Synthesis and Properties of Polyimides and Copolyimides Containing Pyridine Units: A Review

Shahram Mehdipour-Ataei* and Naeemeh Bahri-Laleh

Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

A B S T R A C T

A great number of studies of new polymer syntheses have been focused on the preparation of high-performance polymers. Imide polymers and their copolymers are a well-established class of high-performance polymers that show good combination of mechanical, electrical, and thermal properties. This paper reviews the synthesis and properties of polyimides and copolyimides with different structures specially those containing pyridine ring in their structure. Advantages of using a pyridine nucleus is relayed on two factors. First, high thermal stability derived from its molecular symmetry and aromaticity, and second, improved solubility of the pyridine (in respect to phenyl group) containing polymers because of increased dipole-dipole interactions of polymer-solvent system. This discussion covers different structures of pyridine-based polyimides and their physical and thermal properties. The subtle variations in the structure of the monomers have a great effect on the properties of the final polyimides. Various structural features that are important for understanding the structure/property relationships have been discussed.

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(∗) To whom correspondence to be addressed.
  E-mail: s.mehdipour@ippi.ac.ir

INTRODUCTION

High performance polymers are an important class of polymers and their applications are growing steadily. Many studies on new polymer synthesis are focused on the preparation of these polymers. In general, they show high thermal stability, good chemical resistance, and excellent mechanical properties.

Polyimides have attracted the attention of scientists and engineers more than other polymers in the field of high temperature resistant polymers [1-3]. This attraction is not only due to the desirable combination of their properties, but also to their synthetic potential readiness for specific applications. At the beginning, polyimides found application in a rather restricted number of technologies, as films and varnishes for the aerospace and electrical industries. The advancements in addition polymerization of polyimides and thermoplastic-processable aromatic polyimides, however, have widened the range of properties and application possibilities to a great extent.

At present time, they are considered as versatile polymers with an almost unlimited spectrum of applications as specialty polymers for advanced technologies [4-10]. The first reference to a polyimide was dated at the beginning of the 20th century [11], but the actual emergence of polyimides as a polymer class took place in 1955 with a patent of Edwards et al. on polymers from 1,2,4,5-tetracarboxybenzene and aliphatic diamines [12]. Since then growing interest in polyimides has brought about a big expansion of the science and technology of this family of special polymers which are characterized by excellent mechanical and electrical properties along with outstanding thermal stability.

From the beginning, the major proportion of research efforts on polyimides was directed to the development of wholly aromatic species, seeking for high thermal stability. In this respect, the all-aromatic polyimides are such materials that can retain their properties and structurally remain almost unchanged at 250-300ºC for long periods of time. It was then realized that the application of aromatic polyimides, and in general, of polyheterocycles types was not possible from the melt procces. Furthermore, their extreme structural rigidity and high density of cohesive energy rendered them insoluble in many organic media. Therefore, some significant synthetic efforts in the area of high temperature resistant polymers have been focused on improving their processability and solubility through the design and synthesis of new monomers [13-16].

POLYIMIDE SYNTHESIS

Two-step Polycondensation Method
The most widely practiced procedure in polyimide synthesis is a two-step poly(amic acid) process. It involves reacting a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent such as *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidinone (NMP) to yield an intermediary poly(amic acid) which is then cyclized into the final polyimide (Scheme I).

The mechanism of poly(amic acid) formation involves a nucleophilic substitution reaction at the carbonyl group of the dianhydride with a diamine.
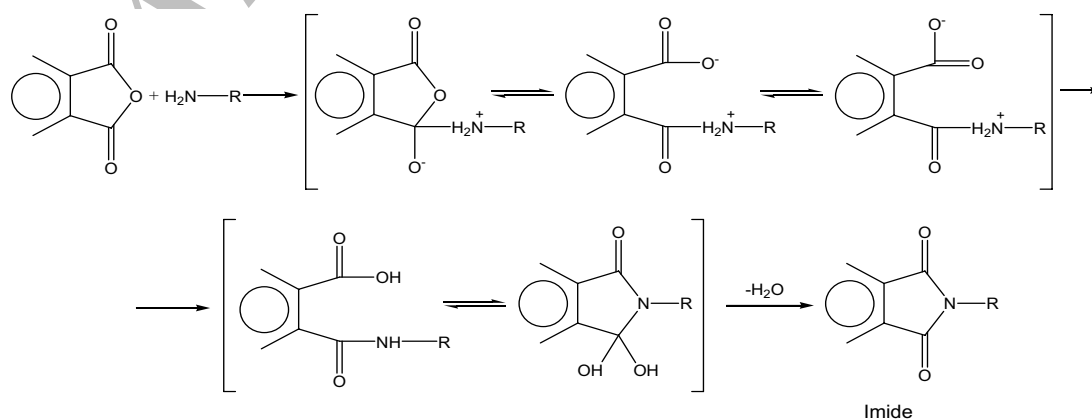
Scheme I. Two step method for polyimide synthesis.

Hence, the reaction is expected to depend upon the electrophilicity of the carbonyl of the dianhydride and the nucleophilicity of the amino group of the diamine.

It is important to note that the poly(amic acid) formation is exothermic and the equilibrium is favoured at lower temperatures [7]. Another important factor affecting the reaction equilibrium is the monomer concentration. As the forward reaction is bimolecular and the reverse reaction is unimolecular, increasing the monomer concentration favours high molecular weight products. It was also found that the order and the mode of monomer addition strongly influence the final molecular weight and the highest molecular weights obtained when solid dianhydrides are added to a solution of diamines. The increase in molecular weights is entirely due to the avoidance of the side reactions [17].

Poly (amic acid)s can be converted to corresponding polyimides by chemical imidization or thermal imidization methods. Chemical imidization is normally promoted by acetic anhydride in combination with organic bases for instance, pyridine or triethylamine, while other dehydrating agents such as propionic anhydride, trifluoroacetic anhydride, N,N-dicyclo-hexylcarbodiimide, etc. can be used as well. Although it can be performed on polyimide films, chemical imidization is mostly carried out in solution with the final polyimide being collected as a precipitate which by convenience remains soluble all over the process. When the reaction is conducted at room temperature a period of 24 to 48 h is needed for total imidization, while some few hours would only be enough if the chemical cyclodehydration reaction is allowed to proceed at 100ºC.

The intermediate poly(amic acid) is usually converted to the final polyimide by a thermal imidization route. This process is especially useful when the final product is desired as a film or a coating resin. Films are first cast on a substrate and then let pass through a thermal cycle by heating the poly(amic acid) mixture to 100°C and holding it for 1 h, and then again heating the mixture from 100°C to 200°C and holding it for another 1 h. Finally, the mixture is heated from 200°C to 300°C and then being held for further 1 h, followed by slow cooling to room temperature [18-21].

One-step Polycondensation Method
This technique is employed for the synthesis of polyimides which are being soluble in organic solvents at polymerization temperatures. The process involves heating a stoichiometric mixture of monomers in a high boiling solvent or in a mixture of solvents at 180-220°C. The imidization proceeds rapidly at these temperatures and the water generated due to the reaction is distilled off continuously as an azeotrope mixture along with the solvent.

The commonly utilized solvents are nitrobenzene, m-cresol, and dipolar aprotic amide solvents. The high temperature solution polymerization is often performed in the presence of catalysts. An acidic catalyst such as benzoic acid is added in the first step, which promotes the formation of trans-isoimide. It has been proposed that a basic catalyst such as isoquinoline is then needed to convert the trans-isoimide into polyimide [22-23]. This process is especially useful for polymerization involving unreactive dianhydrides and diamines. An interesting feature of this method is that it often yields materials with a higher degree of crystallinity than those obtained by two-step methods. This may be due to the increased solubility of the monomers in the solvent medium [24].

Other Methods
Condensation of Dianhydrides and Diisocyanates
The reaction takes different pathways depending on the conditions employed. In the absence of catalyst the reaction has been claimed to proceed through a seven-membered polycyclic intermediate (Scheme II) that finally gives rise to polyimide with evolution of
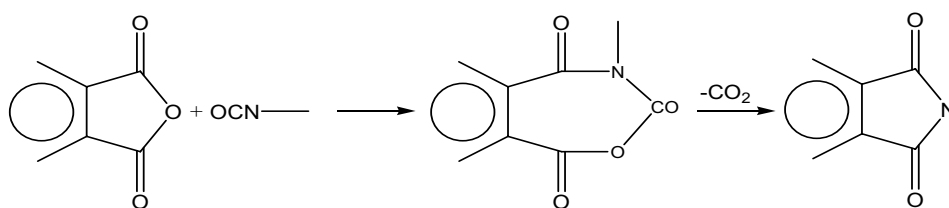
Scheme II. Mechanism of polyimide synthesis from dianhydrides and diisocyanates.

carbon dioxide [25-26].

The reaction is conducted in solution of aprotic solvents in the presence of reagents at low temperature and a maximum reaction temperature of ~130°C. On the other hand, to this date, polyimides of very high molecular weight have not been reported by this method.

In the presence of catalysts, the mechanism is different. Catalytic quantities of water or alcohols facilitate imide formation with possible formation of intermediates such as ureas and carbamates which then react with anhydrides to yield polyimides. Other conventional catalysts have been widely used to accelerate this reaction, for which the tertiary amines, alkali metal alcoholates, metal lactams, and even mercury

organic salts have been reported [27].

