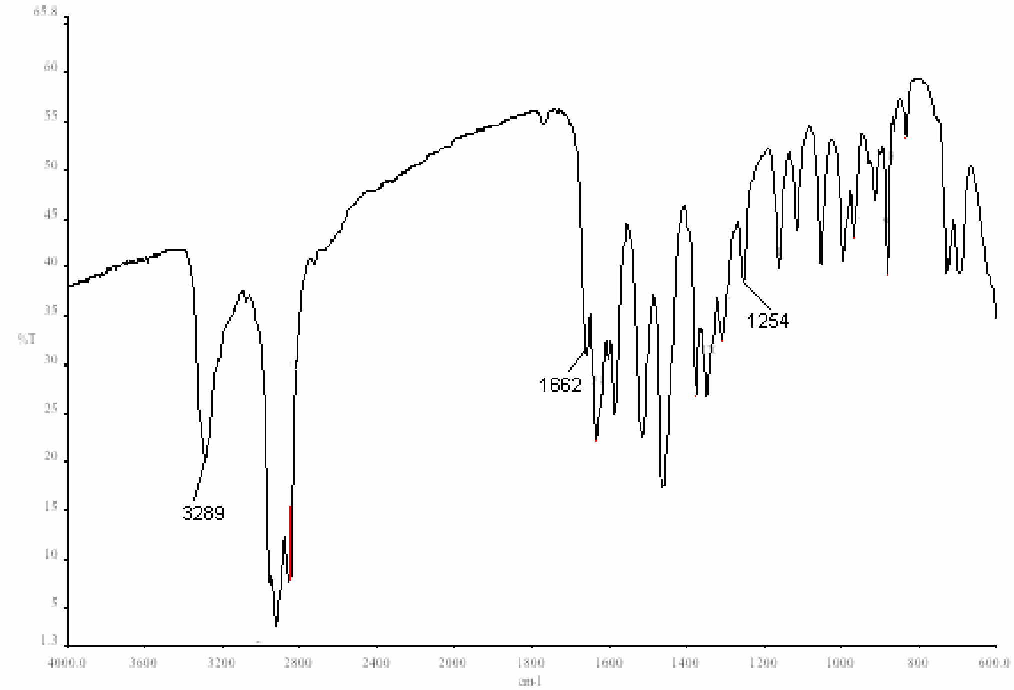


Figure 3.20: IR spectrum of 5-hexadecyloxyisophthalic acid dihydrazide in nujol mull.

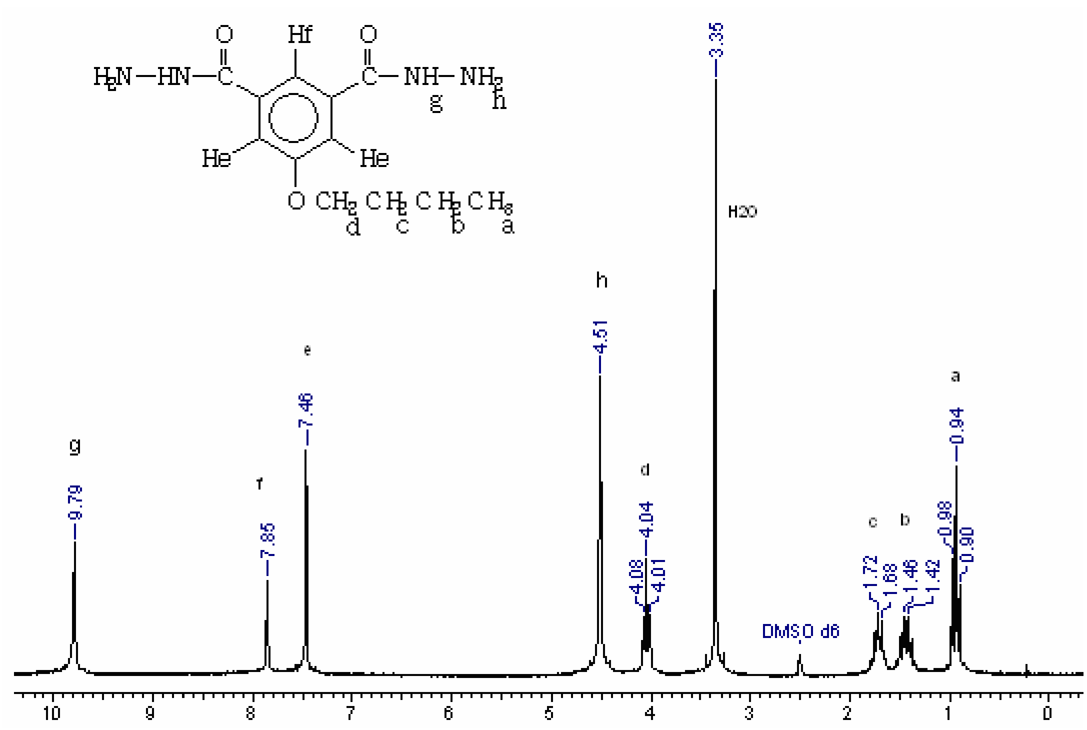


Figure 3.21: ^{1}H-NMR spectrum of 5-butyloxyisophthalic acid dihydrazide in DMSO- d_6.

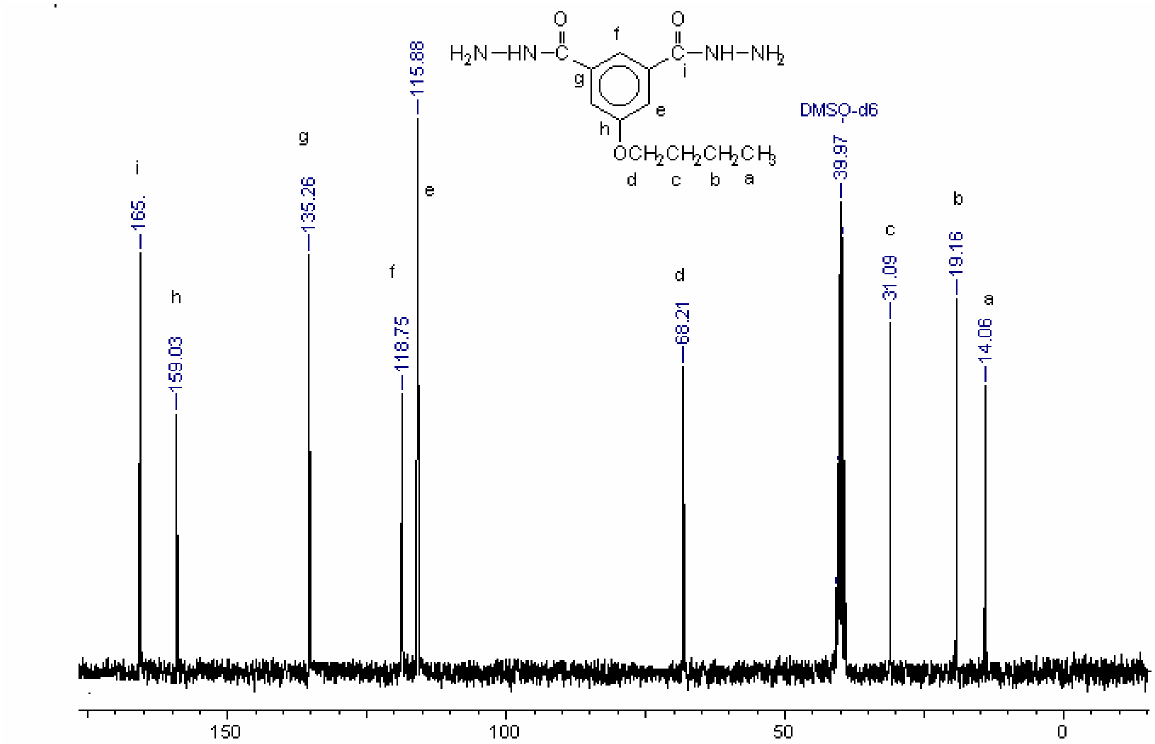
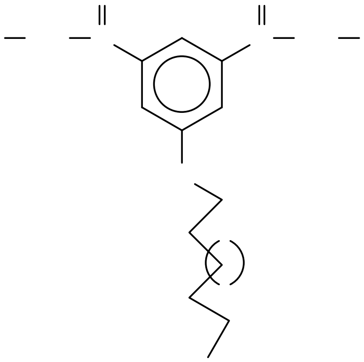


Figure 3.22:^{13}C-NMR spectrum of 5-butyloxyisophthalic acid dihydrazide in DMSO- d_6.

The chemical shifts in the ^{13}C-NMR spectra for the respective carbon atoms of the diacylhydrazides are shown in **Table 3.14.**

Table 3.14: ^{13}**C-NMR spectral data of 5-alkoxyisophthalic acid dihydrazide**



C-Atom	OIADH (δ ppm) n=3	DDIADH (δ ppm) n=7	HDIADH (δ ppm) n=11
a	14.16	13.97	13.97
b	22.39	22.21	22.21
c	25.78	25.63	25.63
d	27.80-29.0	27.50-29.17	27.50-29.17
e	31.55	31.46	31.46
f	68.20	68.11	68.11
g	158.78	158.70	158.70
h	115.54	115.51	115.51
i	135.0	134.89	134.89
j	118.55	118.38	118.38
k	165.50	165.35	165.35

Mass spectrum (**Figure 3.23**) of 5-butyloxyisophthalic acid dihydrazide showed the molecular ion peak at 266 confirming the proposed structure. The mass spectral data of the diacyl hydrazides is given in **Table 3.15** which were in good agreement with the proposed structures.

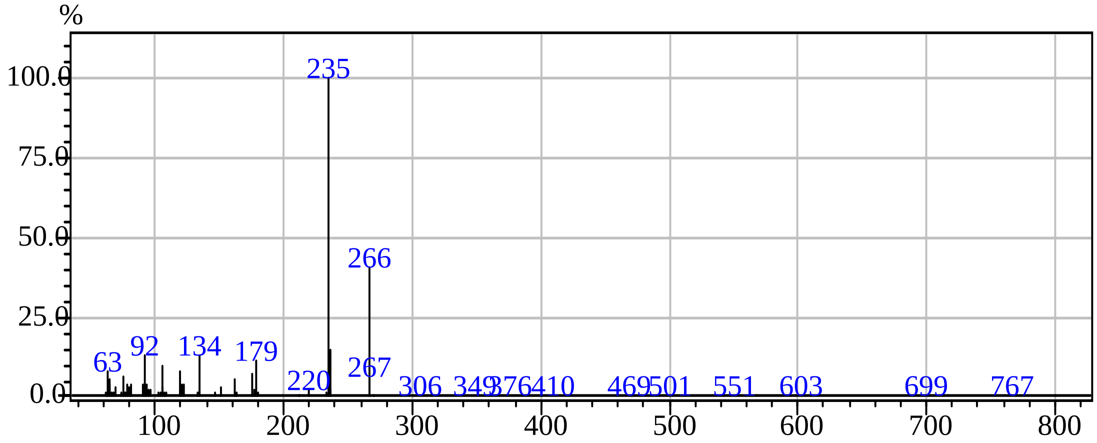


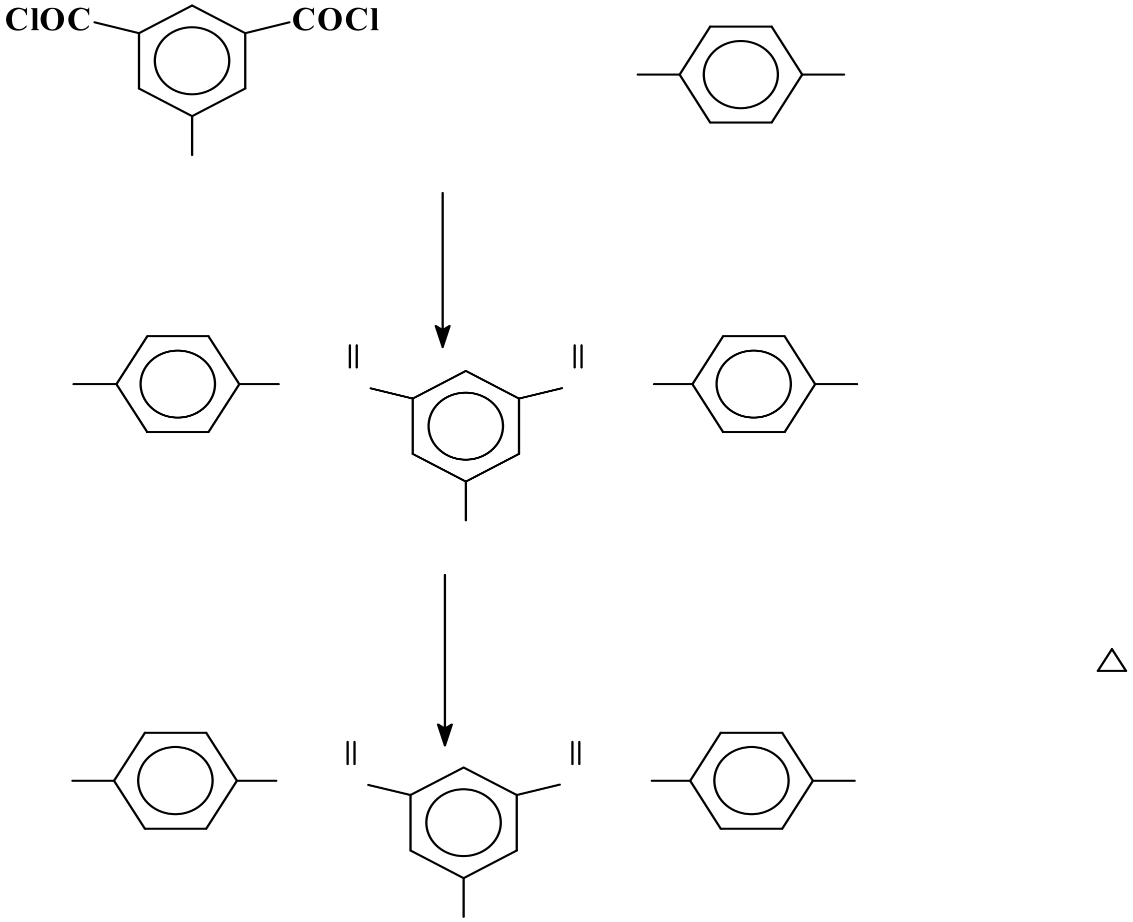
Figure 3.23: Mass spectrum of 5-butyloxyisophthalic acid dihydrazide

Table 3.15: Mass spectral data of 5-alkoxyisophthalicacid dihydrazides

Diacyl hydrazide	**m/z, relative intensity (%)**
BIADH	266 (M^+, 40), 235 (100)
OIADH	322 (M^+, 30), 291 (100)
DDIADH	378 (M^+, 55), 347 (100)
HDIADH	434 (M^+, 90), 403 (100)

3.4.5 Synthesis of 5-alkoxy-N,N’-bis(4-aminophenyl) isophthalamides

The route adapted for the synthesis of new aromatic diamines containing pre-formed amide linkages and possessing pendent alkoxy side-chain, viz., 5-alkoxy-N,N’-bis(4-aminophenyl)isophthalamides is shown in **Scheme 3.5**.



Scheme 3.5: Synthesis of 5-alkoxy-N,N’-bis(4-aminophenyl)isophthalamides.

The corresponding 5-alkoxyisophthaloyl dichloride was reacted with p-nitroaniline in the presence of triethylamine as hydrogen chloride scavenger in DMF at room temperature. The following five dinitro compounds were synthesized and their physical and spectral characterization data is collected in **Table 3.16.**

5-Butyloxy-N,N’-bis(4-nitrophenyl) isophthalamide (BNI)
5-Octyloxy-N,N’-bis(4-nitrophenyl) isophthalamide (ONI)
5-Dodecyloxy-N,N’-bis(4-nitrophenyl) isophthalamide (DDNI)
5-Hexadecyloxy-N,N’-bis(4-nitrophenyl) isophthalamide (HDNI)
N,N’-Bis(4-nitrophenyl) isophthalamide (NI)

Table 3.16: **Physical and spectral characterization data of 5-alkoxy-N,N'-bis(4-nitrophenyl) isophthalamide.**

No.	Dinitro Compd.	Yield (%)	M.P. (^{o}C) (Lit. M.P. ^{o}C)	IR (cm^{-1})	^{1}H-NMR (δ ppm), DMSO-d_6
1	BNI	85	265	3378(-NH), 1682(-C=O), 1534,1340(-NO_2), 1244(Ar-O-C)	0.96 (3H, t, -CH_3), 1.40-1.60 (2H, m,-CH_2), 1.60-1.90(2H,m,-CH_2), 4.15(2H,t, -OCH_2), 7.75 (2H,s, ArH *ortho* to ether), 8.08 (4H, d, ArH *meta* to –NO_2), 8.16 (1H, s, ArH *ortho* to both –C=O), 8.29(4H, d, ArH *ortho* to –NO_2), 10.92 (2H, br, s,-NH-)
2	ONI	85	262	3378(-NH), 1682(-C=O), 1534,1340(-NO_2), 1244(Ar-O-C)	0.85 (3H, t, -CH_3), 1.25-1.57 (10H,m, -CH_2), 1.65-1.89(2H,m,CH_2), 4.13 (2H, t,-OCH_2), 7.74 (2H,s, ArH *ortho* to ether), 8.10 (4H, d, ArH *meta* to –NO_2), 8.16 (1H, s, ArH *ortho* to both –C=O), 8.26(4H, d, ArH *ortho* to –NO_2), 10.92 (2H, br, s,-NH-)
3	DDNI	88	251-252	3378(-NH), 1682(-C=O), 1534,1340(-NO_2), 1244(Ar-O-C)	0.85 (3H,t, -CH_3), 1.21-1.58 (18H,m, -CH_2), 1.65-1.89 (2H,m,-CH_2), 4.15 (2H,t, -OCH_2), 7.75 (2H,s, ArH *ortho* to ether), 8.08 (4H, d, ArH *meta* to –NO_2), 8.16 (1H, s, ArH *ortho* to both –C=O), 8.26(4H, d, ArH *ortho* to –NO_2), 10.90 (2H, br, s,-NH-)
4	HDNI	90	153-154	3378(-NH), 1682(-C=O), 1534,1340(-NO_2), 1244(Ar-O-C)	0.94 (3H, t,-CH_3), 1.21-1.57(26H,m, -CH_2), 1.65-1.89 (2H, m,-CH_2), 4.15 (2H,t, -OCH_2), 7.75 (2H,s, ArH ortho to ether), 8.08 (4H, d, ArH *meta* to –NO_2), 8.15 (1H, s, ArH *ortho* to both –C=O), 8.25(4H, d, ArH *ortho* to –NO_2), 10.90(2H, br, s,-NH-)
5	NI	87	1350 (377, dec.)[77]	3378(-NH), 1682(-C=O), 1534,1340(-NO_2), 1244(Ar-O-C)	7.76 (1H, t, ArH meta to both–C=O), , 8.09(4H,d, *meta* to –NO_2),8.20 (2H, d, ArH *ortho* to –NO_2), 8.29 (4H, d, ArH *ortho* to -NO_2), 8.58(1H, s, ArH *ortho* to both –C=O),10.89 (2H, br, s,-NH-)

A representative IR spectrum of 5-octyloxy-N,N’-bis(4-nitrophenyl) isophthalamide is shown in **Figure 3.24.** An absorption band at 3378cm^{-1} is due to NH of the amide group. Absorption band at 1682 cm^{-1} is assigned to the carbonyl of the amide goup. The absorption bands characteristic of the nitro group were observed at 1534 cm^{-1} (asymmetric stretching) and 1340 cm^{-1} (symmetric stretching).

^{1}H-NMR spectrum of 5-butyloxy-N,N’-bis(4-nitrophenyl) isophthalamide is shown in **Figure 3.25** as an example. The amide NH appears as a singlet at 10.92 δ ppm. Aromatic protons *ortho*- and *meta*- to nitro exhibited a doublet each at 8.29 δ ppm and 8.08 δ ppm, respectively. Aromatic proton flanked by amide groups exhibited a singlet at 8.16 δ ppm while the two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.75 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.15 δ ppm and a multiplet centered at 1.78 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.40 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.96 δ ppm.

^{13}C-NMR spectrum of 5-butyloxy-N,N’-bis(4-nitrophenyl) isophthalamide along with assignments of the carbon atoms is shown in **Figure 3.26**, as an example.

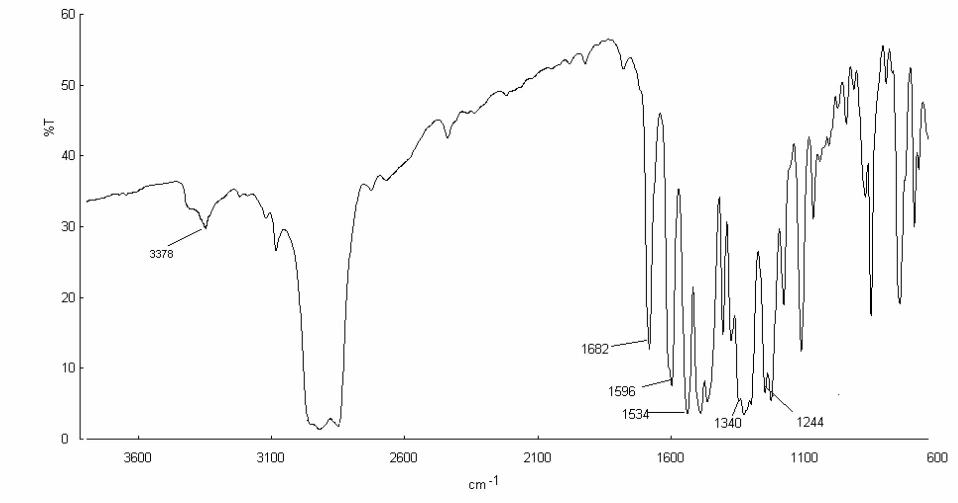


Figure 3.24: IR spectrum of 5-octyloxy-N,N’-bis(4-nitrophenyl) isophthalamide (ONI) in nujol mull.

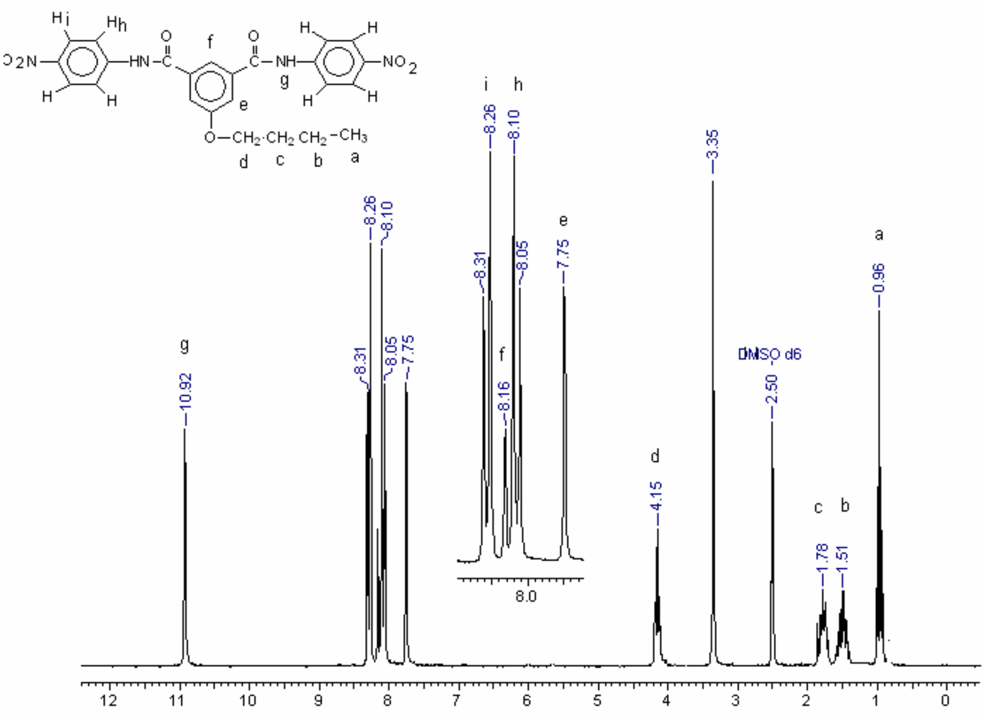


Figure 3.25: ^{1}H-NMR spectrum of 5-butyloxy-N,N’-bis(4-nitrophenyl) isophthalamide in DMSO-d_6.

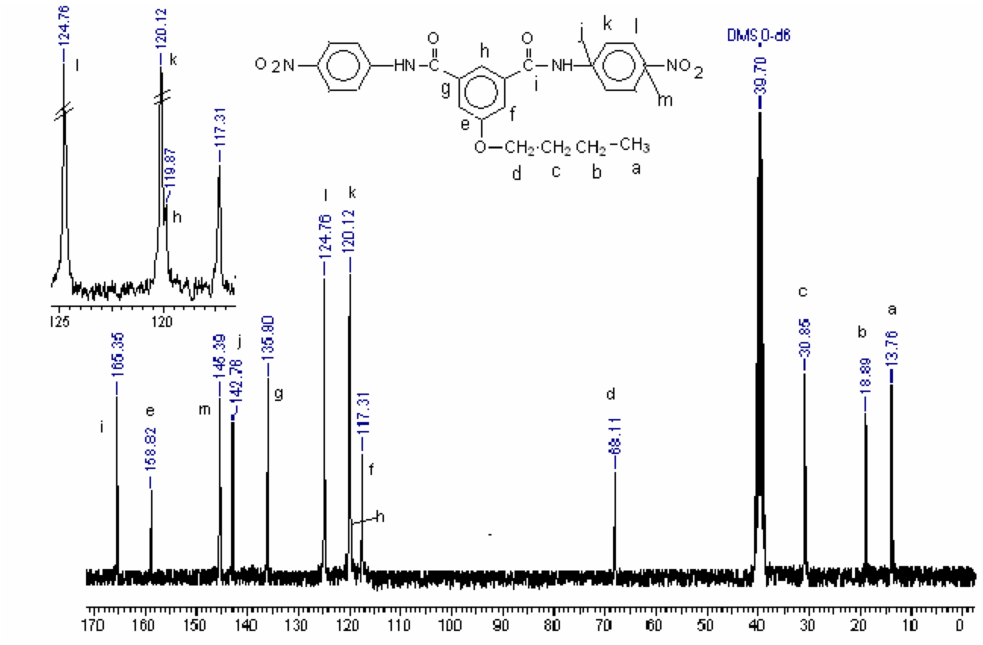


Figure 3.26: ^{13}C NMR spectrum of 5-butyloxy-N,N’-bis(4-nitrophenyl) isophthalamide in DMSO-d_6.

5-Alkoxy-N,N'-bis(4-aminophenyl)isophthalamides were synthesized by reduction of the corresponding dinitro compounds. Reduction of an aromatic nitro compound to an aromatic amine can be carried out using a number of reagents,[78] e.g. the catalytic hydrogenation (H2 / Pd-C), HCl and metal or metal salt, or hydrazine hydrate / Pd-C.

In the present work, the dinitro compounds were reduced with hydrazine hydrate / Pd-C. The following four 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides were successfully synthesized and their physical and spectral characterization data is given in **Table 3.17.**

5-Butyloxy-N,N'-bis(4-aminophenyl)isophthalamide (BAI)
5-Octyloxy-N,N'-bis(4-aminophenyl)isophthalamide (OAI)
5-Dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide (DDAI)
5-Hexadecyloxy-N,N'-bis(4-aminophenyl) isophthalamide (HDAI)
N,N'-Bis(4-aminophenyl) isophthalamide (AI)

Table 3.17: Physical and spectral characterization data of 5-alkoxy-N,N'-bis(4-aminophenyl) isophthalamides.

No	Diamine	Yield (%)	M.P. (^{o}C) (Lit. M.P. ^{o}C)	I.R (cm^{-1})	^{1}H-NMR (δppm), DMSO-d_6
1	BAI	75	227	3400-3250 (-NH_2,- NH) 1646(-C=O) 1250(Ar-O-C)	0.96 (3H, t,-CH_3),1.25-1.60(2H,m,-CH_2), 1.62-1.80 (2H, m,-CH_2), 4.11(2H,t, -OCH_2), 4.95 (4H, br, s, -NH_2), 6.56(4H, d, ArH *ortho* to –NH_2), 7.39 (4H,d, ArH *meta* to –NH_2), 7.60 (2H, s, ArH *ortho* to ether), 8.04 (1H, s, ArH *ortho* to both–C=O), 9.97 (2H, br,s,-CONH).
2	OAI	78	190	3400-3250 (-NH_2, -NH) 1646(-C=O) 1250(Ar-O-C)	0.89 (3H,t,-CH_3), 1.15-1.55(10H,m,-CH_2), 1.60-1.80 (2H, m,-CH_2) 4.13(2H, t, -OCH_2), 4.98 (4H,br, s, -NH_2) ,6.60(4H,d, ArH ortho to –NH_2), 7.40(4H,d, ArH *meta* to –NH_2), 7.60(2H,s, ArH *ortho* to ether), 8.05(1H,s, ArH *ortho* to both–C=O), 9.99(2H, br,s,-CONH).
3	DDAI	73	101	3400-3250 (-NH_2,- NH) 1646(-C=O) 1250(Ar-O-C)	0.90 (3H,t,-CH_3), 1.15-1.57 (18H,m,-CH_2-), 1.60-1.80 (2H,m,-CH_2), 3.91 (2H,t, -OCH_2), 4.96 (4H, br, s, -NH_2), 6.60(4H, d, *ortho* to –NH_2), 7.29(4H,d, ArH *meta* to –NH_2), 7.60(2H, ArH *ortho* to ether), 8.04 (1H, s, ArH *ortho* to both–C=O), 9.96(2H, br, s,-CONH).
4	HDAI	76	87-88	3400-3250 (-NH_2,- NH) 1646(-C=O) 1250(Ar-O-C)	0.96 (3H,t,-CH_3), 1.00-1.55 (26H,m,-CH_2-), 1.65-1.80 (2H,m,-CH_2) 3.91(2H,t, -OCH_2), 4.96 (4H, br, s,-NH_2) ,6.55(4H, d, ArH *ortho* to –NH_2), 7.39(4H, ArH *meta* to –NH_2), 7.60(2H,d, ArH *ortho* to ether), 8.02 (1H,s, ArH *ortho* to both –C=O), 9.96 (2H, br, s,-CONH).
5	AI	75	245-246 (242)[77]	3400-3250 (-NH_2, -NH) 1646(-C=O)	4.94 (4H, br, s, -NH_2), 6.57(4H,d, ArH *ortho* to -NH_2), 7.37(4H, d, ArH *meta* to –NH_2), 7.61(1H, t, ArH *meta* to both –C=O), 8.03 (2H, d, ArH *para* to –C=O), 8.43(1H,s, ArH between two –C=O), 10.0 (2H,br, s,-CONH).

A representative IR spectrum of 5-hexadecyloxy-N,N'-bis(4-aminophenyl) isophthalamide is shown in **Figure 3.27.** Absorption bands at 3400 and 3328 cm^{-1} are attributable to -NH_2 of the amino group and -NH of the amide group. Absorption band at 1646 cm^{-1} is assigned to the carbonyl of the amide group. The absorption bands characteristic of the nitro group were not observed indicating complete reduction of the nitro compound to the amine.

^{1}H-NMR spectrum of 5-butyloxy-N,N'-bis(4-aminophenyl)isophthalamide is shown in **Figure 3.28** as an example. The amide NH appears as a singlet at 9.97 δ ppm. Aromatic proton flanked by amide groups exhibited a singlet at 8.04 δ ppm while the two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.60 δ ppm. Aromatic protons *meta*- and *ortho*- to amino group exhibited a doublet each at 7.39 δ ppm and 6.56 δ ppm, respectively. A broad singlet at 4.95 δ ppm is ascribed to the amino group. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.11 δ ppm and a multiplet centered at 1.76 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.25 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.96 δ ppm.

^{13}C-NMR spectrum of 5-butyloxy-N,N'-bis(4-aminophenyl) isophthalamide along with the assignments of carbon atoms is shown in **Figure 3.29**, as an example.

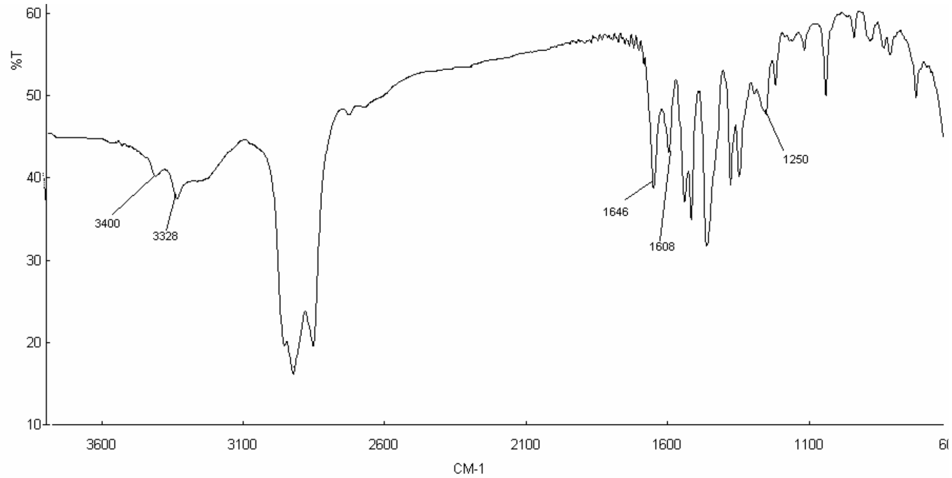


Figure 3.27: IR spectrum of 5-hexadecyloxy-N,N'-bis(4-aminophenyl) isophthalamide in nujol mull.

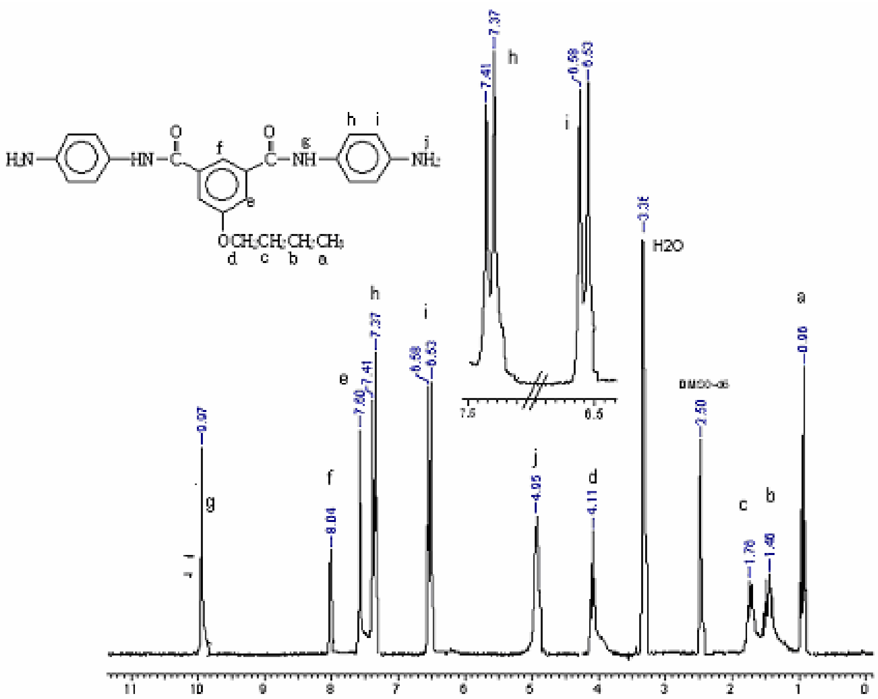


Figure 3.28: ^{1}H-NMR spectrum of 5-butyloxy-N,N’-bis(4-aminophenyl) isophthalamide in DMSO-d$_6$.

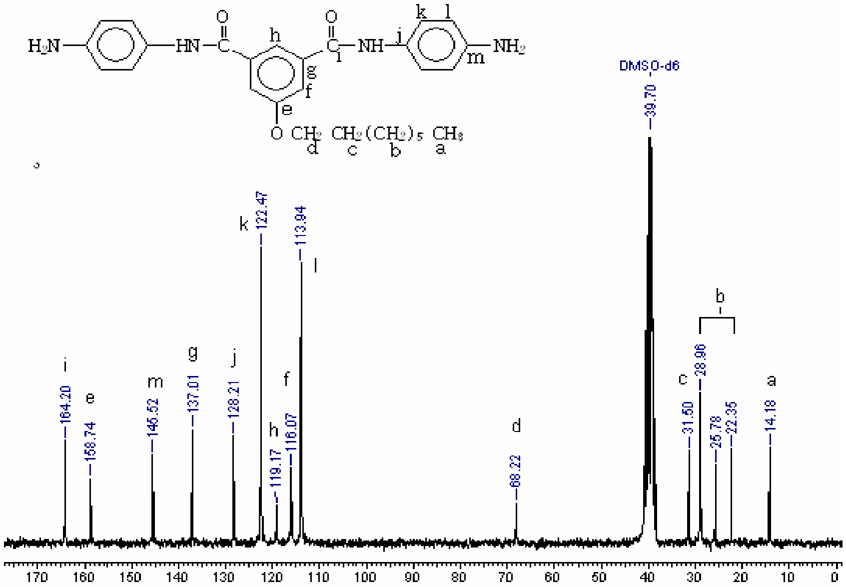
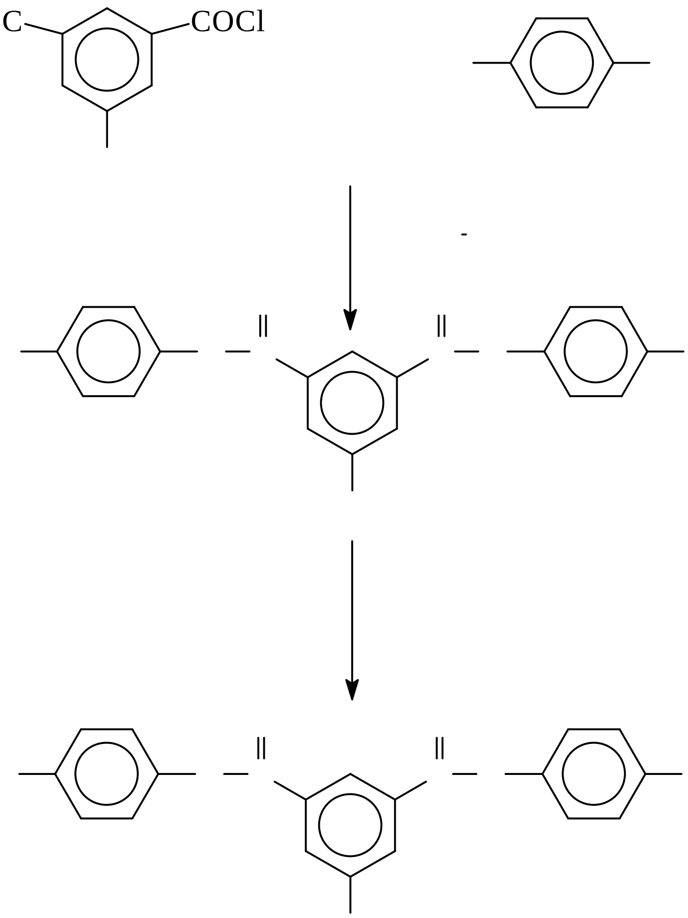


Figure 3.29: ^{13}C-NMR spectrum of 5-octyloxy-N,N’-bis(4-aminophenyl) isophthalamide in DMSO-d$_6$.

3.4.6 Synthesis of 5-alkoxyisophthalicacid bis(4-aminophenyl) esters

The route adapted for the synthesis of new aromatic diamines containing pre-formed ester linkages and pendent flexible alkoxy chains, namely 5-alkoxyisophthalicacid bis(4-aminophenyl) esters is depicted in **Scheme 3.6.**



Scheme 3.6: Synthesis of 5-alkoxyisophthalic acid bis(4-aminophenyl) esters.

The corresponding 5-alkoxyisophthaloyl dichloride was reacted with p-nitrophenol in the presence of triethylamine as hydrogen chloride scavenger in DMF at room temperature. The following two dinitro compounds were synthesized and their physical and spectral characterization data is collected in **Table 3.18.**

5-Octyloxyisophthalic acid bis(4-nitrophenyl) ester (OINE)
5-Dodecyloxyisophthalic acid bis(4-nitrophenyl) ester (DINE)

Table 3.18: Physical and spectral characterization data of 5-alkoxyisophthalic acid bis(4-nitrophenyl) ester

No	**Dinitro compound**	**Yield (%)**	**M.P. (^oC)**	**IR (cm^{-1})**	**^1H-NMR (δ ppm), DMSO-d_6**
1	OINE	86	130	1750(-C=O) 1522,1350 (-NO_2) 1208(Ar-O-C)	0.87 (3H,t,-CH_3), 1.10-1.59 (10H,m, -CH_2), 1.72-1.90 (2H,m,-CH_2), 4.11 (2H, t,-OCH_2), 7.44 (4H,d, ArH *meta* to -NO_2), 7.96 (2H, s, ArH *ortho* to ether), 8.33(4H,d, ArH, *ortho* to -NO_2), 8.55 (1H, s, ArH *ortho* to both –C=O)
2	DINE	85	120-123	1750(-C=O) 1522,1350 (-NO_2) 1208(Ar-O-C)	0.86 (3H, t, -CH_3), 1.10-1.60 (18H,m, -CH_2), 1.71-1.90 (2H, m,-CH_2), 4.11 (2H, t,-OCH_2), 7.44 (4H,d, ArH *meta* to NO_2), 7.97 (2H, s, ArH *ortho* to ether), 8.33(4H,d, ArH *ortho* to NO_2), 8.56(1H,s, ArH *ortho* to both –C=O)

A representative IR spectrum of 5-octyloxyisophthalic acid bis(4-nitrophenyl) ester is shown in **Figure 3.30.** Absorption band at 1750 cm^{-1} is assigned to the carbonyl of the ester group. The absorption bands characteristic of the nitro group were observed at 1522 cm^{-1} (asymmetric stretching) and 1350 cm^{-1} (symmetric stretching).

^{1}H-NMR spectrum of 5-dodecyloxyisophthalic acid bis(4-nitrophenyl) ester is shown in **Figure 3.31** as an example. Aromatic proton flanked by ester groups exhibited a singlet at 8.56 δ ppm. Aromatic protons *ortho*- and *meta*- to nitro exhibited a doublet each at 8.36 δ ppm and 7.44 δ ppm, respectively. The two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.97 δ ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.11 δ ppm and a multiplet centered at 1.81 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.0 δ ppm to 1.60 δ ppm. Methyl protons of the aliphatic chain appeared as a distorted triplet at 0.86 δ ppm.

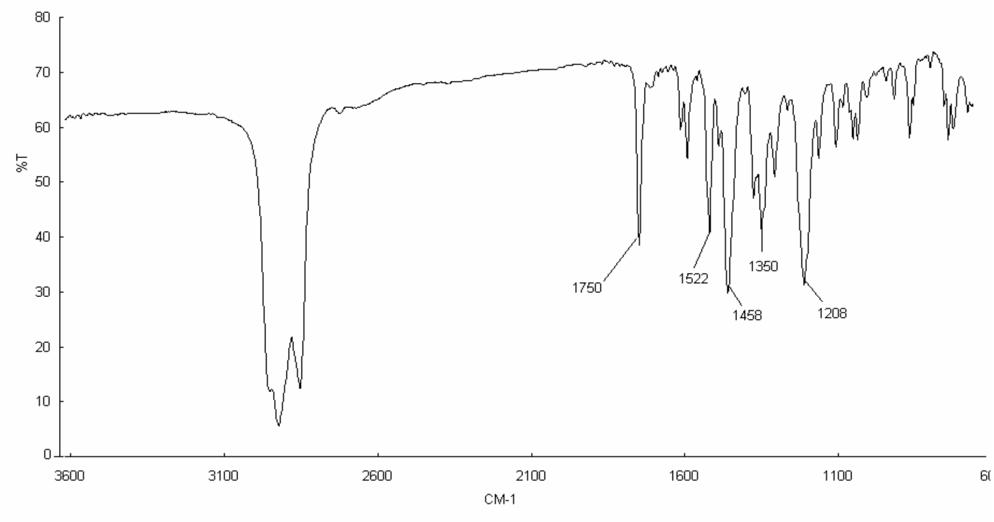


Figure 3.30: IR spectrum of 5-dodecyloxyisophthalicacid bis(4nitrophenyl) ester in nujol mull.

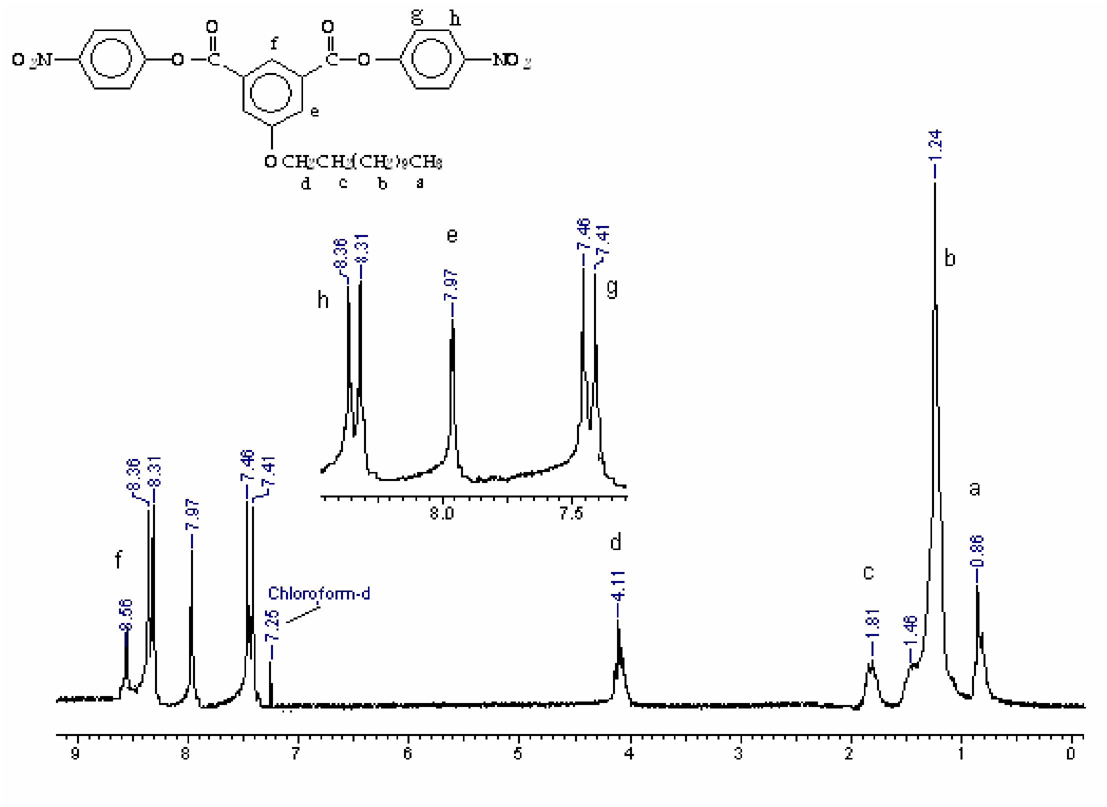


Figure 3.31: ^{1}H-NMR spectrum of 5-dodecyloxyisophthalic acid bis(4nitrophenyl) ester in DMSO-d$_6$.

The following two new 5-alkoxy-isophthalic acid bis(4-aminophenyl) esters were synthesized by catalytic hydrogenation (H_2/ Pd/C) of the corresponding dinitro compounds.[79]

5-Octyloxyisophthalic acid bis(4-aminophenyl) ester (OIAE)

5-Dodecyloxyisophthalic acid bis(4-aminophenyl) ester (DIAE)

Physical and spectroscopic characterization data of the 5-alkoxyisophthalic acid bis(4-aminophenyl) esters are presented in **Table 3.19**.

Table 3.19: Physical and spectral characterization data of 5-alkoxyisophthalic acid bis(4-aminophenyl) esters.

No	Diamine	Yield (%)	M.P (^{o}C)	IR (cm^{-1})	^{1}H-NMR (δ ppm), DMSO-d_6
1	OIAE	80	150	3338 (-NH) 1737(-C=O) 1216(Ar-O-C)	0.84(3H,t,-CH_3), 1.10-1.50 (10H, m,-CH_2),1.60-1.80(2H,m,-CH_2-), 4.13(2H,t, -OCH_2), 5.81 (4H, br, s, -NH_2), 6.65(4H,d, ArH *ortho* to –NH_2), 6.96(4H, ArH *meta* to –NH_2), 7.83(2H, ArH *ortho* to ether), 8.28 (1H,s, ArH *ortho* to both –C=O)
2	DIAE	85	122	3340 (-NH) 1738(-C=O) 1216(Ar-O-C)	0.84(3H,t,-CH_3),1.10-1.50(18H,m,-CH_2),1.62-1.80(2H,m,-CH_2-), 4.11(2H,t, -OCH_2), 5.17 (4H, br,s, -NH_2), 6.62(4H,d, ArH *ortho* to –NH_2), 6.92 (4H,d, ArH *meta* to –NH_2), 7.82(2H,s, ArH *ortho* to ether), 8.28 (1H,s, ArH *ortho* to both –C=O)

A representative IR spectrum of 5-octyloxyisophthalic acid bis(4-aminophenyl) ester is shown in **Figure 3.32.** Absorption band at 3340 cm^{-1} is attributed to the amino group. Absorption band at 1738 cm^{-1} is assigned to the carbonyl of the ester group.