Condensation of Diimides
Diimides of tetracarboxylic acids can be used for the synthesis of polyimides. Several reactions have been used:

1- Polycondensation of diimides with dihalides (Scheme III)

2- Aminolysis of diimides by diamines (Scheme IV)

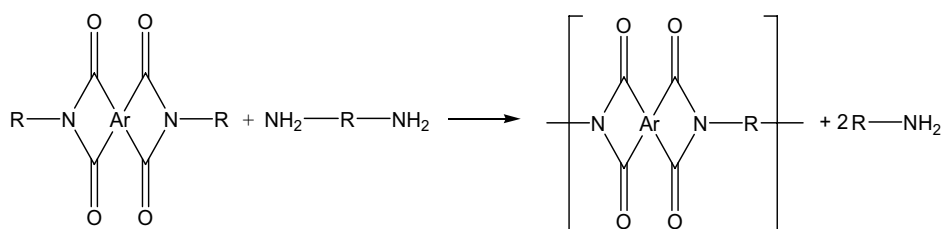3- Transimidization (Scheme V)

Condensation of Silylated Diamines
This method has been successfully applied to the synthesis of aromatic polyimides and can be considered
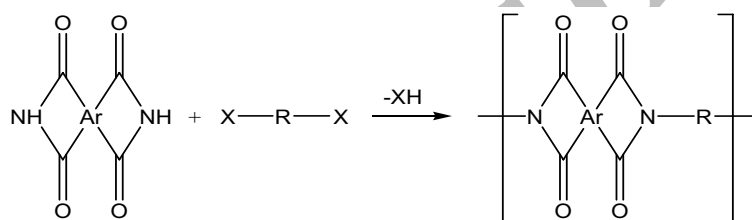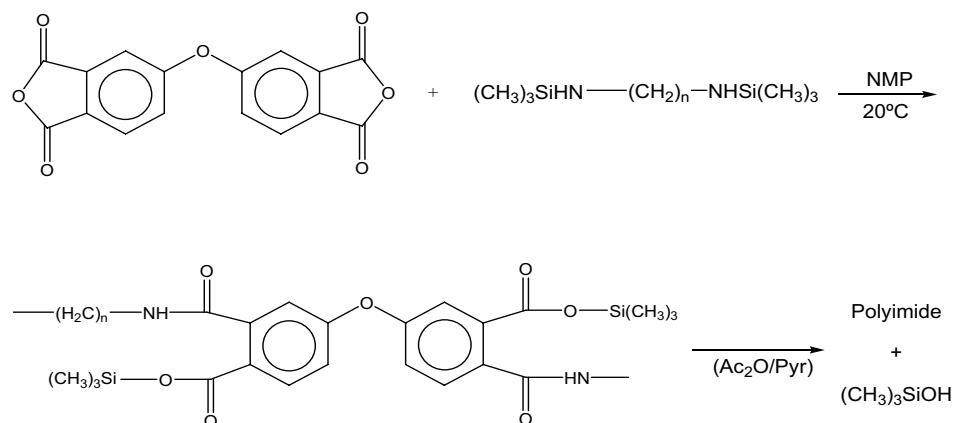

Scheme III. Synthesis of polyimides from diimides and dihalides.
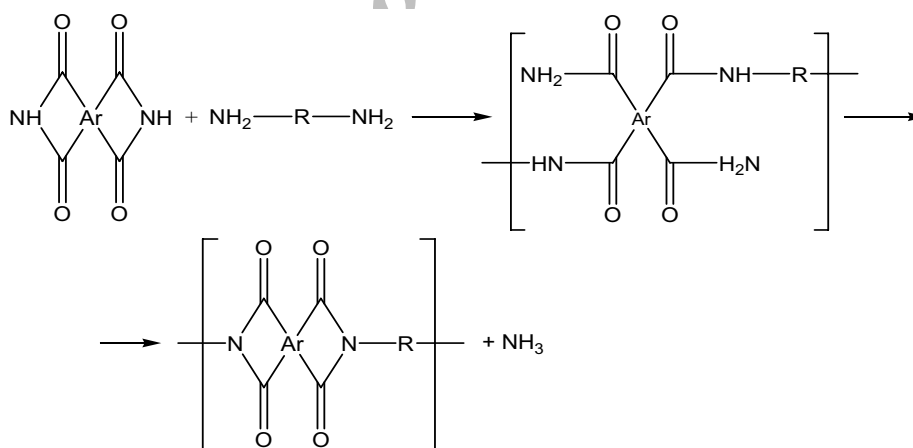
Scheme IV. Polyimide synthesis from diimides and diamines.

**Scheme V.** Mechanism of transimidization in polyimide synthesis.

Scheme VI. Polyimide synthesis by silylated diamines.

as a recommendable method in some instances, particularly for less reactive diamines, such as silylated aromatic diamines which are proved to be more nucleophilic than free diamines. By this method, a poly(amic trimethyl silyl ester) is produced in the first step which can be converted into polyimide by chemical means (Scheme VI) [28,29].

Addition Reactions
During the last three decades, there has been a trend towards structural modification of polyimides to improve their solubility and processability. Thus, the

synthesis of telechelic oligoimides has developed as the thermosetting telechelic oligomer precursors of thermostable networks as well as telechelic oligomer precursors of block copolymers. The number-average molecular weight of these oligoimides must be rather limited (around 2000 g. mol^{-1}) to reach the best compromise between processability and thermal and mechanical performances. Up to now, in order to prepare thermosetting prepolymers leading to thermostable networks after curing, most of the oligoimides have ended by cross-linking functional groups such as maleimide, nadimide, nadic allyl,
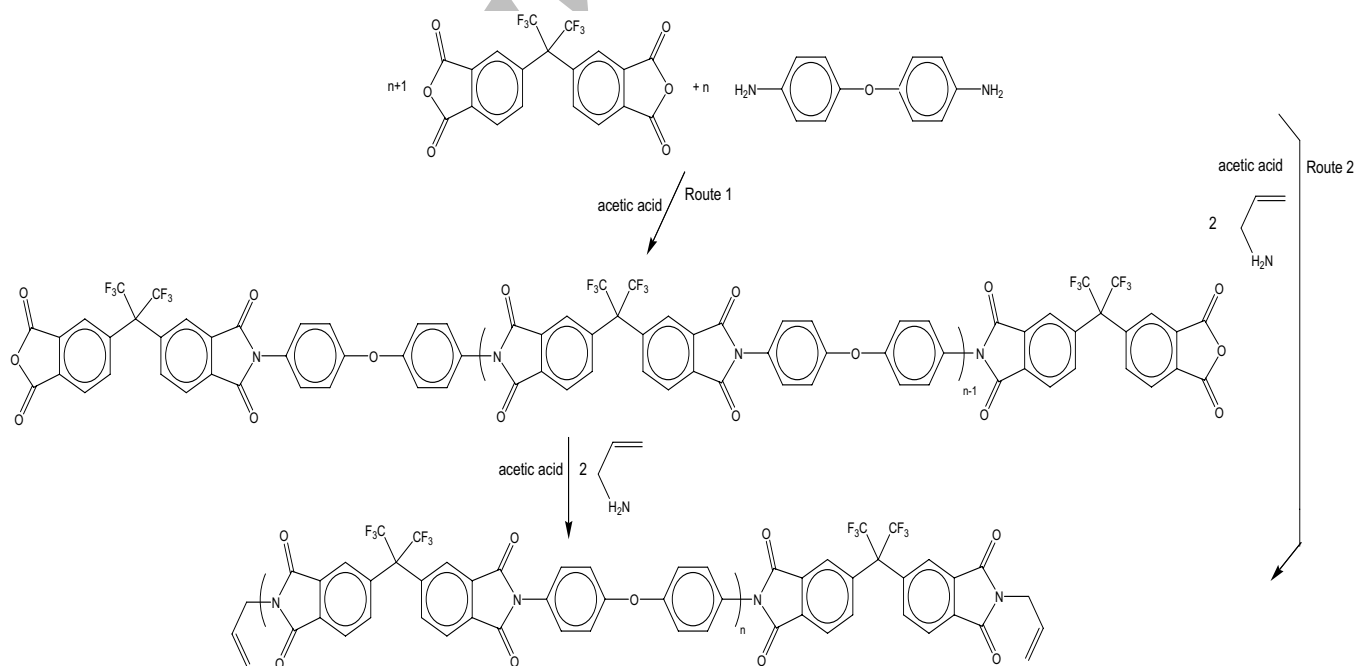
Scheme VII. Synthesis of allyl terminated oligoimide.

acetylene, and benzocyclobutene [30,31]. For instance, a procedure for the synthesis of allyl terminated oligoimide is shown in Scheme VII [32].

As it is shown, telechelic oligoimides end-capped with anhydride or allyl groups have been successfully synthesized in an acid medium. This method essentially enables a very high reaction rate followed by a simple treatment. Two methods have been studied to obtain this oligoimide. The first method consists of mixing a dianhydride, diamine, and monoamine in onestep. Whereas, the second one involves the synthesis of an oligoimide in two steps, in which the number-average molecular weight is easier to control. Such precursors by controlling the imide structural blocks would lead to copolymers which contain alternating oligoimide moieties with different physical properties.