^{1}H-NMR spectrum of 5-octyloxyisophthalic acid bis(4-aminophenyl) ester is shown in **Figure 3.33** as an example. Aromatic proton flanked by ester groups exhibited a singlet at 8.28 δ ppm while the two aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.83 δ ppm. Aromatic protons *meta*- and *ortho*- to amino group exhibited a doublet each at 6.96 δ ppm and 6.65 δ ppm, respectively. A broad peak at 5.81 δ ppm is ascribed to the amino group. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.13 δ ppm and a multiplet centered at

1.77 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.10 δ ppm to 1.50 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.84 δ ppm.

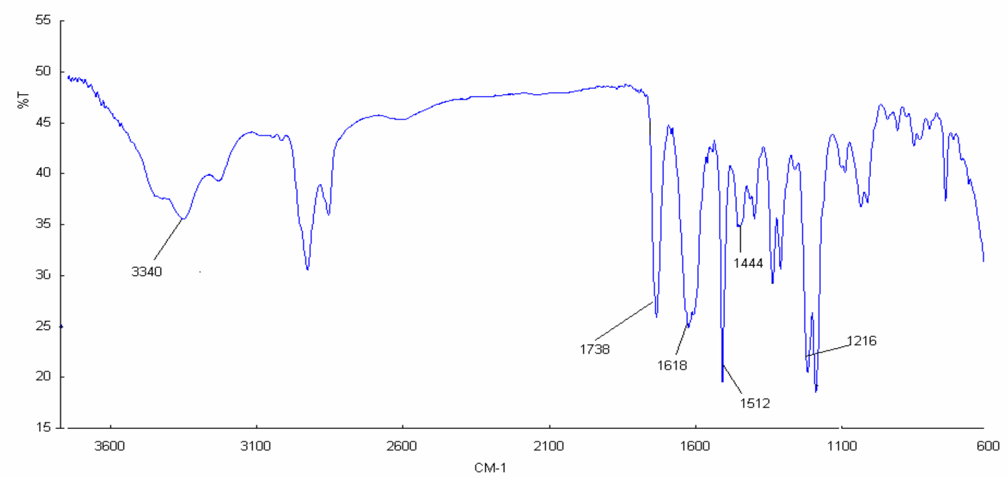


Figure 3.32 : IR spectrum of 5-octyloxyisophthalic acid bis(4-aminophenyl) ester in nujol mull

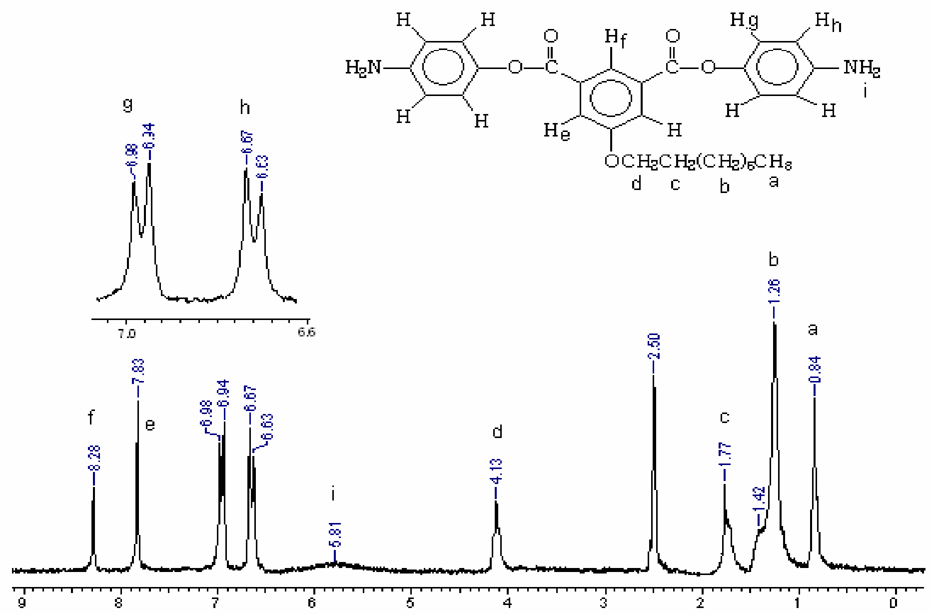


Figure 3.33: ^{1}H-NMR spectrum of 5-octyloxyisophthalic acid bis (4-aminophenyl) ester in DMSO-d_6

3.4 Conclusions

1. Five 5-alkoxyisophthalic acids were synthesized and characterized by spectral methods.
2. Five 5-alkoxyisophthaloyl dichlorides were synthesized and characterized by spectral methods.
3. Four new 5-alkoxy- 1,3- phenylenediisocyanates were synthesized starting from 5-alkoxyisophthalic acids by Curtius rearrangement reaction and were characterized by spectral methods. Diisocyanates represent valuable monomers for synthesis of polyurethanes, polyureas and a host of thermally stable polymers, such as polyimides, polyamides, poly(amideimide)s, etc.
4. Four new 5-alkoxyisophthalic acid dihydrazides were synthesized and characterized by spectral methods. Diacylhydrazides represent useful monomers for the synthesis of polyhydrazides, poly(1,3,4-oxadiazole)s, etc.
5. Four new aromatic diamines containing pre-formed amide linkages and possessing pendent alkoxy groups were synthesized and characterized by spectral methods. These diamines represent suitable monomers for the synthesis of regularly alternating poly(amideimide)s.
6. Two new aromatic diamines containing pre-formed ester linkages and possessing pendent alkoxy groups were synthesized and characterized by spectral methods. These diamines represent promising monomers for the synthesis of perfectly alternating poly(esterimide)s, and poly(esteramide)s.

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Chapter 4a. Synthesis and Characterization of Polyimides from Aromatic Diisocyanates Containing Pendent Alkoxy Groups and Aromatic Dianhydrides

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4a.1 Introduction

Polyimides exhibit excellent thermal and mechanical properties and have extensive engineering and microelectronics applications. Since conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly(amicacid) precursors and then either thermally or chemically imidized. However, there are some problems owing to the instability of poly(amicacid)s and the liberation of water in the imidization process. Therefore, soluble polyimides that are processable without difficulty are desired.

There are several approaches that have been tried with varying degrees of success for improvement of the solubility and / or processability of aromatic polyimides.[1-5] The attachment of flexible side chains has been drawing particular interest in polyimide synthesis because it increases not only the processability of polyimides but also the pretilt angle of liquid crystal molecules on rubbed polymer surfaces.[6-8] A large array of monomers containing pendent flexible linkages that have been reported in the literature listed in **Tables 3.1-3.6 (Chapter 3).**

Considering the two most routinely practiced routes for the synthesis of polyimides, viz, diamine – dianhydride reaction and diisocyanate – dianhydride reaction, three options are available to attach flexible side chains to aromatic polyimides. They are, i) diamine modification,[9-11] ii) dianhydride modification,[8] and iii) diisocyanate modification.[12-17]

The purpose of the present work was to synthesize aromatic polyimides based on *meta*-oriented aromatic diisocyanates containing pendent flexible alkoxy chains of varying carbon lengths with commercially available aromatic dianhydrides and to study the effect of pendent flexible alkoxy chains on properties of the resulting polyimides.

5-Alkoxy-1,3-phenylenediisocyanates,viz.,5-butyloxy-1,3-phenylenediisocyanate, 5-octyloxy-1,3-phenylenediisocyanate, 5-dodecyloxy-1,3-phenylenediisocyanate and 5-

hexadecyloxy-1,3-phenylenediisocyanate were each polycondensed with aromatic dianhydrides, namely, 4,4’-oxydiphthalic anhydride (ODPA), 3,3′,4,4'-(hexafluoroisopropylidene)diphthalic anhydride (FDA) and 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA) in benzonitrile in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst to obtain a series of polyimides. Polyimides were characterized by inherent viscosity measurements, IR and NMR spectroscopy, UV-vis spectroscopy, solubility tests, X-ray diffraction, thermogravimetric analysis and differential scanning calorimetery. Polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA was evaluated for liquid crystal alignment layers.

4a.2 Experimental

4a.2.1 Materials

5-Alkoxy-1,3-phenylenediisocyanates were synthesized as described in **Chapter 3, Section 3.3.7**. Dianhydrides, ODPA, FDA, and BTDA (Aldrich) were sublimed under reduced pressure before use. Benzonitrile was dried over phosphorous pentoxide for 12 h and then distilled under reduced pressure prior to use. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was recrystallized from pet-ether and dried under reduced pressure at 50°C. N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), tetrachlorethane (TCE), dimethylsulfoxide (DMSO), pyridine, dichloromethane (DCM), chloroform, and *meta*-cresol were purified as per literature procedures.[18]

4a.2.2 Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of polyimide in *meta*-cresol or concentrated sulfuric acid at 30 ± 0.1 °C using an Ubbelohde suspended level viscometer.

Inherent viscosity was calculated using the equation

$$\eta_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$$

where t and t_o are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

FTIR spectra were recorded using polyimide films or powders on a Perkin-Elmer 599B spectrophotometer.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker NMR (200 or 500 MHz) spectrometer at room temperature using $CDCl_3$ as solvent.

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

Differential scanning calorimetric (DSC) measurements were performed on Perkin-Elmer DSC-7 at a heating rate of 40^oC / minute under nitrogen atmosphere.

X-Ray diffractograms of polymer films were obtained on a Rigaku Dmax 2500 X-ray diffractometer. The system consists of a rotating anode generator with a copper target ($CuK\alpha$) and the sample was scanned at the rate of 2^o / minute at room temperature. Soluble polyimides were analyzed as films while others were analyzed as powders. Films were cast from *meta*-cresol solution on a clean petridish. *meta*-Cresol was evaporated at 100^oC in an oven to get a semi-dried film. The film was finally dried at 120^oC under reduced pressure for 4 days to get a film of ~30 μm thickness.

UV-visible spectra were recorded on Shimadzu UV-1601 UV-vis spectrophotometer. Films of 15-20 μm thickness were prepared from *meta*-cresol.

The solubility of polyimides was determined at 3 wt % concentration in various solvents at room temperature or on heating.

4a.2.3 Cell preparation for pretilt angle measurements

Indium tin oxide (ITO) coated glass (25 mm x 25 mm) was obtained from M/s Merck, Germany. The ITO coated glass substrate was thoroughly washed successively with soap solution, deionised water and ethanol followed by drying. A 1 wt. % solution of polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA (PI-2) was prepared in tetrachloroethane by heating. Spin coating of this polyimide was performed using a Karl Süss CT-62 spin coater (5 s at 1000 rpm, 40 s at 5000 rpm) on the ITO side. After spin coating, the substrate was preheated at 100° C for 10 minutes.

The liquid crystal E7, a mixture consisting of 50.6 % 4'-pentylcyanobiphenyl (5CB), 25.2 % 4'-heptylcyanobiphenyl (7CB), 17.8 % 4'-octyloxycyanobiphenyl (8OCB), and 6.4 % 4'-pentylcyanoterphenyl (5CT), ($T_{N/I}$ = 60° C, $\rho = 1.06$ g/cm^3, $\varepsilon_{//} = 19$ and $\varepsilon_{\perp} = 5.2$, and $\triangle n = 0.225$) was obtained from M/s Merck Ltd., Germany.

Electro-optical cells were constructed using ITO-coated glass coated with the polyimide substrate. Polyimide surface was rubbed uniformly with a velvet cloth. A twisted nematic cell was constructed by placing the two substrates orthogonal to each other with respect to their rubbing direction. The cells were secured with UV curable glue (Norland UV Sealant 91) having 18 µm spacers. The cells were filled with liquid crystal material E7, by capillary action at 80°C, which is 20°C above the nematic-isotropic transition temperature of the liquid crystal.

Electro-optical characteristics were investigated using DMS 703 display measuring system (Autronic-Melchers GmbH). A square wave was used to drive the cells for the dynamic response measurements at 1000 Hz. The pretilt angle was measured directly using the crystal rotation method (Autronic, TBA 107).[19]

4a.2.4 Synthesis of polyimides

A representative procedure for the synthesis of polyimides is described below:

Into a carefully dried 25 ml two-necked round bottom flask fitted with a magnetic stirring bar, a nitrogen inlet and a reflux condenser were placed 5-hexadecyloxy-1,3-phenylenediisocyanate (0.44 g, 1.1 mmol), ODPA (0.34 g, 1.1 mmol), DABCO (0.043 g, 0.37 mmol) and benzonitrile (3.5 ml). The mixture was stirred at 140°C under nitrogen atmosphere for 10 h. At the end of the reaction time, the reaction mixture was poured into excess methanol. The precipitated polymer was collected by filtration at pump, followed by thorough washing with hot methanol. The polymer was dried at 120°C for 12 h under reduced pressure.

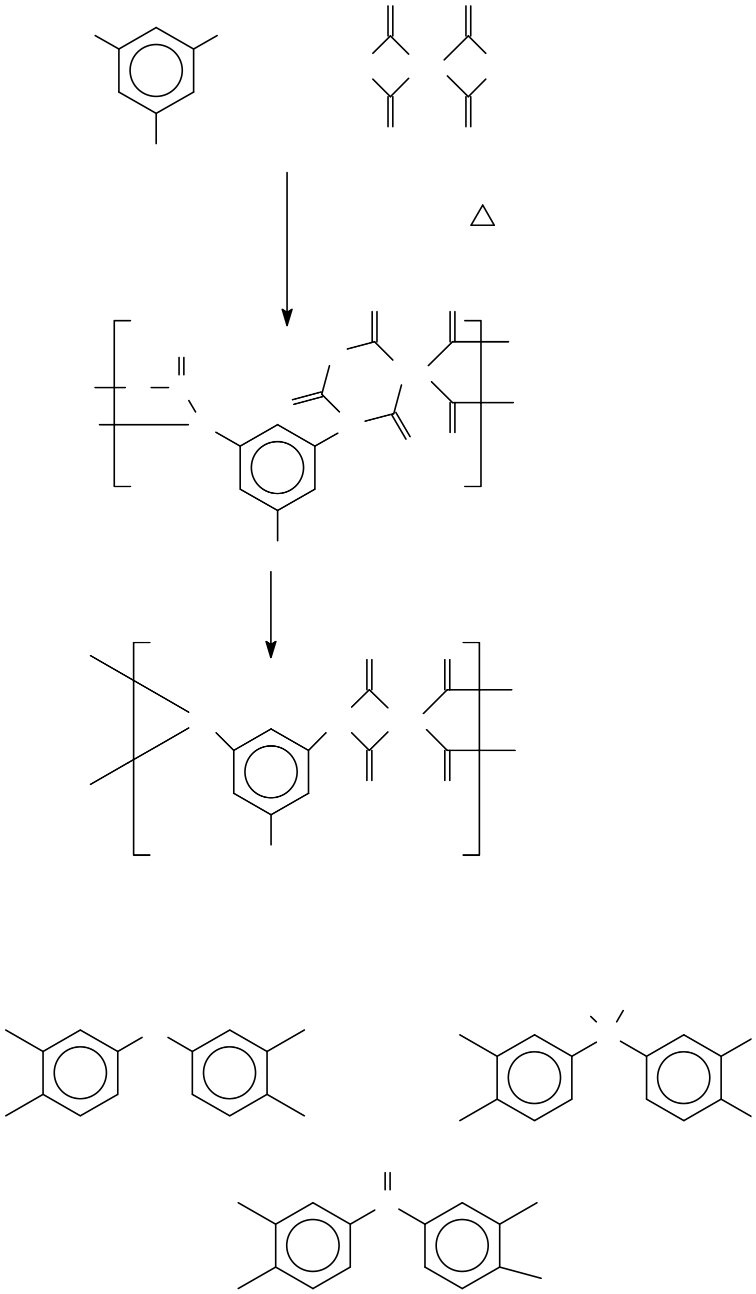
A similar procedure was followed for the synthesis of other polyimides.

4a.3 Results and Discussion

4a.3.1 Synthesis of polyimides from 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides

Polyimides were synthesized by the reaction of stoichiometric quantities of diisocyanates and dianhydrides in benzonitrile in the presence of DABCO as a catalyst (**Scheme 4a.1**) following the procedure reported by Imai and co-workers.[20] The diisocyanate-dianhydride reaction proceeds *via* the formation of a seven membered cyclic intermediate, which decomposes on heating to form a polyimide with the evolution of carbon dioxide.[21]

In synthesis of polyimides from both ODPA and FDA, the reaction mixture was homogeneous throughout the course of polymerization while in the case of BTDA, the reaction mixture became heterogeneous owing to the precipitation of the formed polyimide.



Scheme 4a.1: Synthesis of aromatic polyimides from 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides.

The results of polyimide synthesis are summarized in **Table 4a.1.** Inherent viscosity values of polyimides were in the range 0.16 – 0.42 dL/ g indicating formation of low to moderate molecular weight polymers. BTDA - derived polyimides precipitate out

Table 4a.1: Preparation of aromatic polyimides based on 5-alkoxy-1,3-phenylene-diisocyanates and aromatic dianhydrides.

Polyimide	**Diisocyanate (-R substituent)**	**Dianhydride**	**Yield (%)**	η_{inh} **(dl/g)**[a]
PI-1	$-OC_4H_9$	ODPA	99	0.42
PI-2	$-OC_8H_{17}$	ODPA	96	0.42
PI-3	$-OC_{12}H_{25}$	ODPA	95	0.35
PI-4	$-OC_{16}H_{33}$	ODPA	98	0.36
PI-5	$-OC_4H_9$	FDA	92	0.41
PI-6	$-OC_8H_{17}$	FDA	94	0.43
PI-7	$-OC_{12}H_{25}$	FDA	93	0.29
PI-8	$-OC_{16}H_{33}$	FDA	97	0.27
PI-9	$-OC_4H_9$	BTDA	99	0.18[b]
PI-10	$-OC_8H_{17}$	BTDA	94	0.19[b]
PI-11	$-OC_{12}H_{25}$	BTDA	95	0.16[b]
PI-12	$-OC_{16}H_{33}$	BTDA	96	0.18[b]

a: η_{inh} of polyimide was measured at a concentration of 0.5 dl/g in *meta*-cresol at 30 ± 0.1 °C.

b: η_{inh} of polyimide was measured at a concentration of 0.5 dl/g in sulfuric acid at 30 ± 0.1 °C.

of the reaction medium in the early stages of the reaction limiting molecular weight build-up. Polyimides derived from ODPA and FDA could be cast into transparent and flexible films from their solution in *meta*-cresol or tetrachloroethane.

4a.3.2 FT-IR spectroscopic analysis

A representative IR spectrum of polyimide derived from 5-hexadecyloxy-1,3-phenylenediisocyanate and ODPA is shown in **Figure 4a.1**. The absorption bands at 1780 and 1720 cm^{-1} (imide-I), 1354 cm^{-1} (imide- II), 1142 cm^{-1} (imide- III), and 746 cm^{-1} (imide-IV) were observed. The imide-I band is attributed to the stretching vibration of the two carbonyl groups which are weakly coupled. Imide-II, -III and –IV bands are assigned, respectively, to the axial, transverse and out-of -plane vibrations of the cyclic imide structure.

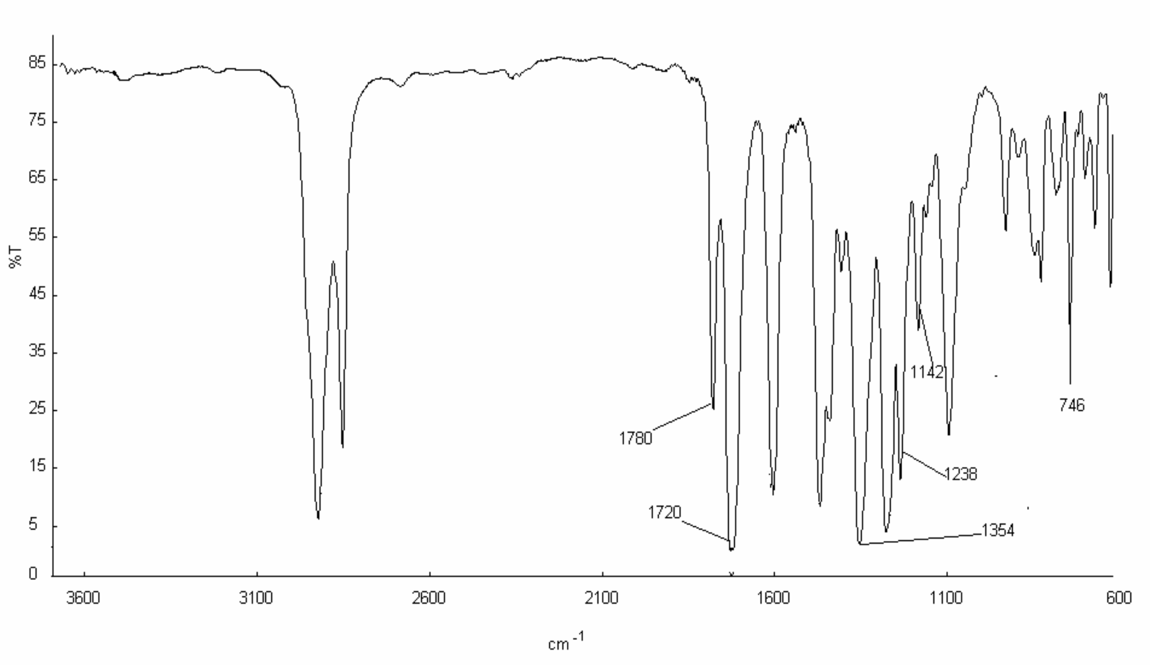


Figure 4a.1: IR spectrum (Film) of polyimide derived from 5-hexadecyloxy-1,3-phenylenediisocyanate and ODPA.

4a.3.3 NMR spectroscopic analysis

^{1}H-NMR spectrum of polyimide (**PI-5**) derived from 5-butyloxy-1,3-phenylene diisocyanate and FDA recorded in $CDCl_3$ is shown in **Figure 4a.2**. Protons *ortho*- to the imide ring appeared as doublet at 8.03 δ, ppm. Protons flanked by imide ring and hexafluoroisopropylidene group showed a singlet at 7.95 δ, ppm while the protons *ortho*- to hexafluoroisopropylidene group appeared as a doublet at 7.85 δ, ppm. Proton *para*- to ether linkage appeared as a singlet at 7.20 δ, ppm while two aromatic protons *ortho*- to ether linkage exhibited a singlet at 7.06 δ, ppm. Methylene protons attached to the ether linkage showed a triplet at 4.0 δ, ppm. Methylene protons attached carbons β and γ to the ether oxygen each showed a multiplet centered at 1.78 and 1.45 δ, ppm. Methyl protons appeared as a triplet at 0.95 δ, ppm.

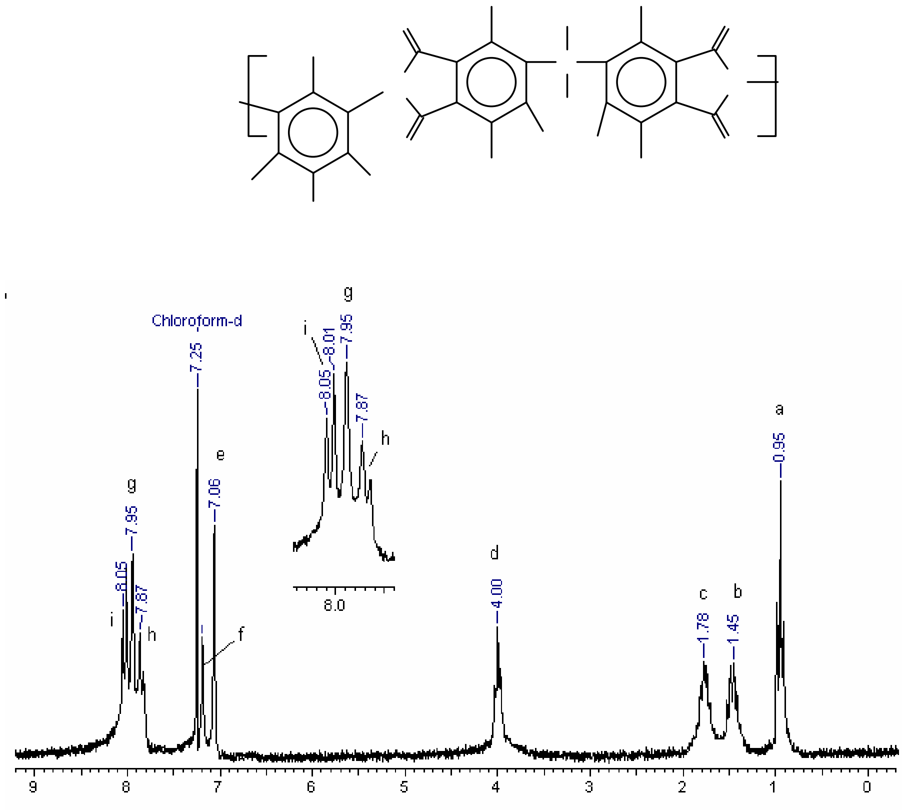


Figure 4a.2: ^{1}H-NMR spectrum of polyimide derived from 5-butyloxy-1,3-phenylene diisocyanate and FDA in $CDCl_3$.

^{13}C-NMR spectrum of polyimide derived from 5-butyloxy-1,3-phenylenediisocyanate and FDA is shown in **Figure 4a.3** along with the assignments of the carbon atoms. Imide carbonyls showed two peaks at 165.34 and 165.18 ppm. The downfield chemical shift was due to the electron withdrawing characteristic of the oxygen atom.

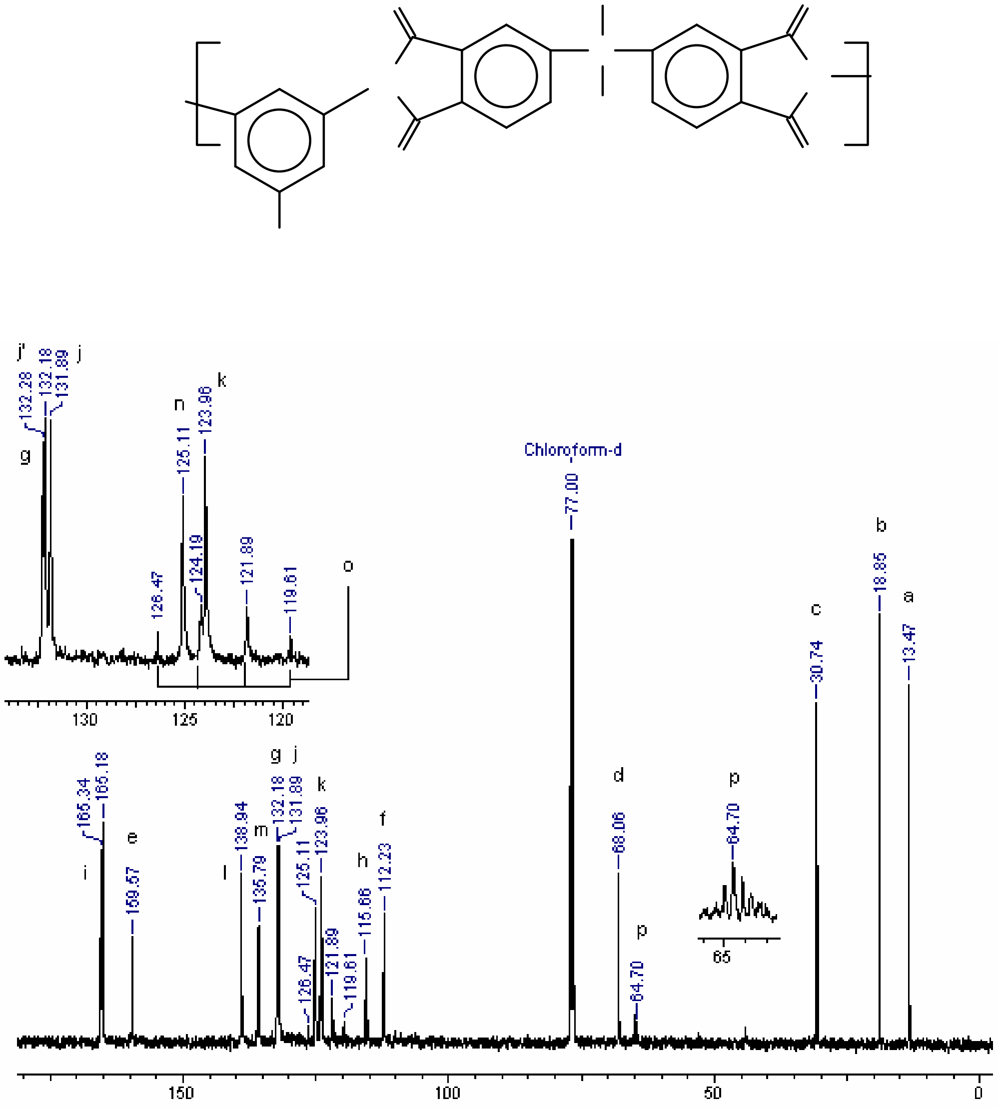


Figure 4a.3: ^{13}C-NMR spectrum of polyimide derived from 5-butyloxy-1,3-phenylenediisocyanate and FDA in $CDCl_3$.

4a.3.4 Properties of polyimides

4a.3.4.1 Solubility of polyimides

Polyimides were tested for solubility at 3 wt % concentration in different solvents and the data is summarized in **Table 4a.2**.

Polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and FDA were soluble in dichloromethane, tetrachloroethane, DMF, DMAc, NMP, *meta*-cresol and pyridine, The solubility of polyimides based on FDA could be attributed to the low cohesive energy provided by the fluorinated groups and the reduction in charge transfer complexes of a conjugated aromatic system.[22] Polyimide derived from FDA and *meta*-phenylene diamine – an analogous polyimide without pendent side- chain is also reported to be soluble in solvents such as DMF, DMAc, and NMP at room temperature.[23] Therefore, the unequivocal role of pendent alkoxy chain for the improvement of solubility of FDA-based polyimides can not be confirmed based on the solubility data.

Polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and ODPA were soluble in *meta*-cresol, NMP, pyridine, and in TCE upon heating. Polyimide derived from meta-phenylene diamine and ODPA – an analogous polyimide without pendent alkoxy chain - is reported to swell in *meta*-cresol.[23,24] (It has been reported that the solubility of a polyimide depends on the method of synthesis also.). Nonetheless, improvement in the solubility of the present series of ODPA-based polyimides may be attributed to the entropy effect of the flexible alkoxy groups.

Polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and BTDA were partially soluble in *meta*-cresol and NMP and were insoluble in DMF, DMAc, TCE, and pyridine. Owing to the relatively rigid BTDA moiety as compared to ODPA moiety, BTDA-derived polyimides were insoluble.

Thus, the solubility of polyimides was governed by both the dianhydride and the diisocyanate structure, the former having a greater influence.

Table 4a.2: Solubility data of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and aromatic dianhydrides.

Poly-imide	Diisocya-nate	Dianhy-dride	DCM	TCE	*m*-Cresol	DMF	DMAc	NMP	Pyri-dine	H_2SO_4
PI-1	-OC_4H_9	ODPA	–	+	++	–	±	++	++	++
PI-2	-OC_8H_{17}	ODPA	–	+	++	–	±	++	++	++
PI-3	-$OC_{12}H_{25}$	ODPA	–	+	++	–	±	++	++	++
PI-4	-$OC_{16}H_{33}$	ODPA	–	+	++	–	±	++	++	++
PI-5	-OC_4H_9	FDA	++	+	++	++	++	++	++	++
PI-6	-OC_8H_{17}	FDA	++	+	++	++	++	++	++	++
PI-7	-$OC_{12}H_{25}$	FDA	++	+	++	++	++	++	++	++
PI-8	-$OC_{16}H_{33}$	FDA	++	+	++	++	++	++	++	++
PI-9	-OC_4H_9	BTDA	–	–	±	–	–	±	–	++
PI-10	-OC_8H_{17}	BTDA	–	–	±	–	–	±	–	++
PI-11	-$OC_{12}H_{25}$	BTDA	–	–	±	–	–	±	–	++
PI-12	-$OC_{16}H_{33}$	BTDA	–	–	±	–	–	±	–	++

++ : soluble at room temperature; + : soluble on heating; ± : partially soluble;
– : insoluble.

4a.3.4.2 X-Ray diffraction studies

X-Ray diffractograms of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and ODPA, FDA and BPDA are shown in **Figures 4a.4**, **4a.5,** and **4.a.6**, respectively.

X-Ray diffractograms of polyimides derived from ODPA and FDA showed broad peak at about 2 $\theta = 19^o$ in the wide angle region. These peaks are so broad that they may be considered as amorphous halos.

BTDA-based polyimides exhibited recognizable peaks near 2θ = 5, 12, 19 and 24°. This means that BTDA- based polyimides are partially crystalline in nature which is also reflected in their poor solubility compared to ODPA- based polyimides (**Table 4a.2,** above). In the middle-angle region (2 θ = 2 - 6°), polyimides containing pendent alkoxy chains has a peak. The peak shifts to smaller angle and its intensity increases as the side chain length increases. These peaks are characteristic of a typical layered structures resulting from ordered packing of the aliphatic side chains. These layered structures develop more tightly with increasing side chain length which may be attributed to the fact that the longer aliphatic side chains facilitate the better packing of the polymer chains. Similar observations have been reported for rigid rod polymers having long flexible side chains.[25-28]

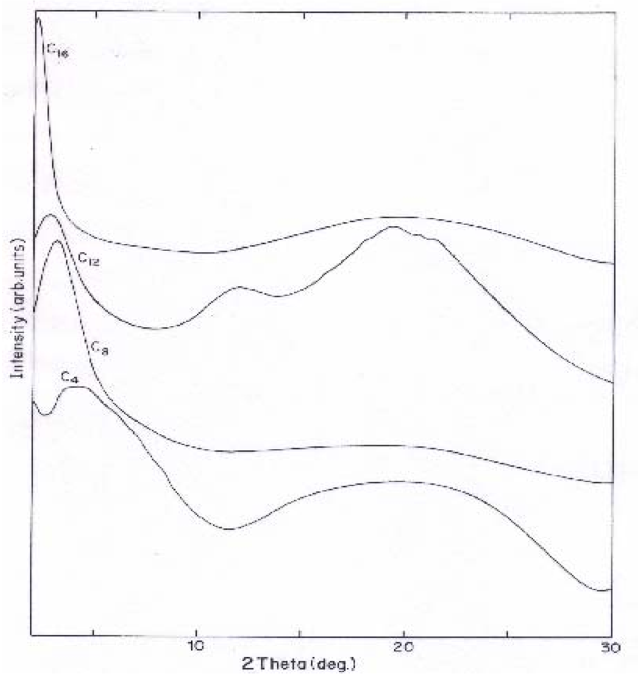


Figure 4a.4: X-Ray diffractograms of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and ODPA (PI-1 to PI-4).

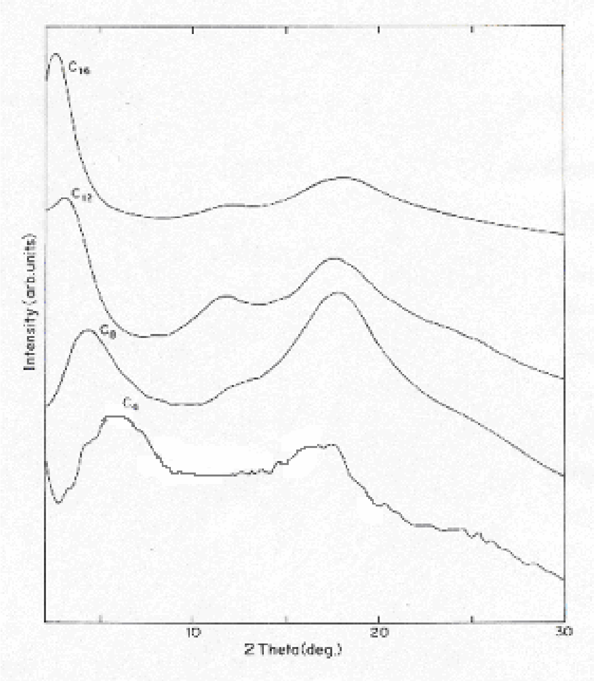


Figure 4a.5: X-Ray diffractograms of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and FDA (PI-5 to PI-8).

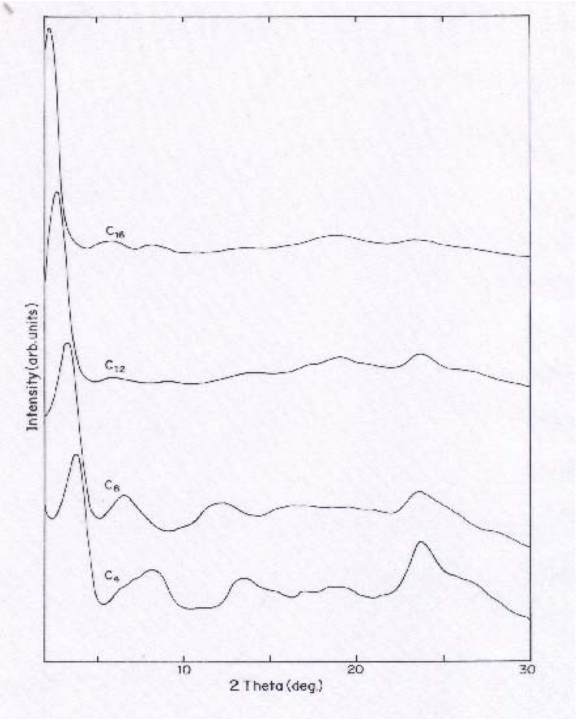


Figure 4a.6: X-Ray diffractograms of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and BTDA (PI-9 to PI-12).

4a.3.4.3 Thermal behaviour of polyimides

Thermal stability of polyimides with alkoxy side chains was investigated by thermogravimetric analysis (TGA) at a heating rate of 10°C / minute in nitrogen. The TG curves are shown in **Figure 4a.7, Figure 4a.8,** and **Figure 4a.9.** Initial decomposition temperature (IDT) and temperature at 10% weight loss are given in **Table 4a.3.**

Thermal degradation of polyimides began in the temperature range 390 - 440°C and showed stepwise degradation with increase in temperature. IDT of polyimides containing pendent alkoxy chains are lower than that of analogous polyimides without alkoxy side chains which are reported to be stable up to 540 – 547°C. [23] The degradation occurring in the first step could be attributed to the decomposition of the labile alkyl group with cleavage occurring at the alkyl-ether bond. The weight loss in the first degradation step increased with increase in the side chain length as can be seen from TG curves (**Figure 4a.7, Figure 4a.8,** and **Figure 4a.9**).

A representative DTG curve for polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA is shown in **Figure 4a.10**. DTG curve shows three distinct regions. Temperature at the first maximum degradation (T_{max1}) (480°C) corresponds to the loss of alkyl group. Temperature at the second maximum degradation (T_{max2}) (620°C) corresponds to the thermal scission of the polyimide backbone. This temperature is comparable to the maximum degradation temperature for aromatic polyimides, implying that the backbone of the polyimide containing the pendent alkoxy chains was mostly maintained even after the scission of the side chains. A third broad DTG profile was observed at around 800°C. This may be attributed to the volatilization of the low mass fractions resulting from the previous degradation processes.

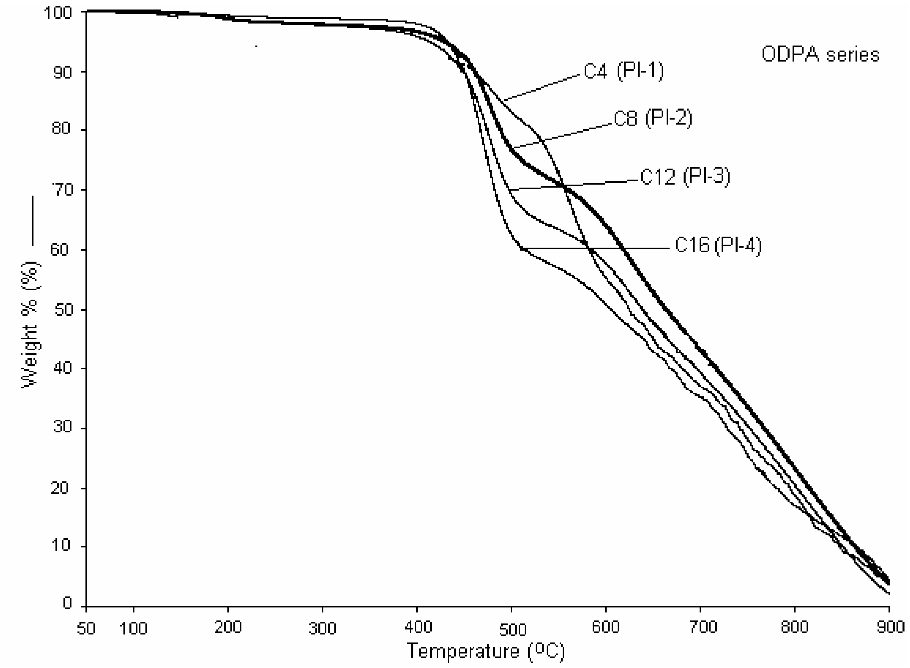


Figure 4a.7: TG curves of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and ODPA (PI-1 to PI-4).

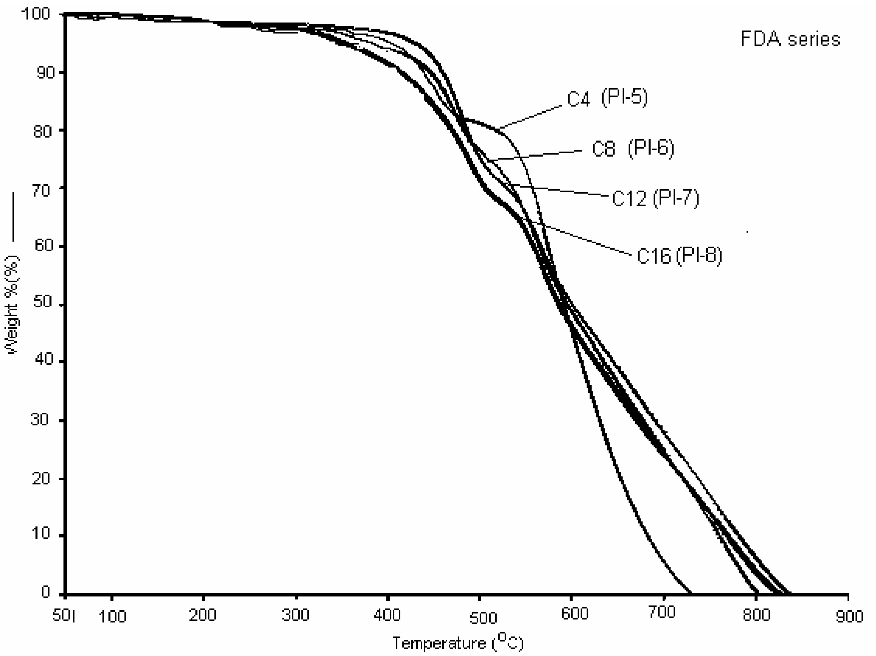


Figure 4a.8: TG curves of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and FDA (PI-5 to PI-8).

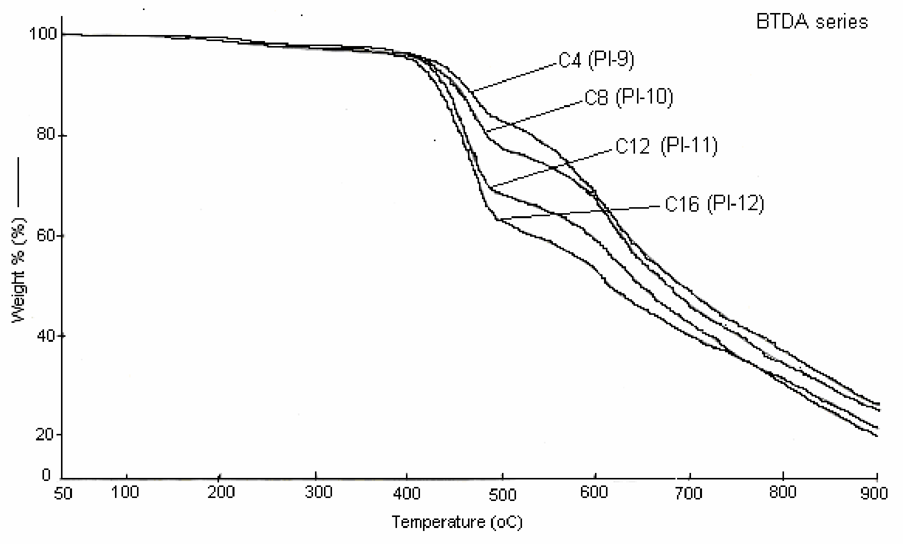


Figure 4a.9: TG curves of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and BTDA (PI-9 to PI-12).

Table 4a.3: Thermal properties of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and aromatic dianhydrides.

Polyimide	Diisocyanate (-R substituent)	Dianhydride	Tg (^{o}C)	TGA	
				IDT (^{o}C)	T_{10} (^{o}C)
PI-1	$-OC_4H_9$	ODPA	237	440	460
PI-2	$-OC_8H_{17}$	ODPA	185	440	455
PI-3	$-OC_{12}H_{25}$	ODPA	162	435	445
PI-4	$-OC_{16}H_{33}$	ODPA	159	435	445
PI-5	$-OC_4H_9$	FDA	246	390	410
PI-6	$-OC_8H_{17}$	FDA	195	420	430
PI-7	$-OC_{12}H_{25}$	FDA	165	440	450
PI-8	$-OC_{16}H_{33}$	FDA	161	415	425
PI-9	$-OC_4H_9$	BTDA	244	420	450
PI-10	$-OC_8H_{17}$	BTDA	195	420	440
PI-11	$-OC_{12}H_{25}$	BTDA	182	410	440
PI-12	$-OC_{16}H_{33}$	BTDA	179	415	445

IDT: Initial decomposition temperature.

T_{10}: Temperature at which 10% weight was observed.

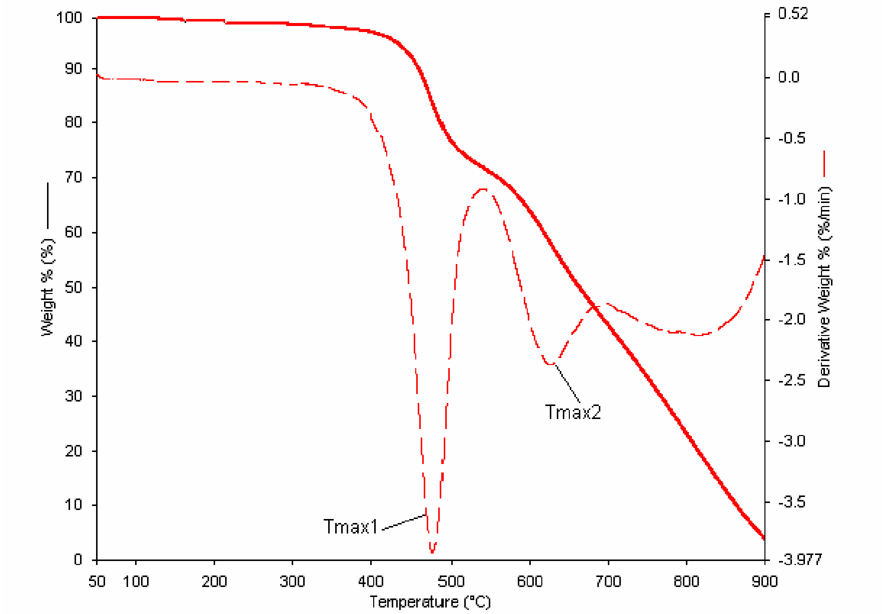


Figure 4a.10: Representative DTG and TG curves of polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA (PI-2).

[DTG curve (T_{max1} = temperature at the first maximum degradation; T_{max2} = temperature at the second maximum degradation)]

Glass transition (T_g) temperatures of the polymers were measured by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polyimide samples at a heating rate of 40°C / minute. DSC curves are shown in **Figures 4a.11, 4a.12 and 4a.13** and T_g values are incorporated in **Table 4a.4**. T_g values of polyimides were in the range 159-246°C. A plot of T_g Vs number of carbon atoms in the pendent alkoxy chains of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and aromatic dianhydrides is shown in **Figure 4a.14**. T_g values for the reference polyimides derived from *meta*-phenylene diamine and respective dianhydrides – analogous polyimides without pendent alkoxy chains - were taken from the literature.[23] T_g values of polyimides containing pendent flexible alkoxy groups were lower than those of the reference polyimides. The depression of T_g values with increase in side chain length indicates that side chains act on main chains as a bound solvent or as an internal plasticizer. The effect of alkoxy chain in lowering T_g value was pronounced upto chain length of 12 carbon atoms. Further increase in the carbon chain length from 12 to 16 did not result in any further significant reduction in T_g values of polyimides.