STRUCTURE/PROPERTY RELATIONSHIPS

Glass Transition Temperature

With increasing the symmetry and rigidity of polymer chains, the glass transition temperature increases. Also, polymers containing aromatic structure have higher T_g than polymers having aliphatic structure. Highly dipolar bridging groups such as carbonyl and sulphonyl impart higher T_g than non-polar groups such as oxo or methylene bridgings.

Flexible pendent groups reduce the glass transition of the polymer by acting as internal diluents which may lower the frictional interaction between the chains. The overall effect would be a reduction in the rotational energy requirements of the backbone. At longer aliphatic side groups, T_g increases as side chain crystallization sets in, hence impending chain motion.

Scheme VIII and Table 1 show the effect of isomeric attachment of diamine and dianhydride on the glass transition temperature, respectively [7]. The glass transition temperature decreases as the polymer goes from all para to all meta catenations. The explanation is that an overall decrease in T_g correlates with backbone flexibility. However, the ortho containing polymers contradict this theory by their T_g being considerably higher than expected. In this structure (Scheme VIII) the presence of ortho linkages can lead to a strong dipolar unit where the imide unit and the carbonyl bridge are in close proximity. The T_g is not changed as much by isomeric variations in the dianhydride unit as in the diamine.

To study the structural effects of pendent groups on the T_g of polyimides, the synthesis of two series of aromatic polyimides containing various-sized alkyl side groups have been presented in Scheme IX. Series of polyimides derived from both BTDA and 6FDA dianhydrides exhibit similar glass transition temperature behaviour. Both series follow a decreasing order of BTDA-MBDMA > BTDA-MDA > BTDA-MBDEA > BTDA-MBDIA and 6FDA-MBDMA > 6FDA-MDA > 6FDA-MBDIA > 6FDA-MBDEA.
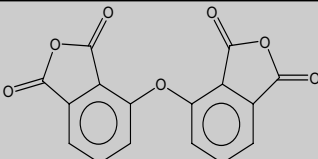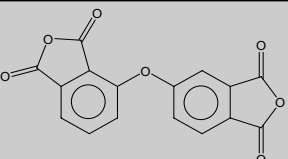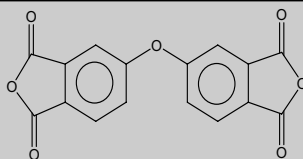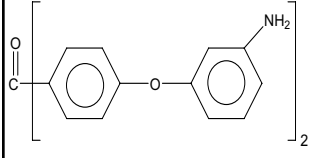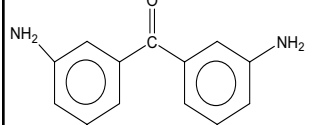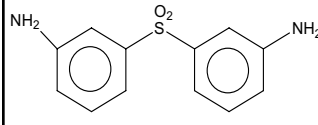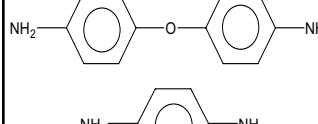
The glass transition temperature increases markedly when hydrogen atoms at ortho positions of aniline rings are replaced with methyl groups, but decreases with growing the alkyl side group size.

The bulky alkyl groups affect the T_g of a polyimide in two manners. First, it reduces the intermolecular interactions and chain packing, thus increases the free volume in polymer systems and so leading to decreased T_g. This effect is enhanced with the increasing sizes of the alkyl groups. Second, attaching bulky alkyl groups next to the imide linkages may severely restrict polymer chain thermal rotation, thus significantly increasing chain stiffness and leading to

Amine attachment	T_g(ºC)
2,2´	289
2,3´	259
2,4´	289
3,3´	264
3,4´	282
4,4´	293
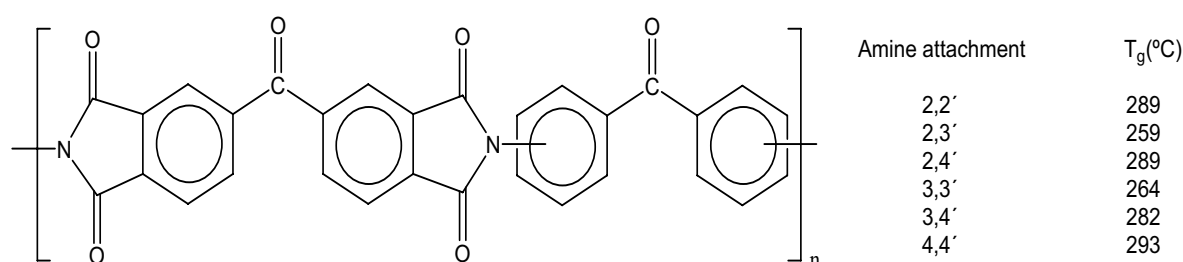
Scheme VIII. Effect of isomeric attachment of diamine on the glass transition temperature of the resulted polyimides.

Table 1. Effect of isomeric attachment of dianhydride on the glass transition temperature of the related polyimides.

Diamine \ Dianhydride			
	198	207	204
	234	243	235
	241	244	253
	246	270	268
	294	313	no T_g observed

increased T_g.

BTDA-MBDMA Polymer has a T_g value which is 30°C higher than that of BTDA-MDA polymer. Notably, a similar relation is also observed for 6FDA-MBDMA and 6FDA-MDA polyimides. Two methyl groups both on ortho positions to the amine group, induce high steric hindrance on the bond rotation

between the phenyl and imide rings. Additionally, the replacement of methyl groups with ethyl or isopropyl larger groups causes an intensive depression rather than further increment in T_g. This reduction in T_g is attributed to the increased free volume in the polymer system resulting from the growth of the alkyl group.

Therefore, these differences in T_g can be attributed

Dianhydrides:
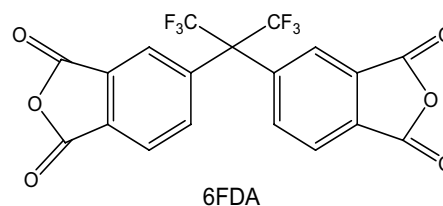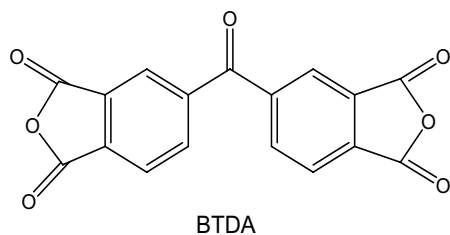
Diamines:
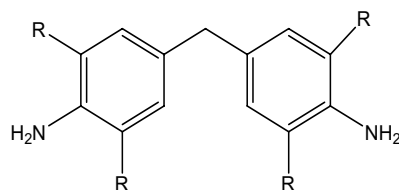
Scheme IX. Aromatic polyimides containing various-sized alkyl side groups.

to two opposite factors, namely the restriction of chain rotation caused by the steric hindrance of pendant groups and the increase of free volume resulting from the reduction of intermolecular interaction and ordered chain-packing [33].

Thermo-oxidative Stability

According to the rule of thermo-oxidative stabilities in polyimides, when the dianhydride and diamine are in a high oxidation state, polyimides should exhibit better oxidation resistance than other polymers of similar molecular weights. Since, all common polyimides based on PMDA, BTDA, ODPA, and 6FDA have dianhydrides that are in high oxidation states, the thermo-oxidative instability in general must be related to the more oxidation susceptibility of the diamine derived units.

If the stoichiometry is based on the presence of the excess dianhydride (0.5-2%), a better thermo-oxidative stability would be obtained than that in the case of excess diamine. Very high molecular weight polyimides generally exhibit better thermo-oxidative stability than their corresponding lower weight species.

Effect of Chain Structure on Crystallinity

Few factors appear to be distinctly important for inducing crystallinity in polyimides. Para-substituted dianhydrides and diamines appear to favour the crystallization while, increasing meta-substitution seems to reduce the ability of the polymer to crystallize. While, para- and meta-substituted ether linked diamines seem to be the best candidates for inducing crystallinity in the polyimides, increasing the flexibility by introducing ortho-substitution often inhibits the presence of crystallinity. This is because the ortho-substitution pack often controls the chain symmetry and thus makes it harder for the chain to arrange into crystal lattice. Introduction of bulky bridging groups or pendant side groups in the chain backbone also inhibits crystallinity and is actually often one of the practiced means when developing soluble polyimides. Another feature related to the ability of polyimides to crystallize is the nature of the dianhydride. For most polyimides using common dianhydrides, the ability to crystallize often goes with the order of BTDA>PMDA>BPDA~ODPA, although, some exceptions, however, do exist to this rule.

Liu et al. [34] have studied the incorporation of various side chains containing biphenyl unit on the crystalline morphology and properties of the resulted polyimides. Several polyimides derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,5-diaminobenzoate containing various side chains with biphenyl unit (PP0DA without spacer, PP2DA with ethylene spacer, PP6DA with hexylene spacer, and CN6DA with hexylene spacer and cyano group) were prepared by thermal imidization. As a reference, polyimides without side chains have also been prepared by polycondensation of *m*-diaminobenzene (MPDA) with the same aromatic dianhydride. For BTDA/MPDA polyimide sample, in the initial stage of thermal imidization, the PAA films look totally dark under polarized light.