As expected, polyimides derived from flexible dianhydride (ODPA) revealed lowest Tg values in the series of polyimides.

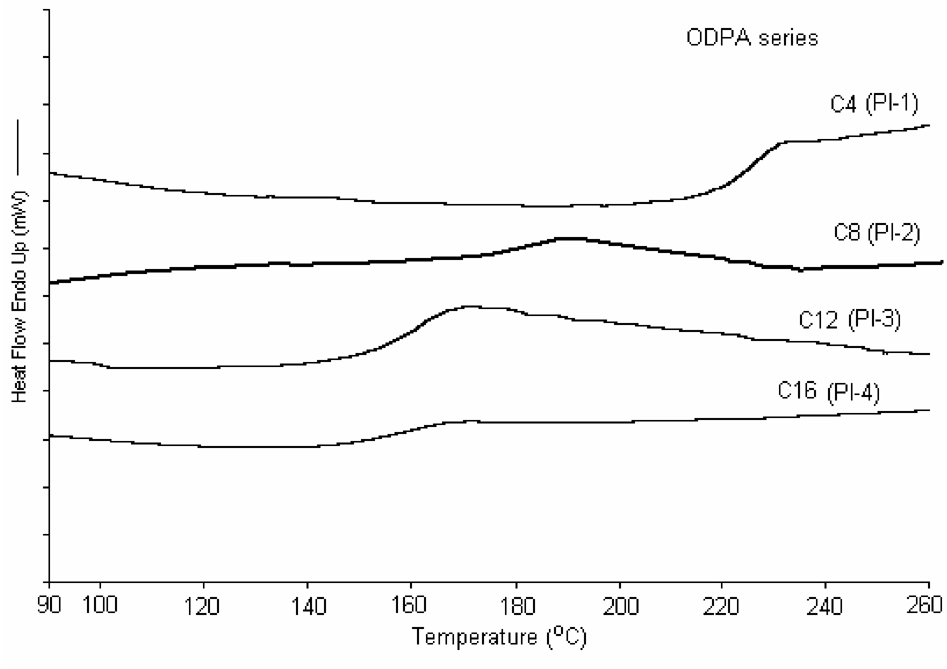


Figure 4a.11: DSC curves of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and ODPA (PI-1 to PI-4).

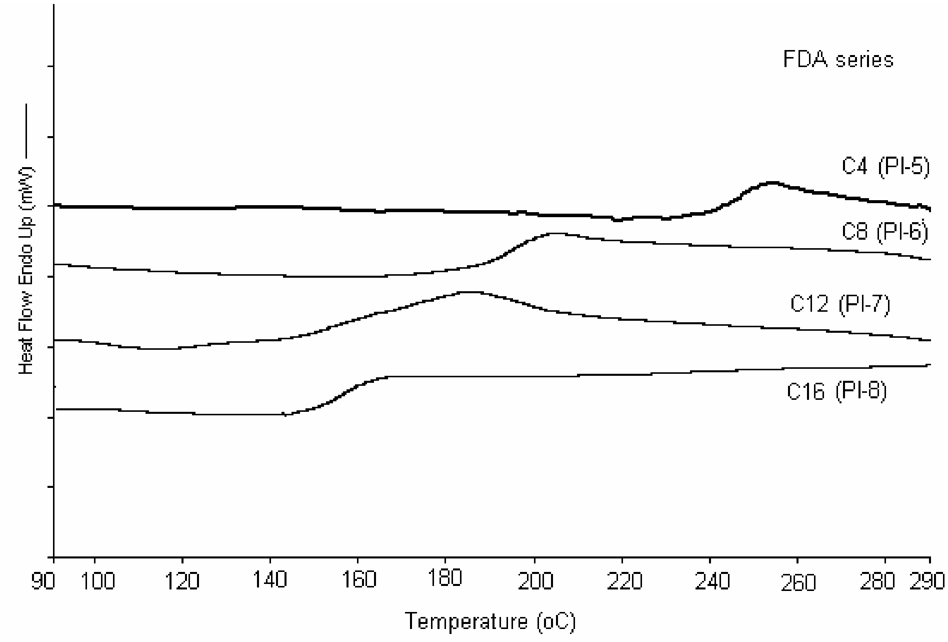


Figure 4a.12: DSC curves of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and FDA (PI-5 to PI-8).

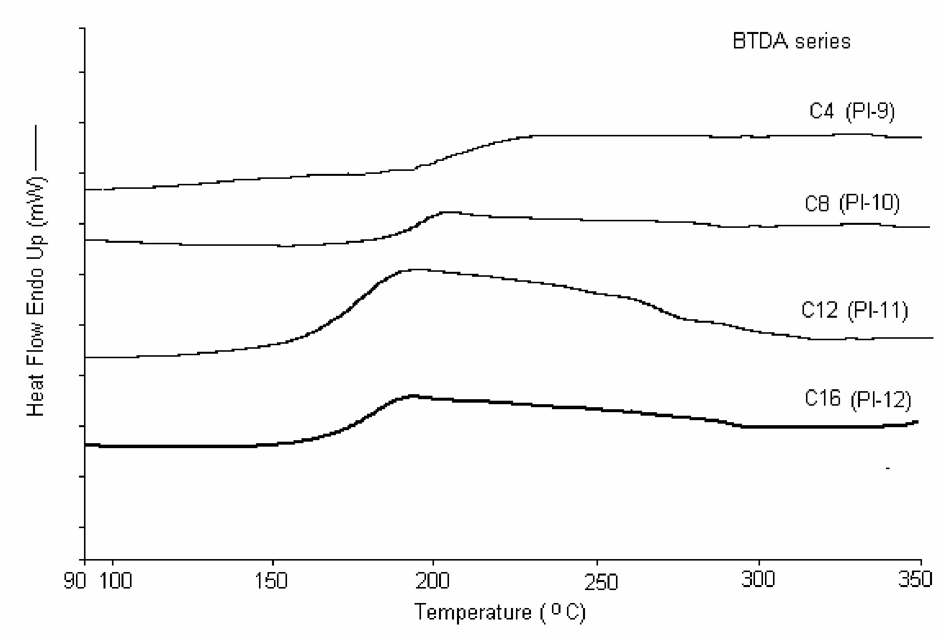


Figure 4a.13: DSC curves of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and BTDA (PI-9 to PI-12).

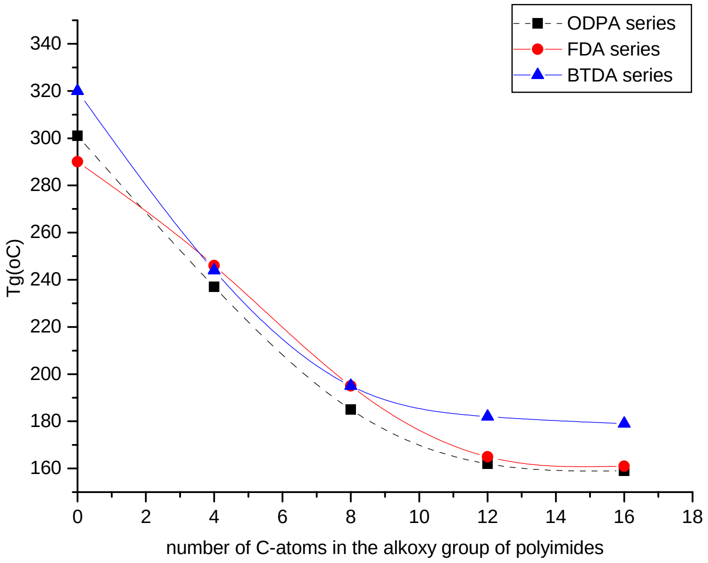


Figure 4a.14: Plot of Tg values Vs number of carbon atoms in the alkoxy group of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides.

4a.3.4.4 Optical transparency

Thin films (15-20 μm thickness) of polyimides derived from 5-butyloxy-1,3-phenylenediisocyanate and ODPA and FDA were measured for optical transparency using UV-vis absorption spectra. **Figure 4a.15** shows UV-vis spectra of polyimide films. The cut off wavelength (absorption edge, λ_o) values and the percentage transmittance at 500 nm (the solar maximum) from these spectra are presented in **Table 4a.4**. Polyimides based on 5-alkoxy-1,3-phenylenediisocyanates and FDA and ODPA produced fairly transparent and almost colorless polyimide films. **Figure 4a.15** shows that polyimides derived from 5-butyloxy-1,3-phenylenediisocyanate and ODPA and FDA showed high transmittance of 80% and 81 %, respectively at wavelength of 500 nm. In case of ODPA-derived polyimide, high transmittance is due to the presence of ether oxygen which functions as a separator linkage and enhances chain mobility. The high transmittance in case of FDA-derived polyimide is due to the presence of bulky and electron withdrawing hexafluoroisopropylidene linkage which leads to a reduction of intermolecular charge transfer complex (CTC) formation.[29, 30]

Optical transparency of polyimide films is of special importance in application as orientation films in liquid crystal display devices.[7]

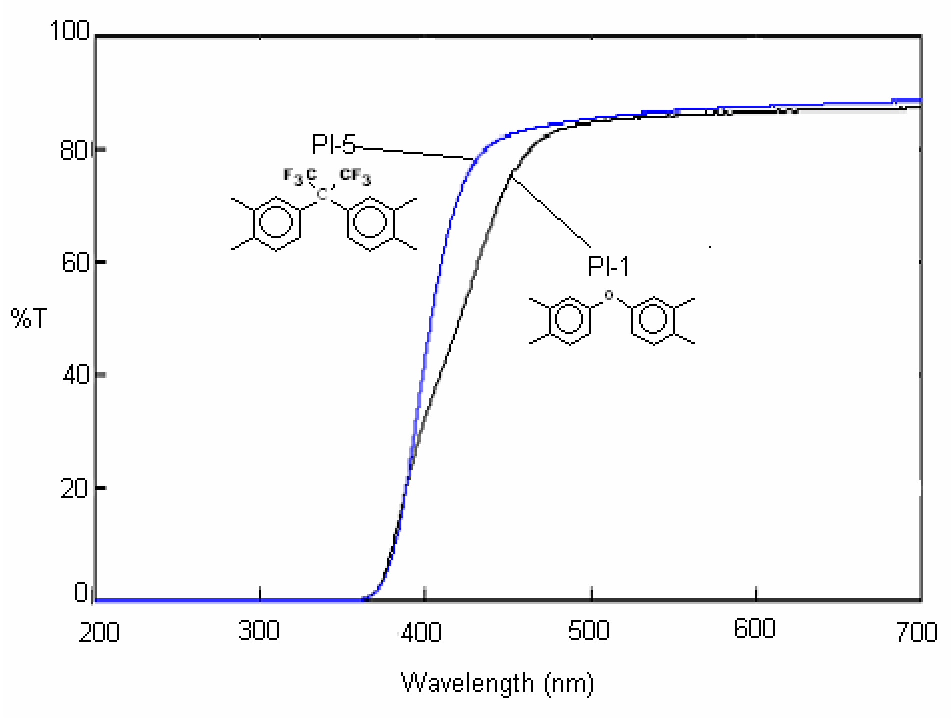


Figure 4a.15: UV-vis absorption spectra of polyimide films derived from 5-butyloxy-1,3-phenylenediisocyanate and ODPA (PI-1)and FDA (PI-5).

Table 4a.4: Optical transparency data of polyimides derived from 5-butyloxy-1,3-phenylenediisocyanate and ODPA and FDA.

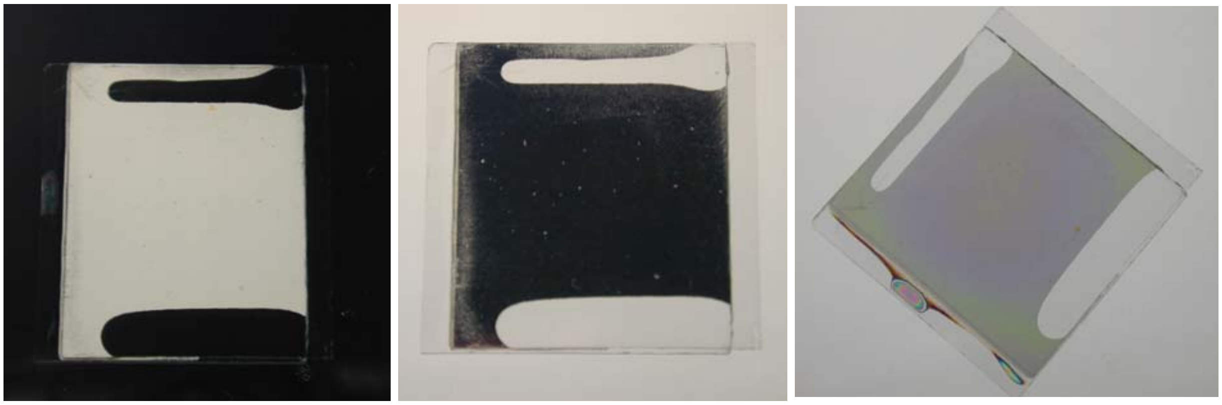
Polyimide	**Diisocyanate (-R substituent)**	**Dianhydride**	**Cut off wavelength λ_o, (nm)**	**% Transmittance (500 nm)**
PI-1	$-OC_4H_9$	ODPA	365	80
PI-5	$-OC_4H_9$	FDA	365	81

4a.4 Pretilt angle and electro-optical characteristics of polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA.

The liquid crystal cells were prepared as described in **section 4a.2.3** and the measurements were done by crystal rotation method.[19] The pretilt angle was then calculated from the obtained incident angle.

Figure 4a.16 shows the photographs of the twisted nematic cell between crossed and parallel polarizers made from polyimide derived from 5-octyloxy-1,3-phenylene diisocyanate and ODPA (PI-2). Uniform alignment of liquid crystals was observed. This opens the route for this polyimide to be used as an alignment layer for liquid crystal displays. A pretilt angle of 2.97^o was observed for PI-2, which is adequate for display applications. Low LC pretilt angle is particularly attractive for In-Plane-Switching or twisted-nematic LCD modes. Organo-soluble polyimides are desirable as their processing temperature is low – a feature particularly important for low temperature poly-silicon-thin-film transistor-liquid crystal display (TFT-LCD) processes.[6,7]

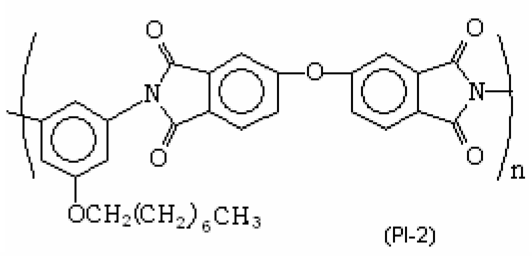
It is reported that polyimide main chain structure greatly influences the liquid crystal pretilt angle of the alkyl-branched polyimide films. An asymmetric and flexible main chain structure would lead to a small pretilt angle while a symmetric and rigid main chain structure would generate a high pretilt angle. One of the possible explanations for the low pretilt angle of polyimide PI-2 is the presence of flexible ether linkage in its backbone and *meta*-catenation. To be able to draw definitive conclusions on what factors govern the pretilt angle, further studies are necessary.



(a) (b) (c)

Figure 4a.16: Twisted nematic cell made from polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA (PI-2).
(a) cell between crossed polarizers (b) cell between parallel polarizers (c) cell at 45^0 between crossed polarizers.

Figure 4a.17(a) shows a typical transmittance-voltage curve for normal incidence of the twisted nematic cell. A typical switching curve is observed, with a switching voltage of nearly 3 V. Response and relaxation time of the twisted nematic cell is shown in **Figure 4a.17(b)**, a switching time of 65 ms was observed at 5 V. In the OFF state, due to the 18 µm cell thickness black flow effect is visible in the graph.



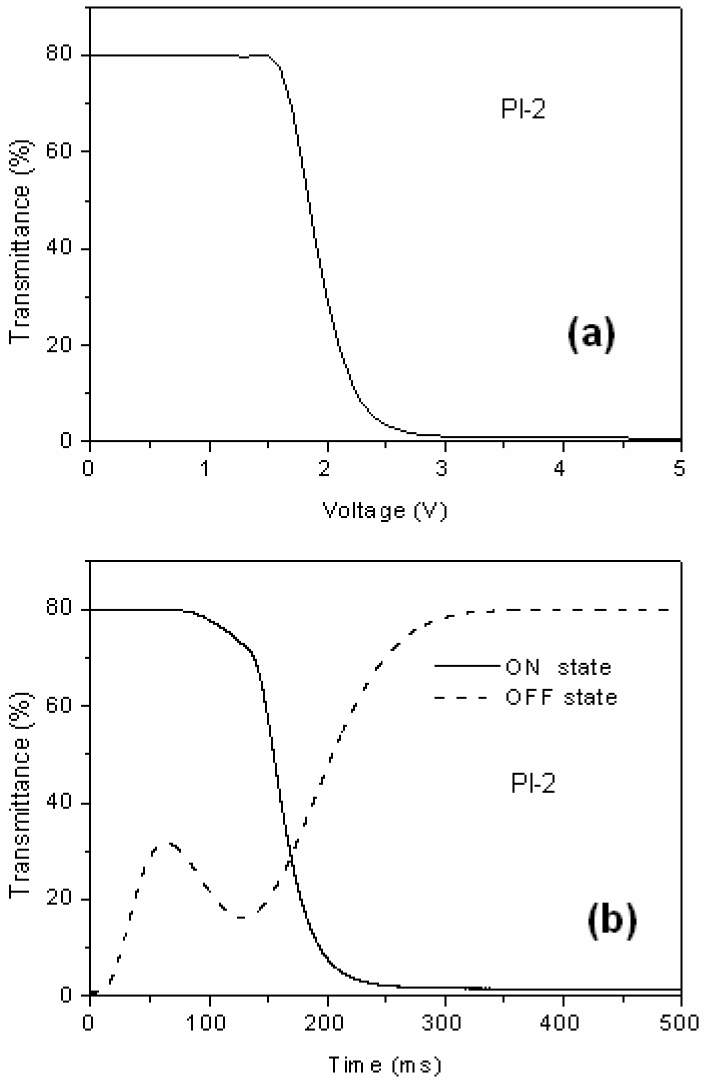


Figure 4a.17(a) Electro-optical characteristics of polyimide (PI-2) orientation layer. (b) Response and relaxation times for polyimide orientation layer, from the non-select to the select state (5 V) at a frequency of 1000 Hz.

4a.5 Conclusion

1. A series of polyimides was synthesized by the polycondensation of 5-alkoxy-1,3-phenylenediisocyanates with commercially available aromatic dianhydrides in benzonitrile in the presence of DABCO as a catalyst. Low to moderate molecular weight polyimides were obtained.
2. The solubility of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and dianhydrides was dependent on the structure of both the diisocyanate and the dianhydride. Polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and FDA and ODPA were soluble in *meta*-cresol, NMP and pyridine. FDA and ODPA-derived polyimides could be cast into transparent and flexible films from *meta*-cresol and TCE**.**
3. Pendent alkoxy chains were effective in lowering the Tg values of polyimides. Polyimides containing pendent alkoxy group with 12 carbon atoms in its alkoxy chain had T_g values which were significantly lower than the corresponding control polyimides without the pendent groups. Further increase in the length of the alkoxy chain did not result in any further significant reduction of T_g values.
4. The introduction of pendent alkoxy chains resulted in decrease in thermal stability of polyimides. Polyimides displayed step-wise degradation behaviour resulting from the degradation of alkoxy side chain followed by the main chain.
5. Wide angle X-ray diffractograms revealed that layered structures were formed for polyimides with longer pendent alkoxy chains.
6. A pretilt angle of 2.97^o was observed for polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA. This opens the route for this organo-soluble polyimide to be used as an alignment layer for liquid crystal displays.

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Chapter 4b. Synthesis and Characterization of Poly(amideimide)s from Diacylhydrazides Containing Pendent Flexible Alkoxy Groups and Aromatic Dianhydrides

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4b.1 Introduction

Aromatic polyimides are thermally stable polymers which exhibit excellent mechanical and electrical properties. However, these polymers are difficult to process because of their high softening temperatures and poor solubility in organic solvents. In order to improve their solubility, several approaches have been proposed based on the incorporation of flexible segments bearing ester, amide, or ether moieties in the polymer backbone without sacrificing the heat resistance.[1-4]

Poly(amideimide)s combine the thermal stability property of polyimides and ease of processability of polyamides and be intermediate in properties between polyimides and polyamides.

In this study, synthesis, characterization and properties of a series of new poly(amideimide)s derived from diacylhydrazides containing pendent flexible alkoxy chains and commercially available aromatic dianhydrides is reported.

In particular, commercially available dianhydrides, viz., 4,4’-oxydiphthalic anhydride (ODPA), 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) were each polycondensed with the following 5-alkoxyisophthalic acid dihydrazides, viz., 5-butyloxyisophthalic acid dihydrazide, 5-octyloxyisophthalic acid dihydrazide, 5-dodecyloxyisophthalic acid dihydrazide and 5-hexadecyloxyisophthalic acid dihydrazide. To bring out the influence of pendent alkoxy chains on the properties of poly(amideimide)s, a series of poly(amideimide)s was synthesized from isophthalic acid dihydrazide and their properties were compared.

Poly(amideimide)s were characterized by inherent viscosity measurements, solubility tests, IR and ^{1}H-NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4b.2 Experimental

4b.2.1 Materials

The diacylhydrazide monomers, namely, 5-alkoxyisophthalic acid dihyrdazides were synthesized as described in **Chapter 3, Section 3.3.8.** The dianhydrides, PMDA, BPDA and ODPA (Aldrich), were purified by sublimation under reduced pressure before use. N,N-Dimethylacetamide (DMAc) was distilled from calcium hydride under reduced pressure. N,N-Dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), pyridine, dichloromethane (DCM), chloroform and *meta*-cresol were dried and distilled as per literature procedures.[5]

4b.2.2 Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of poly(amideimide)s or poly(hydrazide acid)s in DMAc at 30 ± 0.1°C using an Ubbelohde suspended level viscometer.

IR spectra were recorded using poly(amideimide) films on a Perkin-Elmer 599B spectrophotometer.

^{1}H-NMR spectra was recorded on a Bruker NMR spectrometer (200 or 500 MHz) at room temperature using DMSO-d_6 as solvent.

Thermogravimetric analyses (TGA) were performed on Perkin-Elmer TGA-7 analyzer at a heating rate of 10°C / minute under nitrogen atmosphere.

Differential scanning calorimetric (DSC) analysis was performed on Perkin-Elmer DSC-7 at a heating rate of 20°C / minute under nitrogen atmosphere.

X-Ray diffractograms of polymers (samples were made as described in **Chapter 4a**) were obtained on a Rigaku Dmax 2500 X-ray diffractometer.

The solubility of poly(amideimide)s was determined at 3 wt.% concentration in various solvents at room temperature or on heating.

4b.2.3 Synthesis of poly(amideimide)s

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

Into a 25 ml two-necked round bottom flask fitted with a magnetic stirring bar and nitrogen inlet, 5-dodecyloxyisophthalic acid dihydrazide (0.756 g, 2 mmol) and dry DMAc (10 ml) were charged. After complete dissolution of the diacylhydrazide, PMDA (0.436 g, 2 mmol) was added in portions to the stirred solution of diacylhydrazide at room temperature. After the addition of dianhydride was complete, the reaction was allowed to proceed for an additional 18 h at room temperature under nitrogen atmosphere.

A portion of the sample from the reaction mixture was precipitated in methanol for isolation of poly(hydrazide acid). The precipitated polymer was washed several times with methanol and dried at 40^{o}C for 24 h under reduced pressure.

Imidization was effected by two methods

A. Thermal imidization of poly(hydrazide acid)s

Poly(amideimide)s were prepared by thermal imidization technique. The poly(hydrazide acid) solution was cast in to glass petri dish and the solvent was evaporated at 80^{o}C under nitrogen atmosphere for 1 h. The semi-dried film was heated at 220^{o}C for 12 h under reduced pressure to effect imidization.

B. Chemical imidization of poly(hydrazide acid)s

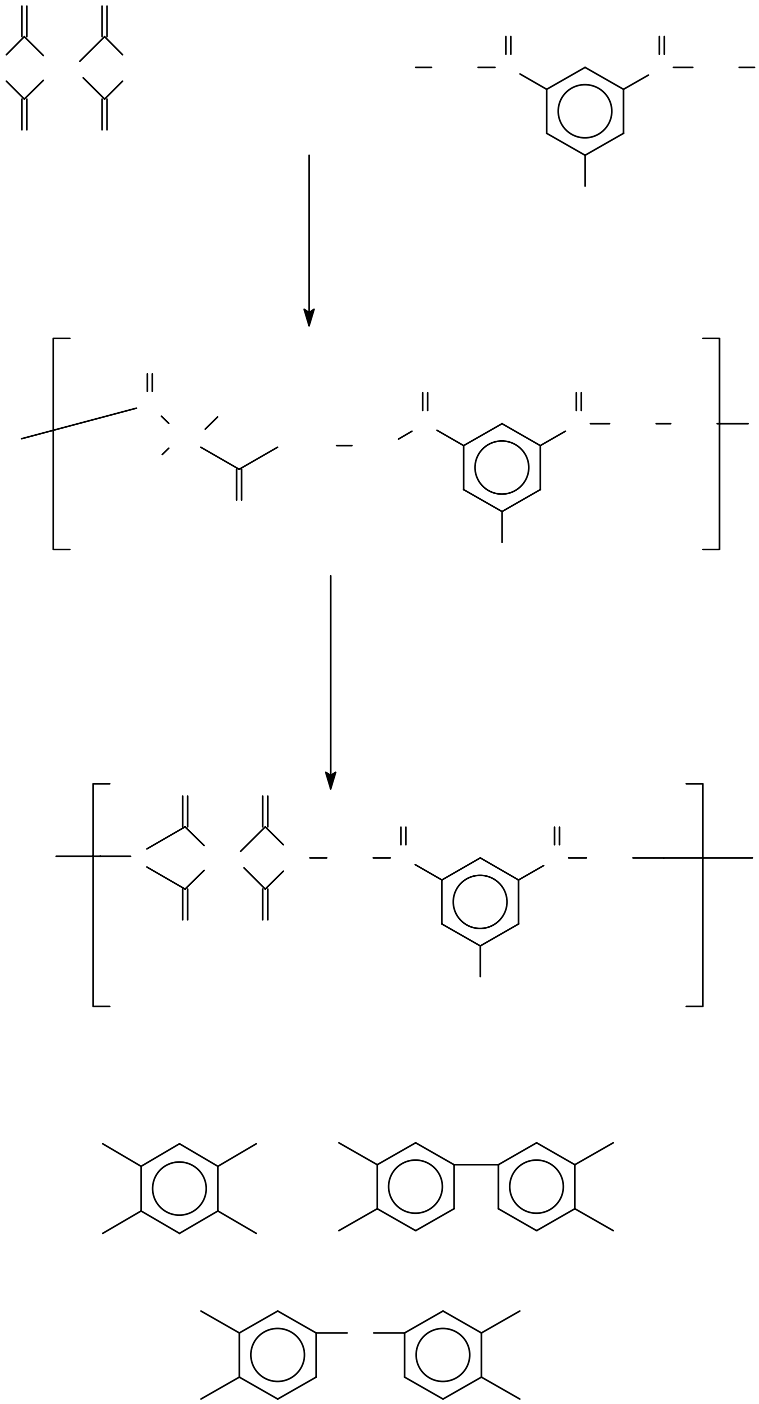
Poly(amideimide)s were also prepared by chemical imidization method. To poly(hydrazide acid) solution, a mixture of acetic anhydride (0.35 ml) and pyridine (0.30 ml) was added and the mixture was stirred at room temperature for 24 h in a draft of nitrogen. The reaction mixture was poured into excess methanol and yellow coloured flakes separated. The flakes were recovered by filtration at pump, washed several times with methanol and dried at 120°C for 12 h under reduced pressure.

4b.3 Results and Discussion

4b.3.1 Synthesis of poly(amideimide)s from diacylhydrazides containing pendent alkoxy groups and aromatic dianhydrides

Scheme 4b.1 outlines the synthesis of poly(amideimide)s.

The preparation of poly(amideimide)s by the reaction of an aromatic diacylhydrazide and a dianhydride is a two stage process.[6-11] The first stage is the ring opening polyaddition reaction of a dianhydride and a diacylhydrazide to form poly(hydrazide acid), while the second step consists of the subsequent cyclodehydration of poly(hydrazide acid) to form poly(amideimide). It has been established that the cyclodehydration reaction involving NH and COOH groups in poly(hydrazide acid) gives selectively imide functions, without formation of any detectable 1,3,4-oxadiazole rings by cyclodehydration of the O = C – NH – NH –C = O moieties.[6, 12,13]



Scheme 4b.1: Synthesis of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and aromatic dianhydrides.

All diacylhydrazides, except 5-hexadecyloxyisophthalic acid dihydrazide, were soluble in DMAc at room temperature. 5-Hexadecyloxyisophthalic acid dihydrazide was solubilized in DMAC by heating to 60°C and the solution was cooled to room temperature before use in polymerization with dianhydrides. The diacylhydrazides in DMAc solution were reacted with ODPA, BPDA, and PMDA at room temperature to obtain respective poly(hydrazide acid)s.

The cyclodehydration of poly(hydrazide acid)s can be achieved either chemically or thermally. In the present work, both the methods were utilized. In the chemical cyclization, the DMAc solution of the poly(hydrazide acid) was treated with acetic anhydride and pyridine when a yellow coloured solution was obtained. The flakes of poly(amideimide)s were obtained by precipitating the polymer solution into methanol. In the thermal cyclodehydration, the solution of poly(hydrazide acid) was spread onto a glass petri dish and the solvent was evaporated at 80°C in a slow stream of nitrogen flow. Then, the semi-dried film was kept in a vacuum oven at 220°C for 12 h to obtain a tough, pale yellow film of poly(amideimide).

Results of synthesis of poly(amideimide)s are summarized in **Table 4b.1.** Inherent viscosities of poly(amideimide)s containing pendent alkoxy chains were in the range 0.55-0.88 dL/g (**Table 4b.1**) indicating formation of reasonably high molecular weight polymers. Poly(amideimide)s derived from isophthalic acid dihydrazide were not soluble in organic solvents, hence the inherent viscosities were measured at poly(hydrazide acid) stage which were in the range 0.35 to 0.51 dl /g. Poly(amideimide)s containing pendent alkoxy chains could be cast in to tough, flexible and transparent films from a solution in DMAc.

Table 4b.1: Preparation of poly(amideimide)s based on 5-alkoxyisophthalic acid dihydrazides and aromatic dianhydrides.

Poly(amide-imide)	Diacylhydrazide (-R substituent)	Dianhydride	Yield (%)	η_{inh} (dL/g)[a]
PAIH-1	-H	ODPA	95	0.42[b]
PAIH-2	$-OC_4H_9$	ODPA	97	0.65
PAIH-3	$-OC_8H_{17}$	ODPA	94	0.88
PAIH-4	$-OC_{12}H_{25}$	ODPA	96	0.69
PAIH-5	$-OC_{16}H_{33}$	ODPA	93	0.63
PAIH-6	-H	BPDA	97	0.35[b]
PAIH-7	$-OC_4H_9$	BPDA	96	0.55
PAIH-8	$-OC_8H_{17}$	BPDA	98	0.87
PAIH-9	$-OC_{12}H_{25}$	BPDA	98	0.76
PAIH-10	$-OC_{16}H_{33}$	BPDA	98	0.68
PAIH-11	-H	PMDA	95	0.51[b]
PAIH-12	$-OC_4H_9$	PMDA	95	0.65
PAIH-13	$-OC_8H_{17}$	PMDA	96	0.65
PAIH-14	$-OC_{12}H_{25}$	PMDA	96	0.59
PAIH-15	$-OC_{16}H_{33}$	PMDA	95	0.56

a: η_{inh} of poly(amideimide) was measured at a concentration of 0.5 g / dl in DMAc at 30 ± 0.1°C

b: η_{inh} of poly(hydrazide acid) was measured in DMAc at a concentration of 0.5 g / dl at 30±0.1°C as corresponding poly(amideimide) was insoluble in DMAc.

4b.3.2 FT-IR spectroscopic analysis

Poly(amideimide)s were characterized by FT-IR spectroscopy. Representative IR spectrum of poly(amideimide) based on 5-dodecyloxyisophthalic acid dihydrazide and PMDA is shown in **Figure 4b.1** as an example. Absorption bands at 1794 cm^{-1} (symmetric C = O), 1738 cm^{-1} (asymmetric C = O), 1338 cm^{-1} (imide –II), 1114 cm^{-1} (imide-III) and 710 cm^{-1} (imide-IV) confirm the formation of imide rings. The absorption bands at 3250 cm^{-1} and 1697 cm^{-1} correspond to the NH and C = O of the amide linkage.

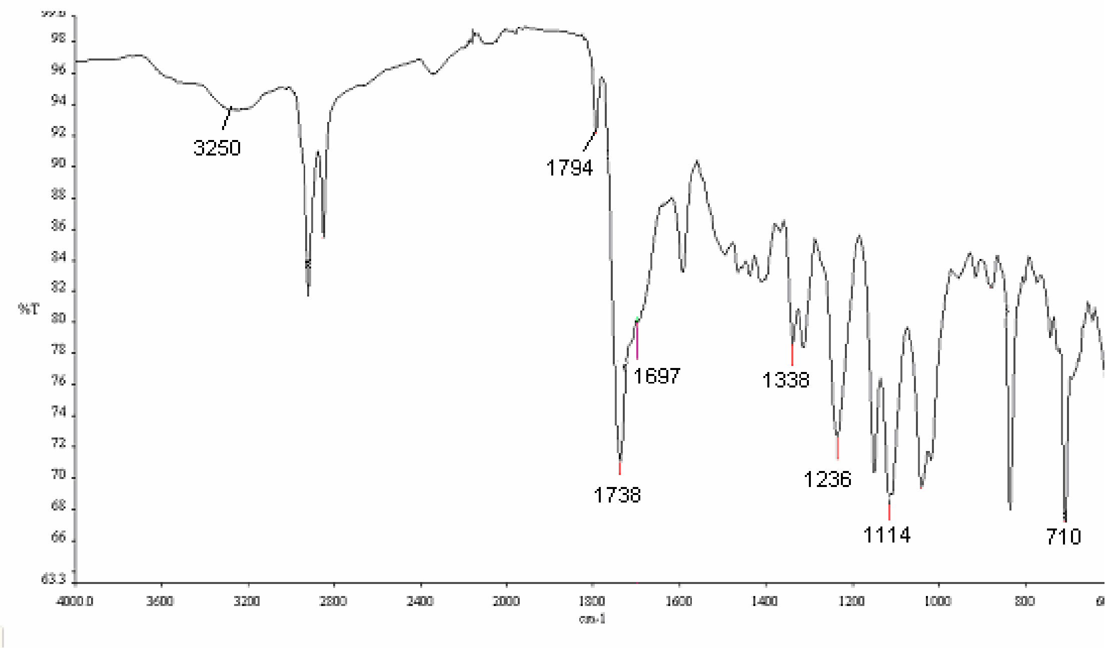


Figure 4b.1: IR spectrum of poly(amideimide) film derived from 5-dodecyloxy-isophthalic acid dihydrazide and PMDA.

4b.3.3 NMR spectroscopic analysis

^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyloxyisophthalic acid dihydrazide and PMDA is shown in **Figure 4b.2.** A broad singlet at 11.82 δ ppm corresponds to -NH of the amide functions. The two aromatic protons flanked by imide carbonyl groups exhibited a singlet at 8.56 δ ppm. The aromatic proton flanked by amide carbonyl groups appeared as a singlet at 8.2 δ ppm while the aromatic protons *ortho* to ether linkage appeared as a singlet at 7.82 δ ppm. The methylene protons α- and β- to ether oxygen appeared as a triplet at 4.17 δ ppm and a multiplet centered at 1.79 δ ppm, respectively. The other methylene protons displayed a multiplet over the range 1.10-1.50 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.84 δ ppm.

Figure 4b.3 shows ^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyloxyisophthalic acid dihydrazide and ODPA along with assignments of the protons.

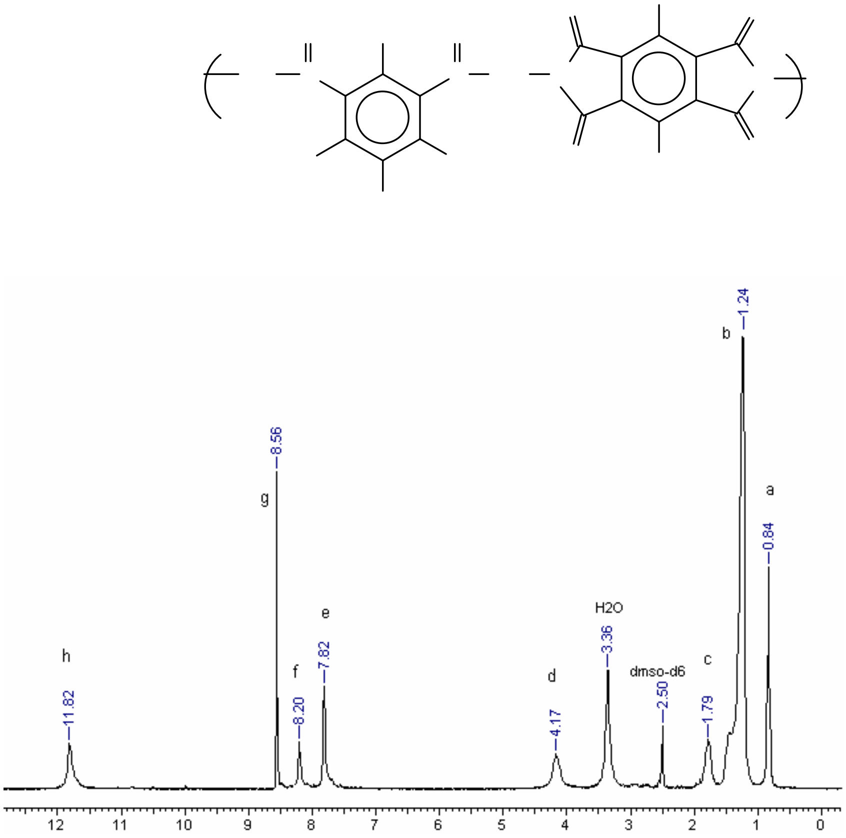


Figure 4b.2: ^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyloxyisophthalic acid dihydrazide and PMDA (PAIH-15) in DMSO-d_6.

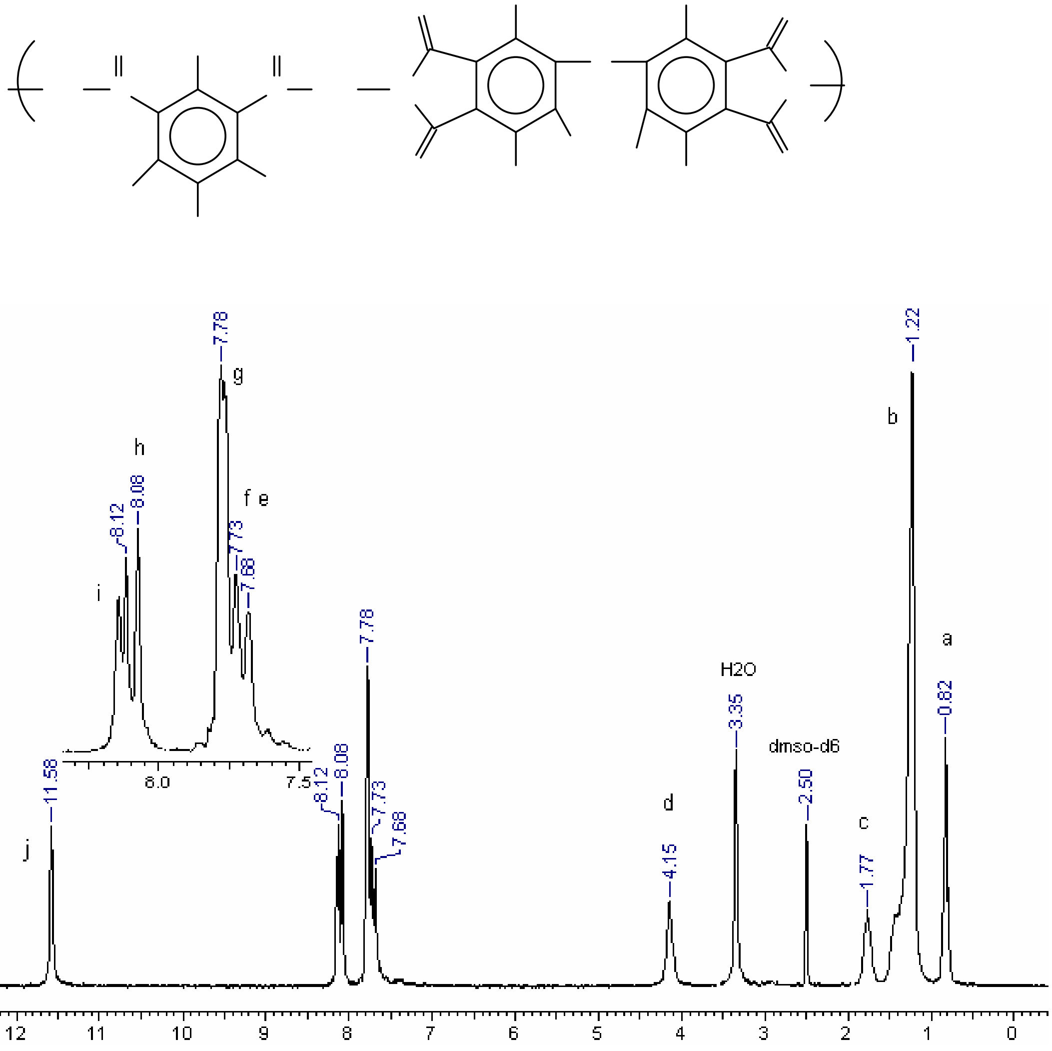


Figure 4b.3: ^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyl-oxyisophthalic acid dihydrazide and ODPA (PAIH-5) in DMSO-d$_6$.

4b.3.4 Properties of poly(amideimide)s

4b.3.4.1 Solubility of poly(amideimide)s

Poly(amideimide)s were tested for solubility at 3 wt % concentration in different solvent and the data is summarized in **Table 4b.2.**

Poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and ODPA, BPDA and PMDA were all soluble in DMAc, DMF, NMP and pyridine. Analogous poly(amideimide)s derived from isophthalic acid dihydrazide were not soluble in the above solvents. It is obvious that introduction of pendent alkoxy chains weakened the intermolecular interactions which conferred good solubility in organic solvents to poly(amideimide)s.

Table 4b.2: Solubility data of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and aromatic dianhydrides.

Poly(amide -imide)	Diacyl hydrazide	Dianhy-dride	$CHCl_3$	DMAc	DMF	NMP	DMSO	m-cresol	Pyridine	THF
PAIH-1	-H	ODPA	–	–	–	–	–	–	–	–
PAIH-2	$-OC_4H_9$	ODPA	–	++	++	++	++	+	++	–
PAIH-3	$-OC_8H_{17}$	ODPA	–	++	++	++	++	+	++	–
PAIH-4	$-OC_{12}H_{24}$	ODPA	–	++	++	++	++	+	++	–
PAIH-5	$-C_{16}H_{33}$	ODPA	–	++	++	++	++	+	++	–
PAIH-6	-H	BPDA	–	–	–	–	–	–	–	–
PAIH-7	$-OC_4H_9$	BPDA	–	++	++	++	±	+	++	–
PAIH-8	$-OC_8H_{17}$	BPDA	–	++	++	++	±	+	++	–
PAIH-9	$-OC_{12}H_{24}$	BPDA	–	++	++	++	±	+	++	–
PAIH-10	$-OC_{16}H_{33}$	BPDA	–	++	++	++	±	+	++	–
PAIH-11	-H	PMDA	–	–	–	–	–	–	–	–
PAIH-12	$-OC_4H_9$	PMDA	–	++	++	++	++	±	++	–
PAIH-13	$-OC_8H_{17}$	PMDA	–	++	++	++	++	±	++	–
PAIH-14	$-OC_{12}H_{24}$	PMDA	–	++	++	++	++	±	++	–
PAIH-15	$-OC_{16}H_{33}$	PMDA	–	++	++	++	++	±	++	–

++ : soluble at room temperature; + : soluble at 60^{o}C; ± : sparingly soluble on heating; - : insoluble

4b.3.4.2 X-Ray diffraction studies

X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and ODPA, BPDA and PMDA are shown in **Figure 4b.4, 4b.5 and 4b.6**, respectively. X-Ray diffractograms of poly(amideimide)s derived from isophthalic acid dihydrazide and the above dianhydrides are also incorporated in the respective figures for comparison. The diffractograms indicate that in the wide angle region the poly(amideimide)s have only very broad peaks at about $2\theta = 20^o$. These peaks are so broad that they may be considered as amorphous halos.

In the X-ray diffractogram of each series of poly(amideimide)s, two diffuse peaks in the middle-angle region ($2\theta = 2 - 8^o$) were observed in case of poly(amideimide)s derived from 5-butyloxyisophthalic acid dihydrazide. This suggests that poly(amideimide)s containing butyloxy pendent group has a loosely packed layered structure, in which the main chains were separated with disordered side chains. However, in poly(amideimide)s containing octyloxy, dodecyloxy and hexadecyloxy pendent group, reflection peaks became much sharper and stronger and shifted to smaller angle. This fact indicates that the order of the layered structures improved with increased side chain length. Similar observations were made in case of polyimides derived from 5-alkoxy-1,3-phenylene diisocyanates and ODPA and FDA as discussed in **Chapter 4a.** These results are in line with the observations made by earlier workers for polymers with stiff main chains and flexible alkyl side chains.[14-18]

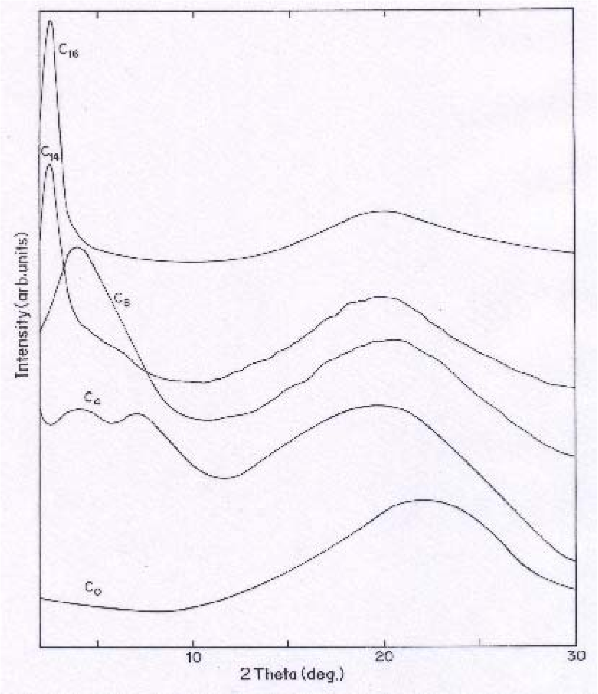


Figure 4b.4: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and ODPA (PAIH-1 to PAIH-5).

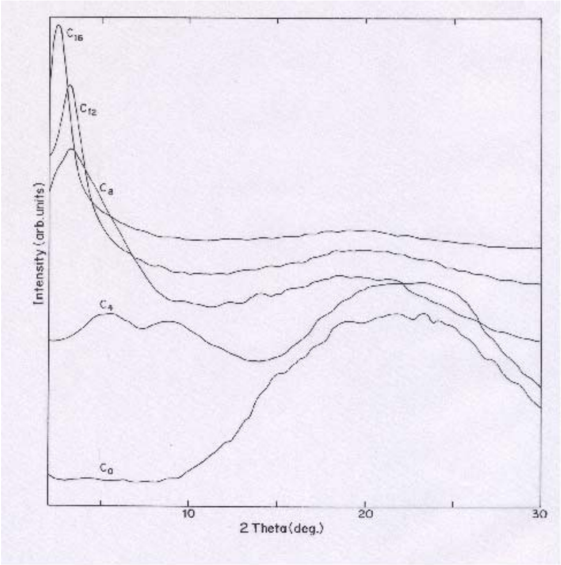


Figure 4b.5: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and BPDA (PAIH-6 to PAIH-10).

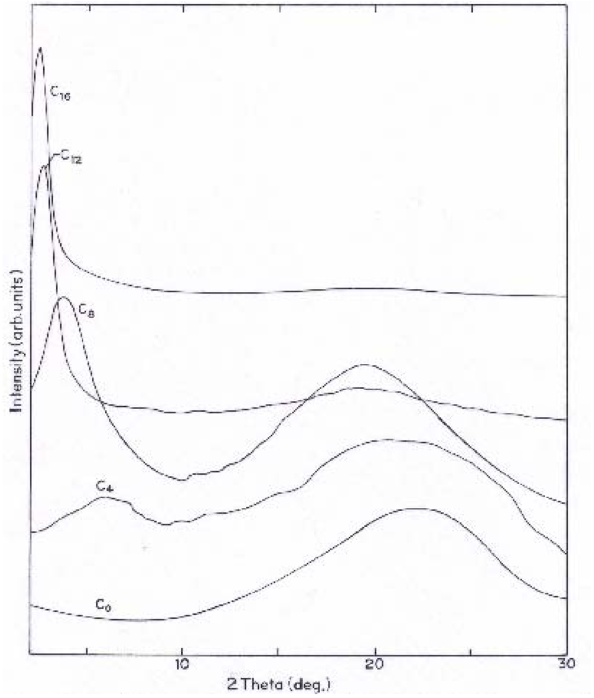


Figure 4b.6: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and PMDA (PAIH-11 to PAIH-15).

4b.3.4.3 Thermal behaviour of poly(amideimide)s

Thermal stability of poly(amideimide)s was determined by thermogravimetric analysis (TGA) at the heating rate of 10°C / minute under nitrogen. The TG curves are shown in **Figure 4b.7, 4b.8 and 4b.9**. Initial decomposition temperature (IDT) and temperature at 10% weight loss (T_{10}) were determined from thermograms and the data is given in **Table 4b.3**. Poly(amideimide)s were stable upto 375-410°C and then drastic degradation occured. All of the poly(amideimide)s left no residue after heating to 700- 900°C.

A representative DTG curve for poly(amideimide) derived from 5-hexadecyloxyisophthalic acid dihydrazide and ODPA (PAIH-5) is shown in **Figure 4b.10**. Temperature at the first maximum degradation (T_{max1}) (445°C) apparently corresponds to the loss of alkyl group and coincides with the main chain degradation. A second broad DTG profile was observed at around 730°C. This may be attributed to the volatilization of the low mass fractions resulting from the previous degradation processes.

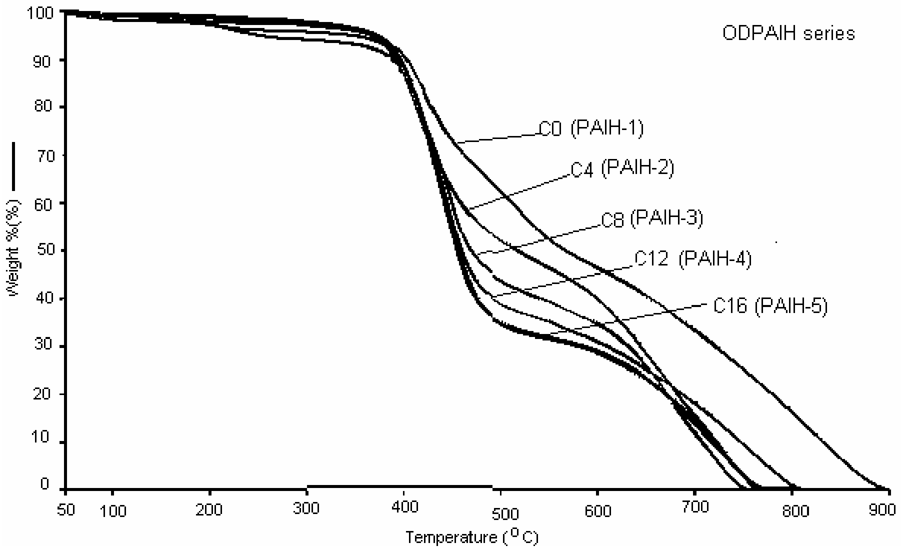


Figure 4b.7: TG curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and ODPA (PAIH-1 to PAIH-5).

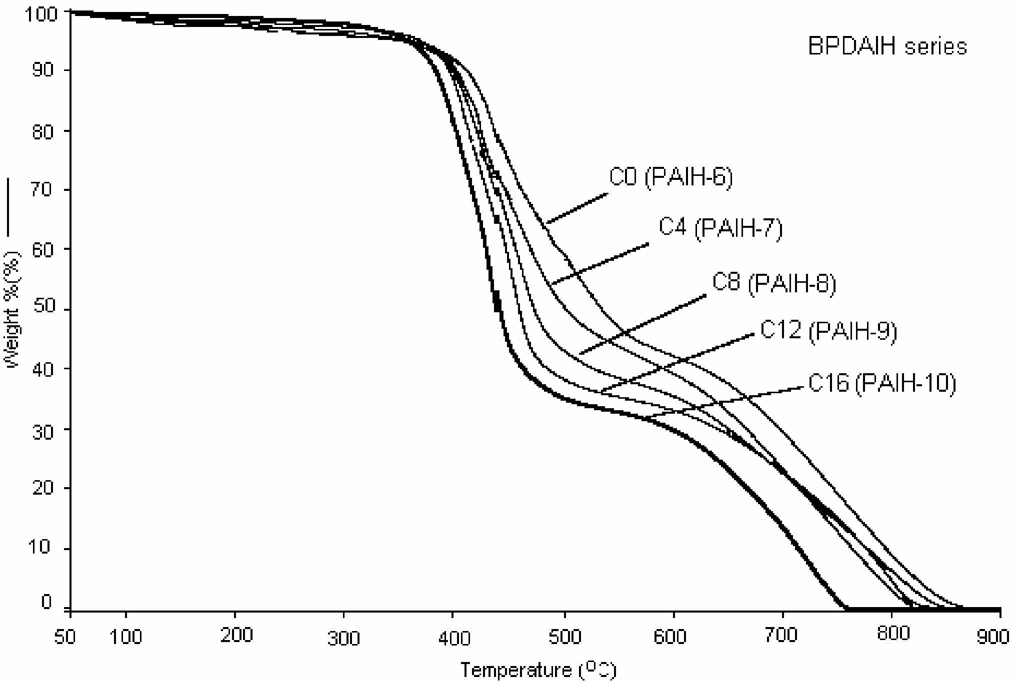


Figure 4b.8: TG curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and BPDA (PAIH-6 to PAIH-10).

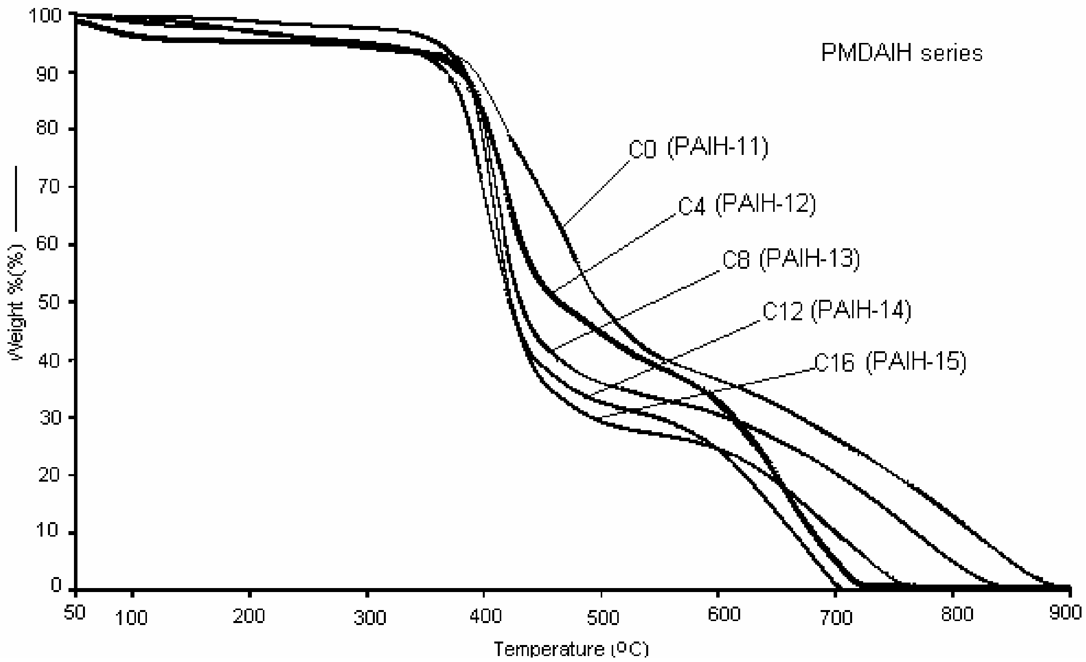


Figure 4b.9: TG curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and PMDA (PAIH-11 to PAIH-15).

Table 4b.3: Thermal properties of poly(amideimide)s derived from 5-alkoxy-isophthalic acid dihydrazides and aromatic dianhydrides.

Poly(amid eimide)	Diacylhydrazide (-R substituent)	Dianhydride	Tg (°C)	IDT (°C)	T_{10}(°C)
PAIH-1	- H	ODPA	261	400	425
PAIH-2	$-OC_4H_9$	ODPA	230	390	395
PAIH-3	$-OC_8H_{17}$	ODPA	220	400	410
PAIH-4	$-OC_{12}H_{25}$	ODPA	213	400	410
PAIH-5	$-OC_{16}H_{33}$	ODPA	215	390	395
PAIH-6	-H	BPDA	ND	410	415
PAIH-7	$-OC_4H_9$	BPDA	240	400	410
PAIH-8	$-OC_8H_{17}$	BPDA	230	390	400
PAIH-9	$-OC_{12}H_{25}$	BPDA	220	390	400
PAIH-10	$-OC_{16}H_{33}$	BPDA	225	375	380
PAIH-11	- H	PMDA	284	390	400
PAIH-12	$-OC_4H_9$	PMDA	243	385	390
PAIH-13	$-OC_8H_{17}$	PMDA	230	390	400
PAIH-14	$-OC_{12}H_{25}$	PMDA	225	375	380
PAIH-15	$-OC_{16}H_{33}$	PMDA	227	375	380

IDT: Initial decomposition temperature
T_{10} : Temperature at 10% weight loss
ND : Not detectable

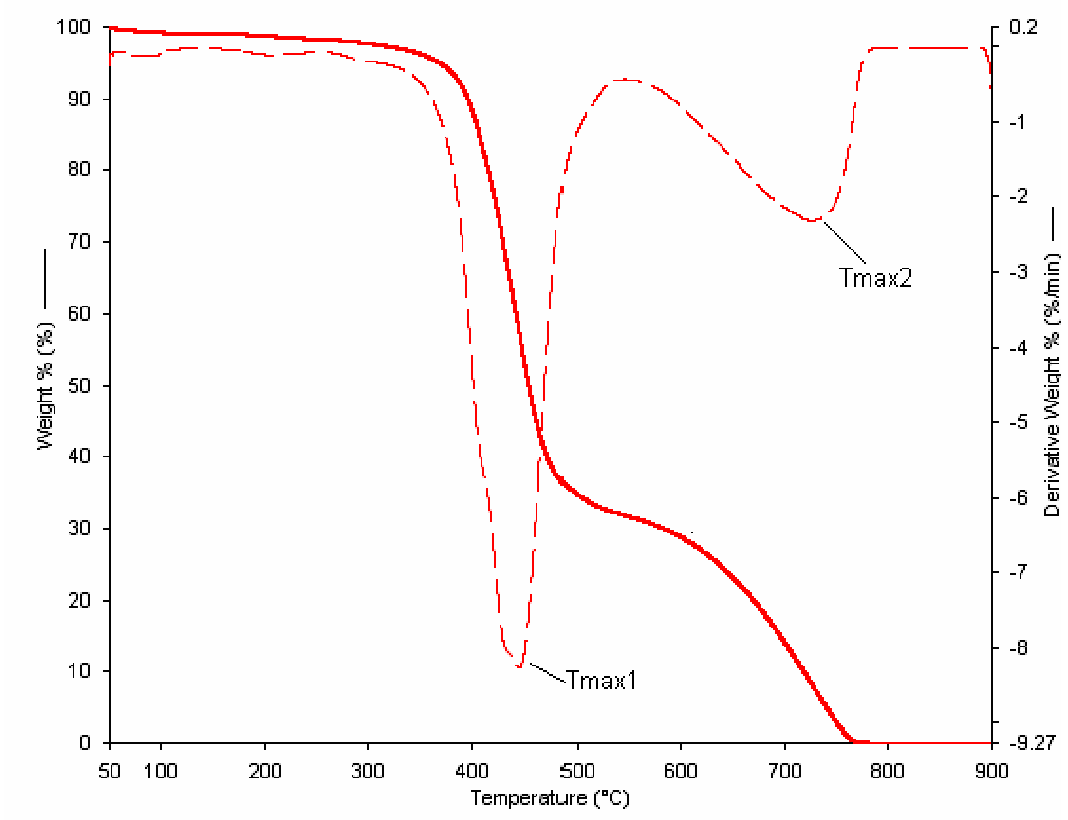


Figure 4b.10: A representative DTG curves of poly(amideimide) derived from 5-hexadecyloxyisophthalic acid dihydrazide and ODPA (PAIH-5).

Derivative curve (T_{max1} = temperature at the first maximum degradation; T_{max2} = temperature at the second maximum degradation)

DSC curves of poly(amideimide)s are shown in **Figures 4b.11, 4b.12 and 4b.13** and T_g values obtained are listed in **Table 4b.3**. T_g values of poly(amideimide)s containing pendent alkoxy groups were in the range 213 - 243°C which are lower than those of the corresponding poly(amideimide)s based on isophthalic acid dihydrazide which were in the range 261-284°C.

A plot of T_g values versus number of carbon atoms in the pendent alkoxy chains of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and aromatic dianhydrides is shown in **Figure 4b.14**. T_g values of poly(amideimide)s containing pendent flexible alkoxy groups were lower than those of the corresponding unsubstituted poly(amideimide)s. This clearly results from the presence of the alkoxy side chains which are responsible for the decrease in the intermolecular interaction which in turn results in decrease in T_g values. The effect of alkoxy chain in lowering the T_g value was pronounced up to chain length of 8 carbon atoms. Further increase in the chain length did not have significant effect in lowering of T_g.

T_g values of poly(amideimide)s derived from three aromatic dianhydrides were found to be in decreasing order of ODPA < BPDA < PMDA. This result is attributed to the rigidity of the dianhydrides (PMDA > BPDA > ODPA) which restricts free mobility of the backbone and hence results in increased T_g values (**Figure 4b.14**).

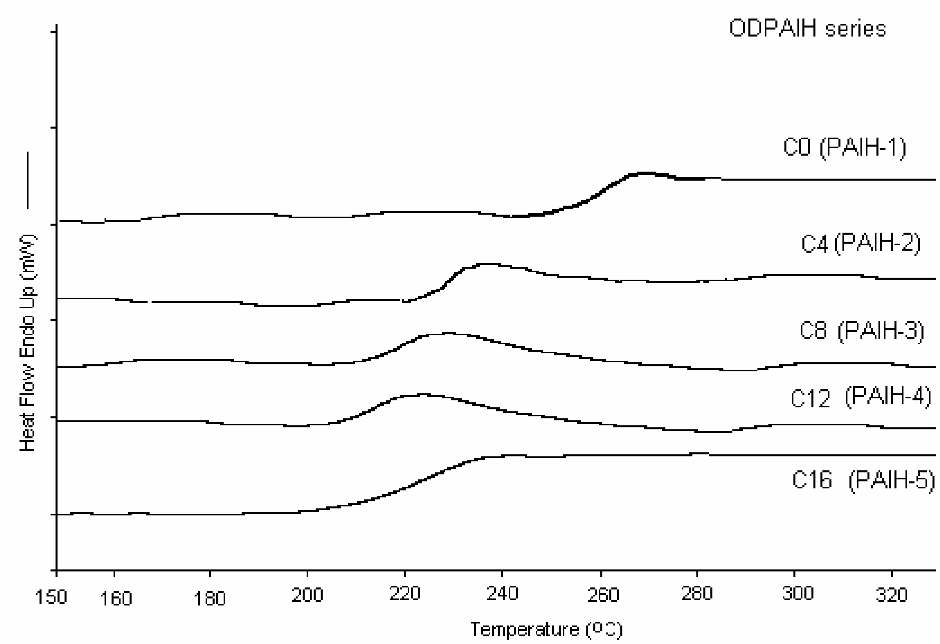


Figure 4b.11: DSC curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and ODPA (PAIH-1 to PAIH-5).

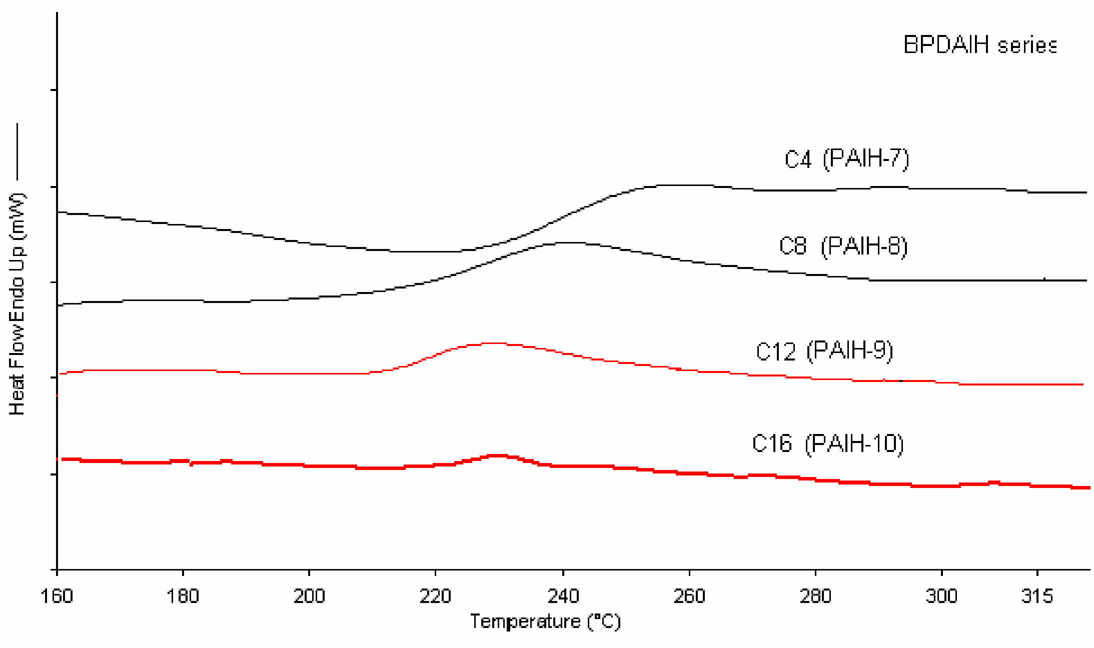


Figure 4b.12: DSC curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and BPDA (PAIH-7 to PAIH-10).

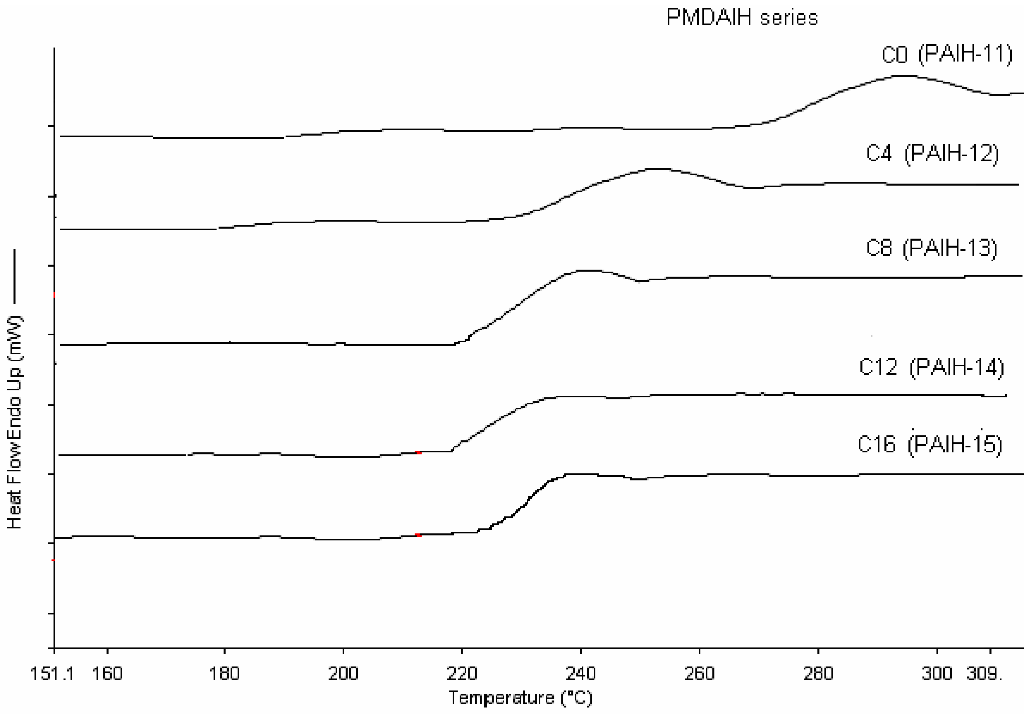


Figure 4b.13: DSC curves of poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and PMDA (PAIH-11 to PAIH-15).

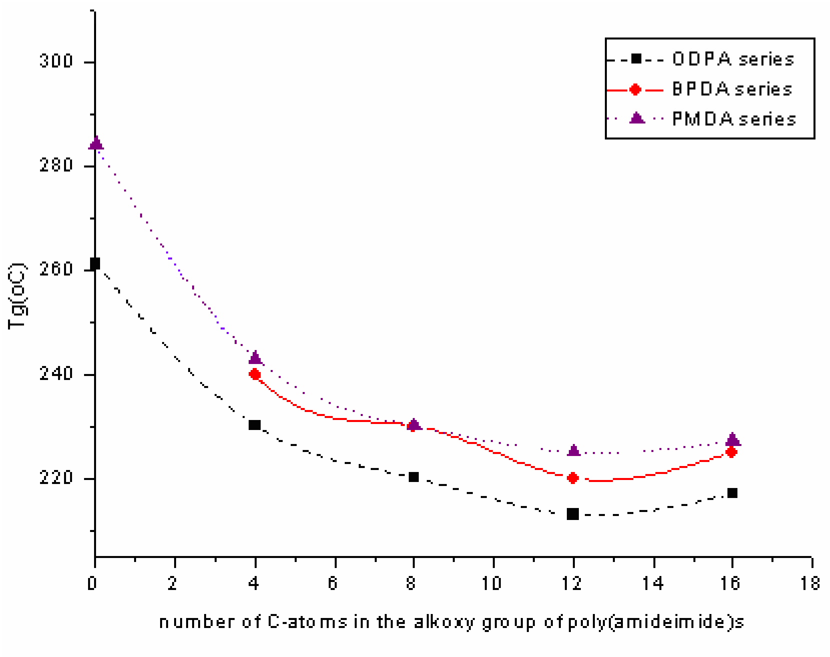


Figure 4b.14: Plot of T_g values as a function of number of carbon atoms in the pendent alkoxy groups of poly(amideimide)s.

4b.4 Conclusion

1. A new series of poly(amideimide)s having pendent flexible alkoxy chains with different chain lengths(C_4, C_8, C_{12}, C_{16}) was synthesized from 5-alkoxyisophthalic acid dihydrazides and aromatic dianhydrides by a two-step solution polycondensation in DMAc *via* the poly(hydrazideacid) intermediate.
2. Poly(amideimide)s were obtained in reasonably high molecular weight as indicated by their inherent viscosity values.
3. Poly(amideimide)s containing pendent flexible alkoxy chains were found to be soluble in organic solvents such as DMAc, DMF, NMP and pyridine whereas poly(amideimide)s based on isophthalic acid dihydrazide – reference poly(amideimide)s without pendent alkoxy chains- were insoluble in these solvents. Rigid dianhydrides such as PMDA and BPDA also gave soluble poly(amideimide)s. This indicates that the incorporation of pendent flexible alkoxy chains leads to a significant improvement in solubility of poly(amideimide)s.
4. Tough, transparent and flexible films could be cast from the solution of poly(amideimide) in DMAc.
5. Thermal analysis showed that the attached side-chains induced the depression of T_g.
6. IDT values of poly(amideimide)s were in the range 375 – 410^o C and then drastic degradation occurred with increase in temperature.
7. X-Ray diffractograms revealed that poly(amideimide)s with longer alkoxy chains had layered structures.

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Chapter 4c. Synthesis and Characterization of Poly(amideimide)s from Diamines Containing Pre-formed Amide Linkages and Aromatic Dianhydrides

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4c.1 Introduction

Aromatic poly(amideimide)s are an important class of high performance polymers having excellent resistance to high temperatures and favourable balance of physical and chemical properties.[1,2] Poly(amideimide)s have been developed as engineering thermoplastic materials, for example, Torlon^{R} (Amoco Chemical Co.), and used as electrical wire enamel, adhesives, and various injection molding and extrusion products. They inherit desirable characteristics from both polyimides and polyamides, and possess good thermal properties compared to polyamides, and better melt processability than polyimides. To further improve processability and solubility in organic solvents of poly(amideimide)s several approaches have been adapted which include introduction of flexible or asymmetric linkages in the backbone, introduction of bulky pendent groups, etc.[3-10]

The present study aims to investigate effect of pendent flexible alkoxy groups on the properties of poly(amideimide)s. Thus, a series of new regularly alternating poly(amideimide)s was synthesized by polycondensation of aromatic diamines containing pre-formed amide linkages and possessing pendent alkoxy groups, namely, 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides with commercially available aromatic dianhydrides, viz. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (FDA), pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA) and 4,4'-oxydiphthalic anhydride (ODPA). As reference materials that do not have alkoxy side chains, a series of poly(amideimide)s was synthesized by polycondensation of N, N'-bis(4-aminophenyl)isophthalamide with the same aromatic dianhydrides. Poly(amideimide)s were characterized by inherent viscosity measurements, FTIR and NMR spectroscopy, UV-vis spectroscopy, solubility tests, X-ray diffraction, thermogravimetric analysis and differential scanning calorimetery. Poly(amideimide)s derived from 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides and PMDA were used to prepare liquid crystal alignment layers.

4c.2 Experimental

4c.2.1 Materials

5-Alkoxy-N,N'-bis(4-aminophenyl)isophthalamides were synthesized as described in **Chapter 3, section 3.3.10**. Dianhydrides, namely, FDA, PMDA, BPDA and ODPA were received from Aldrich and were sublimed under reduced pressure before use. N,N-Dimethylacetamide (DMAc) was distilled from calcium hydride under reduced pressure. N,N-Dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), pyridine, tetrahydrofuran (THF), dichloromethane, chloroform and *meta*-cresol were dried and distilled as per literature procedures.[11]

4c.2.2 Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of poly(amideimide)s in DMAc at 30 ± 0.1°C using an Ubbelhode suspended level viscometer.

FTIR spectra were recorded using poly(amideimide) films on a Perkin-Elmer 599B spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker NMR spectrophotometer at 200 or 500 MHz at room temperature using DMSO-d_6 + $CDCl_3$ mixture as solvent.

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

DSC analysis was performed on Perkin-Elmer DSC-7 at a heating rate of 40^{o}C / minute in nitrogen atmosphere.

X-Ray diffractograms of polymer films were obtained on a Rigaku Dmax 2500 X-ray diffractometer. Polymer samples were dissolved in distilled DMAc and filtered onto a glass petridish. The solvent was then slowly evaporated at 100^{o}C in an oven to get a semi-dried film. The film was dried at 120^{o}C under reduced pressure for 4 days to get a film of ~30 μm thickness.

UV-visible spectra were recorded on Shimadzu UV-1601 UV-vis spectrophotometer using films of 15-20 μm thickness.

Solubility of poly(amideimide)s was determined at 3 wt % concentration in various solvents at room temperature or on heating.

4c.2.3 Liquid crystal (LC) cell preparation and measurement of the LC alignment

Liquid crystal cells were prepared to measure the pretilt angle of LC molecules aligned on poly(amideimide) films. Poly(amideimide) films for LC alignment layers were prepared by the spin coating of 3 wt % of poly(amideimide) solution in DMAc at 3000 rpm for 40 seconds onto clean glass substrate (3.0 cm x 4.0 cm), followed by drying at 120^{o}C for 6 h under reduced pressure. Poly(amideimide) films were subsequently rubbed with a roller covered by a rayon velvet fabric (YA-20-R, Yoshikawa Co.), and the rubbing density (L/l) was calculated as follows:

$$\frac{L}{l} = N\left(\frac{2\pi rn}{60v} - 1\right) \qquad (1)$$

where L (mm) is the total length of the rubbing cloth that touches a certain point of the film; *l* (mm) is the contact length of the rubbing roller circumference; N is the cumulative number of rubbings; ν (cm / s) is the velocity of the substrate stage; and *n* (rpm) and *r* (cm) are the rubbing roller speed and radius, respectively.

LC cells were fabricated from two pieces of rubbed poly(amideimide) films assembled in an antiparallel rubbing direction with 50-µm (cell gap) thick spacers and filled with 4-pentyl-4’-cyanobiphenyl (Aldrich) containing 1.0 wt % Disperse Blue 1 dichroic dye (Aldrich) by the capillary method. The pretilt angles for the fabricated LC cells were measured by a crystal rotation method[12] with a laboratory apparatus equipped with a goniometer, a photodiode detector, a He-Ne Laser with a 632.8-nm wavelength (model 106-1, Spectra-Physics), a polarizer-analyzer pair, and a sample stage (rotating out-of-plane direction).

4c.2.4 Synthesis of poly(amideimide)s

A representative procedure for synthesis of poly(amideimide)s is described below:

Step I: Synthesis of poly(amicacid)

Into a 50 ml two-necked round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet, were placed 5-dodecyloxy-N,N’-bis(4-aminophenyl)isophthalamide (1.06 g, 2 mmol) and dry DMAc (10 ml). After complete dissolution of the diamine, PMDA (0.436 g, 2 mmol) was added in portions to the stirred solution cooled to 10^{o}C. After the addition of dianhydride was completed, the reaction was allowed to proceed for 18 h at room temperature under nitrogen atmosphere. The poly(amicacid) solution thus obtained was spread onto a glass petridish and the solvent was evaporated at 80^{o}C to get a semi-dried film. Then the film was imidized by thermal imidization technique. An aliquot of the poly(amicacid) was taken and precipitated in methanol, filtered and dried under reduced pressure.

Step II: Thermal imidization of poly(amicacid)

Poly(amicacid) solution was cast onto glass petridish and solvent was evaporated at 80°C in nitrogen atmosphere for 1 h. The semi-dried film was heated under reduced pressure at 100°C, 200 °C and 250 °C for 1 h at each temperature.

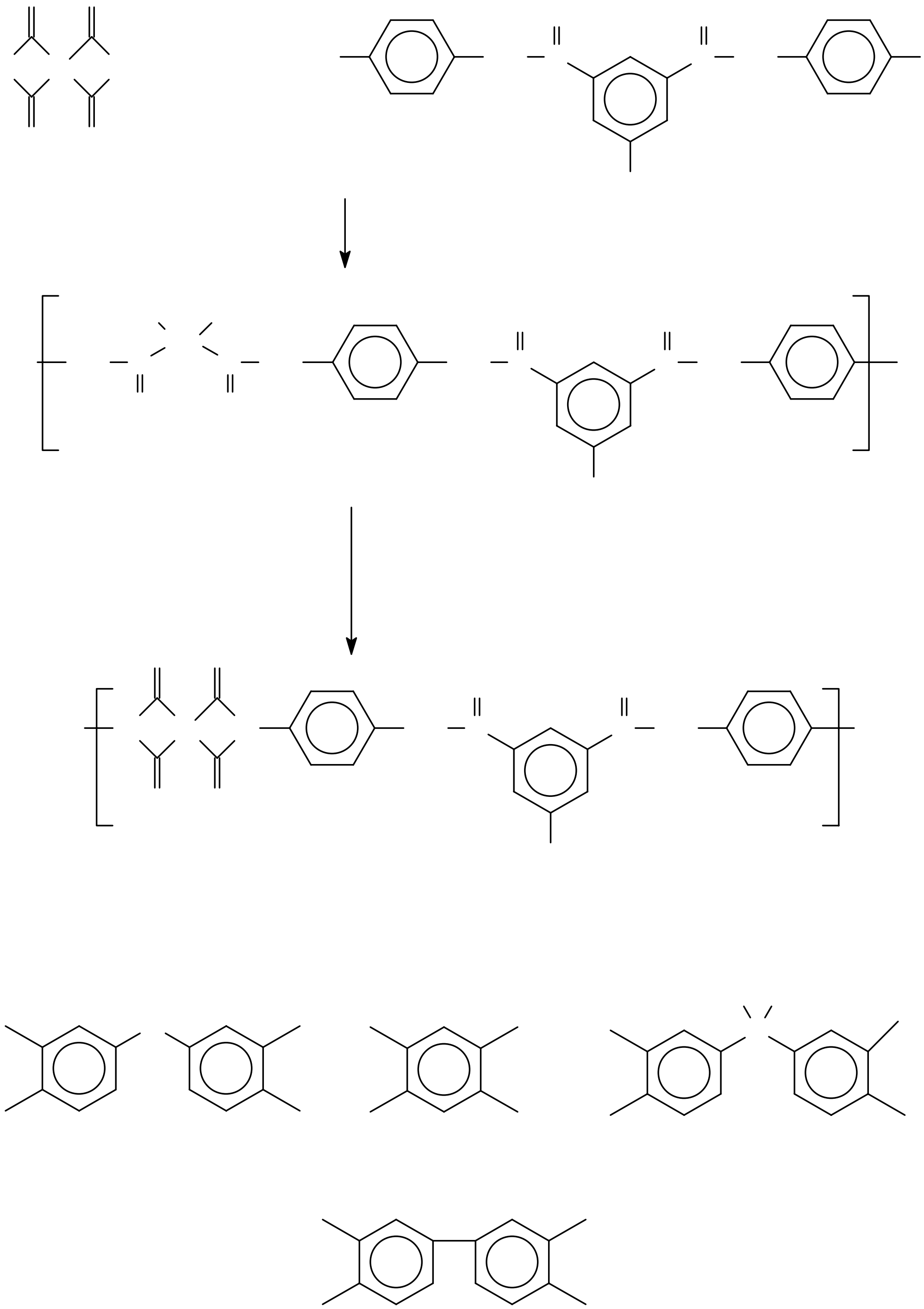
4c.3 Results and Discussion

4c.3.1 Synthesis of poly(amideimide)s

Of the four aromatic diamines containing pre-formed amide linkages and possessing pendent alkoxy groups described in **Chapter 3**, three diamines, namely, 5-octyloxy-N,N'-bis(4-aminophenyl)isophthalamide, 5-dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide, and 5-hexadecyloxy-N,N'-bis(4-aminophenyl)isophthalamide were chosen for polycondensation with commercially available aromatic dianhydrides.

In this study, twelve poly(amideimide)s were synthesized by polycondensation of aromatic diamines containing pre-formed amide linkages and possessing pendent alkoxy groups with aromatic dianhydrides, viz., ODPA, FDA, PMDA and BPDA by a two-step method *via* the poly(amicacid) intermediate. The corresponding four unsubstituted poly(amideimide)s were synthesized from N,N'-bis(4-aminophenyl)isophthalamide by polycondensation with aromatic dianhydrides mentioned above to compare their properties with those of the substituted ones.

Scheme 4c.1 illustrates the synthesis of poly(amideimide)s.



Scheme 4c.1: Synthesis of poly(amideimide)s from 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides and aromatic dianhydrides.

Poly(amicacid)s were prepared by the addition of stoichiometric quantity of solid dianhydride to the diamine solution in DMAc at 10°C followed by stirring for 18 h at room temperature. The molecular weight build up started after one hour of addition of the dianhydride, then the reaction was allowed to proceed for an additional 18 h. Regardless of the diamine monomers containing different side chain lengths and dianhydride monomers, all the polymerization reactions remained homogenous during the entire course of polymerization.

Imidization of poly(amicacid)s can be achieved chemically or thermally. In the present work, thermal imidization method was used in which the solvent was evaporated from the poly(amicacid) solution by heating the solutions at 80°C in a stream of nitrogen flow. The semi-dried polymer film was heated at 100°C, 200 °C and 250 °C for 1 h at each temperature under reduced pressure to obtain poly(amideimide) films.

Thermal imidization of poly(amic acid)s containing flexible aliphatic linkages to the corresponding polyimides is reported to be carried out using a similar heating protocol.[13-16]

Results of the synthesis of poly(amideimide)s are presented in **Table 4c.1** Inherent viscosities of poly(amideimide)s obtained from 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamide and ODPA, FDA and PMDA were in the range 0.73-1.67 dl/g indicating the formation of reasonably high molecular weight polymers. The unsubstituted poly(amideimide)s and poly(amideimide)s derived from BPDA were not soluble in DMAc, hence their inherent viscosities were measured at the poly(amicacid) stage which were in the range 0.50 – 0.75 dl/g.

Poly(amideimide)s containing pre-formed amide linkages and possessing pendent alkoxy groups showed good film forming property. Tough, flexible and transparent films could be cast from the solution of polymer in DMAc or NMP.

Table 4c.1: Preparation of poly(amideimide)s based on 5-alkoxy-N,N'-bis(4-aminophenyl)isophthalamides and aromatic dianhydrides.

Poly(amide-imide)	Diamine (-R substituent)	Dianhydride	Yield (%)	η_{inh} (dL/g)[a]
PAI-1	-H	ODPA	95	0.73[b]
PAI-2	$-OC_8H_{17}$	ODPA	94	1.10
PAI-3	$-OC_{12}H_{25}$	ODPA	96	1.25
PAI-4	$-OC_{16}H_{33}$	ODPA	93	1.28
PAI-5	-H	FDA	97	0.65[b]
PAI-6	$-OC_8H_{17}$	FDA	98	0.85
PAI-7	$-OC_{12}H_{25}$	FDA	98	0.73
PAI-8	$-OC_{16}H_{33}$	FDA	98	1.02
PAI-9	-H	PMDA	95	0.50[b]
PAI-10	$-OC_8H_{17}$	PMDA	96	1.25
PAI-11	$-OC_{12}H_{25}$	PMDA	96	1.52
PAI-12	$-OC_{16}H_{33}$	PMDA	95	1.67
PAI-13	-H	BPDA	95	0.75[b]
PAI-14	$-OC_8H_{17}$	BPDA	96	0.58[b]
PAI-15	$-C_{12}H_{25}$	BPDA	96	0.63[b]
PAI-16	$-OC_{16}H_{33}$	BPDA	95	0.58[b]

a: η_{inh} of poly(amideimide) was measured at a concentration of 0.5 g / dl in DMAc at 30 ± 0.1 °C.

b: η_{inh} of poly(amicacid) was measured in DMAc at a concentration of 0.5 g / dl at 30 ± 0.1 °C as the corresponding poly(amideimide) was insoluble in DMAc.

4c.3.2 FTIR spectroscopic analysis

A representative FTIR spectrum of poly(amideimide) derived from 5-dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide and BPDA is shown in **Figure 4c.1**. The bands at 1773 cm^{-1} (C = O symmetric stretching), and 1712 cm^{-1} (C = O asymmetric stretching), 1371 cm^{-1} (C – N stretching) and 737 cm^{-1} (imide ring deformation) confirmed the formation of imide rings. The absorption band at 3300 cm^{-1} and 1655 cm^{-1} correspond to N-H and –C = O of the amide linkage. The peak at 1242 cm^{-1} was assigned to Ar - O – C - linkage.

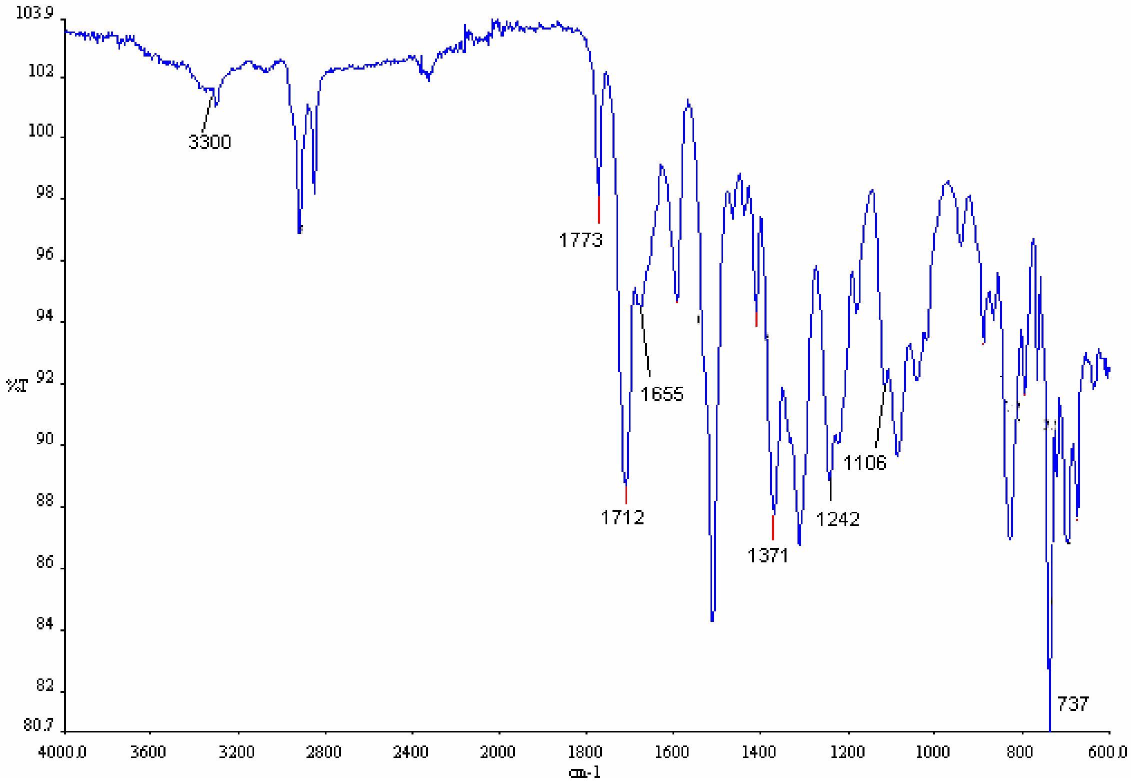
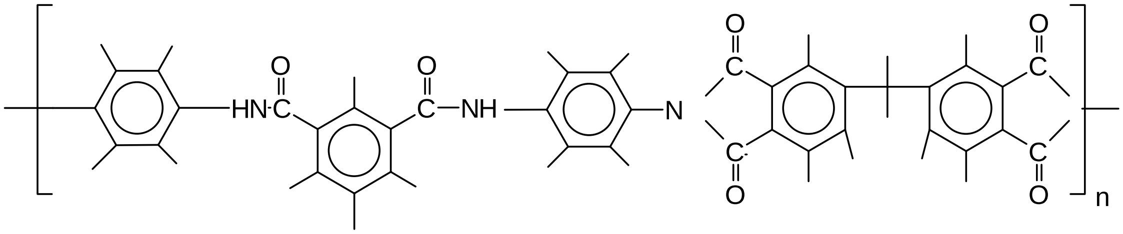


Figure 4c.1: IR spectrum (Film) of poly(amideimide) derived from 5-dodecyloxy-N,N'-bis (4-aminophenyl)isophthalamide and BPDA (PAI-15).

4c.3.3 NMR spectroscopic analysis

^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyloxy-N,N'-bis(4-aminophenyl)isophthalamide and FDA is shown in **Figure 4c.2**. A singlet at 10.55 δ, ppm was assigned to - NH of the amide group. Aromatic proton flanked by amide carbonyl groups exhibited a singlet at 8.19 δ, ppm while the aromatic protons *ortho* to ether linkage appeared as a singlet at 7.70 δ, ppm. The aromatic protons *ortho* to imide carbonyl appeared as doublet at 8.15 δ, ppm. The two aromatic protons flanked by imide carbonyl group and hexafluoroisopropylidene linkage exhibited a singlet at 7.80 δ, ppm. The doublets of aromatic protons *ortho* to hexafluoroisopropylidene linkage and aromatic protons *meta* to NH – CO linkage merged together and appeared in the region 7.90 - 8.05 δ, ppm. The aromatic protons *ortho* to NH – CO linkage appeared as doublet at 7.41 δ, ppm. The methylene protons α- and β- to oxygen atom appeared as a triplet at 4.13 δ, ppm and a multiplet centered at 1.79 δ, ppm, respectively. The other methylene protons displayed a multiplet over the range 1.10 - 1.50 δ, ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.83 δ, ppm. The relative intensities of the peaks agreed with the proposed structure of poly(amideimide).



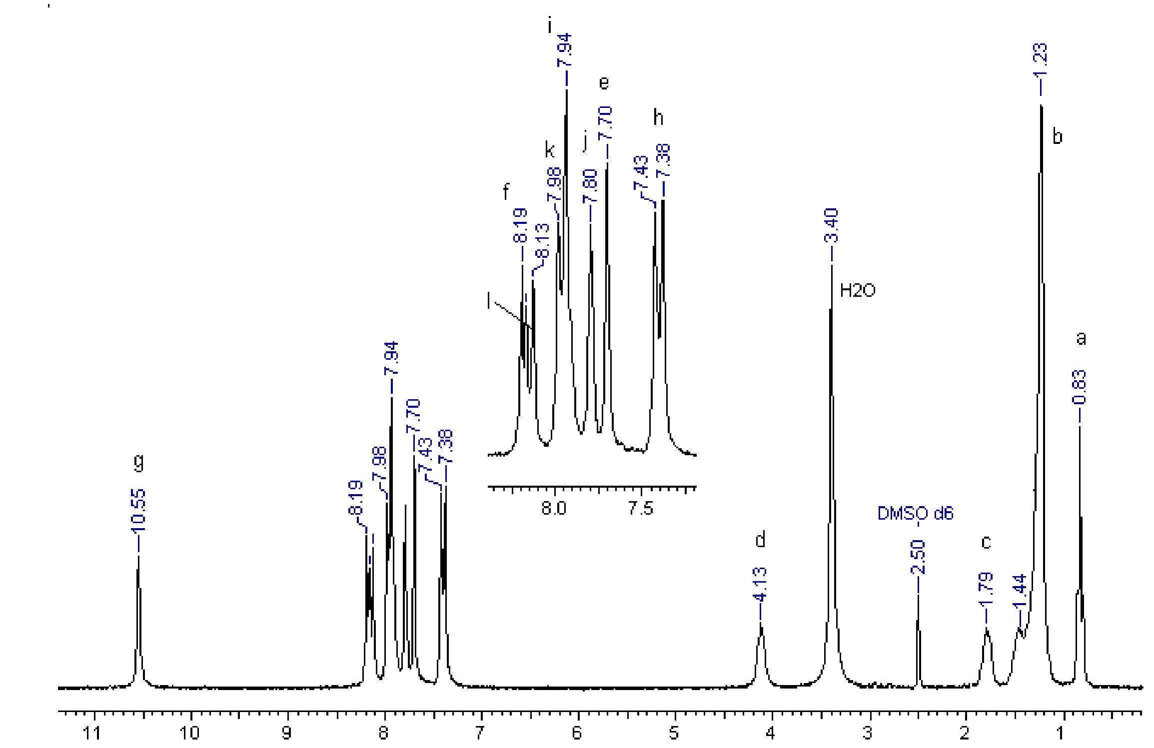


Figure 4c.2: ^{1}H-NMR spectrum of poly(amideimide) derived from 5-hexadecyloxy -N,N’-bis(4-aminophenyl)isophthalamide and FDA (PAI-8) in DMSO-d6 + $CDCl_3$.

4c.3.4 Properties of poly(amideimide)s

4c.3.4.1 Solubility of poly(amideimide)s

Poly(amideimide)s were tested for solubility at 3 wt % concentration in different solvents and the data is summarized in **Table 4c.2**.

Poly(amideimide)s derived from N, N'- bis(4-aminophenyl)isophthalamide and ODPA , PMDA and BPDA were insoluble in DMAc, DMF, NMP, DMSO while those based on FDA were soluble in these solvents. The solubility of poly(amideimide)s based on FDA could be attributed to the presence of hexafluoroisopropylidene group that separates the aromatic rings and hinders interaction between neighbouring molecules (ie., charge transfer complex formation).[17]

Poly(amideimide)s derived from 5-alkoxy-N,N'-bis (4-aminophenyl) isophthalamides and ODPA were soluble in DMAc at room temperature and upon heating in DMF, NMP and *meta*-cresol. This is a significant improvement compared to poly(amideimide) without pendent alkoxy groups and confirms that presence of pendent alkoxy chains imparted improved solubility.

Poly(amideimide)s derived from 5-alkoxy-N,N'-bis (4-aminophenyl) isophthalamides and PMDA were soluble upon heating in DMAc and NMP. Poly(amideimide)s did not precipitate after being dissolved in DMAc and NMP upon cooling.