With the increase in temperature, many spherulites are formed in a relatively short time and a complicated spherulitic morphological feature is clearly observed under the continuous thermal imidization. In addition to the zigzag Maltese cross, the spherulites also show concentric extinction rings, which are characteristics of banded spherulites, and insertion of a sensitive tint plate along the 45° direction, which leads to an identification of negative birefringence.

The introduction of side chains significantly inhibits the formation of perfect spherulite morphology. Under continuous thermal imidization condition, BTDA/PP0DA, BTDA/PP2DA, and BTDA/PP6DA form only fine grainy crystalline particle. While for polyimide with cyano-biphenyl side chains no crystalline may be seen under polarized light.

Solubility

A number of methods have been used to attain solubility in polyimides while maintaining their desirable high temperature characteristics. The majority of these approaches have involved the following structural modifications:

1- The incorporation of flexible or non-symmetrical thermally stable linkages in the polymer backbone such as perfluoroalkyl, oxygen or sulphur linkages, and phosphorus linkages [35].

2- The introduction of large polar or non-polar pendant substituents along the polymer backbone. The effects of polar and non-polar substituents on solubility are similar, but polar substituents do tend to

afford solubility in a greater number of solvents [36,37].

3- The disruption of symmetry and recurrence regularity through the copolymerization of two dianhydrides or two diamines [38].

The main concept behind all these approaches is to reduce the influence of several types of polymer chain-chain interactions, as well as the chain packing and charge transfer of the electronic polarization interactions.

Colour

Colour in polyimides may have many origins such as chromophoric units, impurities from starting materials, side reaction products (isoimides), and charge transfer complexation. Unlike crystalline polymeric materials, amorphous polyimides exhibit good transparency characteristics.

The wholly aromatic polyimides have strong absorbance in the visible region of their UV-visible spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the inter-molecular charge-transfer complex (CTC) formation. A lowering of the CTC generally between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties affords polyimide with lighter colour. For example, the optically transparent and colourless polyimide can be synthesized from a dianhydride and a diamine that have hexafluoroisopropylidene (-C(CF$_3$)$_2$-) groups [39-41]. Hasegawa et al. [42] have reported the general conditions for obtaining transparent polyimides by using lower electron-accepting dianhydrides and lower electron-donating diamines as monomers for weakening the both intra- and inter-molecular charge transfer interactions.

The most effective approach for avoiding colour formation is the use of diamines or dianhydrides which contain alkyl groups that, not only eliminate electronic interactions that may cause colour formation, but also tend to break up extended conjugation along the chain which causes colouration.

Dielectric Constant

Polyimides have been widely utilized as packaging materials and dielectric layers in electronic and microelectronic industries because of their outstanding characteristics such as low dielectric constant, good processability, high mechanical properties, and superior thermal stability [43]. However, polyimides' dielectric constants are not low enough to meet the specifications of intermetal dielectric layers. Therefore, preparation of polyimides with lower dielectric constants has been under development in recent years [44-48]. Among the strategies used to lower the dielectric constant in polyimides, some potential methods are listed as follows:

1- Adopting diamine and dianhydride monomers with minimum polarizability.

2- Constructing polyimides having high degree of free volume.

3- Incorporating fluorine into the polymer chains.

4- Preparing foams by introducing air voids into polyimide matrix.

The methods in strategies (1) and (2) are not efficient for further decrease in the dielectric constant of polyimides, because of the intrinsic properties of the monomers. Although, fluorine incorporation can lead to polyimides with dielectric constants in the range 2.4-2.8, the limitations of this method, however, lie in the synthetic difficulties and in the expenses of mechanical strength, solvent resistant thermal stability, etc. [48]. Based on the fact that air is the substance with the lowest dielectric constant of 1.0, preparing polyimide as foams is an attractive and reasonable approach to achieve low dielectric constant materials [49].

PYRIDINE-BASED POLYIMIDES AND COPOLYIMIDES

Aromatic polyimides are thermally stable polymers that generally show excellent mechanical strength and chemical stability. Due to the increased performance characteristics demanded of polymers in various fields, including aerospace, automobile, and microelectronic industries, use of these aromatic polymers is growing steadily. However, one of the drawbacks to employ these high performance polymers is because of their difficult processing conditions due to their high melting temperatures or high glass transition temperatures. Therefore, some significant synthetic efforts, in the area of high-temperature resistant poly-

mers have been focused on improving their process-ability and solubility through the design and synthesis of new monomers.

The objective for selection of heterocyclic rings in the main chain of the synthetic polymer is to impart certain properties to the polymer. Among different heterocyclic rings, the advantage of using a pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity [50].

Also, presence of nitrogen atom in the structure produces a polarized bond which improves the solu-bility of the prepared polymers due to increased dipole-dipole interactions in the polymer-solvent sys-tem. Therefore, the main advantage of using pyridine in the backbone of polyimides is to increase their sol-ubility while maintaining their thermal stability. In this section, we introduce an overview of the pyridine containing polyimides and copolyimides.

Aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine in N-methyl-2-pyrrolidone as a solvent afford AP and AN pyridine-based ether diamines, respectively

(Scheme X). Polycondensation reactions of the obtained diamines with some commercially available dianhydrides result in six pyridine-based, thermally stable poly(ether imide)s. Structure/property relations of these polymers were investigated. According to the results reported, polyimides derived from AP demon-strate higher thermal stability than the corresponding polyimides based on AN diamine. This is due to the structural symmetry and regularity of the aminophe-noxy group in comparison with the aminonaphthoxy group. The polymers obtained are soluble in dipolar aprotic solvents such as NMP, DMAc, dimethylfor-mamide, and DMSO and also in a less efficient sol-vent (m-cresol) in the range of 0.8-1.4 g/dL. However, the aminonaphthoxy derived polymers are reported to be more soluble than the aminophenoxy-derived poly-mers. In addition to the presence of the flexible groups, this is another feature of the symmetry and its relative disruption in the above mentioned polymers [51].

In another work, the reactions of two diamines (AP and AN) with trimellitic anhydride to prepare
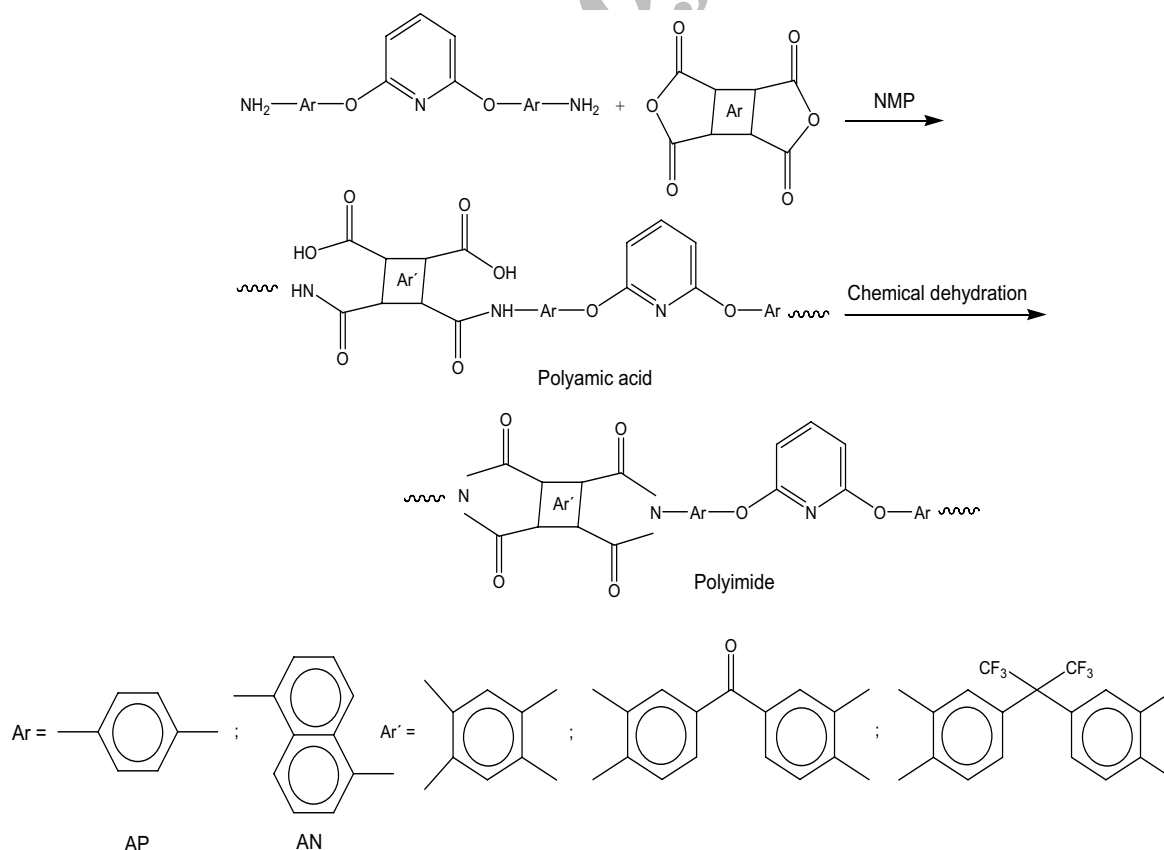
Scheme X. Preparation of poly(ether imide)s.

(a)

(b)

(c)   Continued

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(d)

(e)
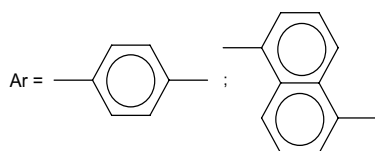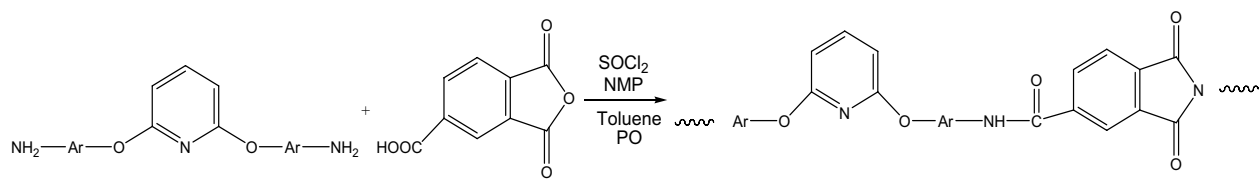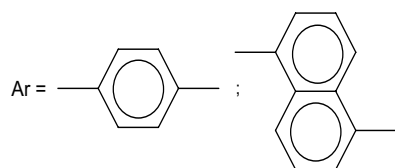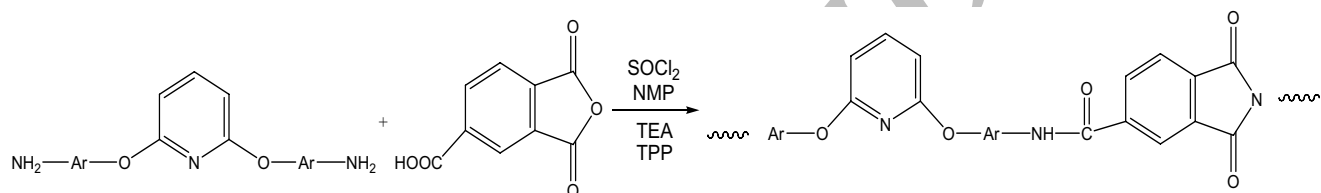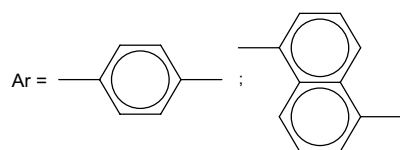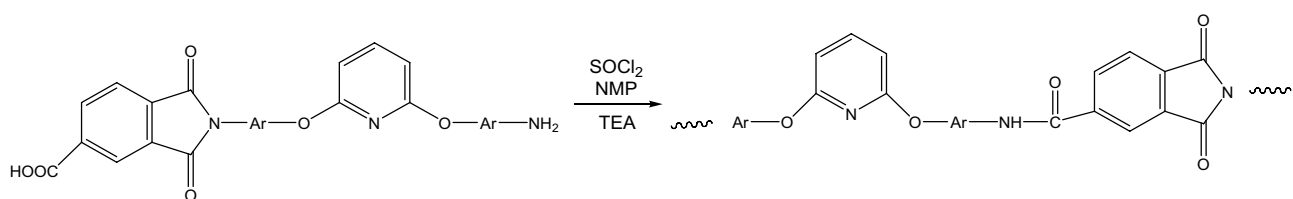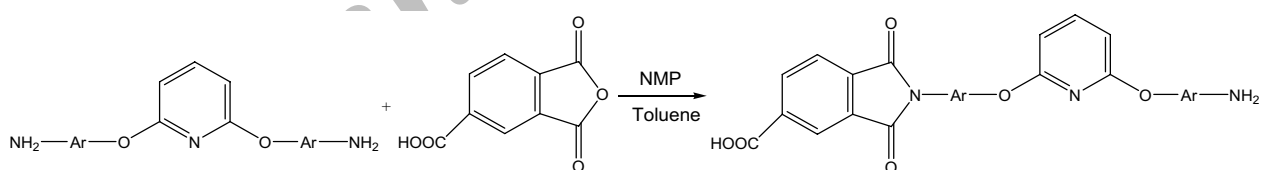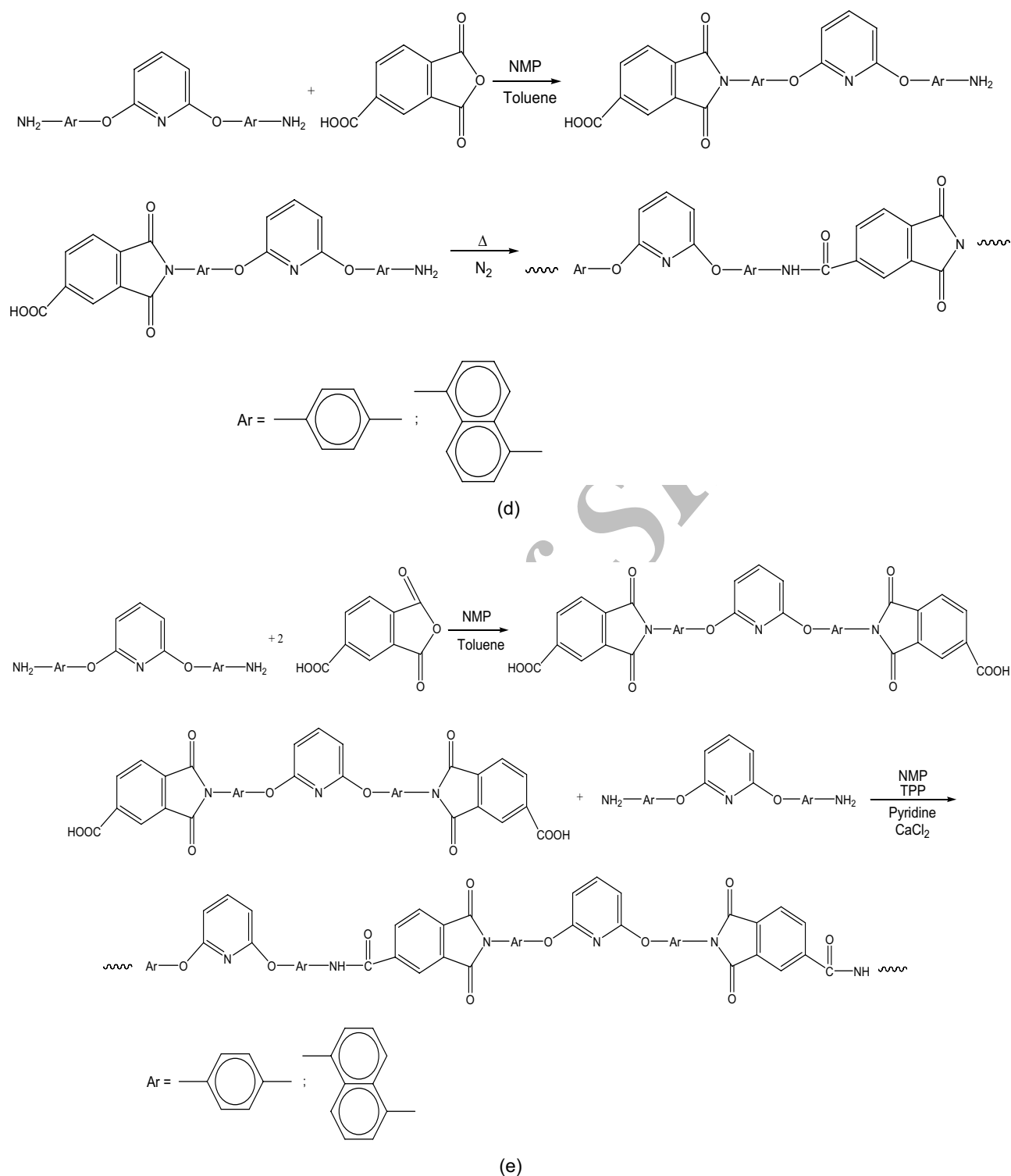
Scheme XI. Preparation of polymers from: (a) method 1, (b) method 2, (c) method 3, (d) method 4, and (e) method 5.

poly(ether amide imide)s have been investigated via five different methods. These methods are shown in Scheme XI [52]. Since the inherent viscosity of the polymers is a good criterion in the estimation of molecular weight and improvement of the reaction,

according to the obtained results, method (5) which is a two-step method via diimide-diacid (DIDA) formation is the best method for preparation of poly(ether amide imide)s. Also, method (2) which is a single step polycondensation method is a good method for prepa-