Poly(amideimide)s derived from 5-alkoxy-N,N'-bis (4-aminophenyl) isophthalamides and BPDA were soluble upon heating in NMP while they were partially soluble on heating in DMAc and DMF.

Table 4c.2: Solubility data of poly(amideimide)s derived from 5-alkoxy-N,N'-bis (4-aminophenyl)isophthalamides and aromatic dianhydrides.

Poly(amide-imide)	Diamine	Dianhydride	DCM/ $CHCl_3$	DMAc	DMF	NMP	DMSO	m-cresol
PAI-1	-H	ODPA	–	–	–	–	–	–
PAI-2	$-OC_8H_{17}$	ODPA	–	++	+	+	±	+
PAI-3	$-OC_{12}H_{24}$	ODPA	–	++	+	+	±	+
PAI-4	$-OC_{16}H_{33}$	ODPA	–	++	+	+	±	+
PAI-5	-H	FDA	++	++	++	++	++	+
PAI-6	$-OC_8H_{17}$	FDA	++	++	++	++	++	++
PAI-7	$-OC_{12}H_{24}$	FDA	++	++	++	++	++	++
PAI-8	$-OC_{16}H_{33}$	FDA	++	++	++	++	++	++
PAI-9	-H	PMDA	–	–	–	–	–	–
PAI-10	$-OC_8H_{17}$	PMDA	–	+	±	+	–	±
PAI-11	$-OC_{12}H_{24}$	PMDA	–	+	±	+	–	±
PAI-12	$-OC_{16}H_{33}$	PMDA	–	+	±	+	–	±
PAI-13	-H	BPDA	–	–	–	–	–	–
PAI-14	$-OC_8H_{17}$	BPDA	–	±	±	+	–	±
PAI-15	$-OC_{12}H_{24}$	BPDA	–	±	±	+	–	±
PAI-16	$-OC_{16}H_{33}$	BPDA	–	±	±	+	–	±

++ : soluble at room temperature; + : soluble on heating; ± : partially soluble on heating;
- : insoluble.

4c.3.4.2 X-Ray diffraction studies

X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxy -N, N’-bis (4-aminophenyl)isophthalamides and ODPA, FDA, PMDA and BPDA are shown in **Figures 4c.3, 4c.4**., **4c.5** and **4c.6**, respectively. X-Ray diffractograms of poly(amideimide) derived from N, N’-bis (4-aminophenyl)isophthalamide and the above dianhydrides are also incorporated in the respective figures for comparison. The diffractograms indicate that in the wide angle region poly(amideimide)s have no sharp peaks but only very broad peak at about $2\ \theta = 15 - 22^o$ indicating an amorphous nature of these polymers. In case of poly(amideimide)s obtained from ODPA, an additional peak was observed at $2\theta \approx 11^o$.

The diffuse peak observed in the middle- angle region ($2\theta \approx 2 - 6^o$) in poly(amideimide)s containing 8 carbon atoms in alkoxy chain became sharper and shifted to lower angle with increasing side chain length. This indicates the presence of layered structure in poly(amideimide)s containing pendent alkoxy chains of 12 and 16 carbon atoms. Hence, it can be concluded that poly(amideimide)s containing C_{12} and C_{16} alkoxy side chains had a layered structure and the order of the layered structure improved with increasing side chain length.

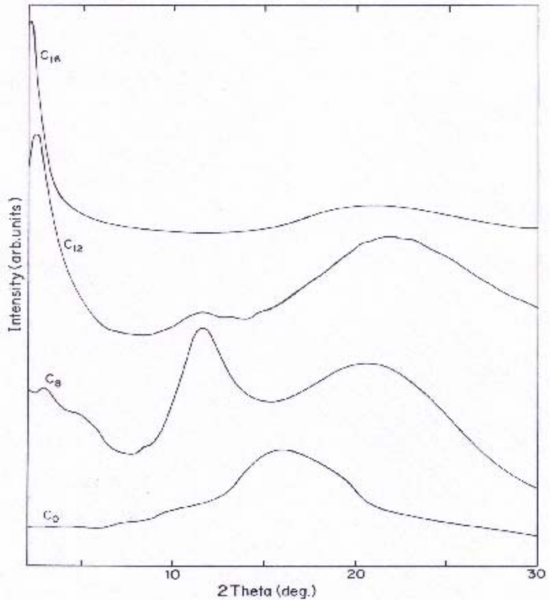


Figure 4c.3: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxy - N, N'-bis (4-aminophenyl)isophthalamides and ODPA (PAI-1 – PAI-4).

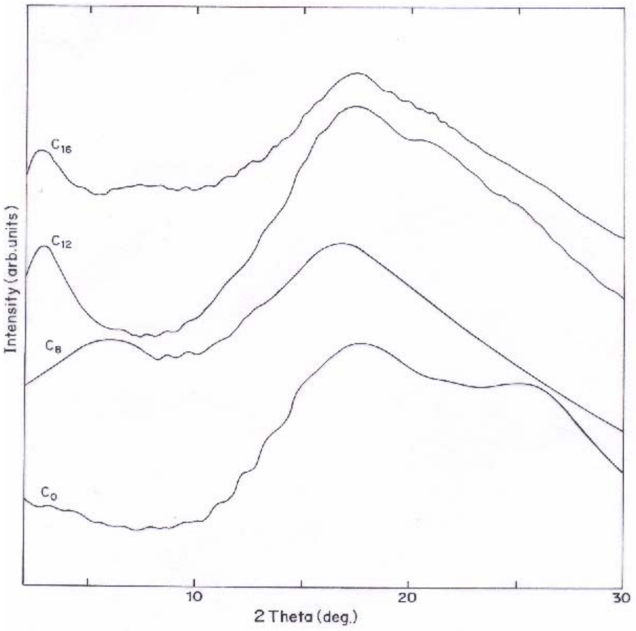


Figure 4c.4: X-ray diffractograms of poly(amideimide)s derived from 5-alkoxy - N, N'-bis (4-aminophenyl)isophthalamides and FDA (PAI-5-PAI-8).

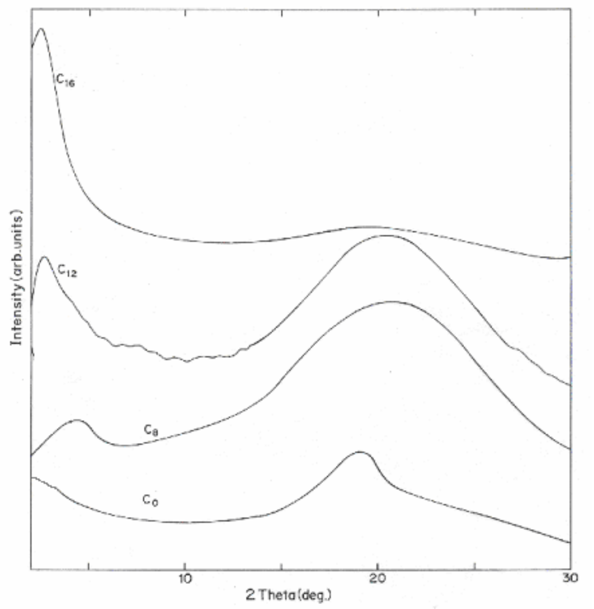


Figure 4c.5: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxy - N, N'-bis (4-aminophenyl)isophthalamides and PMDA (PAI-9-PAI-12).

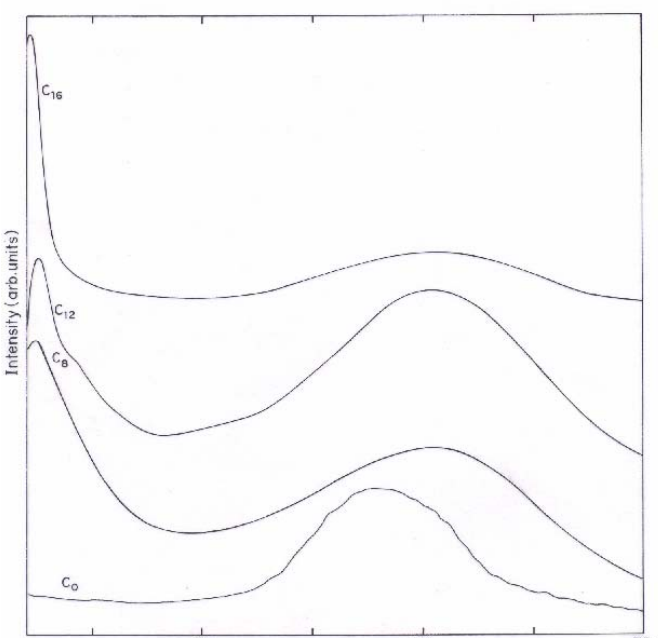


Figure 4c.6: X-Ray diffractograms of poly(amideimide)s derived from 5-alkoxy - N, N'-bis (4-aminophenyl)isophthalamides and BPDA (PAI-13-PAI-16).

4c.3.4.3 Thermal behaviour of poly(amideimide)s

Thermal stability of poly(amideimide)s was investigated by thermogravimetric analysis (TGA) at a heating rate of 10°C / minute in nitrogen. TG curves are shown in **Figure 4c.7, Figure 4c.8, Figure 4c.9 and Figure 4c.10**. Initial decomposition temperature (IDT) and temperature at 10% weight loss are given in **Table 4c.3**.

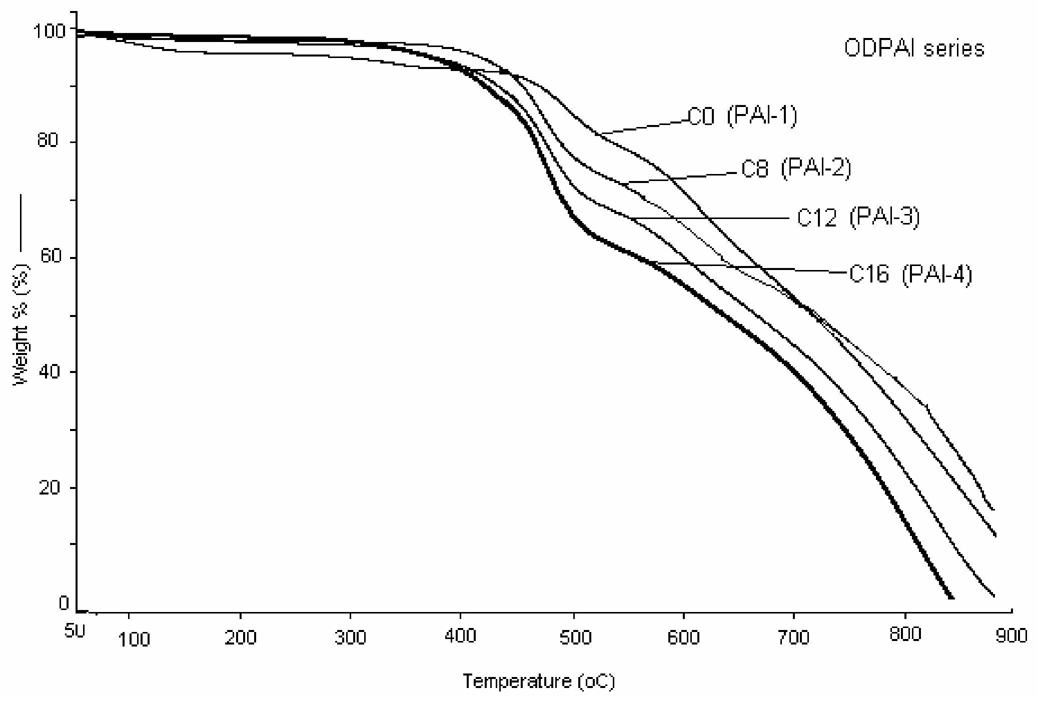


Figure 4c.7: TG curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and ODPA (PAI-1 – PAI-4).

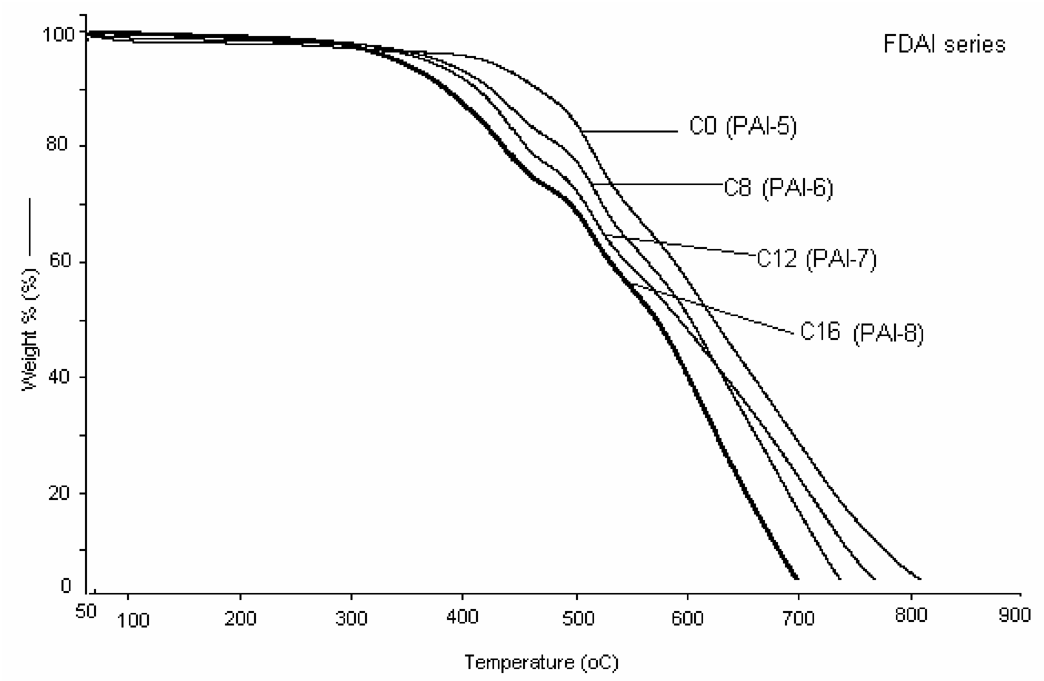


Figure 4c.8: TG curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and FDA (PAI-5-PAI-8).

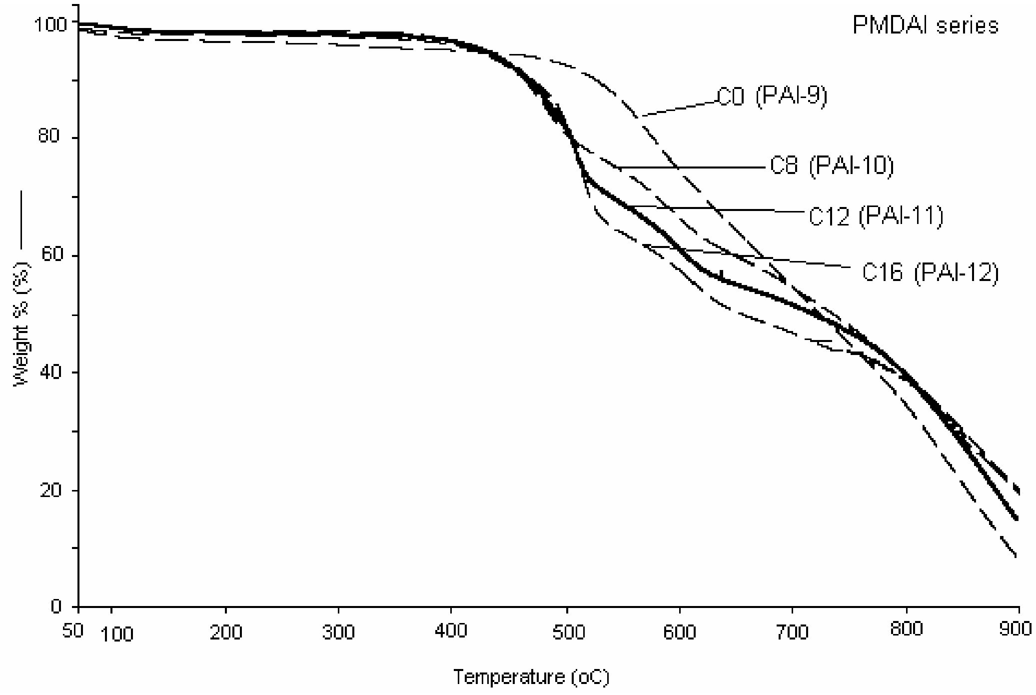


Figure 4c.9: TG curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and PMDA (PAI-9-PAI-12).

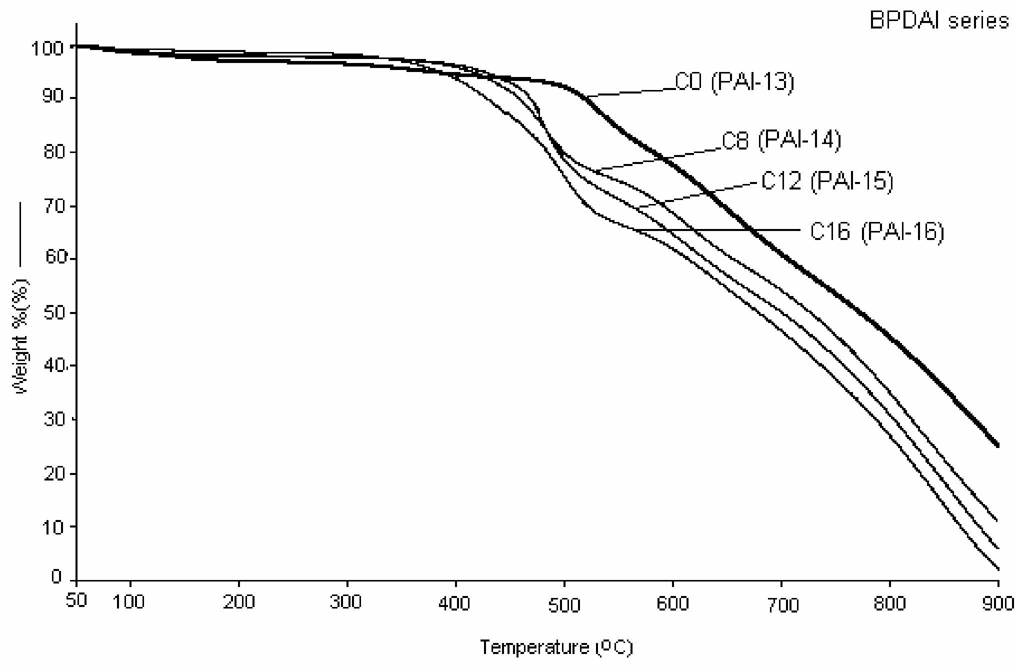


Figure 4c.10: TG curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and BPDA (PAI-13-PAI-16).

T_{10} values of poly(amideimide)s without alkoxy side chains were in the range 480 – 525°C, while that of poly(amideimide)s containing pendent alkoxy chains were in the range 415-465°C indicating lower thermal stability of poly(amideimide)s containing pendent alkoxy chains due to the presence of thermally labile alkoxy chains. The degradation of poly(amideimide)s occurred in a stepwise manner. The first degradation step could be attributed to the decomposition of the labile alkyl group with cleavage occurring at the alkyl - ether bond. The weight loss in first degradation step increased with increase in the side chain length as can be seen from TG curves (**Figure 4a.7, Figure 4a.8, Figure 4a.9 and Figure 4a.10**).

Table 4c.3: Thermal properties of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and aromatic dianhydrides.

Poly(amideimide)	Diamine (-R)	Dianhydride	Tg (^oC)	IDT (^oC)	T_{10}^a (^oC)
PAI-1	-H	ODPA	322	460	480
PAI-2	$-OC_8H_{17}$	ODPA	254	435	465
PAI-3	$-OC_{12}H_{25}$	ODPA	243	430	445
PAI-4	$-OC_{16}H_{33}$	ODPA	237	425	430
PAI-5	-H	FDA	344	500	510
PAI-6	$-OC_8H_{17}$	FDA	269	425	460
PAI-7	$-OC_{12}H_{25}$	FDA	254	425	450
PAI-8	$-OC_{16}H_{33}$	FDA	245	385	415
PAI-9	-H	PMDA	ND	515	525
PAI-10	$-OC_8H_{17}$	PMDA	321	440	460
PAI-11	$-OC_{12}H_{25}$	PMDA	312	440	450
PAI-12	$-OC_{16}H_{33}$	PMDA	309	445	450
PAI-13	-H	BPDA	314	500	515
PAI-14	$-OC_8H_{17}$	BPDA	285	435	450
PAI-15	$-OC_{12}H_{25}$	BPDA	268	449	465
PAI-16	$-OC_{16}H_{33}$	BPDA	266	390	430

IDT : Initial decomposition temperature
a : Temperature at 10 % weight loss
ND : Not detected.

A representative DTG curve for poly(amideimide) derived from 5-dodecyloxy -N, N'-bis (4-aminophenyl)isophthalamide and ODPA is shown in **Figure 4c.11**. DTG curve shows three distinct regions. Temperature at the first maximum degradation (T_{max1}) (480°C) presumably corresponds to the loss of alkyl group. Temperature at the second maximum degradation (T_{max2}) (610°C) corresponds to the thermal scission of the poly(amideimide) backbone. A third broad DTG profile was observed at around 840°C. This may be attributed to the volatilization of the low mass fractions resulting from the previous degradation processes.

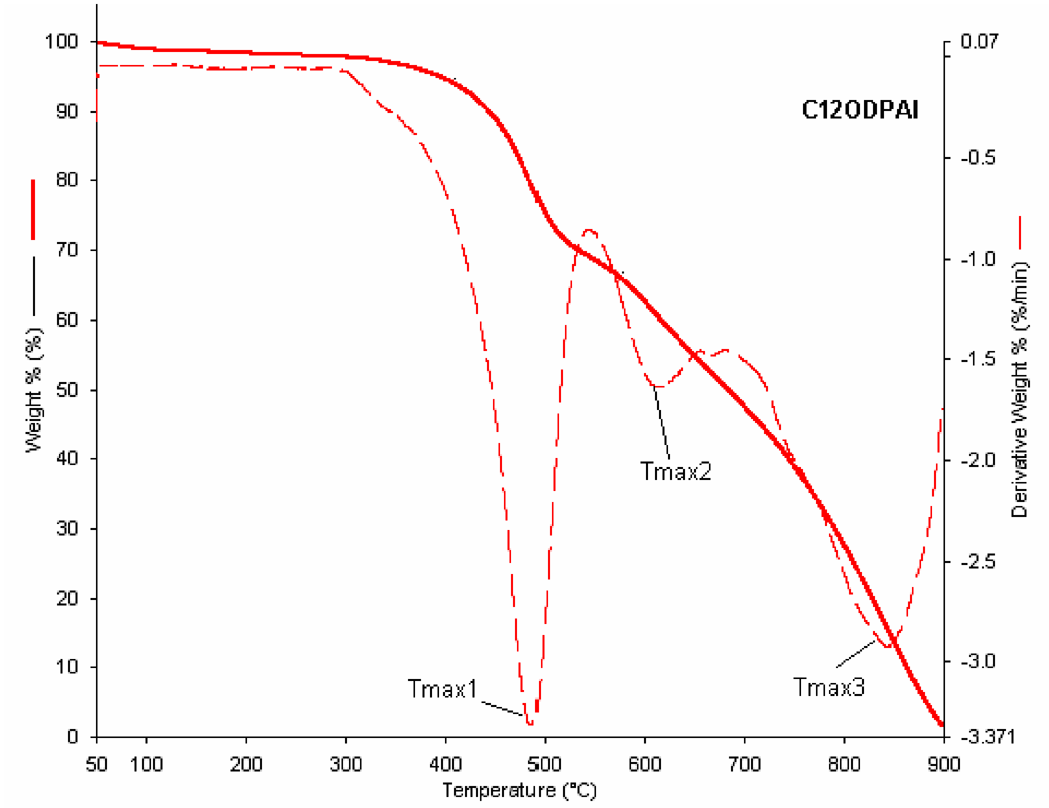


Figure 4c.11:A representative DTG and TG curves of PAI-3, derived from 5-dodecyloxy -N,N'-bis (4-aminophenyl)isophthalamide and ODPA.

DTG (T_{max1} = temperature at the first maximum degradation; T_{max2} = temperature at the second maximum degradation, T_{max3} = temperature at the broad third maximum degradation)

Glass transitions temperature of the poly(amideimide)s were evaluated by differential scanning calorimeter (DSC) at a heating rate of 40°C /minute. T_g values were obtained from second heating scans of polymer samples and the data is presented in **Table 4c.3**. DSC curves of poly(amideimide)s are shown in **Figures 4c.12 to 4c.15**. T_g values of poly(amideimide)s containing pendent alkoxy groups were in the range 237 -321°C while T_g values of analogous poly(amideimide)s derived from N,N-bis(4-aminophenyl)isophthalamide were in the range 314-344°C. A plot of T_g versus number of carbon atoms in alkoxy group of poly(amideimide)s is shown in **Figure 4c.16**. T_g values of the poly(amideimide)s containing pendent flexible alkoxy groups were lower than those of the reference poly(amideimide)s. This clearly results from the presence of the alkoxy side-chains which are responsible for the decrease in the intermolecular interaction which in turn results in decrease in T_g. T_g of the poly(amideimide)s derived from dianhydrides, ODPA, FDA, PMDA and BPDA, decreased in order: ODPA < FDA < BPDA < PMDA depending upon the rigidity of dianhydride.

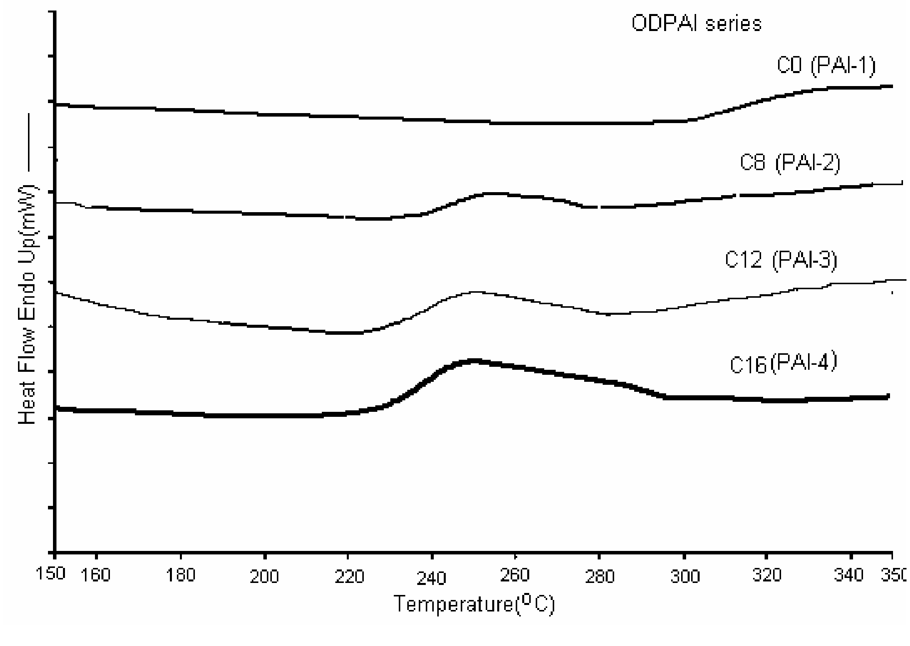


Figure 4c.12: DSC curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and ODPA (PAI-1 – PAI-4).

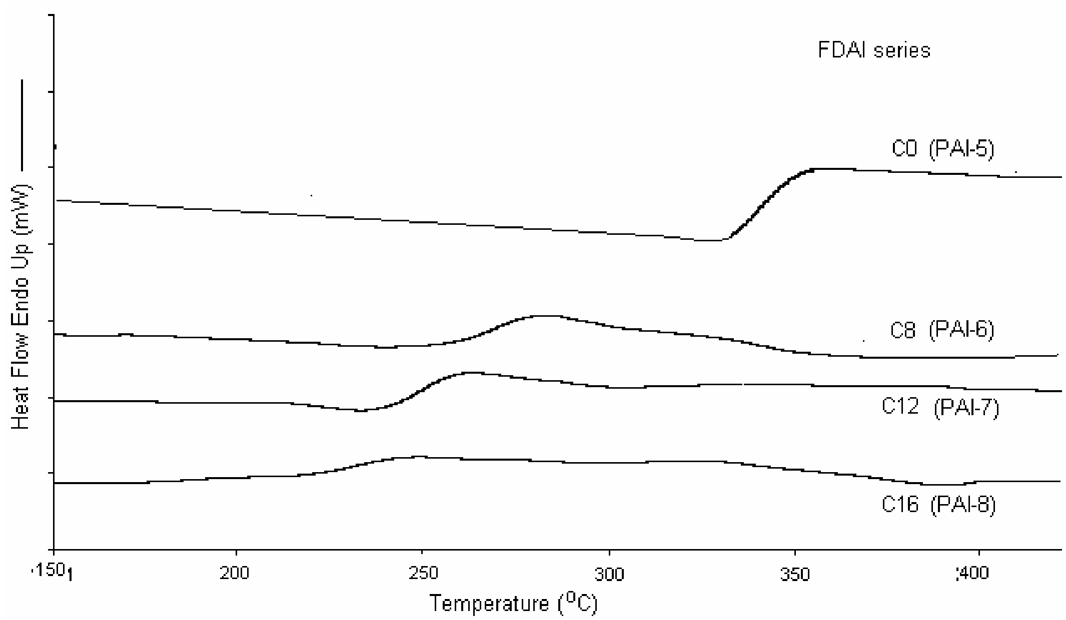


Figure 4c.13: DSC curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and FDA (PAI-5-PAI-8).

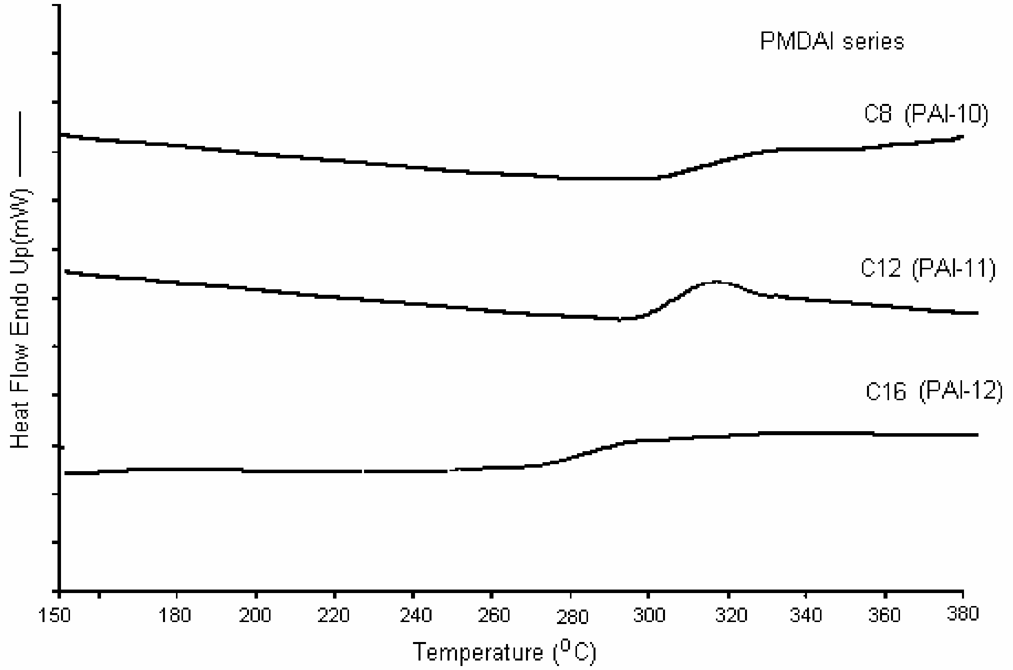


Figure 4c.14: DSC curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamides and PMDA (PAI-9-PAI-12).

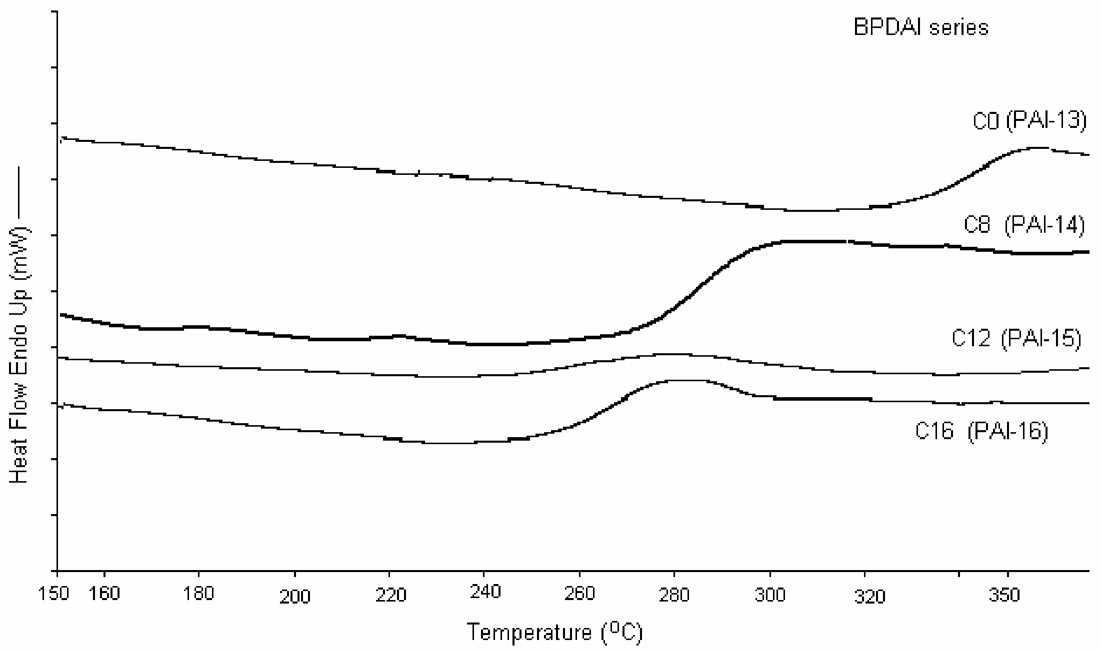


Figure 4c.15: DSC curves of poly(amideimide)s derived from 5-alkoxy -N, N'-bis (4-aminophenyl)isophthalamide and BPDA (PAI-13-PAI-16).

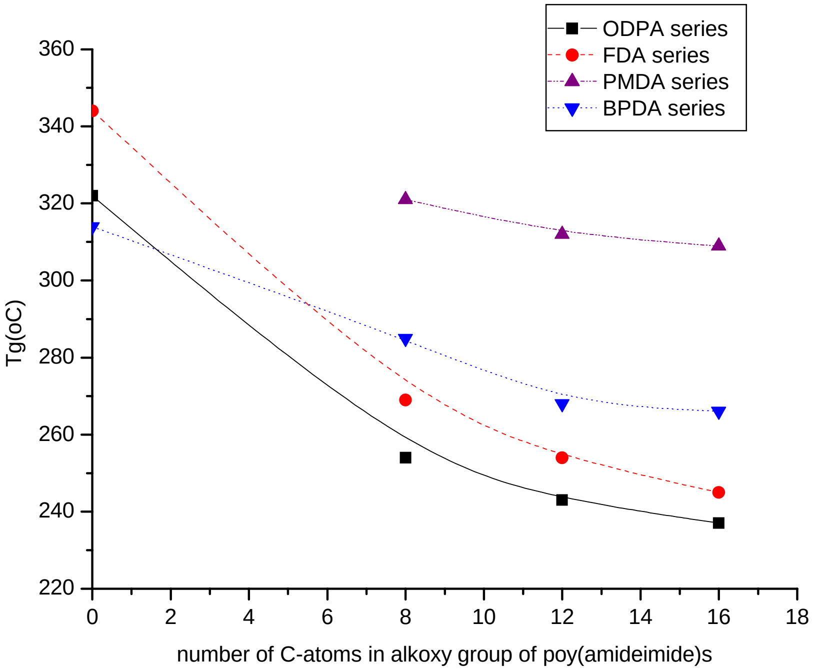


Figure 4c.16: Plot of Tg Vs number of carbon atoms in alkoxy group of poly(amideimide)s

4c.3.4.4 Optical transparency

UV-vis absorption spectra of poly(amideimide)s were recorded on UV-visible spectophotometer in the range 200 - 700 nm wavelength. UV-vis spectra of thin films (15-20 μm thickness) of poly(amideimide)s derived from 5-dodecyloxy-N,N'-bis(4-aminophenyl) isophthalamide and ODPA , FDA and PMDA are shown in **Figure 4c.17.** The cut off wavelength (absorption edge, λ_o) values and the percentage transmittance at 500 nm (the solar maximum) are presented in **Table 4c.4**. Poly(amideimide)s based on 5-dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide and FDA and ODPA produced fairly transparent and almost colorless films, whereas PMDA-derived poly(amideimide) gave pale yellow film. Poly(amideimide)s derived from FDA and ODPA showed transmittance of 87 % and 83 %, respectively at 500 nm whereas PMDA-derived poly(amideimide) showed 65 % transmission at 500 nm. The higher % transmittance values of PAI-7 and PAI-3 could be attributed to the presence of hexafluoroisopropylidene group of FDA and ether linkage of ODPA. Among three poly(amideimide)s, λ_o of PAI-7 is the maximum, PAI-3 revealed a shorter λ_o and PAI-11 showed shortest λ_o. The shortest λ_o and highest transmittance of FDA-derived poly(amideimide) than analogous poly(amideimide)s was attributed to the bulky and electron withdrawing $-CF_3$ group in FDA, resulting in decreased CTC formation between polymer chains through steric hindrance and the inductive effect.[18] The highest λ_o and lowest % transmittance in case of PMDA-derived poly(amideimide) among the three poly(amideimide)s is due to the electronic conjugation structure of PMDA.[19]

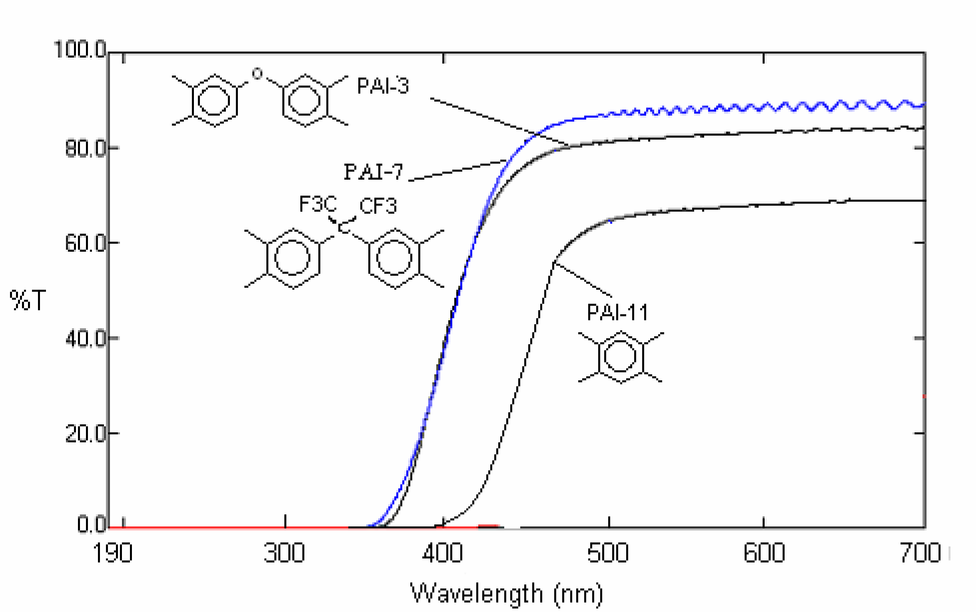


Figure 4c.17: UV-visible spectra of poly(amideimide) films derived from 5-dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide and ODPA, FDA and PMDA

Table 4c.4: Optical transparency data of poly(amideimide)s derived from 5-dodecyloxy-N,N'-bis(4-aminophenyl)isophthalamide and ODPA, FDA and PMDA.

Polymer code	Diamine (-R substituent)	Dianhydride	Cut-off wavelength, (nm), λ_o	% Transmittance (500 nm)
PAI-3	$-OC_{12}H_{25}$	ODPA	363	83
PAI-7	$-OC_{12}H_{25}$	FDA	353	87
PAI-11	$-OC_{12}H_{25}$	PMDA	400	65

4c.4 Application of poly(amideimide)s as liquid crystal alignment layers

To measure the alignment of LC molecules on rubbed polyimide surfaces, spin-coated poly(amideimide) films (~1000 A^o thick) of PAI-10 and PAI-12 were rubbed at four different rubbing densities and used to fabricate standard LC cells. The rubbing density was controlled from 60 to 240 by a cumulative number of rubbings with the rubbing depth fixed at 0.35 mm. The pretilt angles of the LC molecules on rubbed poly(amideimide) films at different rubbing densities measured by crystal rotation method are shown in **Table 4c.5**. PAI-10 and PAI-12 showed a pretilt angle of 12.0 and 17.5^o at a rubbing density of 60. These values are adequate for super-twisted nematic LCD devices.

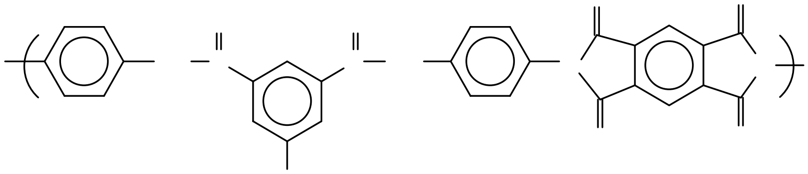
Table 4c.5: Pretilt angles of poly(amideimide)s containing pendent alkoxy chains at various rubbing densities (RD).

Poly(amideimide)	Pretilt angle (^{o})			
	RD= 60	RD=120	RD=180	RD=240
PAI-10 (C_8PMDA)	12.0	11.5	10.5	9.5
PAI-12 (C_{16}PMDA)	17.5	15.5	5.5	3.8

Although the exact mechanism of the LC alignment on the alkyl side-chain poly(amideimide)s is not yet clear, it is thought that two factors are dominant in determining the pretilt angle, ie., van der Waals interactions between LC molecules and alkyl side chains,[20-21] and the inclination angle of polymer backbones increased by alkyl side chains after rubbing.[22-23] As can be seen from results in **Table 4c.5**, pretilt angle increased as the side chain length increased from octyloxy (C_8) to hexadecyloxy (C_{16}). These results strongly suggest that the pretilt angles were mainly governed by van der Waals interactions between the LC molecules and the alkyl side chains.

Variation of the pretilt angles of LC molecules in contact with rubbed poly(amideimide) surfaces with increasing rubbing density is shown in **Figure 4c.18**. For poly(amideimide) PAI-10 (with 8 carbon chain length), the pretilt angle decreased marginally with increasing rubbing density from 60 – 240. However, for poly(amideimide) PAI-12 (with 16 carbon chain length), there was a appreciable decrease in the pretilt angle with increasing rubbing density from 120 to 180. The interpretation of results needs a number of additional experiments such as polar diagrams from optical phase retardation measurements. These studies are in progress.

Overall, poly(amideimide)s containing pendent alkoxy chains exhibited good properties suitable for applications in LCDs.



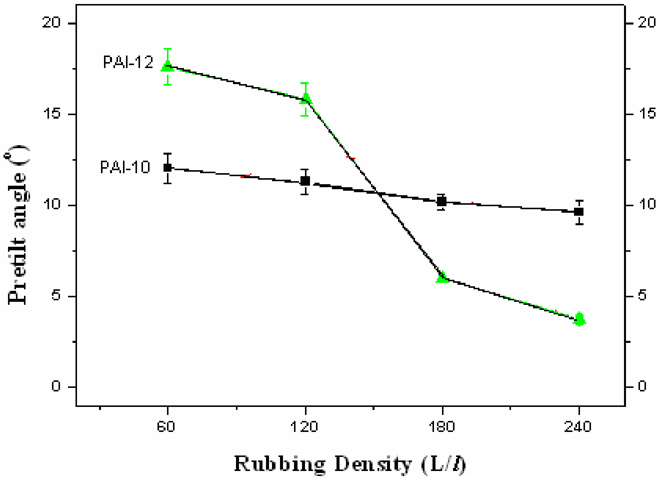


Figure 4c.18: Variations of the pretilt angles of LC molecules in contact with rubbed poly(amideimide) surfaces with increasing rubbing density.

4c.5 Conclusion

1. A new series of regularly alternating poly(amideimide)s bearing pendent flexible alkoxy groups with different chain lengths (C_8, C_{12}, C_{16}) was synthesized from diamines containing pre-formed amide linkage and aromatic dianhydrides such as ODPA, FDA, PMDA and BPDA by a two-step polycondensation in DMAc *via* poly(amicacid) route.
2. Poly(amideimide)s were of reasonably high molecular weights as indicated by their inherent viscosities values. Tough, transparent and flexible films could be cast from their solution in DMAc or NMP.
3. Poly(amideimide)s containing pendent flexible alkoxy groups showed considerably higher solubility than analogous unsubstituted polymers and dissolved in polar aprotic solvents upon heating or even at room temperature in some cases.
4. Thermal analysis showed that the attached side chains induced depression of T_g, and decreased the thermal stability of poly(amideimide)s.
5. X-Ray diffractograms revealed that poly(amideimide)s with longer side chains had layered structures in the solid state. As the side chain length increased from n-octyloxy to n-hexadecyloxy, the extent of layered structure formation increased.
6. Poly(amideimide)s containing pendent alkoxy chains exhibited a good rubbing processability and excellent performance in controlling of both alignment and pretilt of LC molecules in the LC cell. The pretilt of LC molecules was easily achieved in a wide angle range 3.8- 17.5^o, depending upon the rubbing density as well as the length of the alkoxy side chains. Overall, poly(amideimide)s synthesized in this study exhibited good properties suitable for applications in LCDs.

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Chapter 5a. Synthesis and Characterization of Polyesters Containing Pendent Flexible Alkoxy Groups

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5a.1 Introduction

Aromatic polyesters exhibit good thermal stability, solvent resistance and good mechanical properties and are therefore applied widely in the aviation, automobile and electronic industries.[1,2] However, most polyarylates encounter processing difficulties due to their high glass transition or melting temperatures coupled with insolubility in common organic solvents.[3,4] Several approaches have been adapted to improve the processability of aromatic polyesters,[5-21]

(i) Replacement of the conventional monomers with ones containing bulky pendent groups, or

(ii) Introduction of flexible linkages in the main chain or as pendent groups.

Recently, considerable efforts have been devoted to study the effect of incorporation of pendent flexible groups along the backbone of high performance polymers such as polyimides,[22] poly(amideimide)s,[23] polyamides[24] and polyesters.[20] The flexible side chains are thought to act as bound solvent for rigid polymer backbone. In some cases, polymers form novel layered mesophases.[20]

A Japanese patent[25] reports the synthesis of polyesters from 5-alkoxyisophthaloyl dichlorides and bisphenols. However, no data on polymer characterization was available.

The objective of the present work was to synthesize a series of polyesters from 5-alkoxyisophthaloyl dichlorides with different alkoxy side chains (C_1, C_4, C_8, C_{12}, C_{16}) and bisphenols, viz., bisphenol-A (BPA) and 4,4'-(hexafluoroisopropylidene) diphenol (HFBPA), and to investigate the effect of introduction of pendent alkoxy chains on the properties of aromatic polyesters.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Kinetics of thermal degradation of polyesters was studied by TGA.

5a.2 Experimental

5a.2.1 Materials

5-Alkoxyisopthaloyl dichlorides were synthesized as described in **Chapter 3, Section 3.3.5** and were purified by distillation under reduced pressure prior to use in polymerization reaction. Bisphenol-A (BPA) and 4,4'-(hexafluoroisopropylidene)diphenol (HFBPA) (Aldrich) were sublimed under reduced pressure prior to use. Dichloromethane (DCM) was dried over calcium hydride and then distilled. Benzyltriethyl ammonium chloride (BTEAC) (Aldrich) was used as received.

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5a.2.2 Measurements

Inherent viscosity of polyesters was measured with 0.5 %(w/v) solution of polyester in $CHCl_3$ at 30 ± 0.1 ^oC using an Ubbelhode suspended level viscometer.

Molecular weight of polyesters were measured on Thermofinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5 ^oA to 50 ^oA), Detector - RI, room temperature. Polystyrene was used as the calibration standard. The polyester sample (5 mg) was dissolved in 5 ml chloroform and filtered through 0.2 μ SS-filter.

FTIR spectra were recorded using polyester films on a Perkin-Elmer 883 spectrophotometer.

^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker 200 or 500 MHz spectrophotometer using $CDCl_3$ as a solvent.

Thermogravimetric analysis was performed on Mettler Toledo STAR^e system at a heating rate of 10°C / minute under nitrogen atmosphere. Sample weight taken was ~10 mg.

DSC was carried out on Perkin-Elmer DSC-7, at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. The polymer was dissolved in chloroform and filtered on a glass petri dish; the solvent was evaporated slowly at 40°C in a closed oven, and the semi-dried films were dried at 50°C for 5 days under reduced pressure to obtain films for XRD studies.