(a)
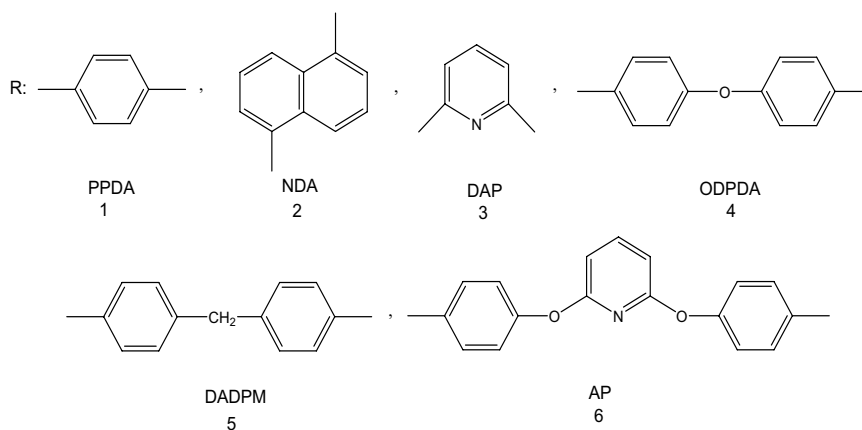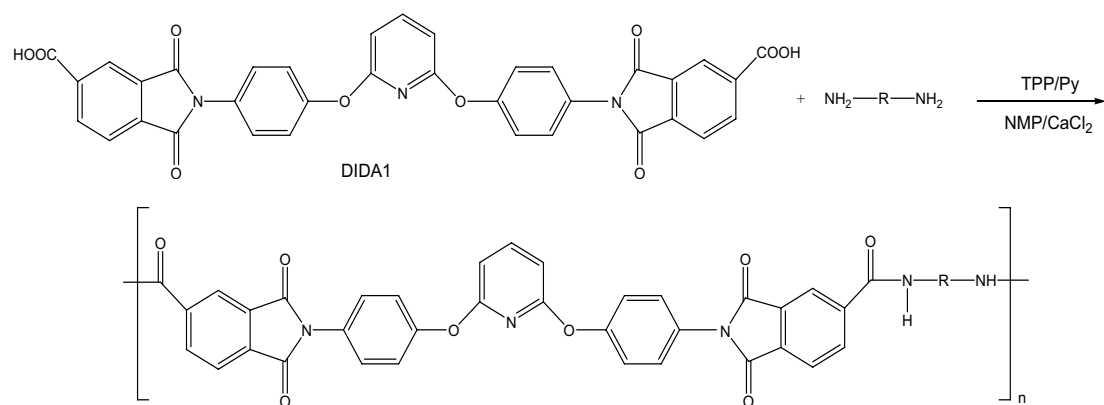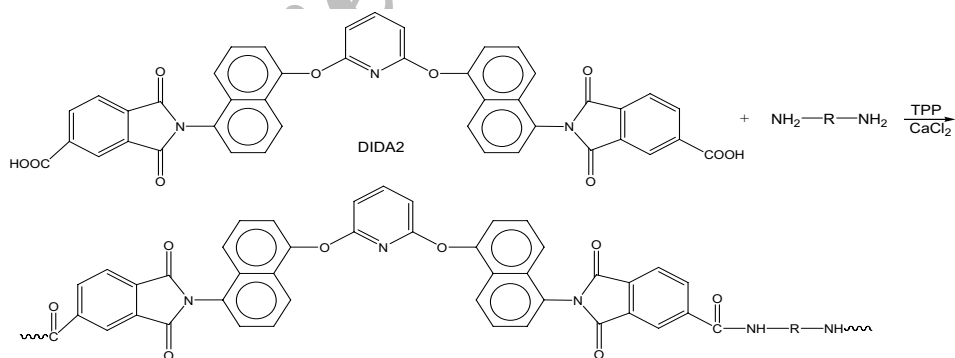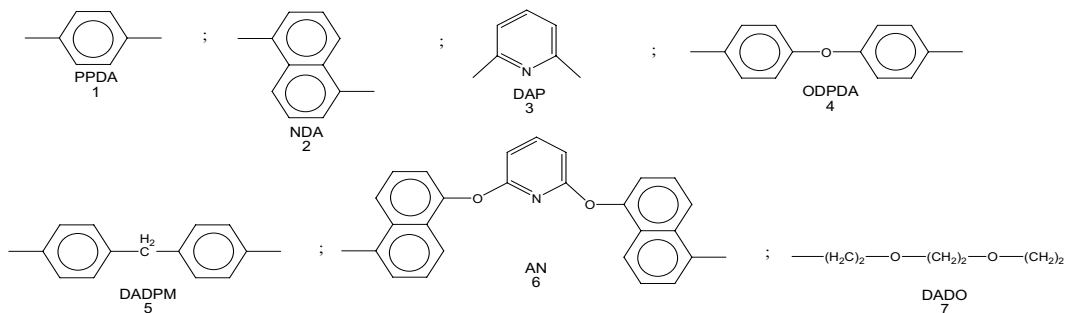
(b)

Scheme XII. Preparation of poly(amide-imide)s.

Table 2. Yield and inherent viscosities of poly (ether amide imide)s.

Method	Polymer (based on diamine)	Yield (%)	Inherent viscosity (dL/g)
1	AP	93	0.13
1	AN	86	0.11
2	AP	90	0.36
2	AN	88	0.31
3	AP	70	0.17
3	AN	67	0.14
4	AP	77	0.21
4	AN	73	0.17
5	AP	91	0.45
5	AN	89	0.46

ration of poly(amide imide). Inherent viscosities of the resulted polymers are collected in Table 2.

Since the polymers obtained from methods (2) and (5) have the highest molecular weights, they show superior thermal properties in comparison to other polymers. Although polymers (2) and (5) have similar structural backbones, their glass transition temperatures are different. This could be attributed to their inherent viscosities and their increased molecular weights. The polymers prepared from method (5) have shown the highest T_g values due to the fact that by increases in their molecular weights, the intermolecular hydrogen bonds and donor/acceptor interactions of amide and imide functions increase as well.

Introduction of pyridine ring, incorporation of an ether linkage, phenylation of the backbone, and disruption of symmetry have been the main structural modifications that Mehdipour et al. have used to obtain soluble, thermally stable poly(imide amide)s (Scheme XII) [53,54]. In their report, the syntheses of two pyridine-based diamines by reaction of 4-aminophenol or 5-amino-1-naphthol with 2,6-dichloropyridine have been introduced. Reactions of

the prepared diamines with trimellitic anhydride have afforded two diimide-diacid (DIDA) compounds. Polycondensation reaction of these diacids with different diamines in the presence of triphenyl phosphite has resulted in preparation of thermally stable poly(ether imide amide)s. Thermal behaviour and properties of these polymers are tabulated in Tables 3 and 4. The solubility of the polymers has been tested in dipolar aprotic solvents including NMP, DMAc, DMF, and DMSO. Solubility of the polymers derived from DIDA1 that include phenyl unit is about 0.6-0.9 g/dL and that of the polymers derived from DIDA2 that include naphthyl unit is about 0.65-3 g/dL. The substitution of phenyl unit with bulky naphthyl unit leading to decreased chain to chain interactions causes some interruptions in close packing of polymer chains, thereby leading to an enhanced solubility of the polymers.

In their further efforts, Mehdipour et al. have synthesized two series of poly(ether imide ester)s, by the polycondensation reactions of the prepared diacids (DIDA1 and DIDA2) with different diols (Scheme XIII). Comparison of the physical properties of

Table 3. Thermal analysis characteristic data of DIDA1 derived poly(amide-imide)s.

| Sample No.	T_g (ºC)	T_0 (ºC)	T_{10} (ºC)	T_{max} (ºC)	Char yield at 600ºC (%)
1	245	285	505	590	75
2	235	255	495	565	65
3	231	248	492	585	63
4	229	235	490	588	60
5	228	232	468	555	73
6	225	234	465	543	74
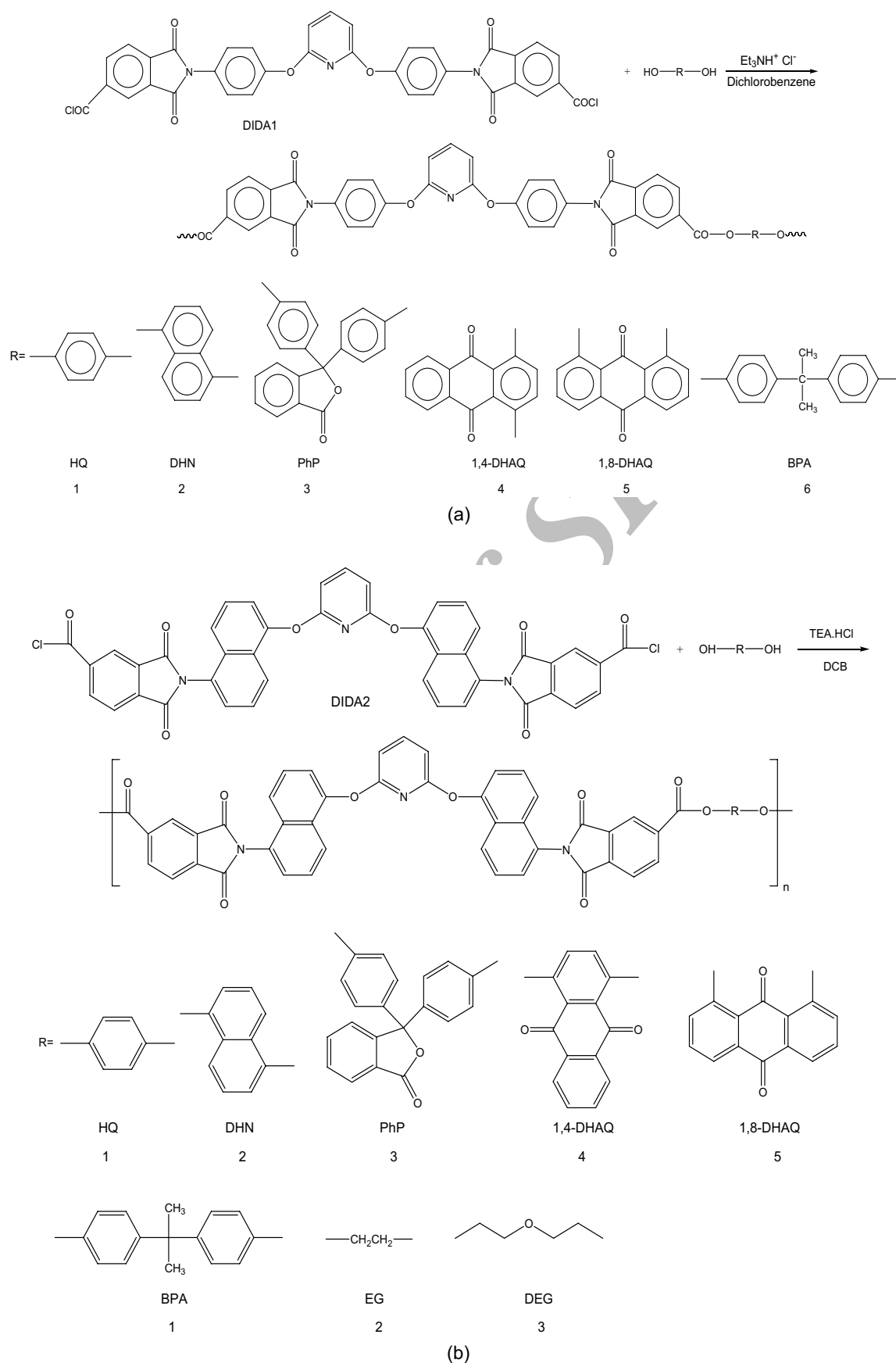
Scheme XIII. Preparation of poly(ether imide ester)s from: (a) DIDA1, (b) DIDA2.