5a.2.3 Synthesis of polyesters

A representative procedure for synthesis of polyesters is described below.

Into a 100 ml two-necked round bottom flask equipped with a high-speed mechanical stirrer and an additional funnel, BPA (1.14 g, 5 mmol) dissolved in 1M NaOH (10.2 ml) was charged. Thereafter, BTEAC (30 mg) was added to the reaction mixture. A solution of 5-butyloxyisophthaloyl dichloride (1.375 g, 5 mmol) dissolved in dichloromethane (12 ml) was added in one lot to the reaction mixture which was cooled to 10°C and the mixture was stirred vigorously at 2000 rpm at 10-15°C for 1 h. The reaction mixture was poured into hot water; the precipitated polymer was filtered and washed several times with water. The polymer was dissolved in dichloromethane and reprecipitated in methanol:water (1:1, v/v) mixture. Polymer was filtered, washed with methanol and dried at 80°C under reduced pressure for two days.

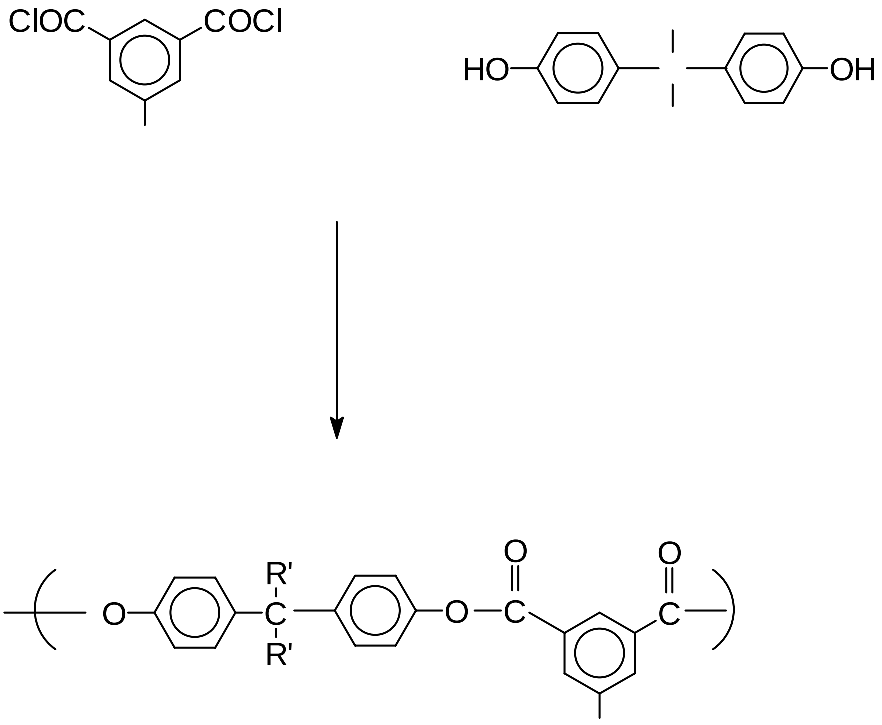
A similar procedure was followed for the synthesis of other polyesters.

5a.3 Results and Discussion

5a.3.1 Synthesis of polyesters from 5-alkoxyisophthaloyl dichlorides and diphenols.

Scheme 5a.1 illustrates the synthesis of polyesters from 5-alkoxyisophthaloyl dichlorides and bisphenols.

Phase transfer-catalysed two phase polycondensation of 5-alkoxyisophthaloyl dichlorides and bisphenols *viz.* BPA and HFBPA in the presence of BTEAC as a phase transfer catalyst was used to synthesize a series of polyesters. As reference polymers that do not have pendent alkoxy chains, two polyesters were synthesized by interfacial polycondensation of isophthaloyl dichloride and BPA and HFBPA. The results of polymerizations are summarized in **Table 5a.1**.



Scheme 5a.1: Synthesis of aromatic polyesters from 5-alkoxyisophthaloyl dichlorides and diphenols.

With the exception of polyester derived from 5-methoxyisophthaloyl dichloride and BPA (PES-3) whose inherent viscosity was 0.47 dl/g, inherent viscosities of the polyesters were in the range 0.85 - 3.0 dl/g indicating formation of reasonably high molecular weight polymers.

The results of GPC measurements on polyesters PES-4 to PES-11 are presented in **Table 5a.2.** Number average molecular weights (Mn) were in the range 1,01,050 to 3,99,400 with polydispersity in the range 1.9-2.6. GPC data indicates the formation of reasonably high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

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

Table 5a.1: Preparation of polyesters from 5-alkoxyisophthaloyl dichlorides and diphenols.

Polyester	Diacid chloride (-R substituent)	Diphenol	Yield (%)	η_{inh} (dL/g)[a]
PES-1.	-H	BPA	95	0.85[b]
PES-2	-H	HFBPA	95	0.90
PES -3	$-OCH_3$	BPA	96	0.47[b]
PES -4	$-OC_4H_9$	BPA	94	1.79
PES -5	$-OC_4H_9$	HFBPA	98	1.92
PES -6	$-OC_8H_{17}$	BPA	97	2.35
PES -7	$-OC_8H_{17}$	HFBPA	98	1.67
PES -8	$-OC_{12}H_{25}$	BPA	98	1.92
PES -9	$-OC_{12}H_{25}$	HFBPA	96	1.72
PES -10	$-OC_{16}H_{33}$	BPA	98	1.59
PES -11	$-OC_{16}H_{33}$	HFBPA	97	3.0

a: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in chloroform at 30 ± 0.1°C.

b: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in a mixture of phenol:TCE (60:40, v/v) at 30 ± 0.1°C.

Table 5a.2: GPC data of polyesters derived from 5-alkoxyisophthaloyl dichlorides and diphenols.

Polyester	**Diacid chloride (-R)**	**Diphenol**	**Molecular weight**[a]		**Polydispersity M_w/M_n**
			M_n	**M_w**	
PES-4	$-OC_4H_9$	BPA	1,03,480	2,64,860	2.6
PES-5	$-OC_4H_9$	HFBPA	1,35,780	3,28,400	2.4
PES-6	$-OC_8H_{17}$	BPA	2,04,150	4,52,290	2.2
PES-7	$-OC_8H_{17}$	HFBPA	1,09,420	2,35,250	2.2
PES-8	$-OC_{12}H_{25}$	BPA	1,54,000	3,35,000	2.2
PES-9	$-OC_{12}H_{25}$	HFBPA	1,01,050	2,60,100	2.6
PES-10	$-OC_{16}H_{33}$	BPA	1,46,040	3,06,680	2.1
PES-11	$-OC_{16}H_{33}$	HFBPA	3,99,400	7,45,700	1.9

a : measured by GPC in chloroform, polystyrene was used as a calibration standard.

5a.3.2 FT-IR spectroscopic analysis

The formation of polyesters was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. FTIR spectra of polyesters derived from 5-dodecyloxyisophthaloyl dichloride and BPA, and HFBPA are reproduced in **Figure 5a.1** and **5a.2**, respectively. Ester carbonyl band in BPA-derived polyesters was observed at 1733 cm^{-1} while that in HFBPA-derived polyesters was observed at 1740 cm^{-1}.

The stretching frequency of the carbonyl bond in HFBPA-based polyester was at a higher wave number than that of carbonyl stretching frequency of BPA-based polyester. The observed shift arises from a decrease in electron density at the carbonyl carbon due to the electron withdrawing effect of hexafluoroisopropylidene group which results in a greater partial positive charge and a stronger C - O bond (and greater vibrational force constant).

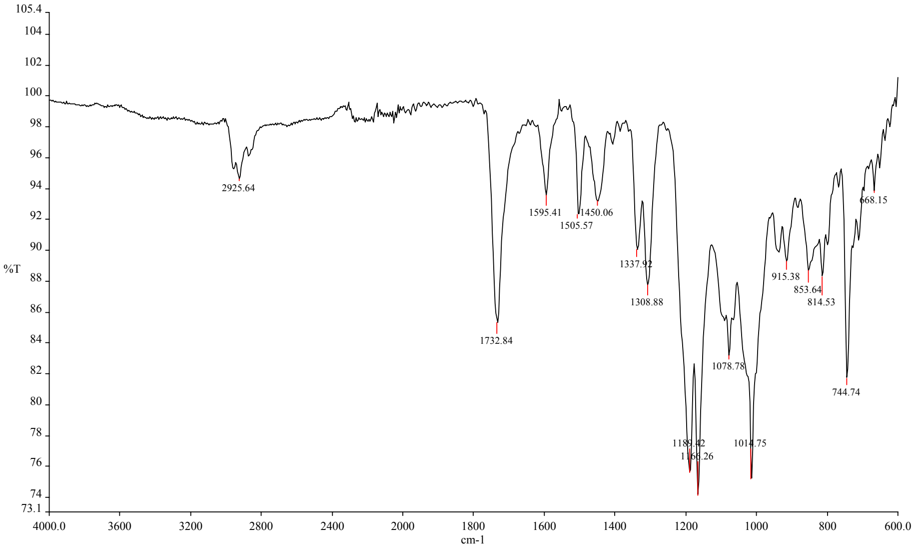


Figure 5a.1: IR spectrum (Film) of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA.

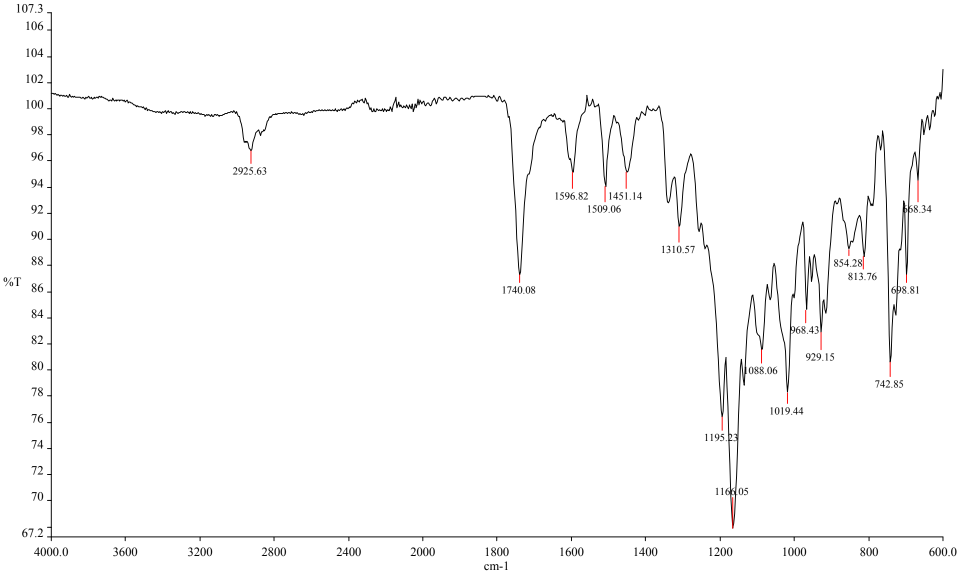


Figure 5a.2: IR spectrum (Film) of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA.

5a.3.3 NMR spectroscopic analysis

Representative NMR spectra of polyesters derived from 5-dodecyloxy-isophthaloyl dichloride and BPA, and HFBPA are reproduced in **Figure 5a.3** and **5a.4**, respectively.

In the ^{1}H-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA (**Figure 5a.3**), the singlet observed at 8.59 δ, ppm was assigned to proton flanked by ester carbonyl groups. Aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.95 δ, ppm. The two doublets at 7.34 and 7.16 δ, ppm were assigned, respectively, to the aromatic protons *meta* and *ortho* to the isopropylidene linkage. The methylene protons attached to the ether linkage appeared as a triplet at 4.10 δ, ppm. The chemical shift due to *gem*-dimethyl group protons appeared at 1.73 δ, ppm. The methylene protons β to the ether oxygen appeared as a multiplet over the region 1.50 to 1.90 δ, ppm and merged with the peak due to the protons of the *gem*-dimethyl group. The other methylene protons appeared as a multiplet over the range 1.05 to 1.50 δ, ppm. The methyl group protons exhibited a triplet at 0.88 δ, ppm.

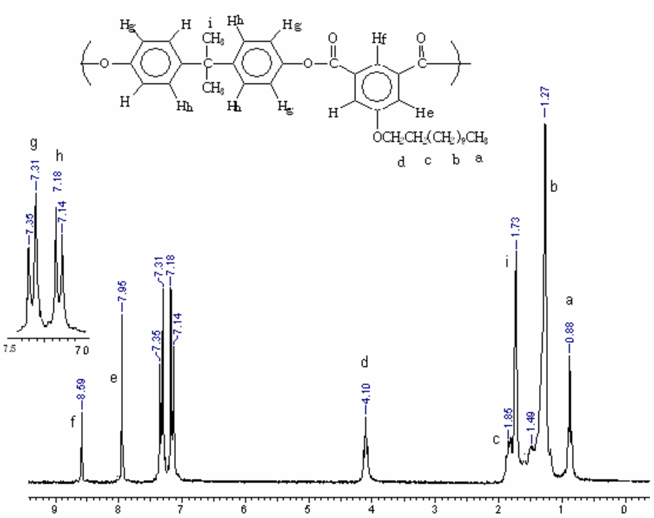


Figure 5a.3: ^{1}H-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA (PES-8) in $CDCl_3$.

In the ^{1}H-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA (**Figure 5a.4**), the singlet observed at 8.62 δ, ppm was assigned to proton flanked by ester carbonyl groups. Aromatic protons *ortho* to the ether linkage appeared as a singlet at 7.99 δ, ppm. The two doublets at 7.55 and 7.34 δ, ppm were assigned, respectively, to the aromatic protons *ortho* and *meta* to the hexafluoroisopropylidene linkage. The downfield chemical shift of aromatic protons *ortho* to hexafluoroisopropylidene linkage is due to the strongly electron withdrawing character of 6F-moiety. The methylene protons attached to the ether linkage appeared as a triplet at 4.14 δ, ppm. The methylene protons β to the ether oxygen appeared as a multiplet over the region 1.70 to 1.95 δ, ppm. The other methylene protons appeared as a multiplet over the range 1.10 to 1.75 δ, ppm. The methyl group protons exhibited a triplet at 0.90 δ, ppm.

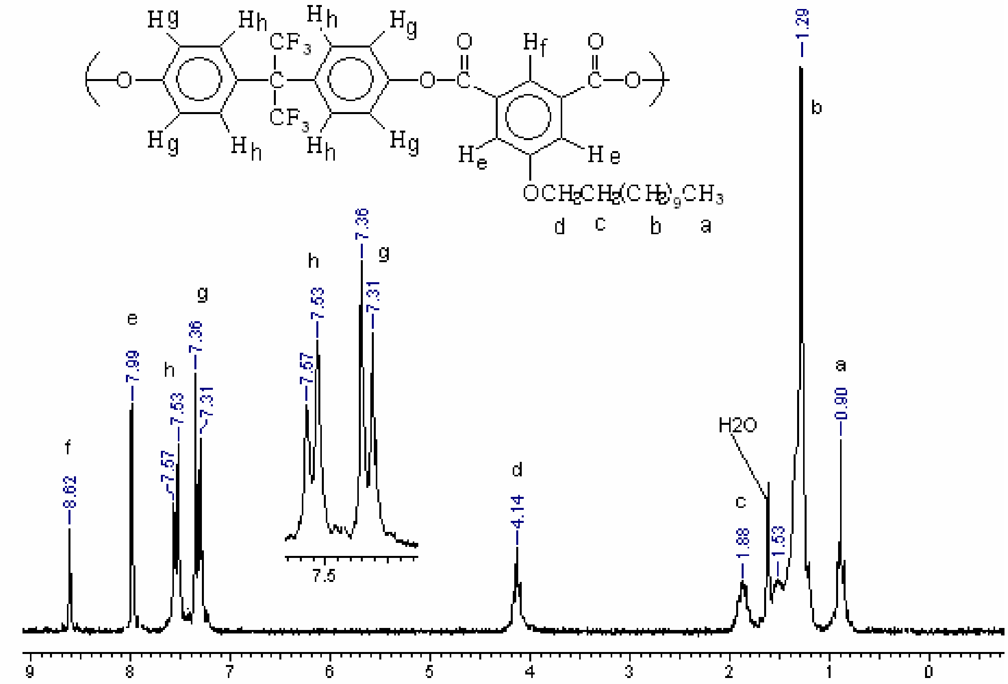
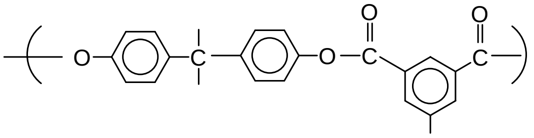


Figure 5a.4: ^{1}H-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA(PES-9) in $CDCl_3$.

Representative ^{13}C-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA is reproduced in **Figure 5a.5**, along with the assignment of the carbon atoms. The assignments of carbon atoms were confirmed by DEPT NMR spectrum (**Figure 5a.6**).



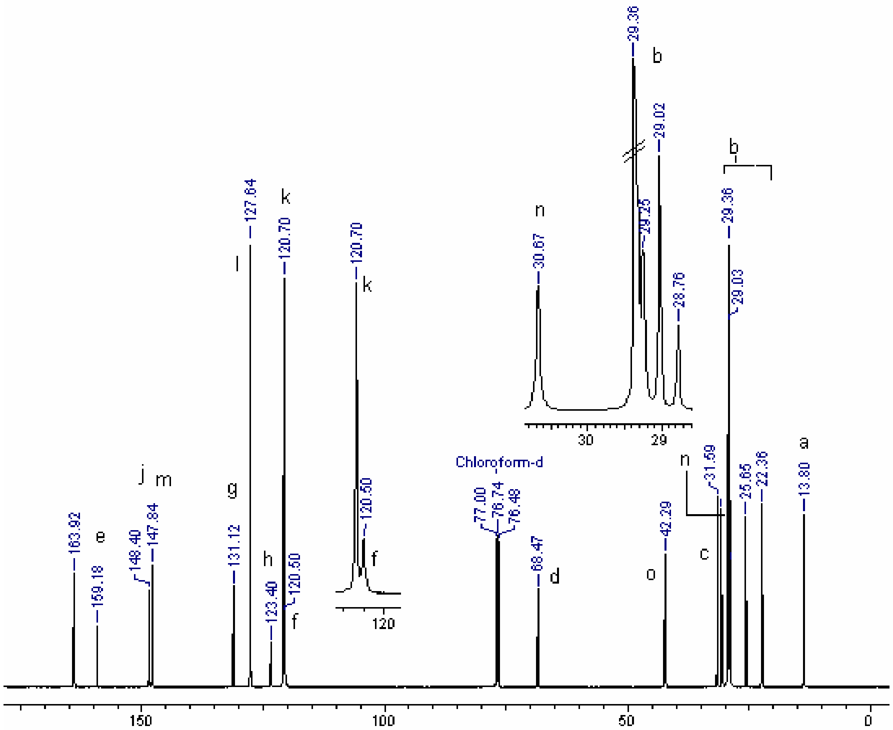


Figure 5a.5: ^{13}C-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA (PES-8) in $CDCl_3$.

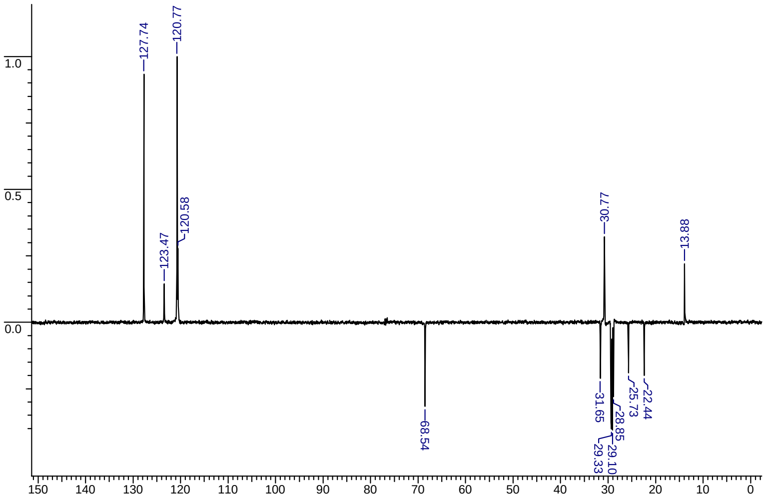


Figure 5a.6: ^{13}C-NMR spectrum (DEPT) of polyester derived from 5-dodecyloxyisophthaloyl dichloride and BPA (PES-8) in $CDCl_3$.

Representative ^{13}C-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA is reproduced in **Figure 5a.7**, along with the assignment of the carbon atoms. The quartet centered at 123.76 δ, ppm was assigned to hexafluoroisopropylidene carbon and is because of the heteronuclear ^{13}C-^{19}F coupling. The assignments of carbon atoms were confirmed by DEPT NMR spectrum (**Figure 5a.8**).

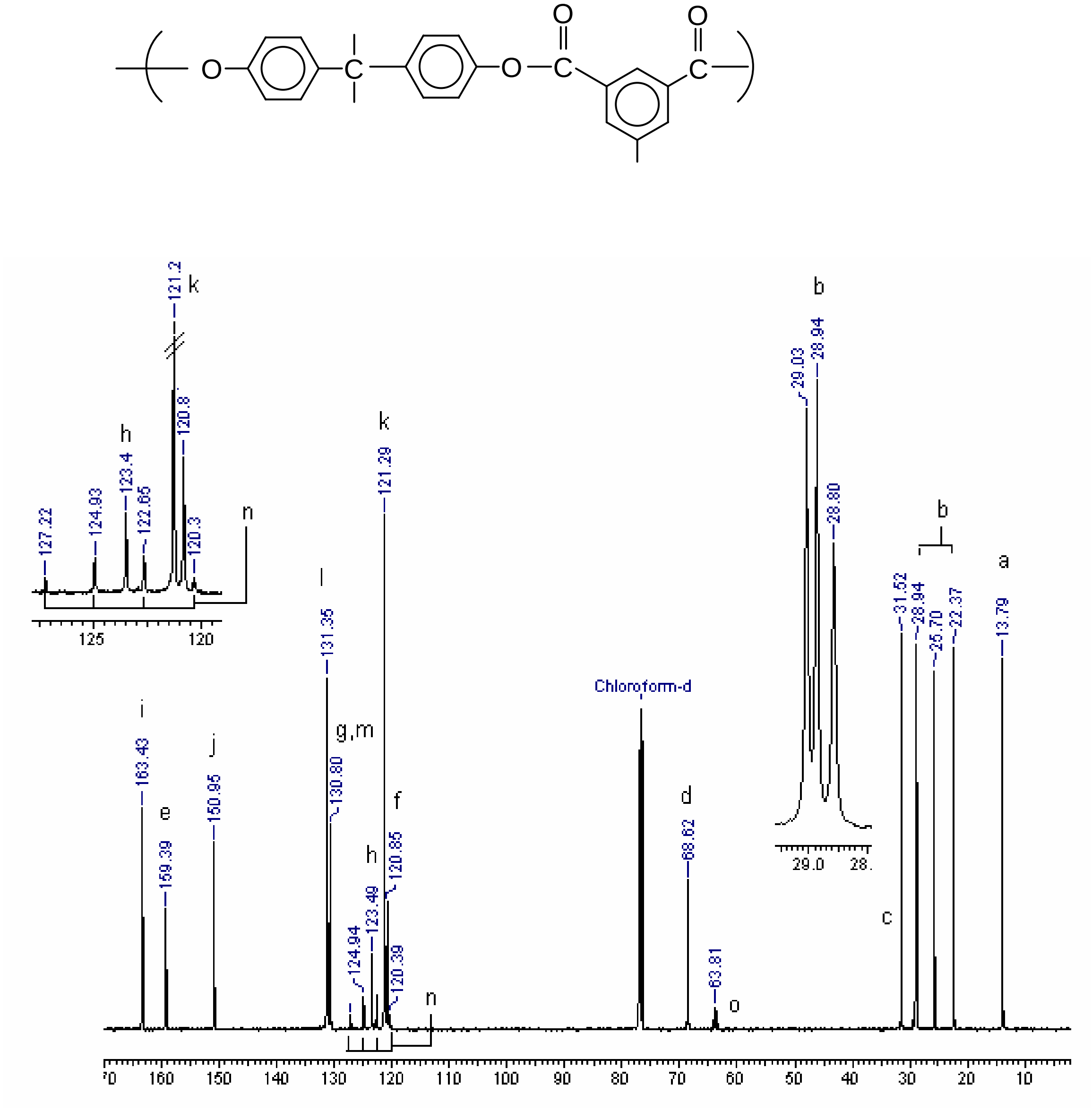


Figure 5a.7: ^{13}C-NMR spectrum of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA (PES-9) in CDCl$_3$.

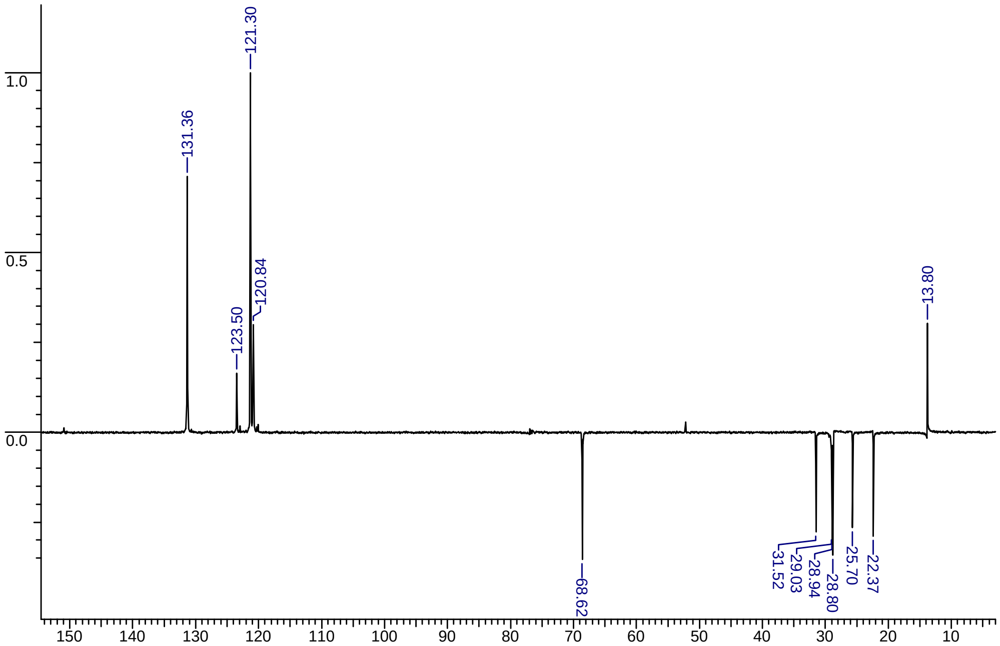


Figure 5a.8: ^{13}C-NMR spectrum (DEPT) of polyester derived from 5-dodecyloxyisophthaloyl dichloride and HFBPA (PES-9) in $CDCl_3$.

5a.3.4 Properties of polyesters

5a.3.4.1 Solubility of polyesters

Solubility of polyesters was tested in various organic solvents at a 3 wt % (w/v) concentration and the data is summarized in **Table 5a.3.** HFBPA-based polyesters were soluble in all the organic solvents tested. Except for polyesters derived from isophthaloyl dichloride and 5-methoxyisophthaloyl dichloride, polyesters derived from 5-alkoxyisophthaloyl dichloride and BPA were found to be soluble in organic solvents like dichloromethane, $CHCl_3$, TCE, DMAc, NMP and pyridine at room temperature. Polyesters derived from isophthaloyl dichloride and 5-methoxyisophthaloyl dichloride were soluble in TCE upon heating. The solubility data indicated that pendent methoxy group was not large enough to sterically hinder intermolecular interactions sufficiently to impart solubility in common organic solvents such as dichloromethane and chloroform. Incorporation of butyloxy groups imparted solubility to the polyester in common organic solvents such as dichloromethane and $CHCl_3$. Butyloxy group decreases intermolecular interactions and also provides additional ‘handles’ for interaction with solvents.

Table 5a.3: Solubility data of polyesters derived from 5-alkoxyisophthaloyl dichlorides and diphenols.

Polyester	**Diacid chloride (-R)**	**Diphenol**	**DCM**	**$CHCl_3$**	**TCE**	**DMF**	**DMAC**	**NMP**	**Pyridine**
PES-1	-H	BPA	–	–	+	–	–	–	–
PES-2	-H	HFBPA	++	++	++	++	++	++	++
PES-3	$-OCH_3$	BPA	–	–	+	–	–	–	–
PES-4	$-OC_4H_9$	BPA	++	++	++	+	++	++	++
PES-5	$-OC_4H_9$	HFBPA	++	++	++	++	++	++	++
PES-6	$-OC_8H_{17}$	BPA	++	++	++	+	++	++	++
PES-7	$-OC_8H_{17}$	HFBPA	++	++	++	++	++	++	++
PES-8	$-OC_{12}H_{25}$	BPA	++	++	++	+	++	++	++
PES-9	$-OC_{12}H_{25}$	HFBPA	++	++	++	++	++	++	++
PE-10	$-OC_{16}H_{33}$	BPA	++	++	++	+	++	++	++
PE-11	$-OC_{16}H_{33}$	HFBPA	++	++	++	++	++	++	++

++: soluble at r.t; +: soluble on heating; –: insoluble

5a.3.4.2 X-Ray diffraction studies

X-ray diffractograms of polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA and HFBPA are shown in **Figures 5a.9 and 5a.10,** respectively. X-ray diffractograms of polyesters derived from BPA and HFBPA showed broad peaks at about $2\ \theta = 17\text{-}20^{o}$ in the wide angle region. These peaks are so broad that they may be considered as amorphous halos.

In case of BPA series, polyesters containing pendent alkoxy chain of 4, 8 and 12 carbon atoms showed diffuse peaks in the middle-angle region ($2\theta = 5\text{-}7^{o}$) in addition to the diffuse peak at $2\theta = 17\text{-}20^{o}$. The peak in the middle-angle region shifted to $2\theta = 3^{o}$ with increased intensity in case of polyester derived from 5-hexadecyloxyisophthaloyl dichloride. This peak is characteristic of a typical layered structures resulting from ordered packing of the aliphatic side chains.

In case of HFBPA series, polyesters containing pendent alkoxy chain of 4 and 8 carbon atoms showed two diffuse peaks, one in the middle-angle region ($2\theta = 5^{o}$) and two peaks in the wide-angle region ($2\theta = 12^{o}$ and $17\text{-}20^{o}$). The peak in the middle–angle region shifted to $2\theta \sim 3^{o}$ with increased intensity for polyesters containing pendent alkoxy chain with 12 and 16 carbon atoms. This peak is characteristic of a typical layered structure resulting from ordered packing of the aliphatic side chains. These layered structures develop more tightly with increasing side chain length which may be attributed to the fact that the longer aliphatic side chains facilitate the better packing of the polymer chains.

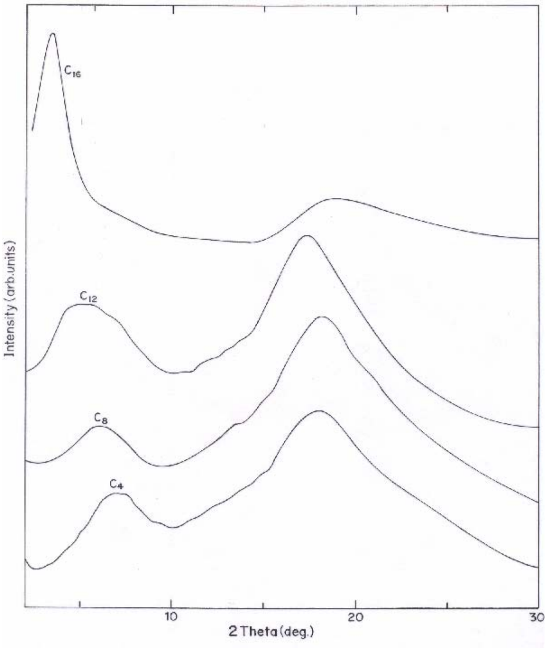


Figure 5a.9: X-Ray diffractograms of polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA (PES-4, 6, 8, 10).

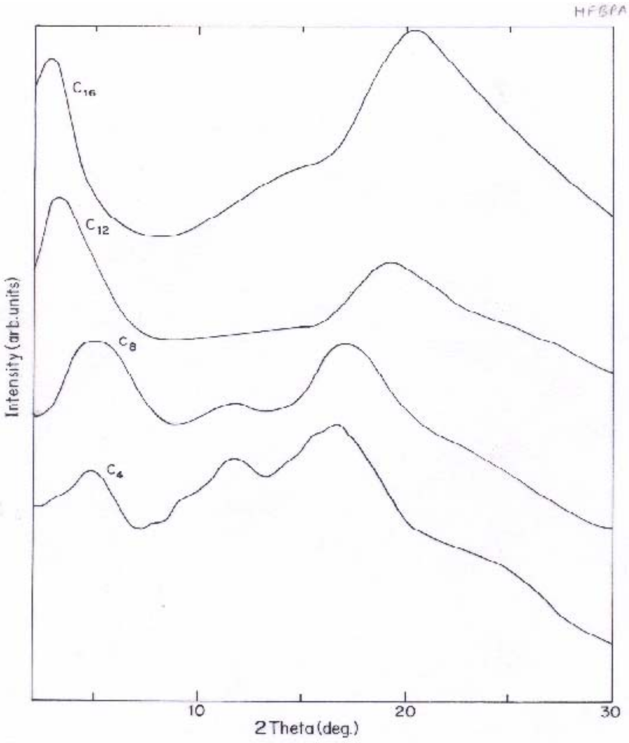


Figure 5a.10: X-Ray diffractograms of polyesters derived from 5-alkoxyisophthaloyl dichloride and HFBPA (PES-5, 7, 9, 11).

5a.3.4.3 Thermal behaviour of polyesters

In the present study, thermal stability of the polyesters was determined by thermogravimetric analysis (TGA) at a heating rate of 10°C /minute under nitrogen. The initial decomposition temperature (IDT) and the decomposition temperature at 10% weight loss (T_{10}) for polyesters are given in **Table 5a.4**. IDT for polyester derived from isophthaloyl dichloride and BPA was 475°C and that for polyester derived from isophthaloyl dichloride and HFBPA was 460°C. An examination of the data on polyesters containing pendent alkoxy chains showed that IDT varied in the range 380-420°C. This indicates that there was a decrease in the thermal stability of polyesters containing pendent alkoxy chains. It was observed from **Figure 5a.11 and Figure 5a.12** that there is a single step degradation in the polyesters derived from BPA, whereas two step degradation was observed in the polyesters derived from HFBPA.

Table 5a.4: Thermal properties of polyesters derived from 5-alkoxyisophthaloyl dichlorides and diphenols.

Polyester	**Diacid chloride (-R substituent)**	**Diphenol**	**IDT (^oC)**	**T_{10} (^oC)**	**T_{max1} (^oC)**	**T_{max2} (^oC)**	**T_g (^oC)**
PES-1	-H	BPA	475	490		-	190
PES-2	-H	HFBPA	460	470	530	-	207
PES-4	$-OC_4H_9$	BPA	420	440	470	-	152
PES-5	$-OC_4H_9$	HFBPA	410	440	460	540	167
PES-6	$-OC_8H_{17}$	BPA	420	425	465	-	94
PES-7	$-OC_8H_{17}$	HFBPA	410	425	455	535	101
PES-8	$-OC_{12}H_{25}$	BPA	405	425	470	-	68
PES-9	$-OC_{12}H_{25}$	HFBPA	400	420	445	530	79
PES-10	$-OC_{16}H_{33}$	BPA	405	420	470	-	44
PES-11	$-OC_{16}H_{33}$	HFBPA	380	400	460	530	60

IDT : initial decomposition temperature
T_{10} : Temperature at 10 % weight loss
T_{max1} and T_{max2}: Temperature at maximum degradation for first and second step, respectively from DTG.

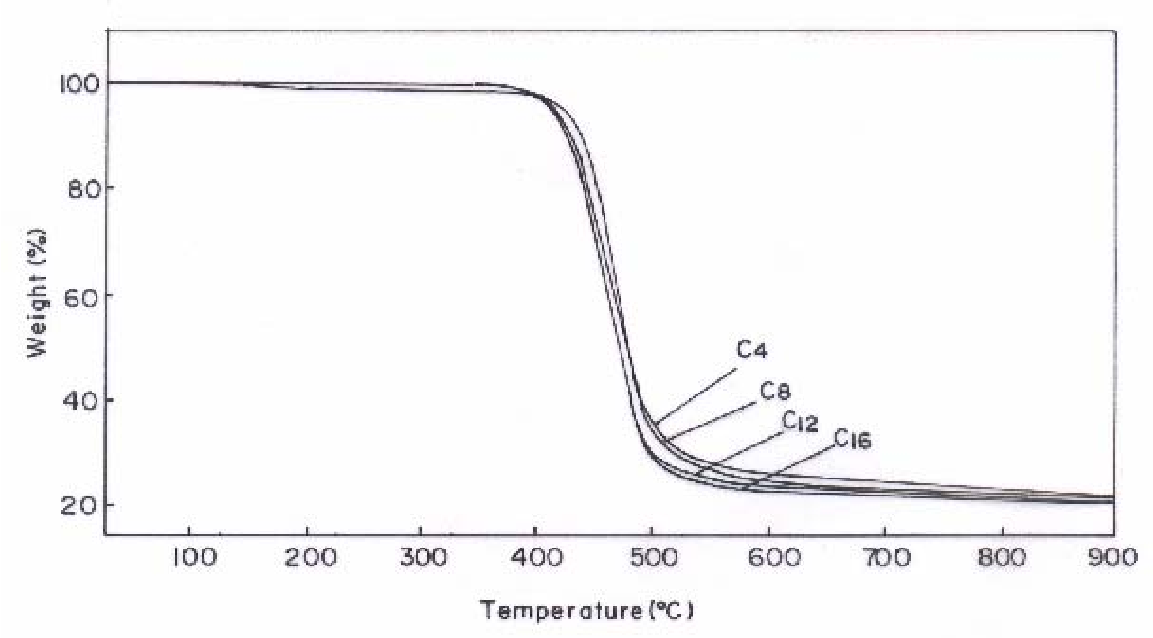


Figure 5a.11: TG curves of polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA (PES-4,.6,.8,.10).

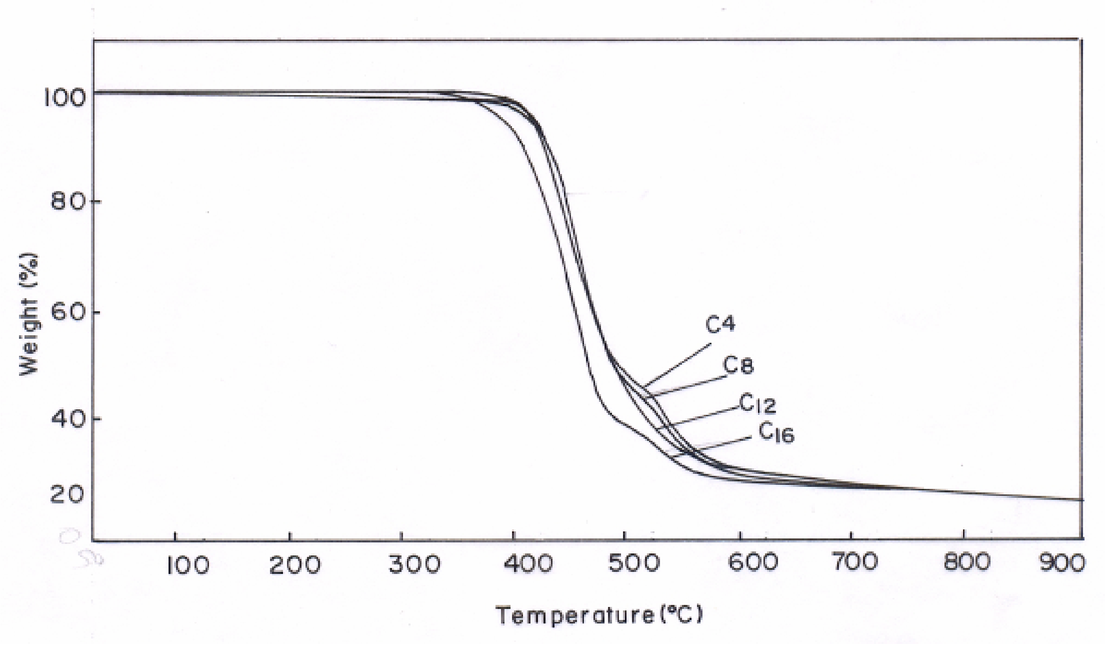


Figure 5a.12: TG curves of polyesters derived from 5-alkoxyisophthaloyl dichlorides and HFBPA (PES-5, 7, 9, 11).

Glass transition (T_g) temperature of the polyesters was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polyester samples at a heating rate of 10^oC / minute. DSC curves are shown in **Figure 5a.13 and 5a.14** and T_g values are given in **Table 5a.4**. T_g values of polyesters derived from BPA and HFBPA, respectively, were in the range 44-152^oC and 60-167^oC. A plot of T_g versus number of carbon atoms in the pendent alkoxy chains of polyesters derived from 5-alkoxyisophthaloyl dichlorides and diphenols is shown in **Figure 5a.15**. T_g values for the reference polyester derived from isophthaloyl dichloride and BPA was 190^oC and that of polyester from HFBPA was 207^oC. T_g values of polyesters containing pendent flexible alkoxy groups were lower than those of the reference polyesters. This clearly results from the presence of the pendent flexible alkoxy chains which are responsible for the increase in the chain mobility which in turn results in decrease in T_g.

As expected, polyesters derived from HFBPA revealed higher T_g values than the corresponding polyesters derived from BPA.

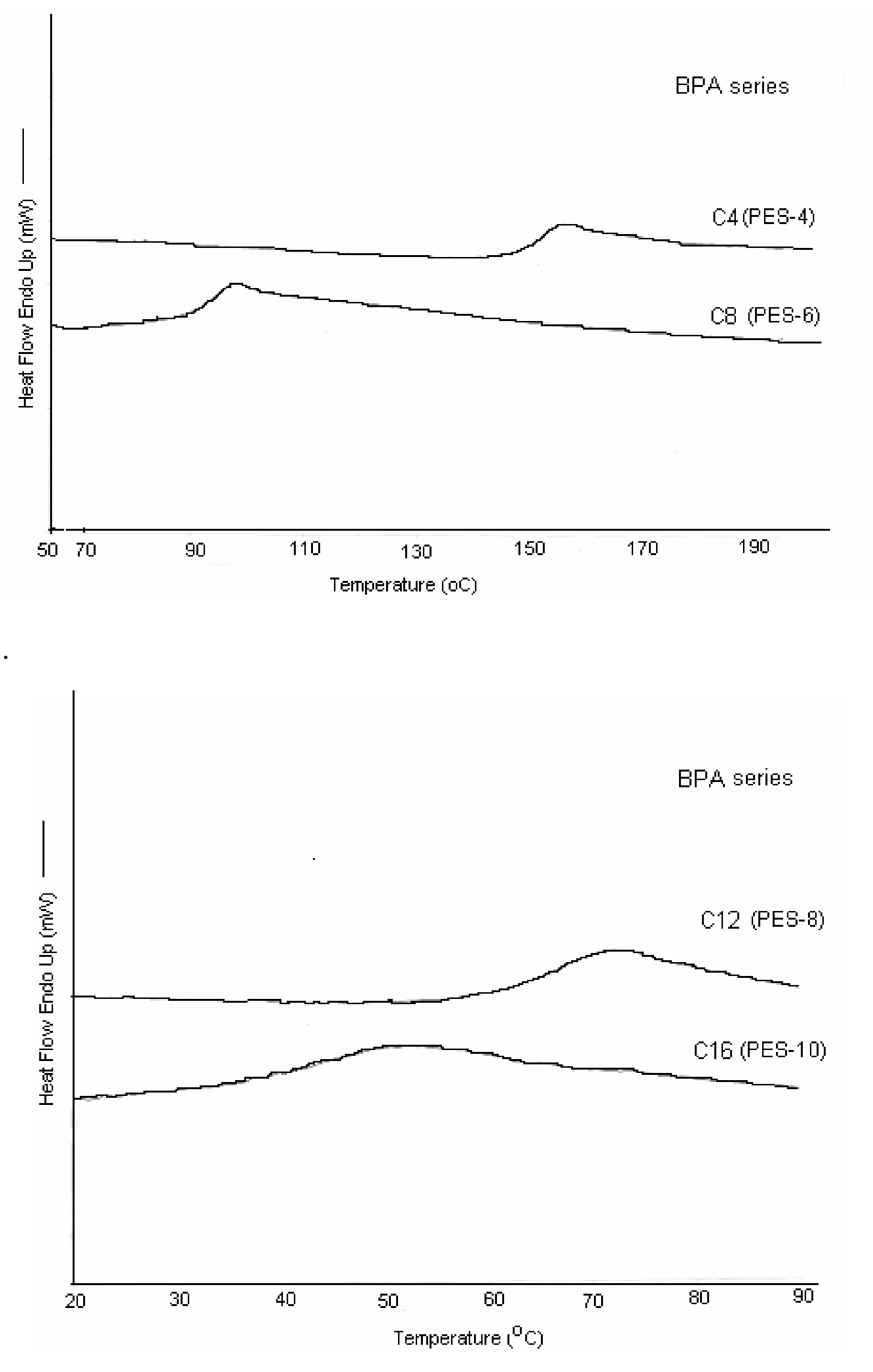


Figure 5a.13: DSC curves of polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA (Top: PES-4 and PES-6, and Bottom: PES-8 and PES-10).

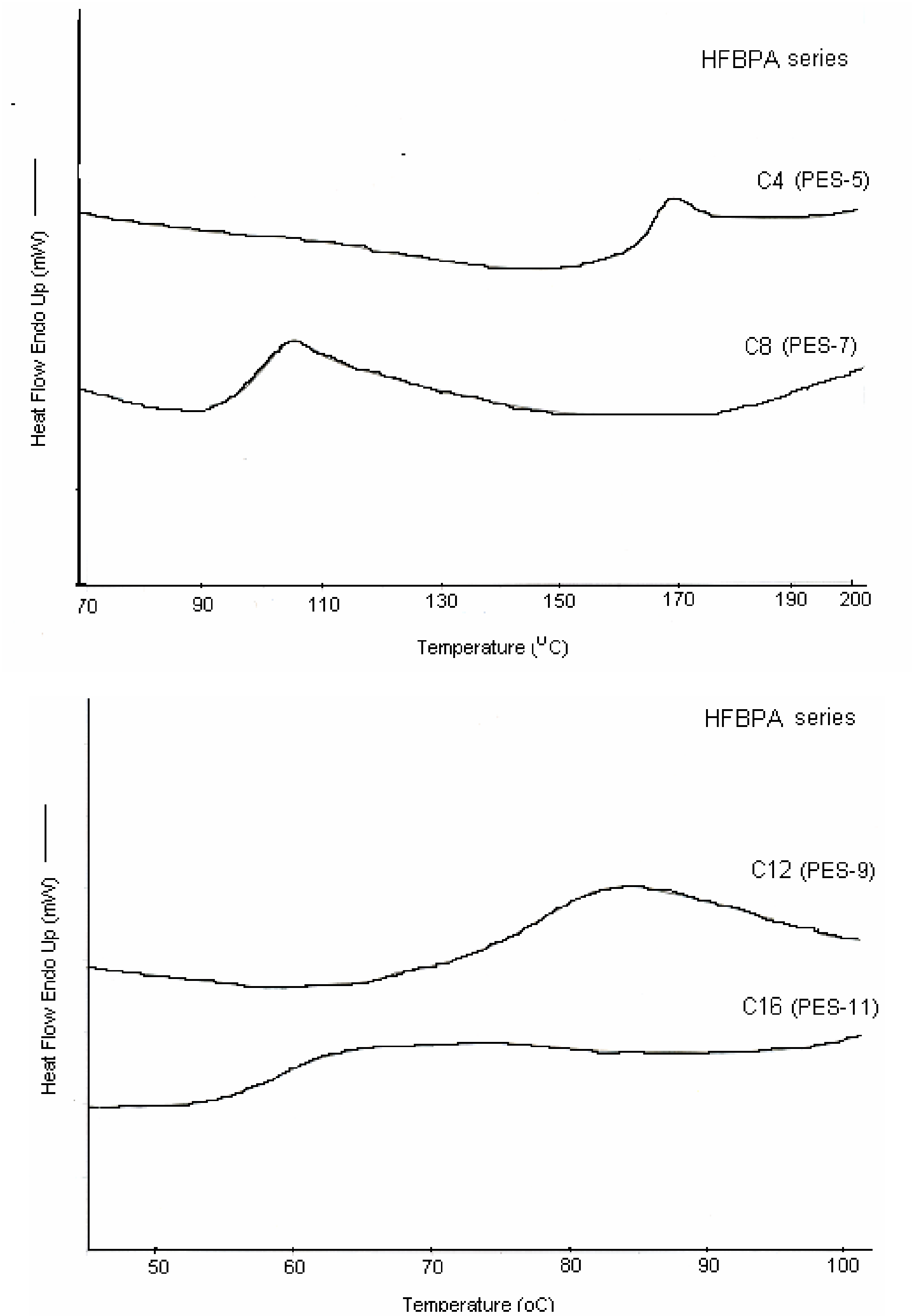


Figure 5a.14: DSC curves of polyesters derived from 5-alkoxyisophthaloyl dichlorides and HFBPA (Top: PES-5 and PES-7, and Bottom: PES-9 and PES-11).

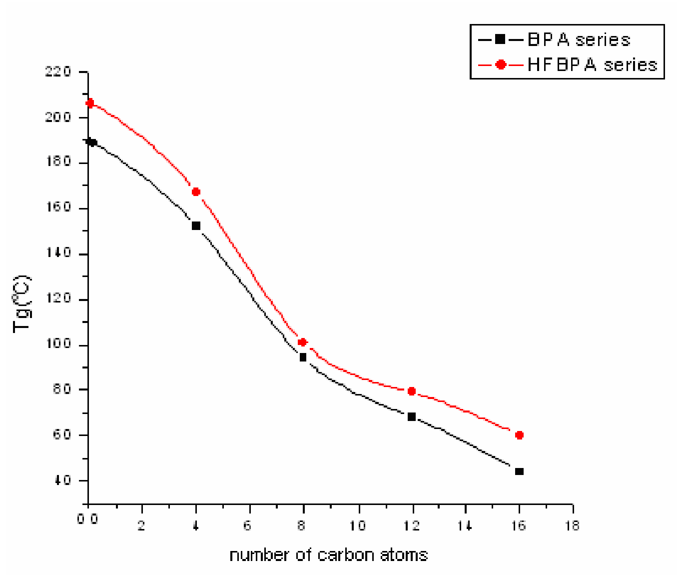


Figure 5a.15: Plot of Tg as function of number of carbon atoms in alkoxy side chains of polyesters.

5a.3.4.4 Kinetics of thermal degradation of polyesters

Eight aromatic polyesters synthesized *via* interfacial polycondensation were analysed for their thermogravimetric properties. Of these, four aromatic polyesters were derived from BPA and the other four polyesters were derived from HFBPA. Thermal properties of these polyesters were compared. These polyesters had varying length of pendent carbon chain on isophthalic unit from C_4 to C_{16} (viz. C_4, C_8, C_{12}, C_{16}).

The superimposed differential thermogram (DTG) plots for BPA and HFBPA-based aromatic polyesters are presented in **Figure 5a.16** and **Figure 5a.17**, respectively. It is evident from these figures that BPA-based aromatic polyesters showed single stage degradation pattern in the temperature range 390°C – 520°C, whereas the HFBPA-based polyesters showed two stage degradation behaviour in the temperature range 360- 580°C. This indicates that HFBPA containing aromatic polyesters show broad degradation pattern as compared to BPA-based aromatic polyesters. The DTG peak relating to this stage was separated out and corrected for area using the Anderson methodology,[26] details of which are represented in **Figure 5a.18**. The separation of two peaks could have been done by peak resolution software, however it was not available to us at the time of analysis. Hence, this technique was used for the simplicity of analysis.

Two nonisothermal integral methodologies were used to deduce the activation energies. The equations used are the following :

(A) Coats – Redfern Equation I (CR I)[27]

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{\left((1-n)T^2\right)}\right]=\log\frac{AR}{\alpha E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad \textbf{(1)}$$

(B) Coats – Redfern Equation II (CR II)

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\log\frac{AR}{\alpha E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad \textbf{(2)}$$

(C) Horowitz- Metzer Method (HM)[28]

$$\ln[-\ln(1-\alpha)]=E\theta/RT_s^2 \qquad \textbf{(3)}$$

where $\alpha = (W-W_f) / (W_o - W_f)$ (W_o, W_f and W are the initial mass, final mass and mass remaining at temperature T [equivalent to final degradation state]), $\theta = T - T_s$, and T_s = the temperature at $W/W_o = 1/e$. CR II is valid for reactions with order parameter (n) equal to 1 and CR I is applicable for reaction order parameters other than 1.

Order parameter ‘n’ was evaluated using CRI and II. The plots of the left hand side function (LHS) vs. 1/T were drawn for different values of n in the range 0-1, excepting n = 1. CR II was used for n = 1. The superimposed plots of the LHS function in CR I or CR II vs 1/T for the polyesters are presented in **Figure 5a.19**.

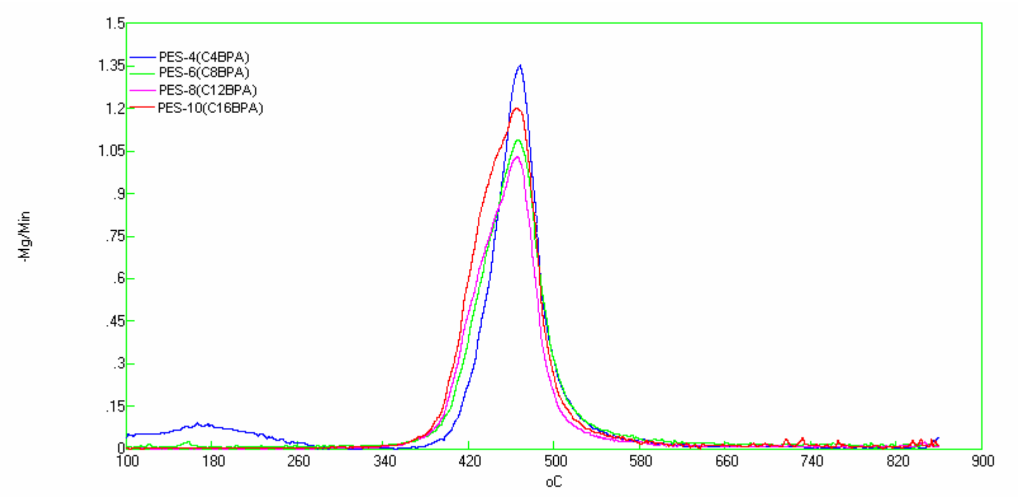


Figure 5a.16: The superimposed differential thermograms (DTG) plots for BPA- based aromatic polyesters (PES-4, 6, 8, 10)

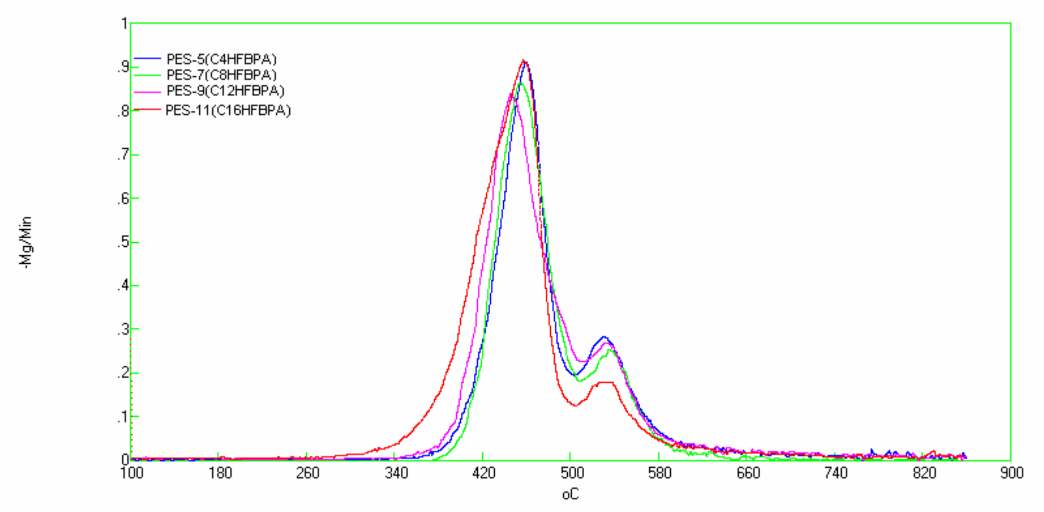


Figure 5a.17: The superimposed differential thermograms (DTG) plots for HFBPA- based aromatic polyesters (PES-5 ,7, 9, 11)

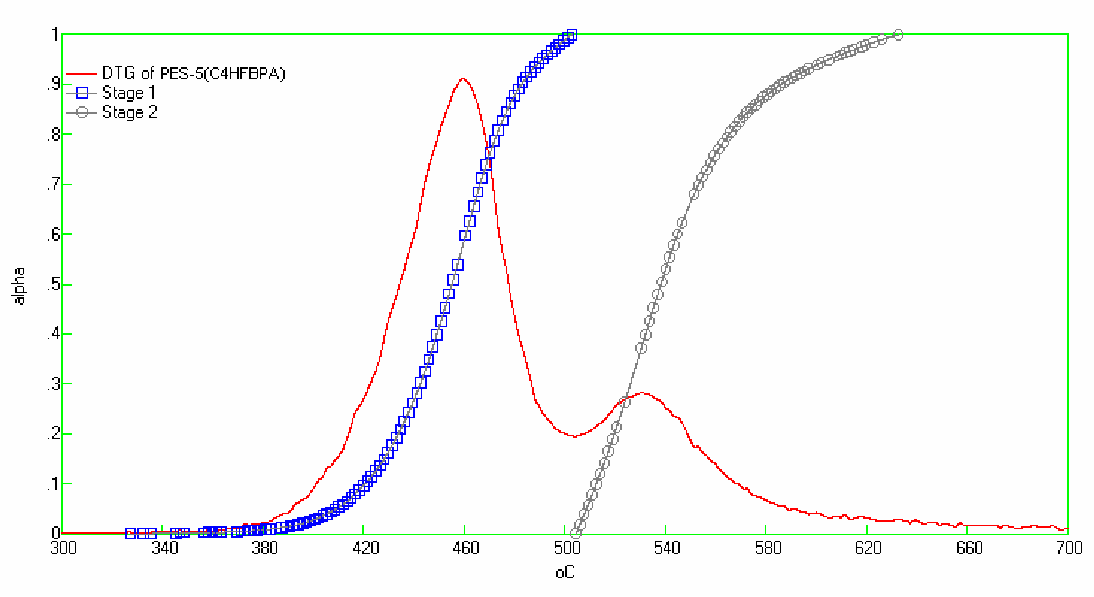


Figure 5a.18: Strategy used to fragment the two stage DTG indicating two separate α vs T curves (PES-5)

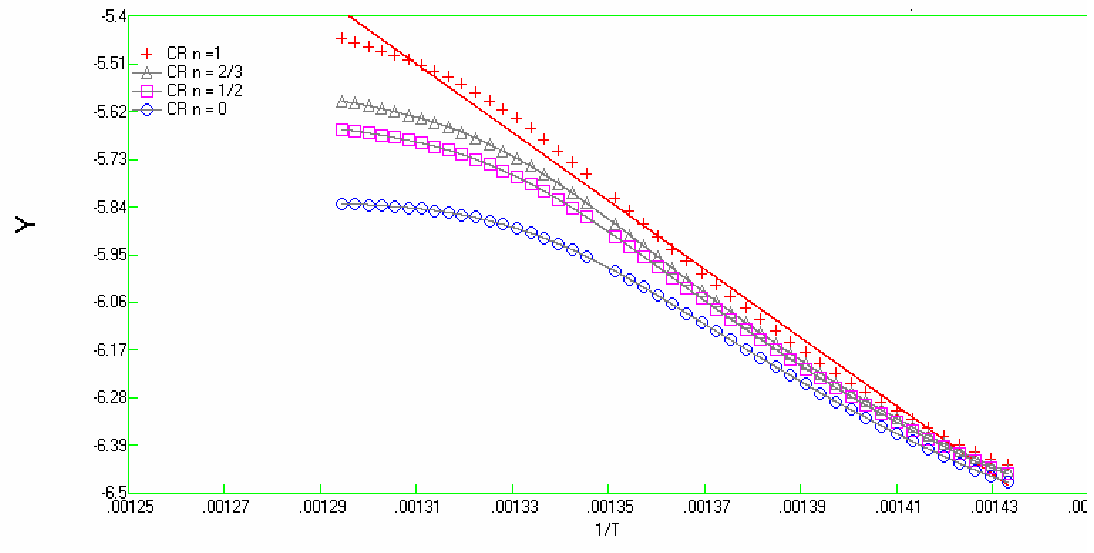


Figure 5a.19: Coats-Redfern plots for 0PES-4 (C_4BPA) polyester at n = 0, 1, 1/2 and 2/3

For n = 0, 1/2 and 2/3 (CR I), a linear relationship was not observed, whereas for n = 1 (CR II), $\log [-\ln (1 - \alpha)]$ against $1/T$ was linear. This indicates that degradation in these stages followed first order kinetics. This was confirmed through Horowitz- Metzer (HM) equation.

The plot of $\log [(1 - \alpha)^{-1} / T^2]$ vs. $1/T$ (CR II) and $\ln [(1 - \alpha)]$ vs. θ (HM equation) were plotted and the energy of activation (E) was evaluated from the slope of straight line for the eight polyesters. The correlation coefficients '*r*' for the plots were also determined in each case. These were found to be near unity for the 24 plots, reflecting linearity of the curves.

The superimposed Horowitz-Metzger and Coats-Redfern plots for the degradation stages of BPA as well as HFBPA derived aromatic polyesters with C_4 pendent groups are represented in **Figures 5a.20** and **5a.21**. Horowitz- Metzger plot i.e. $\ln [-\ln (1 - \alpha)]$ vs θ is presented in **Figure 5a.20** and Coats-Redfern plot i.e. $\log [-\ln (1 - \alpha)/ T^2]$ vs $1/T$ is presented in **Figure 5a.21**.

Similar figures for polyesters containing C_8, C_{12} and C_{16} alkoxy chains are presented in **Figures (5a.22, 5a.23), (5a.24, 5a.25) and (5a.26, 5a.27)**, respectively.

The temperature ranges and extent of degadration (α) within which analysis was performed for BPA and HFBPA-based aromatic polyesters are presented in **Table 5a.5 and Table 5a.6,** respectively. The α ranges presented in these **Tables** are fractional decomposition decomposed in each stage. The second stage kinetics parameters for HFBPA-derived polyesters were analyzed in the α range of 0.60–0.99. The initial 60 % degradation zone was by-passed to avoid errors due to an overlap from the previous zone.[29]

The activation energies (E) were calculated from the slopes of the HM and CR plots and these values are presented in **Table 5a.5 and Table 5a.6** along with its correlation- coefficient (R^2). Higher values obtained by using Horowitz-Metzger method arise from the inexact approximation used in the derivation.[30]

Chemical structure-thermal behavior will be discussed by using values obtained by Horowitz-Metzger method.

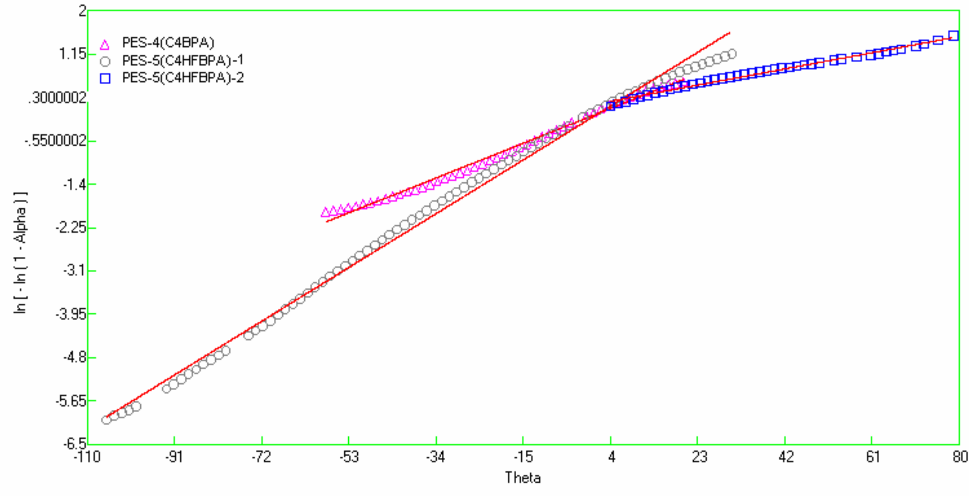


Figure 5a.20: Horowitz-Metzger plots for PES-4(C_4BPA) and PES-5(C_4HFBPA) units containing aromatic polyesters.

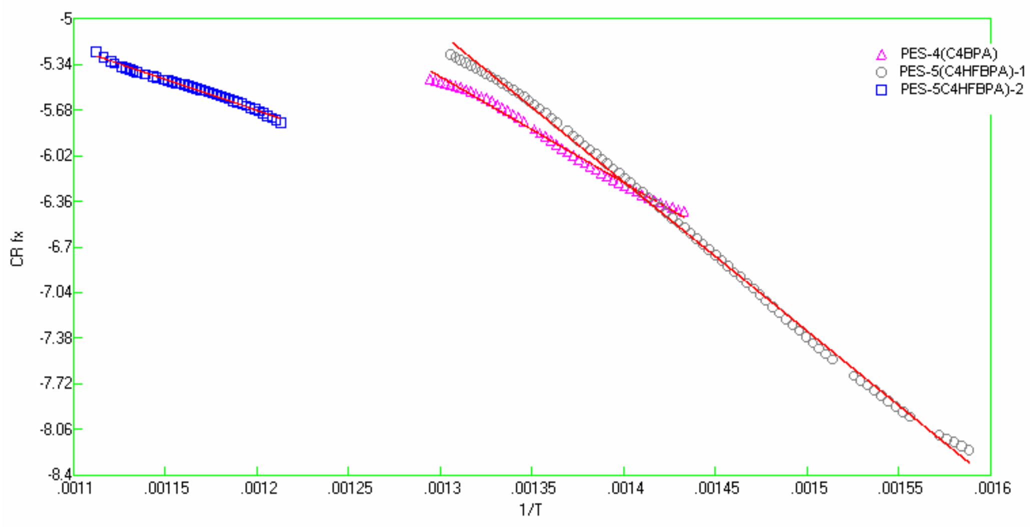


Figure 5a.21: Coats-Redfern plots for PES-4(C_4BPA) and

PES-5(C$_4$HFBPA) units containing aromatic polyesters.

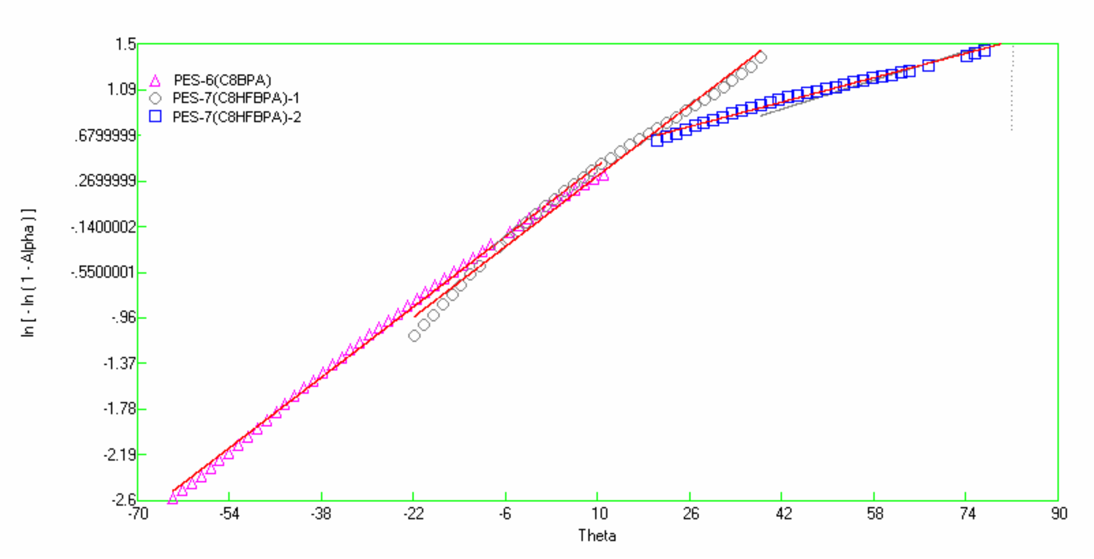


Figure 5a.22: Horowitz-Metzger plots for PES-6 (C$_8$BPA) and PES-7 (C$_8$HFBPA) units containing aromatic polyesters.

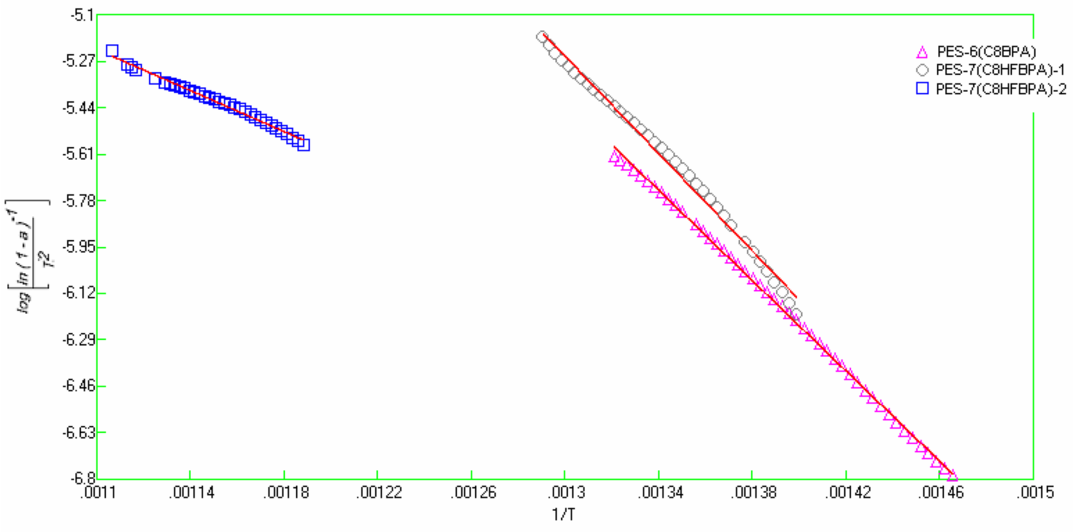


Figure 5a.23: Coats-Redfern plots for PES-6 (C$_8$BPA) and PES-7 (C$_8$HFBPA) units containing aromatic polyesters.

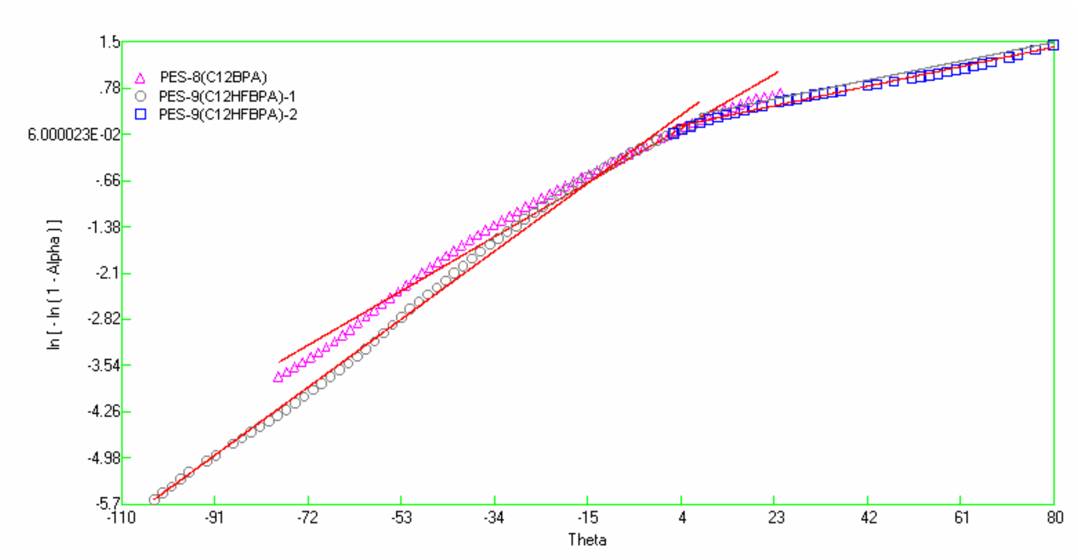


Figure 5a.24: Horowitz-Metzger plots for PES-8 (C_{12}BPA) and PES-9(C_{12}HFBPA) units containing aromatic polyesters.

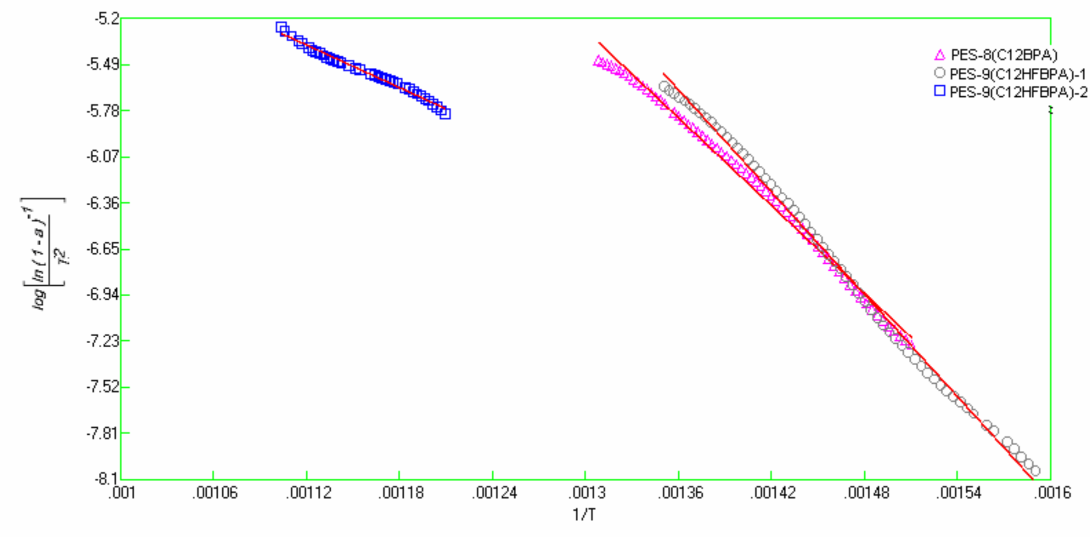


Figure 5a.25: Coats-Redfern plots for PES-8 (C_{12}BPA) and PES-9 (C_{12}HFBPA) units containing aromatic polyesters.

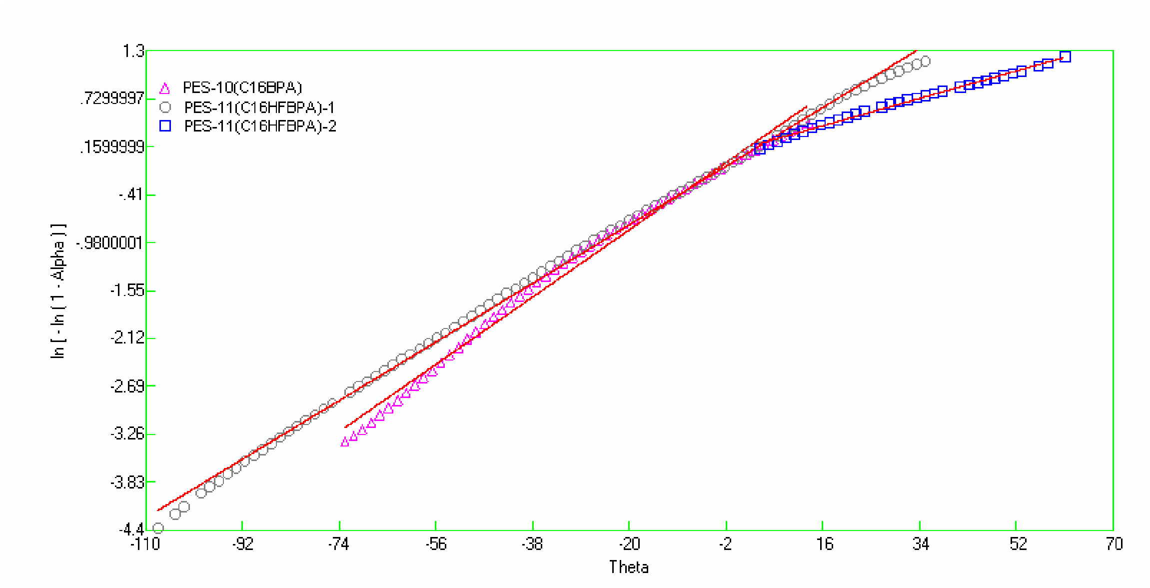


Figure 5a.26: Horowitz-Metzger plots for PES-10 (C_{16}BPA) and PES-11 (C_{16}HFBPA) units containing aromatic polyesters.

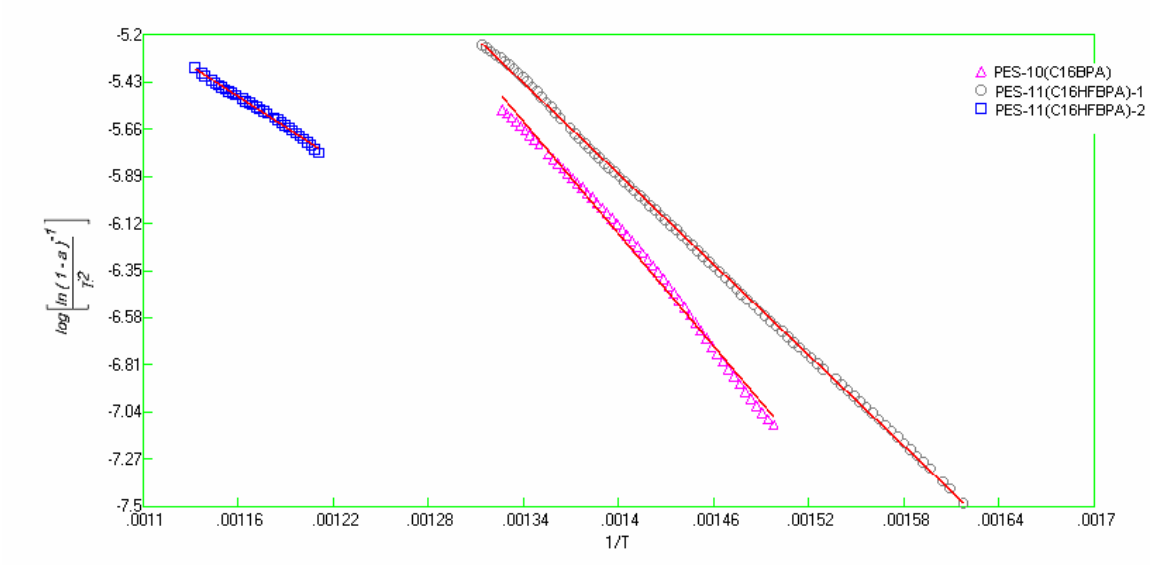


Figure 5a.27: Coats-Redfern plots for PES-10(C_{16}BPA) and PES-11 (C_{16}HFBPA) units containing aromatic polyesters.

Table 5a.5: Decomposition activation energies for BPA- based aromatic polyesters

No	**Polymer Code**	**Sample**	**Data Analysis Range**				**Coats-Redfern**			**Horowitz-Metzger**			
			Temp K		α								
			Start	End	Start	End	slope	R2 error	E (Kcal/mol)	slope	Ts K	R2 error	E (Kcal/mol)
1	**PES-4**	C4BPA	686	764	0.13	0.84	-7886.1	0.993	36.00	3.59E-02	744.5	0.992	39.40
2	**PES-6**	C8BPA	682	757	0	0.75	-8270.7	0.999	37.75	3.96E-02	746	0.997	43.66
3	**PES-8**	C12BPA	662	764	0	0.86	-9187.2	0.992	41.94	4.44E-02	740.1	0.987	48.19
4	**PES-10**	C16BPA	667	754	0	0.79	-9127.8	0.995	41.66	4.44E-02	740.5	0.99	48.30

Table 5a.6: Decomposition activation energies for HFBPA-based aromatic polyesters

No	**Polymer Code**	**Sample**	**Data Analysis Range**				**Coats-Redfern**			**Horowitz-Metzger**			
			Temp K		α								
			Start	End	Start	End	slope	R2 error	E (Kcal/mol)	slope	Ts K	R2 error	E (Kcal/mol)
1	**PES-5**	C4HFBPA-1	629	766	0	0.96	-11108.2	0.998	50.70	5.55E-02	735.4	0.995	59.44
		C4HFBPA-2	824	899	0.68	0.99	-4621.7	0.99	21.10	1.67E-02	820.4	0.99	22.28
2	**PES-7**	C8HFBPA-1	715	775	0.28	0.98	-8916.6	0.989	40.70	3.97E-02	736.6	0.989	42.66
		C8HFBPA-2	842	904	0.84	0.99	-3758	0.991	17.15	1.37E-02	821.3	0.991	18.32
3	**PES-9**	C12HFBPA-1	629	740	0	0.72	-10718.1	0.997	48.92	5.57E-02	732.2	0.996	59.21
		C12HFBPA-2	827	906	0.66	0.99	-4467	0.988	20.39	1.61E-02	824.4	0.991	21.65
4	**PES-11**	C16HFBPA-1	618	761	0	0.96	-7372.3	0.999	33.65	3.87E-02	726	0.998	40.44
		C16HFBPA-2	826	883	0.68	0.97	-4985.5	0.995	22.76	1.81E-02	821.8	0.995	24.23

The variation in thermal properties as a function of chemical structure is discussed in three sections. They are:

- I Effect of pendent chain length on BPA-containing polyesters
- II Effect of pendent chain length on HFBPA-containing polyesters during first stage
- III Effect of pendent chain length on HFBPA-containing polyesters during second stage

I] Effect of pendent chain length on BPA derived polyesters:

Increasing activation energies with increasing pendent chain length from C_4 to C_{12} was observed (**Table 5a.5, Table 5a.6)** in these polyesters and activation energy levels off at C_{16} unit containing polyesters. This behavior can be explained on the basis of glass transition temperature of these materials (**Table 5a.4**). The reduction in glass transition temperature as a function of pendent chain length was observed in these four polyesters. This indirectly indicates that chain mobility is more for polyesters with low Tg as compared to polyesters with high T_g at constant temperature of degradation i.e. around 470°C in these polyesters. This also reflects on the DTG peak broadening as pendant chain length is increased. Restrictions due to chain mobility retards rate of evolution of degradation products from polymer matrix.

The polyester matrix with high mobility will give out the degradation product easily. This behavior results in high energy of activation for polyesters with longer chain length (or lower Tg), since the energy of activation strongly depends on matrix mobility. As rate of evolution of degradation products, in case of polymer degradation, is highly controlled by diffusion of degradation products through polymer matrix. Many times this activation energy is termed as apparent energy of activation. Activation energies calculated by using HM and CR methods are based on fraction decomposition (α).

II] Effect of pendent chain length on HFBPA- derived polyesters during first stage:

The trend that was observed for BPA-based polyesters was not noticed in HFBPA-derived polyesters, even though their glass transition temperature showed identical trend. This indicates that the degradation mechanism for these polyesters is quite different. To explain this behavior, molecular weight parameters were calculated and the values are given in **Table 5a.7**. In this table, the ratio of repeat unit molecular weights for BPA and HFBPA-derived polyesters, DTG peak area ratio and correlation ratio along with their energy of activation are presented.

The value of correlation ratio (**Table 5a.7**) close to unity, which was observed in case of PES-11 polyester, indicate that thermal behaviour of such polymer has some correlation between its chemical structure and degradation pattern. In this polyester, the observed energy of activation (E) is 40.44 Kcal/mol and hydrocarbon segment fraction is 0.85. Similarly, activation energy ratio (E_{BPA}/E_{HFBPA}) for C_{16} unit containing polyester is 0.84. This is in close agreement with each other. This clearly indicates that majority of hydrocarbon containing segment take part during first stage of degradation and fluoro segment decomposes during second stage.

Such behaviour was not observed for the polyesters with large difference in their molecular weights e.g PES–5 and PES–6, and PES-9 and PES–10 (**Table 5a.1**). Detailed pyrolysis GCMS study is necessary to show the complex behavior of degradation of these polyesters and these studies are underway.

III] Effect of pendent chain length on HFBPA-derived polyesters during second stage:

Two stage degradation pattern was observed in case of HFBPA-derived polyesters. The activation energy (E) obtained for this stage was in the range of 18-24 Kcal/mol (**Table 5a.6**). The marginal variation in energy of activation observed for this stage reveals that degradation during this stage has some consistent behavior that is independent of pendent chain length. In other words, pendent chain took part in initial degradation stage. This resulted in constant value of energy of activation. The lower values of activation energies can be attributed to highly diffusion-controlled processes occuring during this stage. The drastic reduction in rate of degradation, as indicated by height of 2nd peak maximum in DTG, is mainly due to evolution of gaseous degradation products through rigid polymer matrix. Such low values are generally observed in case of degradation of BPA- based epoxy thermosets.

Table 5a.7: Relationship between chemical structure and energy of activation (E).

No.	**Chain length**	**Alkoxy Side Chain Molecular Weight**	**RU mol. Wt.,**		**A/B (C)**	**DTG Ratio (D)**	**Co-rrelation Ratio D/C**	**E Kcal/mol**
			A	**B**				
1	C4	57	429	537	0.80	0.73	0.91	59.44
2	C8	113	480	588	0.82	0.78	0.96	42.66
3	C12	169	536	644	0.83	0.76	0.91	59.21
4	**C16**	**225**	**592**	**700**	**0.85**	**0.84**	**0.99**	**40.44**

A = repeat unit formula weight for BPA moiety containing polyester

B = repeat unit formula weight for HFBPA moiety containing polyester

C = Hydrocarbon fraction i.e. ratio A/B

D = DTG peak area fraction (ratio of area under 1st peak to total area)
Correlation ratio is ratio D/C.

E = Energy of activation in Kcal/mol observed for 1st stage decomposition.

5a.4 Conclusion

1. A series of aromatic polyesters bearing pendent flexible alkoxy chains was synthesized by phase-transfer catalyzed interfacial polycondensation of 5-alkoxyisophthaloyl dichlorides with bisphenols, namely, BPA and HFBPA.
2. Polyesters containing pendent alkoxy chains having 4, 8, 12 and 16 carbon atoms showed inherent viscosity values in the range 1.59-3.0 dL/g indicating formation of high molecular weight polyesters.
3. Polyesters derived from BPA and 5-alkoxyisophthaloyl dichlorides having alkoxy groups with number of carbon atom 4 and above showed an enhanced solubility in common organic solvents such as chloroform and dichloromethane than polyester derived from BPA and isophthaloyl dichloride.
4. Tough, transparent and flexible films of polyesters could be cast from chloroform solution of polyesters.
5. Wide-angle X-ray diffractrograms revealed that layered structures were formed for polyesters with alkoxy side chains having carbon atoms greater than 12.
6. The introduction of pendent alkoxy chains caused a decrease in Tg of the polyesters.
7. Polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA showed a single stage weight loss while those derived from HFBPA showed two-stage weight loss.
8. Thermal degradation kinetics of 5-alkoxyisophthaloyl dichloride-based polyesters was studied by non-isothermal methods of Coats-Redfern and Horowitz-Metzger. In the BPA-series of polyesters, increasing activation energy with increase in pendent chain length was observed upto chain length of twelve carbon atoms and levels off at sixteen carbon atoms. A definitive

trend was not observed for HFBPA-derived polyesters during first degradation step due to their complex degradation behaviour. The degradation behaviour of C_{16}HFBPA polyesters indicated that majority of hydrocarbon segment was lost during first stage whereas fluorocarbon moiety degraded during latter stage of degradation. The marginal variation in energy of activation was observed for second stage of degradation in HFBPA-based polyesters indicating pendent side chain length- independent degradation behaviour.

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Chapter 5 b. Gas Permeability Studies in Polyesters and Poly(amideimide)s Containing Pendent Flexible Alkoxy Groups

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5b.1 Introduction

Gas permeation using polymeric membranes is gaining growing importance due to techno-economical demands from various industrial gas separation applications. Membrane- based processes are modular in nature and thus are easy to scale-up. They need lower operational costs, lower maintenance and have operational simplicity over conventional processes like cryogenic and pressure swing adsorption (PSA). The main drawbacks of polymeric membrane- based gas separation processes are that (i) achieving very high level of purity is cost intensive and (ii) operations can not be done at high temperatures due to polymer material characteristics. In such cases, the hybrid technology combining membranes with conventional ones are coming forward as promising alternatives. Newer polymeric materials are being investigated to meet demands of various types. The basic understanding towards polymer structure-gas permeation property is required to systematically architecture the polymer structure for required applications to meet a particular demand. For example, the separation of He from natural gas or breathing gas would need polymeric materials that have high diffusivity selectivity; while the separation of hydrocarbon mixtures is achieved with materials that have high solubility selectivity.

5b.1.1 Theoretical considerations and structure- property relationship

The permeability of a gas in polymer membrane is expressed as

$$P = D \times S$$

where P = Intrinsic permeability, D= Diffusivity of penetrant in polymer matrix, and S = Solubility of penetrant in polymer matrix

The ideal selectivity (α) for two gases a and b with intrinsic permeability Pa and Pb can be expressed as

$$\alpha = P_a/P_b = (Da/Db) \times (Sa/Sb)$$

where (Da/Db) = diffusivity selectivity and (Sa/Sb) = solubility selectivity.

Both the nature of the polymer as well as nature of penetrant affect D and S. The diffusivity depends mainly on packing density, chain and subgroup mobility and gas- polymer interactions; while solubility mainly depends upon gas-polymer interactions, condensability of the gas and packing density.

The applicability of a polymer as a membrane material depends on its intrinsic permeability and selectivity. The ideal membrane should thus have high permeability and selectivity for a desired gas. This can be achieved by appropriate structural modifications of a polymer. A proper understanding of structure – property relationship is necessary to obtain desired permeation characteristics. Several studies have been reported in the literature that correlate the effect of structural modifications on the gas permeation properties and are summarized below. The substituent group in the polymer can be incorporated either at monomer level or can be introduced in the polymer *via* polymer modification reaction. The following section briefly outlines some of the attempts reported in the literature towards this direction.

5b.1.2 Effect of structural modification on gas permeation

Several types of structural modifications have been reported in the literature while varying bulk of the substituent, its nature (polarity, aliphatic, aromatic, etc.),[1,2] substituent site, etc. Robeson has discussed the permeation properties of a variety of polymers containing different structural modifications and proposed that the upper-bound exists for permeability and selectivity. The hexafluoroisopropylidene linkage in bisphenol or diamine has been found to increase gas permeability of resulting polyarylates[3,4] polycarbonate[5,6], polysulfone[7,8] or polyimide[9,10] with marginal changes in selectivity. A typical isomerism effect in polyarylates derived from same bisphenol is observed, wherein 1-3 linkages at the diacid site offered more permeability but lower selectivity, while 1-4 linkages resulted in higher permeability but lower selectivity than earlier case.[11,12] The effect of connector group of bisphenol plays an important role in governing permeation properties of polycarbonates[6], polysulfones[8] and polyarylates[4]. The effect of substituent symmetry on bisphenol moiety plays an important role in governing the gas permeation properties of polyarylates[12] and polysulfones[13]. The asymmetric substitution generally leads to higher permselectivity than either unsubstituted or symmetrically substituted bisphenol- based polymers. The effect of substituent on the acid moiety of polyarylates is largely determined by the bulk, nature and site of the substitution. A two fold increase in permeability for He, while five fold increase for methane as a result of increase in diffusivity as well as selectivity in case of polyaryletherketone containing *tert*- butyl group has been reported by Garcia et. al.[14]. It is also reported that the smaller gases are less affected by changes in the free volume than the bulkier ones. The substitution of polar groups like nitro, bromo in combination with asymmetric substitution on bisphenol increases permselectivity upto six times while decreasing permeability by half the value than unsubstituted case.[15]

It was found that the bulky substituent like isopropyl on the phenylene rings of poly(arylethersulfone) were advantageous for gas permeability, while intermolecular hydrogen bonds and ionic bonds resulted in a considerable increase in gas permselectivity.[16] The cause of this trend were interpreted according to free volume, interchain distance and glass transition temperature together with the respective contribution of gas solubility and diffusivity to the overall permeability. It is also stated that the simultaneous substitution of bulky isopropyl and pendant carboxylic acid group led to 377 % higher oxygen permeability and 5.3 % higher O_2/N_2 selectivity. An investigation on gas permeation properties of poly(etherketone)s obtained with various types of substituents on bisphenol-bridge position revealed that only fraction of total fractional free volume (v_f) is actually accessible to the gas particles during the diffusion process.[17]

The trimethylsilyl as a pendant group is shown to increase gas permeability in PPO.[18]. A substitution by 4-trimethylsilyl-α-hydroxybenzyl as a pendant group on polysulfone resulted up to thirteen fold increase in gas permeability owing to decrease in packing density, which is ascribed to the steric interactions caused by this group. The retention of good permselectivity in this case is imparted by the rigidity of the substituent. Polyimides derived from bisetheranhydrides gave membranes with high free volume and gas permeabilities closer to the Robeson upper-bound.[19] It was reported by Kawakami et. al.[20] that introduction of oligodimethyl siloxane in the main chain or side chain of aromatic polyamides and polyimides reduced Tg significantly while increasing the permeability of nitrogen and oxygen. A study on effect of side chain of silicone polymers by Shah et. al,[21] showed that the solubility of the penetrant gases decreased with increasing bulkiness of the polymer side chains and with decreasing critical temperature of the penetrant.

It is reported by Abajo. et al.[22] that gas permeability through polyimides and polyamides can be increased by introducing bulky side groups, using non-planar monomers and combining these elements on both monomers: diamine and dianhydride or diamine and diacid. The addition of pendant phenyl substituents increased permeability but decreased selectivity of polyamide relative to unsubstituted polymers[23]. Kim. et al.[24] reported that the incorporation of fluorinated side groups into the polyimide membranes decreased their surface free energies, solubility parameters, and fractional free volume and therefore enhanced the permeabilities for CO_2, N_2, O_2 and CH_4 gases but reduced the selectivities for CO_2/CH_4, O_2/N_2, and CO_2/N_2 gas pairs depending upon the structure of dianhydride monomers.

The bisphenol bridge substitution by ethyl, isobutyl, phenyl and methyl propionate in resulting polyarylates revealed that at constant intersegmental packing density, a decrease in the mobility of specific groups in the polymer chain correlates with increased permeability without significant changes in selectivity.[25] The introduction of tosylate group into the five membered ring of the polynorbornene main chain results in increase of T_g and significant improvement in O_2/N_2 selectivity.[26]

The gas transport of side chain crystalline poly(octyl acrylate) observed a 'permeation switch' to be as high as two orders of magnitude upon traversing the melting point.[27] These authors also studied the gas permeability of poly(alkyl acrylate)s with increased side chain length as a function of temperature in both the amorphous and crystalline state. It was found that the penetrant permeability in the amorphous phase increases as the side chain length becomes longer but showed mixed trend in the crystalline state. The alkyl-substituted polyaryletherketone bearing a pendant bulky propyl group on the cardo ring simultaneously exhibited 62.5% higher H_2 permeability and 59.8% higher H_2/N_2 selectivity[28]. In case of polycarbonates, replacement of geminal dimethyl of bisphenol (bridge position) with longer chain alkyl substituents progressively increased oxygen permeability[29]. The gas permeation behavior of poly(dialkylfumarate)s with various bulky ester side chains has been studied by Choi et al.[30]. It was stated that the thermal molecular motion and intermolecular distance depended on the bulkiness of ester side groups and permeation behavior was strongly influenced by thermal molecular motion and density of polymers. The oxygen and nitrogen gas permeability in case of poly(N-n-alkylmaleimide)s was found to increase as the chain length of the side chain increases[31]. These membranes had high permeability coefficient even below their T_g due to the facile permeation through the alkyl chain in the side group. The permeability of poly(alkyl acetylene)s to various gases increased with an increase in the length of linear side chain[32]. An increase in the length of the linear alkyl side chain of poly(2-alkyl acetylene)s led to lowering of fractional free volume, higher permeability and higher mixed gas n-butane/methane selectivity.[33]. The improvement in the permeability of n-butane and its selectivity over methane was ascribed to increase in side chain mobility as the side chain length increases. Conversely, as the size of the alkyl group in silicone membranes of the type (MeSiRO) increased, the permeability decreased markedly, whereas the O_2 / N_2 selectivity remained more or less constant.[34]. The gas permeation study of thirteen different gases for constitutionally identical polyphosphazenes, which differ only in the arrangement of carbons in the side groups[35] showed that as the side chain becomes bulky, the permeability decreases and permselectivity increases.

The study of local molecular motion of four homologous series of poly(oxy[alkylsulfonyl]ethylene) as measured by proton rotating-frame spin-lattice relaxation time showed that slower local motion due to the shorter side chains imparted a lower oxygen permeability.[36].