Table 4. Thermal analysis data of DIDA2 derived poly(amide-imide)s.

Sample No.	T_g (ºC)	T_0 (ºC)	T_{10} (ºC)	T_{max} (ºC)	Char yield at 600ºC (%)
1	225	240	432	450	58
2	218	229	420	435	70
3	215	225	416	430	56
4	207	216	401	418	54
5	202	215	397	415	51
6	180	203	392	409	50
7	138	155	326	380	39

poly(ether imide amide)s with poly(ether imide ester)s has shown that the presence of amide has given rise to better thermal stability, but lower solubility than the polymers with ester in their backbone. This may be accounted to higher chain interactions in polymers containing amide functional group, which increase close packing and therefore, decrease the penetration of solvent molecules into the polymer backbone [55,56]. Thermal properties of these two series of polymers are shown in Tables 5 and 6.

The presence of a pyridine ring and ether units in the diacid structure, and also incorporation of flexible groups and disruption of symmetry from the diol moieties have been applied to improve the solubility of the polymers. Comparison of the physical properties of polymers derived from DIDA1 with the polymers derived from DIDA2 shows that substitution of phenyl units with naphthyl units in the DIDA1 would lead to improved solubility and reduced crystallinity of the polymers without too much relinquishment of their thermal stability.

A series of new poly(amide-imide)s, 5a-5c and 6a-6c, were prepared by direct polycondensation of the diimide-dicarboxylic acids, 3a and 3b, with various diamines, 4a-4c, using CaCl$_2$-promoted polymerization with thionyl chloride in *N*-methyl-2-pyrrolidone (Scheme XIV). The polymers showed good solubilities in a number of organic solvents, such as NMP, DMAc, DMF, and DMSO. The solubilities of the polymers in a variety of organic solvents are presented in Table 7. The incorporation of meta-catenated units into the polymer backbone may have interrupted the chain packing, thus leading to improved solubility. In these polymers, the solubility of polymer 5c (or 6c) is better than those of polymers 5b (or 6b) and 5a (or 6a) because of the presence of the bulky units containing a phenyl pendant group in the main chains of the polymers. Also, due to the totally aromatic structures of these PAIs, excellent thermal stabilities have been obtained for the derived polymers [57]. The results obtained indicate that incorporation of phenyl and *p*-biphenyl pendant groups that attach to pyridine ring of the polymer main chains effectively enhances the solubility and thermal stability of the rigid polymer backbone.

Among the several methods, modified Chichibabin reaction is one of the best methods for the preparation of a pyridine ring. Tamami et al. [58]

Table 5. Thermal properties of poly(ether imide ester)s derived from DIDA1.

Sample No.	T_g (ºC)	T_0 (ºC)	T_{10} (ºC)	T_{max} (ºC)	Char yield at 600ºC (%)
1	240	215	480	494	64
2	230	210	469	478	63
3	225	200	445	474	60
4	204	180	386	438	53
5	201	176	384	425	55
6	196	169	375	410	45

Table 6. Thermal properties of poly(ether imide ester)s derived from DIDA2.

Sample No.	T_g (ºC)	T_0 (ºC)	T_{10} (ºC)	T_{max} (ºC)	Char yield at 600ºC (%)
1	218	175	385	475	42
2	215	171	372	435	44
3	208	164	364	421	41
4	197	155	340	395	39
5	192	157	334	382	37
6	177	149	309	344	31
7	121	140	278	308	24
8	117	132	270	301	22
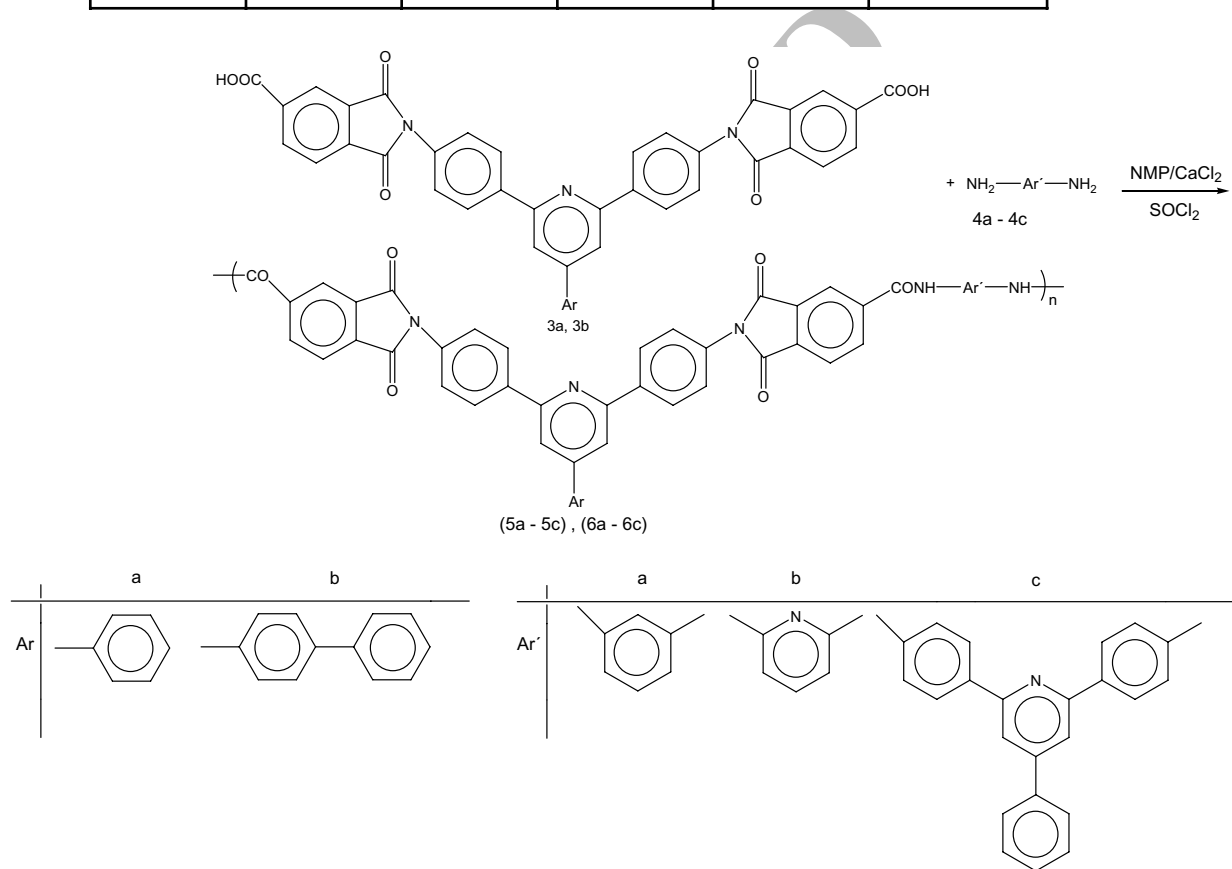
Scheme XIV. Synthesis of poly(amide-imide)s using diimide-dicarboxylic acids.

Table 7. Solubility behaviour of PAIs.