The PPO acylation by long alkyl chain containing myristoyl chloride prominently increased CH_4 permeability than that of CO_2 or N_2.[37]The silylation of polyphosphazene showed that as the length of the alkyl or fluoro alkyl group on the silyl moiety varied from 3-18 carbons, Tg ranges from –20°C to 39° C. Hydrophobicity and gas permeability was also significantly increased by this modification.[38]

5b.2 Experimental

5b.2.1 Materials

Polyesters and poly(amideimide)s were synthesized as described in **Chapter 5a** and **Chapter 4b**, respectively.

Dense membrane preparation for gas permeation

The dense membranes were prepared by solution casting method. A 3-5 % (w/v) solution of polyester in chloroform was prepared, filtered through 5μ ss-filter and poured onto a flat bottom glass surface. The solvent was allowed to evaporate under dry conditions and ambient temperature. The formed film was peeled off and kept in vacuum oven at 50°C for seven days. These films were used for pure gas permeability determination by variable volume method at 35°C and 10 Kg/cm^2 upstream pressure.

Poly(amideimide)s films were cast from DMAc solution following the procedure as mentioned above and dried under vacuum at 100°C for seven days.

The density of polyester films was determined by floatation method at 40°C using aqueous potassium carbonate solution. Minimum five samples of each polyester were used for density determinations and the obtained values were averaged. Using these density values, solubility parameter (δ) was calculated by Small's method[39], while fractional free volume (v_f) was calculated by Van Krevelen's method.[40]

5b.2.2 Measurement of gas permeability

There are two methods which are most commonly used for measurement of gas permeability of polymer membranes. The variable volume method[41] measures the amount of gas permeating through the polymeric membrane; while constant volume-variable pressure method[42] (which is also known as time lag method) rely on sensing the change in permeate side pressure as permeation proceeds. These methods have their own advantages and disadvantages. There are many modifications reported to suit various requirements such as low permeation rate[43], high temperature,[44] high pressure[45] and nature of gas.[46]

In the present work, the variable volume method was used to determine permeability of He, N_2, O_2 and CO_2 . The purity of the gases used was minimum 99 %. The permeability measurements were carried out at 35°C and upstream pressure of 10 Kg/cm^2 while maintaining permeate side at ambient pressure. The schematic diagram of the permeation apparatus is given in **Figure 5b.1**.

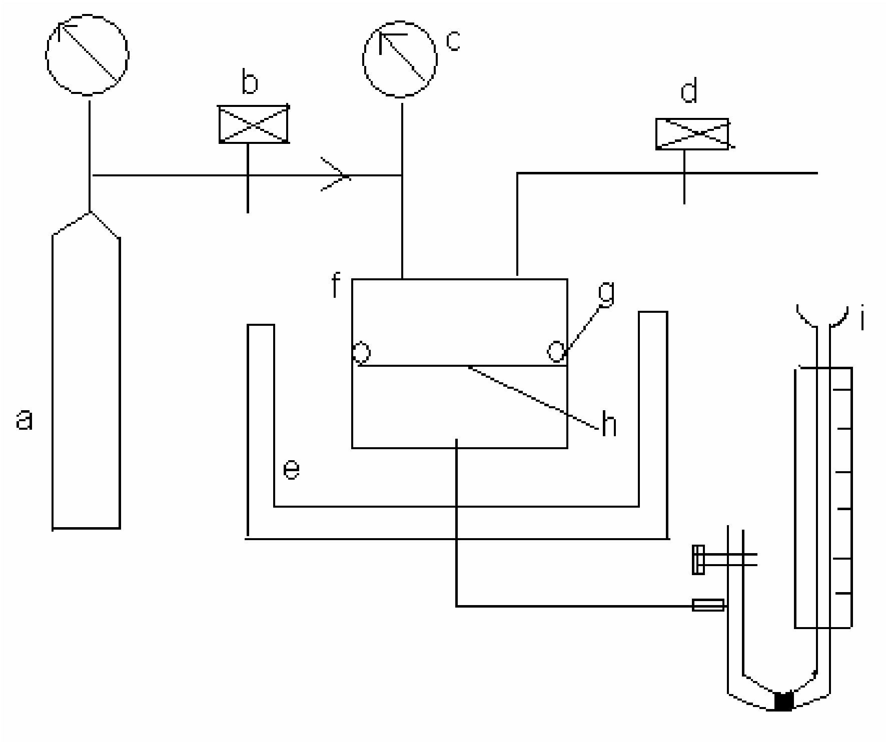


Figure 5b.1: Schematic diagram for gas permeability measurement

(a: Gas cylinder; b: Inlet valve; c: Pressure gauge; d: Outlet valve; e: Thermostat; f: Permeation cell; g: 'O' ring; h: Membrane; i: Calibrated flow meter).

5b.2.3 SOP for gas permeation measurement

The permeation cell was opened and circular coupon (size: 49 mm) of membrane was mounted in the cell. An O-ring was placed on the top of membrane (vacuum grease was applied to the O-ring to ensure the leak-proof assembly). The cell was fixed with inlet (connected to the gas cylinder and a pressure gauge) and outlet tubing and tightened.

Using the regulator knob and the inlet valve, the pressure was adjusted in the cell while keeping the exhaust closed. Gas was flushed through the outlet valve seven to eight times in the system to ensure the removal of earlier gas to the maximum possible extent. The flow meter was attached to the permeate side through a flexible pipe. A desired pressure was applied to the upstream side of the cell while outlet valves were kept closed.

The amount of gas permeated per unit time was recorded after a certain period of time. The readings were continued till enough data generated to ensure the equilibrium had reached (depends on the gas used and membrane mounted in the cell). The initial and final pressure on the gauge was also recorded while taking the readings. The gas permeability was calculated for each reading using the equation given below and the consistent data was averaged.

At the end of the experiment, cell was depressurized and disconnected from the cylinder.

$$p_{avg} = (p_{\text{int}} + p_{final})/2$$

$$\Delta p = p_{avg} - p_{ambient}$$

$$Permeability(P) = \frac{14.7 \bullet distance \bullet \ flow\ meter\ constant \bullet thickness}{76 \bullet area\ of\ \ the\ membrane \bullet \Delta p \bullet time} \text{........(1)}$$

$$selectivity\,\alpha_{(A/B)} = P_A / P_B$$

Δp was recorded in psi, P is the gas permeability in barrer (1 barrer = 10^{-10} cm^3 (STP). cm/cm^2 .s.cm Hg).

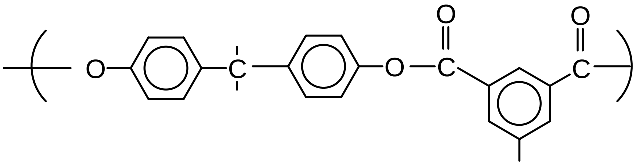
From the permeability coefficients obtained by the **equation (1)**, the ideal separation factor for different pairs of gases was calculated .

5b.3. Results and discussion

5b.3.1 Gas permeability studies in polyesters containing pendent alkoxy groups

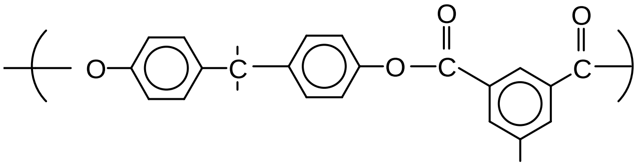
In the present work, the permeability studies of four gases viz He, N_2, O_2 and CO_2 in two series of polyesters derived from bisphenols and 5-alkoxyisophthalic acid dichlorides were carried out. Polyesters based on BPA and HFBPA, selected for gas permeability studies are shown below. The bisphenol moiety provides necessary backbone rigidity for good thermal resistance and mechanical behavior. Moreover, polyesters offer an advantage in that modification of the diacid structure enables variation in physical properties that affect gas permeation properties.

Polyesters derived from 5-alkoxyisophthalic acid dichlorides and BPA.



Polymer code	R
PES-1	-H
PES-4	$-OC_4H_9$
PES-8	$-OC_{12}H_{25}$

Polyesters derived from 5-alkoxyisophthalic acid dichlorides and HFBPA.



Polymer code	R
PES-2	-H
PES-5	$-OC_4H_9$
PES-9	$-OC_{12}H_{25}$

Among the two series of polyesters investigated, one contained bisphenol-A as one of the monomer while other contained 4,4'-(hexafluoroisopropylidene)diphenol (HFBPA) as the bisphenol. The isophthalic acid moiety containing pendent flexible alkoxy chain at its 5th position was used in both the cases. The physical properties and gas permeability study of these polyester membranes (in dense film form) were investigated in order to study the effect of long alkoxy chains as well as effect of nature of bisphenol moiety on gas permeability property.

The packing density of polyesters is evaluated by two ways: (i) by calculating the d-spacing from Wide Angle X-ray Diffraction spectra (WAXD) and (ii) by estimating fractional free volume based on measured density. The results are tabulated in **Table 5b.1.**

Table 5b.1: Physical properties of polyesters containing pendent alkoxy groups governing gas permeation analysis.

Polyester	T_g (^oC)	Density (g/cm^3)	v_f ($cm^3.cm^{-3}$)	Solubility parameter $(cal.cm^{-3})^{1/2}$	d-spacing[a] (A^o)
PES-1	190	1.257	0.329	10.28	5.06 (17-20^o)
PES-4	152	1.1543	0.364	9.489	5.07 (17-20^o), 12.62 (5-7^o)
PES-8	68	1.0833	0.363	9.192	4.85 (17-20^o), 20.53 (5^o)
PES-2	207	1.412	0.381	9.025	5.9 (17-18^o)
PES-5	167	1.334	0.375	9.063	5.30 (17-20^o), 7.55 (12^o), 18.78 (5^o)
PES-9	79	1.236	0.365	8.973	5.09 (17-20^o), 23.23 (3^o)

a: Values in parenthesis are 2θ obtained from WAXD

X-Ray diffractograms of these polyesters (**Chapter 5a, Figure 5a.9 and Figure 5a.10)** showed that all these polymers are amorphous in nature. In both the series of BPA and HFBPA, the d-spacing decreased as chain length increased. In both the series, the additional peak at low angle was observed. The presence of such peak for the polymers containing long alkyl chain is reported in the literature and is attributed to the presence of a layered structure.[47] The other parameter for expressing free volume is determination of v_f based on measured density. In the present case, the density of these polyesters was found to decrease by substitution of long alkoxy chain as anticipated. Similar behavior of decrease in density by increased chain length was observed for oxyalkylene polymers bearing varying side chain length.[48]. Exceptions to this behavior are also known wherein the increase in density is reported with increase in side chain length of polyalkyl acetylenes.[49]. The density based fractional free volume determination of both the series studied here showed opposite trend. The v_f for BPA- series of polymers increased while the same for HFBPA- series decreased with increase in side chain length. This behavior could be explained as follows. The v_f on PES-1 was 0.329, which increased to 0.364 and 0.363 by substitution of alkoxy chain containing C_4 and C_{12} side-chain, respectively. Conversely, the originally high v_f of PES-2 (0.381) got reduced to 0.375 and 0.365 by substitution of C_4 and C_{12} carbon atom containing alkoxy groups, respectively. The reduction in free volume may be because the incorporation of alkoxy chain in the PES-2 could accommodate the bulk of added chain in the already available high free volume, which could not be possible in earlier case of PES-1 since the packing density was initially high. The decrease in v_f by substitution of long alkyl chain is known for polyalkylacetylenes.[49]. It is interesting to note that the v_f of PES-4, PES-5 and PES-9 are almost same. A general decrease in solubility parameter was observed as the side chain length increases. This is as anticipated since the addition in the parent polyester is only by alkoxy chains, which are nonpolar in nature. Similar decrease in solubility parameter was noted in polyimides by substitution of long alkyl chain.[24].

Four polyesters *viz* PES-4, PES-8, PES-5 and PES-9 were chosen for analyzing the effect of flexible alkoxy groups on their gas permeation properties. The data for two reference polyesters *viz*. PES-1 and PES-2 was taken from the literature.[3,12] The results are summarized in **Table 5a.2.**

Table 5b.2: Permeability coefficients (P)[a] and selectivities (α)[b] of polyesters containing pendent alkoxy groups .

Permeation property	**PES-1**[c]	**PES-4**	**PES-8**	**PES-2**[d]	**PES-5**	**PES-9**
P(He)	8.8	16.8	16.4	47.8	45.3	24
P(N_2)	0.09	0.55	1.08	1.11	1.91	1.6
P(O_2)	0.49	2.58	3.41	5.23	6.52	4.6
P(CO_2)	2.1	8.89	17.5	19.1	28.3	22.7
α (He/N_2)	97.8	30.8	15.2	43.1	23.8	15.0
α (O_2/N_2)	5.4	4.7	3.2	4.7	3.4	2.9
α (CO_2/N_2)	23.3	16.2	16.3	17.2	14.8	14.2
α (He/CO_2)	4.2	1.9	0.9	2.5	1.6	1.1

[a]: In units of 10^{-10} [cm^3(STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$] at 10 kg/cm^2 upstream pressure and at 35 °C.

[b]: Selectivity, the ratio of pure gas permeability of respective gases.

[c]: Data taken from reference 12.

[d]: Data taken from reference 3.

The results show that both these series exhibit characteristic trends for gas permeability. The permeability of polyesters based on HFBPA is more than that of bisphenol-A based polyester derived from the same diacidchloride. This is as anticipated since hexafluoroisopropylidene group is known to enhance permeability due to higher free volume of polymers containing this linkage. This difference goes on decreasing as the chain length increases. This shows that the effect of hexafluoroisopropylidene group is masked by the effect induced by long alkoxy chain, which also leads to general increase in permeability. Alternatively, the effect of bisphenol (BPA to HFBPA) is diminished as the chain length increases. For polyesters based on BPA series, the gas permeability increases and selectivity decreases as the chain length increases. An increase in permeability occurred because of introduction of flexible groups. Such an increase in permeability by introduction of flexible group, accompanied by loss in selectivity is commonly observed in many cases.[24,31,38] This increase in permeability is due to the increased free volume by substitution of long alkoxy chain and also due to the added flexibility as revealed by decrease in T_g after substitution. Though v_f of PES-4 and PES-8 is closer, the higher permeability of latter polymer could be because of its lower T_g as a result of higher chain length of pendent alkoxy group. Since T_g is decreased with incorporation of alkoxy chain, the polymer matrix also looses its capability to discriminate between permeating gas molecules, thus results in lower selectivity. An interesting behavior was also seen for CO_2 permeation properties of these materials. The permeability of CO_2 increased to the larger extent than for any other gas as side chain length increased. The CO_2 permeability for PES-8 was almost similar to its He permeability. This indicates that the added long chain alkoxy groups also leads to increase in solubility of condensable gases in polymer matrix.

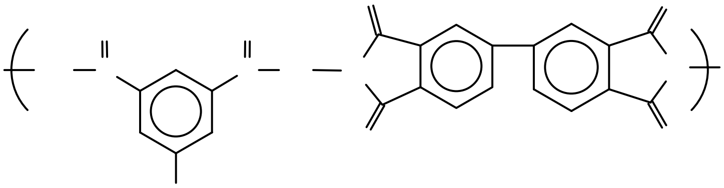
In case of HFBPA series, higher permeability in comparison to BPA series originates primarily because of hexafluoroisopropylidene linkage. It is known that incorporation of hexafluoroisopropylidene group into polymers results in an increase in permeability. In the present HFBPA-based polyester series also, a general increase in permeability, lowering in selectivity and decrease in T_g was observed as like in BPA series, though the trend is different and could be explained based on the effect of added bulk occupying available high free volume. An increase in permeability was observed from PES-2 to PES-5, but in case of PES-9, the permeability showed a general decrease. This could be because the flexible chain may be occupying the higher free volume that is created by hexafluoroisopropylidene group and results in lowering in permeability. This postulation is also supported by the observed decrease in v_f in the series as chain length increases. The reference polyester, PES-2 has high v_f, which after substitution of C_4 or C_{12} alkoxy chain reduces gradually. The small increase in permeability of PES-5 in comparison to PES-2, in spite of its decreased v_f, could be attributed to increased flexibility. In case of PES-9, an increased chain length reduces v_f further and leads to reduced permeability. Such a behavior of decrease in permeability with increase in side chain length is reported. In present case, though the decrease in selectivity, as a result of added flexibility is also evident in HFBPA series as in BPA series, the decrease was not as rapid as seen in latter case. This slower decrease in selectivity and the trends observed for permeability supports the occlusion of added bulk in the free volume created by hexafluoroisopropylidene group.

Interestingly, in both these series, He/CO_2 selectivity decreased with increased chain length. In case of polyesters containing C_{12}-alkoxy side chain, the CO_2 permeability is comparable with He permeability, while in case of most of the rigid polymers such as aromatic polyesters, polyimides, polyamides etc., the permeability of He is higher than for CO_2. This enhancement of CO_2 permeability with increase in chain length shows that the increased solubility of CO_2 could be contributing to this increase. Since the method used for permeability determination was based on variable volume, the quantification of solubility and other parameters could not be done.

5b.3.2 Gas permeability studies in poly(amideimide)s containing pendent alkoxy groups

Two poly(amideimide)s which were selected for gas permeability studies are shown below:

Poly(amideimide)s derived from 5-alkoxyisophthalic acid dihydrazides and BPDA



Polymer code	R	T_g
PAIH-8	$-OC_8H_{17}$	230
PAIH-10	$-OC_{16}H_{33}$	225

The permeation properties of poly(amideimide)s containing pendent octyloxy (PAIH-8) and hexadecyloxy (PAIH-10) group are given in **Table 5b.3**.

Table 5b.3. Permeability coefficients (P)[a] and selectivities (α)[b] of poly(amideimide)s containing pendent alkoxy groups.

Permeation property	**PAIH-8**	**PAIH-10**
P(He)	5.6	9.8
P(N_2)	0.11	0.78
P(O_2)	0.46	2.2
P(CO_2)	2.7	13.2
α (He/N_2)	51	12.6
α (O_2/N_2)	4.2	2.8
α (CO_2/N_2)	24.5	16.9
α (He/CO_2)	2.1	0.74

[a]: In units of 10^{-10} [cm^3(STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$] at 10 kg/cm^2 upstream pressure and at 35 °C.

[b]: Selectivity, the ratio of pure gas permeability of respective gases.

The permeability for poly(amideimide) containing hexadecyloxy pendent chain (PAIH- 10) was higher due to the longer chain length that imparts more flexibility to the backbone as also revealed by its lower T_g. The increase in permeability is associated with decrease in selectivity, as was observed in the polyester series. The peculiar observation shown by polyesters as described above of fast increase in CO_2 permeability and decrease in He/ CO_2 selectivity with increasing chain length was observed in this series of poly(amideimide) also. The C_{16} side-chain containing poly(amideimide) in fact exhibited reverse selectivity for He/ CO_2, indicating strong influence of CO_2 solubility in polymer matrix with increased chain length. The comparison of C_8 side-chain containing polyester and C_8 side-chain containing poly(amideimide) reveals that the latter has lower permeability and higher selectivity, which can be attributed to its more rigid structure. This is further supported by the higher CO_2 based selectivity for poly(amideimide) than for the corresponding polyester.

5b.4 Conclusion

1. The gas permeability investigations on both BPA and HFBPA-based polyesters revealed that not only the length of alkoxy chain, but also nature of the bisphenol play an important role in governing gas permeation properties. The two opposing trends in governing permeability upon incorporation of alkoxy side chain were observed in the permeation properties of both these series. The increase in chain length of pendent alkoxy group in BPA-based polyesters increased the permeability and reduced the selectivity. However, in HFBPA-based polyesters the permeability initially increased marginally and then lowered as chain length of pendent group increased, presumably due to the incorporation of added flexible bulk in the available free volume created by hexafluoroisopropylidene group.
2. Poly(amideimide) series showed a behavior as that of BPA series, wherein gas permeability increased and selectivity decreased with increased chain length. This also confirms that the hexafluoroisopropylidene group is responsible for the different permeation behavior of HFBPA- based polyesters. The CO_2 permeability was largely influenced by the presence of alkoxy chain than for any other gas, possibly due to increased solubility of this condensable gas in the resultant polymer matrix.

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Chapter 6. Synthesis and Characterization of Polyamides Containing Pendent Flexible Alkoxy Groups

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6.1 Introduction

Wholly aromatic polyamides are characterized by their excellent balance of thermal and mechanical properties, which make them useful as high performance materials for advanced technologies.[1] However, they encounter processing difficulties due to their extremely high transition temperatures, which may exceed their decomposition temperatures, and their poor solubility in common organic solvents. Therefore, many efforts have been made to enhance their processability and solubility by chemical modification of their structure with a variety of methods: [2-15]
(i) introduction of bulky side groups, (ii) use of *meta*-oriented or asymmetrically substituted monomers, (iii) incorporation of flexible chains into the polymer backbone or as pendent groups. These modifications work by breaking chain symmetry and regularity and by destroying hydrogen bonds and generally lead to better solubility and improved processability.

A Japanese patent reports the synthesis of polyamides from 5-alkoxyisophthalic acids and various diamines.[16] However, detailed characterization data has not been reported in the patent. Valiyaveettil et al.[9] reported polyamides based on 5-alkoxyisophthaloyl dichlorides containing carbon chain length of 11 – 18 with *meta*-phenylene diamine and 2,6-diaminopyridine. Polyamides with improved solubilites were obtained.

As a natural extention of the synthesis of 5-alkoxyisophthalic acid monomers, a study was undertaken to synthesize aromatic polyamides from 5-alkoxyisophthalic acids containing alkoxy side-chains of varying lengths (C_4, C_8, C_{12}, C_{16}) by direct polycondensation with 4,4’-oxydianiline (ODA) using triphenyl phosphite (TPP) and pyridine as a condensing agent. The primary aim of this work was to examine the effect of pendent alkoxy chains on the properties of polyamides such as solubility and thermal behaviour.

6.2 Experimental

6.2.1 Materials

5-Alkoxyisophthalic acids were synthesized as described in **Chapter 3**. 4,4'–Oxydianiline (ODA) (Aldrich) was sublimed before use. Anhydrous lithium chloride (Aldrich) was dried at 180°C for 8 h under reduced pressure. Triphenyl phosphite (TPP) (Fluka) was purified by distillation under reduced pressure. 1-Methyl-2-pyrrolidone (NMP) and pyridine were dried over calcium hydride and distilled under reduced pressure. N,N-Dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *meta*-cresol, pyridine, chloroform and tetrahydrofuran (THF) were purified as per literature procedures.[17]

6.2.2 Measurements

The inherent viscosity measurements were made with 0.5% (w/v) solution of polyamide in DMAc at 30 ± 0.1 ^{o}C using an Ubbelohde suspended level viscometer.

IR spectra were recorded using polyamide films on a Perkin-Elmer 599B spectrophotometer.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 analyzer at a heating rate of 10^{o}C / minute under nitrogen atmosphere.

DSC was performed on Perkin-Elmer DSC-7 at a heating rate of 10^{o}C / minute under nitrogen atmosphere.

X-Ray diffractograms of polyamides were obtained on Rigaku Dmax 2500 X-ray diffractometer.

The solubility of polyamides was determined at 3 wt % concentration in various solvents at room temperature or on heating.

6.2.3 Polyamide synthesis

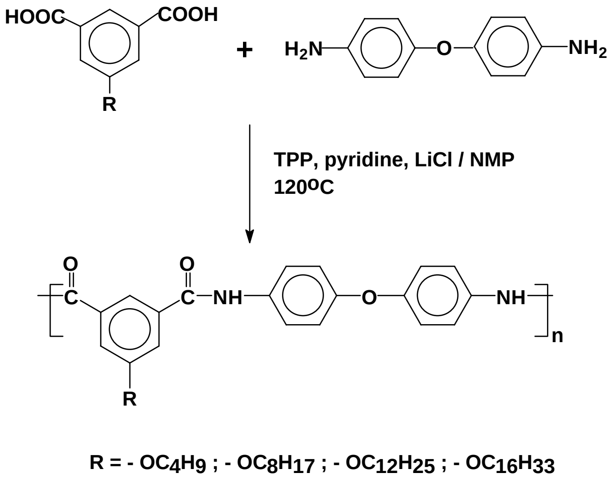
A representative procedure for the synthesis of polyamide is given below:

Into a 50 ml two-necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring bar were charged NMP (12 ml), 5-octyloxyisophthalic acid (0.44 g, 1.5 mmol), ODA (0.30 g, 1.5 mmol), lithium chloride (0.57 g), TPP (0.93 g, 3 mmol), and pyridine (2.65 ml). The mixture was heated with stirring at 120°C for 8 h. The viscous reaction mixture was poured into methanol (100 ml) when a fibrous precipitate was obtained which was filtered, washed thoroughly with methanol and hot water. The polymer was dried at 120°C for 12 h under reduced pressure.

6.3 Results and Discussion

6.3.1 Synthesis of polyamides

Scheme 6.1 depicts the synthesis of polyamides from the 5-alkoxyisophthalic acids and ODA. The direct polycondensation of diacids with aromatic diamines in a typical Yamazaki-Higashi reaction was adopted for the synthesis of aromatic polyamides.[18-20]



Scheme 6.1: Synthesis of polyamides from 5-alkoxyisophthalic acids and 4,4'-oxydianiline (ODA).

Polymerization reactions proceeded in a homogeneous solution. Polyamides were isolated by precipitating the reaction mixture into excess methanol. The results of synthesis of polyamides are presented in **Table 6.1**. Polyamides were isolated as white fibrous materials with inherent visocities in the range 0.55 – 0.63 dl / g indicating the formation of poymers with moderate molecular weights. Tough, transparent, and flexible films of polyamides could be cast from DMAc solution.

Table 6.1: Synthesis of polyamides from 5-alkoxyisophthalic acids and 4,4'-oxydianiline.

Polyamide	**Diacid (-R substituent)**	**Diamine**	**Yield, (%)**	**η_{inh}^{a}, (dL/g)**
PA-1	$-OC_4H_9$	ODA	98	0.60
PA-2	$-OC_8H_{17}$	ODA	96	0.63
PA-3	$-OC_{12}H_{25}$	ODA	99	0.57
PA-4	$-OC_{16}H_{33}$	ODA	98	0.55

a : η_{inh} measured at a concentration 0.5 g dl^{-1} in DMAc at 30 ± 0.1 °C.

6.3.2 FT-IR spectroscopic analysis

IR spectroscopy was used to confirm the formation of polyamides. **Figure 6.1** shows FTIR spectrum of polyamide drived from 5-dodecyloxyisophthalic acid and ODA as an example. FTIR spectra of all polyamides showed -NH stretching frequency as a broad band around 3300 cm^{-1}. This lowering of frequency could be attributed to the involment of NH groups in hydrogen bonding. The amide-I band, associated with stretching vibration of the carbonyl group appears at around 1655 cm^{-1}. The amide-II band, ascribed to the coupling of the N-H bending and C-N stretching of the C-N-H group appears around 1540 cm^{-1}.

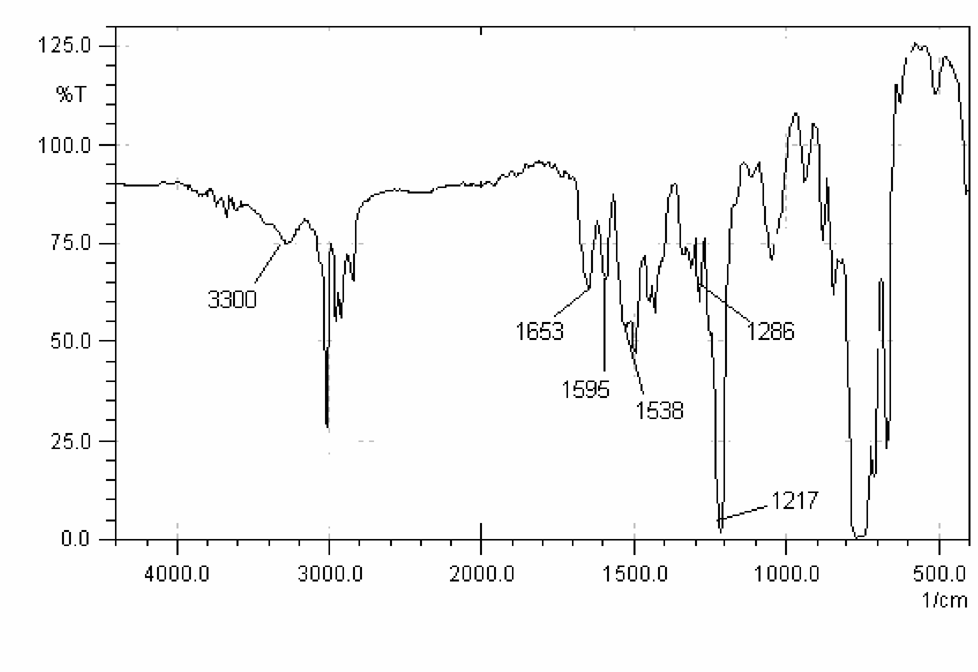


Figure 6.1: IR spectrum of polyamide derived from 5-dodecaloxyisophthalic acid and ODA.

6.3.3 Polyamide properties

6.3.3.1 Solubility of polyamides

Polyamides were tested for solubility at 3 wt % concentration in different solvents and the data is summarized in **Table 6.2**.

Polyamides derived from 5-alkoxyisophthalic acids and ODA were soluble in DMF, DMAc, NMP and pyridine, and upon heating in *meta*-cresol and were insoluble in THF and chloroform.

Table 6.2: Solubility data of polyamides derived from 5-alkoxyisopthalic acids and 4,4’-oxydianiline.

Polyamide	**DMF**	**DMAc**	**NMP**	**Pyridine**	**m-Cresol**	**THF**	**$CHCl_3$**
PA-1	++	++	++	++	+	–	–
PA-2	++	++	++	++	+	–	–
PA-3	++	++	++	++	+	–	–
PA-4	++	++	++	++	+	–	–

++ : Soluble at room temperature; +: Soluble on heating; –: Insoluble

6.3.3.2 Thermal behaviour of polyamides

Thermogravimetric analysis of polyamides was performed on Perkin-Elmer TGA-7 at a heating rate of 10°C /minute under nitrogen atmosphere. **Table 6.3** summarises the thermal behaviour data of polyamides.

Polyamides showed a single step decomposition behaviour similar to polyesters derived from BPA (**Chapter 5a, Figure 5a.11**). It was observed that the initial decomposition temperature varied in the range 320 – 375°C indicating reasonable thermal stability for these polymers.

Differential scanning calorimetric (DSC) analysis was performed on Perkin-Elmer DSC-7 at a heating rate of 10°C /minute under nitrogen atmosphere. DSC curves of polyamides are shown in **Figure 6.2** and the T_g values obtained are incorporated in **Table 6.3**.

The T_g values are in the range 166 – 255°C which are lower than the polyamide based on isophathalic acid and ODA ($T_g = 280^oC$)[21].

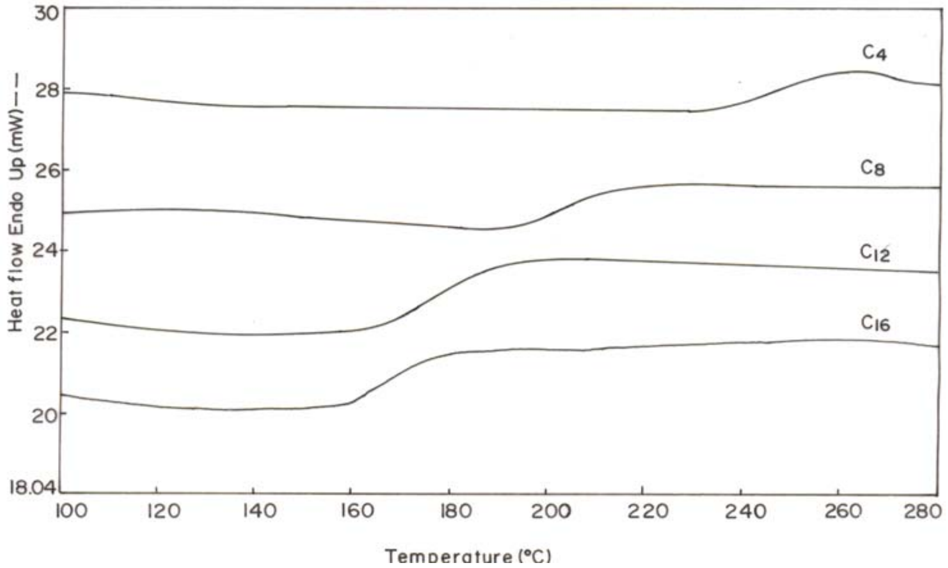


Figure 6.2: DSC curves of polyamides derived from 5-alkoxyisophthalic acids and 4,4'-oxydianiline (PA-1 to PA-4).

Table 6.3: Thermal characteristics of polyamides derived from 5-alkoxyisophthalic acids and 4,4'-oxydianiline.

Polyamide	**IDT (°C)^a**	**T_{10} (°C)^b**	**T_g(°C)^d**
PA-1	375	406	255
PA-2	360	397	208
PA-3	355	393	177
PA-4	320	353	166

a: Initial decomposition temperature (IDT) from TGA;
b: Temperature at which 10% weight (T_{10}) loss was observed;
c: Glass transition temperature (T_g) determined by DSC.

Figure 6.3 is a plot of T_g as a function of the number of carbon atoms in the pendent alkoxy chains of polyamides. For polyamide without the alkoxy side chain, i.e. polyamide derived from isophthalic acid and ODA, literature value (280°C) of T_g was taken. As can be seen from **Figure 6.3**, T_g values decrease with increase in side chain length which is in agreement with an increased flexibility of the polymer.

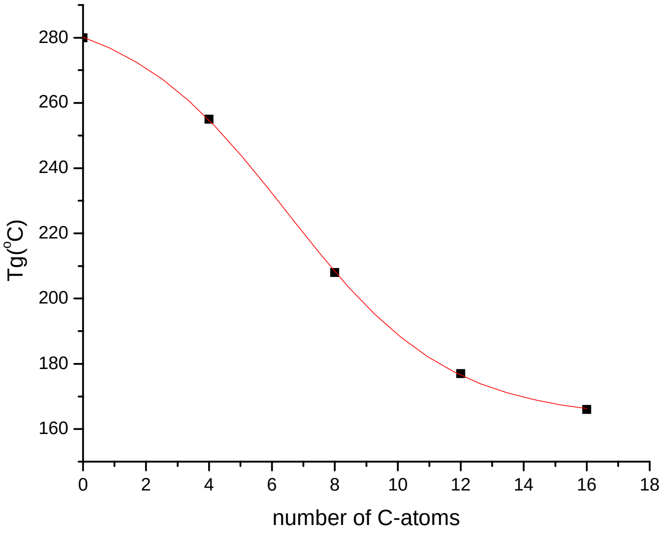


Figure 6.3: Plot of T_g Vs number of carbon atoms in alkoxy side chains of polyamides derived 5-alkoxyisophthalic acids and ODA.

Additional work on polyamides based on 5-alkoxyisophthalic acids and aromatic diamines was not pursued further.

6.4 Conclusion

1. A series of polyamides bearing pendent alkoxy chains was synthesized from 5-alkoxyisophthalic acids and ODA employing Yamazaki-Higashi reaction.
2. Polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and upon heating in *meta*-cresol. Tough, transparent and flexible films of polyamides could be cast from DMAc solution.
3. The incorporation of pendent flexible alkoxy chains along the polyamide backbone decreased the Tg values which ranged from 166 to 255^{o}C.
4. Polyamides were stable up to 320-375^{o}C under nitrogen atmosphere.

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Chapter 7. Summary and Conclusions

The main objective of the present research was to design and synthesize processable high performance polymers such as polyimides, poly(amideimide)s, polyamides, and polyesters by making use of difunctional monomers containing pendent flexible alkoxy chains. Another objective was to study the applications of selected poly(amideimide)s and a polyimide as alignment layers for liquid crystal display devices. Polyesters and poly(amideimide)s were also evaluated as membrane materials for gas separations.

Thus, four series of new alkoxy-substituted difunctional monomers such as aromatic diisocyanates, diacyl hydrazides, and aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages were designed and synthesized starting from 5-hydroxyisophthalic acid, a commercially available chemical, employing simple organic transformations. A total of 16 new difunctional monomers were synthesized and characterized by spectral methods.

5-Alkoxy-1,3-phenylenediisocyanates were polycondensed with commercially available aromatic dianhydrides to obtain a series of polyimides varying in chain length of the pendent alkoxy groups. There was a marginal improvement in the solubility of alkoxy group-containing polyimides in organic solvents. Wide angle X-ray diffractograms revealed that layered structures were formed for polyimides with long alkoxy chains. Depression in Tg of polyimides was observed by introduction of flexible pendent alkoxy groups (Tg values were in the range 159^o –246^oC) indicating their plasticizing effect. Polyimides were stable upto 390^o - 440^oC in nitrogen atmosphere. A large window between glass transition and polymer degradation temperature was observed. This gives an opportunity for these polyimides to be melt-processed or compression molded. The application of organo-soluble polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and

4,4’-oxydiphthalic anhydride (ODPA) as alignment layer for liquid crystal display was evaluated in brief. A pretilt angle of 2.97^o was observed which is adequate for display applications.

5-Alkoxyisophthalic acid dihydrazides were polycondensed with aromatic dianhydrides to obtain a series of new poly(amideimide)s varying in the chain length of the alkoxy group. Compared to the unmodified analogues, alkoxy- containing poly(amideimide)s exhibited significantly improved solubility in polar organic solvents. Exemplary case is the solubility observed for poly(amideimide) derived from 5-butyloxyisophthalic acid dihydrazide and PMDA. Poly(amideimide)s could be cast into tough, transparent and flexible films for their DMAc solution. Wide angle X-ray diffractograms revealed that layered structures were formed for poly(amideimide)s containing long pendent alkoxy chains.

A series of new regularly alternating poly(amideimide)s was synthesized by polycondensation of alkoxy group-containing aromatic diamines possessing pre-formed amide linkages and aromatic dianhydrides. The presence of pendent flexible alkoxy chains brought about improvement in solubility of poly(amideimide)s over that of unsubstituted analogues as exemplified by poly(amideimide)s based on rigid pyromellitic dianhydride(PMDA). Thermal analysis showed that pendent alkoxy chains induced the depression of both T_g values and thermal degradation temperatures. Poly(amideimide)s containing an aromatic ring between amide and imide linkages had greater heat resistance than the analogues poly(amideimide)s synthesized from aromatic diacylhydrazides and aromatic dianhydrides and possessing an amide bond directly attached to the imide ring.

Poly(amideimide)s containing octyloxy and hexadecyloxy side chains exhibited a good rubbing processability and excellent performance in controlling of both the alignment and the pretilt of LC molecules in the LC cell. The pretilt angle of LC molecules was easily achieved in a wide range of 3.8 – 17.5^o depending upon the rubbing density as well as the length of the alkoxy chain. These values are in the desirable range for super twisted nematic (STN) LCD devices.

Aromatic polyesters were synthesized by phase-transfer catalyzed interfacial polycondensation of 5-alkoxyisophthaloyl dichlorides and commercially available bisphenols, viz., BPA and HFBPA. It was observed that the presence of butyloxy pendent group at the 5-position of isophthaloyl dichloride brought about improvement in solubility of the polyester in common organic solvents like chloroform and dichloromethane. (Cf. polyester derived from isophthaloyl dichloride and BPA). Polyesters containing pendent alkoxy chains could be cast into tough, transparent and flexible films from their solution in chloroform.

Thermal degradation kinetics of polyesters revealed that degradation obeyed first order kinetics. The relationship between the chemical structure of polyesters and their thermal degradation behaviour was established.

Gas permeability studies on polyesters derived from 5-alkoxyisophthaloyl dichlorides and BPA showed increase in permeability and decrease in selectivity as length of pendent alkoxy group increases. However, HFBPA-derived polyesters behaved differently owing to the presence of bulky hexafluoroisopropylidene group. The permeability behaviour of poly(amideimide)s was similar to that of BPA – polyester series. The marked increase in CO_2 permeability than permeability of other gases tested namely He, O_2 and N_2 indicated potential of these membrane materials for CO_2 – based separation applications.

Polyamides were synthesized from 5-alkoxyisophthalic acids and 4,4’-oxydianiline (ODA) by Yamazaki-Higashi reaction. Polyamides of moderate molecular weights were obtained and could be cast into films from DMAc solution.

Overall, the pendent alkoxy chains did influence properties of polyimides, poly(amideimide)s, polyamides and polyesters by aiding solubility in organic solvents and reducing T_g. Additionally, poly(amideimide)s and a polyimide with pendent alkoxy chains are favourable for the generation of adequate liquid crystal pretilt angles – an application area where the requirements in terms of thermal properties are not very stringent.

Perspectives

High performance / high temperature polymers such as polyimides, poly(amideimide)s, polyamides and polyesters are of great interest in view of their excellent versatility in various applications. In this context an understanding of the structure-property relationship in high performance polymers is of significant contemporary interest. There is a continuing need to examine approaches to address the issues related to their limited solubility in common organic solvents and poor processability.

The present work on the synthesis of new difunctional monomers has expanded the range of condensation monomers available for preparation of high performance polymers with improved processability albeit a compromise in thermal properties.

It would now be interesting to synthesize other classes of high performance polymers making use of the synthesized difunctional monomers. For example, aromatic diamines containing pre-formed ester linkages are potentially useful monomers for the synthesis of regularly alternating poly(esterimide)s and poly(esteramide)s.

The present work was focused on the synthesis and thermal characterization of polyimides, poly(amideimide)s, polyamides and polyesters. Detailed studies using high temperature WAXD and 13C solid-state NMR spectroscopy would yield useful information on the packing mode and conformational transitions of the alkoxy side chains.

It would be interesting to examine the key factors that determine the pretilt angles of liquid crystal alignment – an issue that was not addressed adequately in the present work.

Synopsis of Thesis entitled
‘Synthesis and Characterization of Polyamides, Polyimides and Polyesters Containing Flexibilizing Groups’

Introduction

High performance / high temperature polymers such as polyimides, polyamides and polyesters have been the subject of numerous studies in order to extend the applications of organic materials to perform under harsh conditions.[1-8] These polymers are well known for their excellent thermal stability and mechanical properties. However, the poor solubility, and high glass transition or melting temperatures caused by rigid polymer backbone leads to their processing difficulty. The ordering and varying of backbone functions has a profound effect on the final properties of the polymer.[9-11] One of the most important criteria that decides the final properties of a polymer is the monomer structure, and by judicious selection of suitable monomers the properties of a polymer can be tailored. Therefore in the synthesis of a polymer the first step constitutes the synthesis of desired monomers that can give rise to polymers with expected / targeted properties. The following approaches were suggested to improve the processability of high performance / high temperature polymers.

These approaches include: (1) introducing kinks or flexible units in the main chain,[12,13] (2) use of 1,3-disubstituted instead of 1,4-disubstituted monomers, and / or asymmetric monomers[14] , and (3) replacing the conventional monomers with ones containing pendent groups.[15,16] One of the attempts to improve polymer processability is *via* internal plasticization. Plasticization normally involves the incorporation of a low molecular mass additive which improves polymer flow and processability. In internal plasticization, the plasticizer is chemically attached to or incorporated in the polymer backbone. It is reported that the introduction of flexible side groups onto the polymer backbone leads to a dramatic increase in solubility and decrease in the glass transition temperature (Tg).[17,18]

The approach adapted in the present work involves the synthesis of 5-alkoxyisophthalic acids, 5-alkoxyisophthaloyl dichlorides, 5-alkoxy-1,3-phenylene diisocyanates and 5-alkoxyisophthalic acid dihydrazides. The 1,3- position of the reactive groups in the monomer structure was selected for several reasons: The acid / acid chloride / isocyanate / acyl hydrazide groups were placed in the 1 and 3 positions in order to obtain *meta*- catenation in the polymer backbone. Such catenation is known to increase solubility and reduce the Tg[14] . Furthermore, aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages and possessing pendent flexible alkoxy groups were designed and synthesized. By relatively easy and inexpensive chemical routes, difunctional monomers were prepared that provide the structural features needed in the polymer for improvement of processability and / or even more specific properties such as pretilt angle and permeability. The aim of the present investigation was to synthesize processable aromatic polyesters, polyamides, polyimides and poly(amideimide)s by incorporating pendent flexible alkoxy groups along the polymer backbone and to establish a structure-property relationship.

With the above objectives, the following specific work was chosen for the thesis.

Objectives of the Present Research:

1) Synthesis of *meta*-oriented aromatic diacids, diacidchlorides, diisocyanates and diacylhydrazides, containing pendent flexible alkoxy chain starting from 5- hydroxyisophthalic acid – a commercially available chemical.
2) Synthesis of aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages and possessing pendent flexible alkoxy groups.
3) Synthesis and characterization of high performance polymers such as aromatic polyimides, poly(amideimide)s, polyesters and polyamides containing pendent flexible alkoxy groups with varying carbon chain lengths.
4) To study the effect of pendent flexible alkoxy groups of varying carbon chain on the solubility and thermal properties of high performance polymers.
5) To evaluate a few selected polymers containing pendent flexible alkoxy groups as materials for alignment layers for liquid crystals and as membrane materials for gas separation studies.

Chapter 1: Introduction and Literature Survey

This chapter provides a comprehensive review of literature on the synthesis of polyimides, poly(amideimide)s, polyesters and polyamides, their structure-property relationship and applications.

Chapter 2: Scope and Objectives

This chapter deals with the scope and objectives of the thesis.

Chapter 3: Synthesis and Characterization of Difunctional Monomers Containing Pendent Flexible Alkoxy Groups

This chapter provides a study on

a) Synthesis of a series of *meta*-oriented aromatic diacids, diacid chlorides, diisocyanates and diacylhydrazides containing pendant flexible alkoxy groups starting from 5- hydroxyisophthalic acid.

b) Synthesis of aromatic diamines containing pre-formed amide linkages and aromatic diamines containing pre-formed ester linkages and possessing pendent flexible alkoxy groups.

The difunctional monomers and intermediates involved in their synthesis were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy.

Chapter 4: Synthesis and Characterization of Polyimides and Poly(amideimide)s Containing Pendent Flexible Alkoxy Groups

This chapter is subdivided into three sections.

Chapter 4a: Synthesis and Characterization of Polyimides from Diisocyanates Containing Pendent Flexible Alkoxy Groups and Aromatic Dianhydrides

This section describes synthesis of polyimides from diisocyanates containing pendent flexible alkoxy groups and commercially available aromatic dianhydrides, viz., 4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (FDA) and 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA).

Chapter 4b: Synthesis and Characterization of Poly(amideimide)s from Diacylhydrazides Containing Pendent Flexible Alkoxy Groups and Aromatic Dianhydrides

This section deals with synthesis of new poly(amideimide)s from diacylhydrazides containing pendent flexible alkoxy group and aromatic dianhydrides, namely, 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA), ODPA and PMDA.

Chapter 4c: Synthesis and Characterization of Poly(amideimide)s from Diamines Containing Pre-formed Amide Linkages and Aromatic Dianhydrides

This section provides synthesis of new poly(amideimide)s from diamines containing pre-formed amide linkages with aromatic dianhydrides , namely ODPA, FDA, PMDA, and BPDA.

Polyimides and poly(amideimide)s were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, optical transparency, thermogravimetric analysis and DSC. Selected poly(amideimide)s were evaluated as alignment layers for liquid crystals and as membrane materials for gas separation studies.

Chapter 5a: Synthesis and Characterization of Polyesters Containing Pendent Flexible Alkoxy Groups

This chapter provides a study on synthesis of processable aromatic polyesters containing pendent flexible alkoxy groups with 4, 8, 12 and 16 carbon chain. Polyesters were synthesized by phase-transfer catalyzed interfacial polycondensation of 5-alkoxyisophthaloyl dichlorides and two aromatic diols viz. bisphenol-A (BPA) and 4,4’-(hexafluoroisopropylidene) diphenol (HFBPA). The polyesters were characterized by inherent viscosity measurements, solubility tests, gel permeation chromatography (GPC) , IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC. The effect of chain length of pendent alkoxy groups on polymer properties such as solubility and Tg was examined. The selected polyester films were studied as membrane materials for gas separations. The kinetics of the thermal degradation of polyesters was studied by thermogravimetric analysis.

Chapter 5b: Gas Permeability Studies in Polyesters and Poly(amideimide)s Containing Pendent Flexible Alkoxy Groups

This section deals with gas permeability investigations on selected polyesters and poly(amideimide)s containing pendent flexible alkoxy groups. The effect of chain length on permeability of He, O_2, N_2 and CO_2 and selectivity for two commercially important gas pairs, *viz*. CO_2/N_2 and O_2/N_2 was studied by variable volume method at 35°C and 10 kg/cm^2 upstream pressure.

Chapter 6: Synthesis and Characterization of Polyamides Containing Pendent Flexible Alkoxy Groups

This chapter deals with synthesis of aromatic polyamides by Yamazaki's polycondensation method of 5-alkoxyisophthalic acids with aromatic diamines. The polyamides were characterized by inherent viscosity measurements, solubility tests, IR spectroscopy , thermogravimetric analysis and DSC. The effect of varying chain length of pendent alkoxy groups on polymer properties was studied.

Chapter 7: Summary and Conclusions

This chapter summarizes the results and describes salient conclusions of the investigations reported in this thesis.

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