Polymer	NMP	DMAc	DMF	DMSO	Py	*m*-Cresol	THF
5a	++	++	+	-	-	-	-
5b	++	++	+	-	-	-	-
5c	++	++	++	+	+	-	-
6a	++	++	+	+	+	-	-
6b	++	++	++	+	+	-	-
6c	++	++	++	++	+	+	+

Concentration: 5 mg/mL, Soluble at room temperature:++; Soluble after heating at 60ºC: +; Insoluble: -
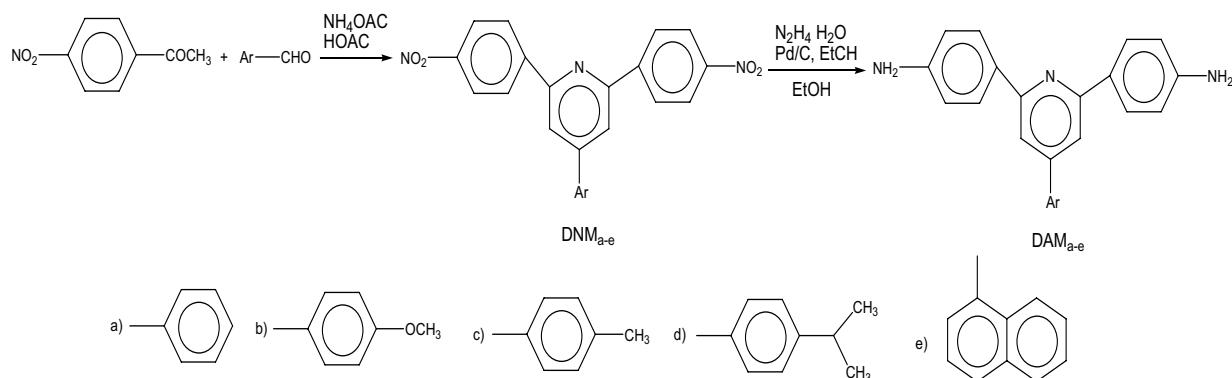
Scheme XV. Preparation of novel diamines from modified Chichibabin method.

have used this method for the preparation of novel diamines according to Scheme XV. 4-Aryl-2,6-bis(4-aminophenyl) pyridines (DAMa-e) have been prepared via a reduction of corresponding 4-aryl-2,6-bis(4-nitrophenyl) pyridines (DNMa-e) using hydrazine hydrate as the source of hydrogen and palladium on charcoal (5 wt%) as the catalyst. DNMa-e monomers had been themselves prepared through the condensation of several aryl aldehydes and 4-nitro acetophenones.

Related polyimides were synthesized from polycondensation of these diamines with some dianhydrides (Scheme XVI).

Solubility of polyimides in different solvents has been studied. The polyimides based on PMDA are insoluble in common polar aprotic solvents, and the polyimides based on BTDA show moderate solubility. However, the polyimides based on 6FDA also show improved solubility. The improvement in solu-

bility of the polyimides on the basis of 6FDA can be attributed to the low cohesion energy provided by fluorinated groups and the reduction in charge-transfer complexes of the conjugated aromatic system. It seems that the stiff and rigid imide structure counteract the effect of the bulky side groups in the diamine monomers, although this effect is less important in polyimides on the basis of dianhydrides with more flexible structures.

Generally, single crystals of molecules, which form noncentral symmetric crystalline forms and have a molecular structure that contains a donor and acceptor group connected by a conjugated backbone, have the capability of frequency doubling of light. Of the many organic molecules investigated, styryl molecules in solution have been found to exhibit some of the highest values of the second order non-linear optical coefficient χ^2 [59,60]. Polyimides have been shown to be poled to form high temperature non-lin-
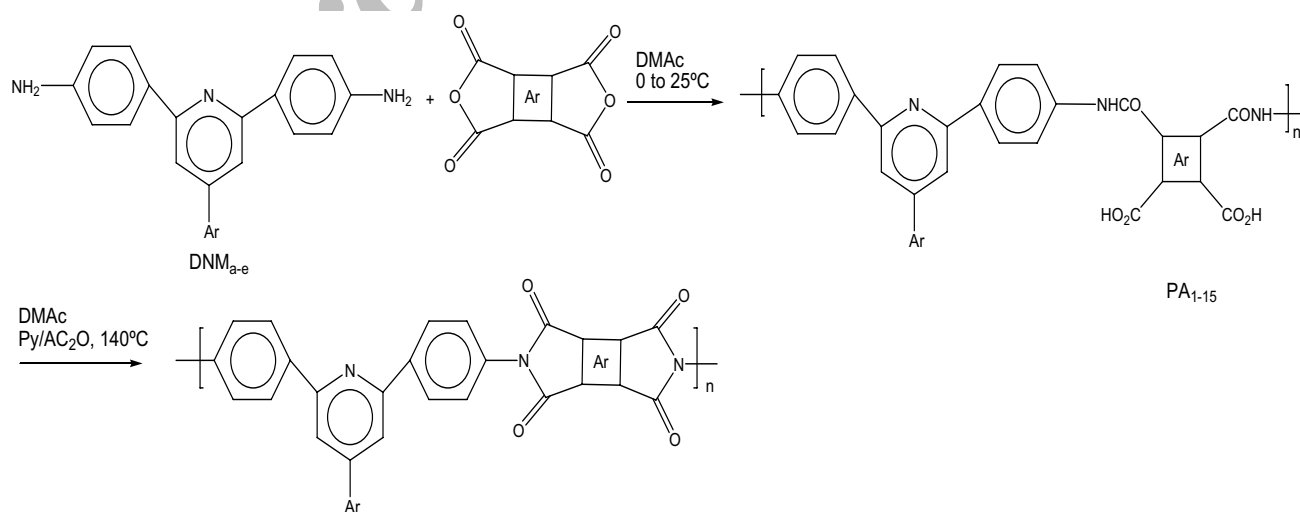
Scheme XVI. Synthesis of polyimides.
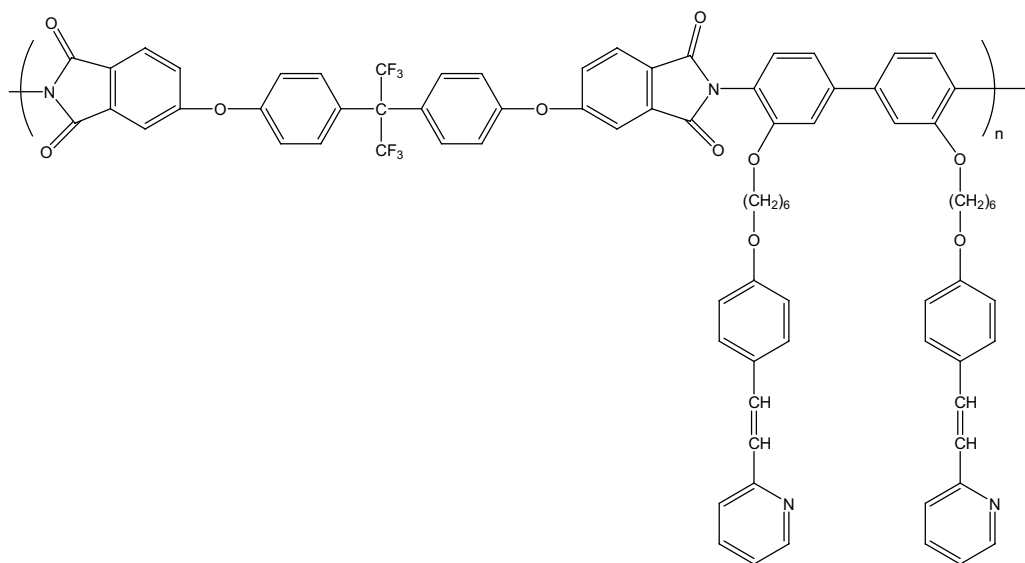
Scheme XVII. Structure of photoreactive polymers containing 2- styrylpyridine.

ear χ^2 materials. A new aromatic polyimide with two fluorinated methyl groups and two hydroxyl groups in the repeating unit has been prepared; a soluble photoreactive polyimide is then prepared by the polymer reaction of the hydroxyl groups in the backbone unit of the polymer with those in the 2-styrylpyridine derivative as the photosensitive compound [61]. The photoreactive polymer and its precursor polymer are soluble in various polar organic solvents and their thin flexible films are easily formed by solution casting. The extent of the photochemical reaction of the photoreactive polymer film has been measured to be 65.8% at exposure energy of 1.5 J/cm². The transmittance of the film is found to be approximately 92% at room temperature and approximately 85% at 200°C. These results suggest that the polyimide is a photosensitive polymer with good photosensitivity and high optical transparency. The structure of this photosensitive polymer is shown in Scheme XVII.

Peesapati et al. [62] have described the synthesis of new thermally stable imides by the insertion of a styrylpyridine group into a polymer backbone (Scheme XVIII). These materials, however, have failed to exhibit non-linear properties. However, the failure to detect such properties reflects the fact that the materials are not poled prior to formation of the rigid backbone structure and hence a random distribution of the dipoles producing a self-cancellation situation, most probably have existed within the polymer.

These polymers have high values of glass transition temperature (T_g) and hence meet the devices processing requirements.

A series of fluorinated poly(amide imide)s, (PAIs) derivatives have been prepared from a new fluorinated imide-containing dicarboxylic acid (BTTB) and various aromatic diamines (Scheme XIX) [63]. Based on the report published, the solubility of the PAIs is improved by the introduction of fluorinated substitutes into the polymer main and side chains which have created more facile processing solution. All of the PAIs are reported to dissolve easily in strong aprotic solvents, such as NMP, DMAc, DMF, DMSO, and cyclopentanone. The excellent solubility of the PAIs
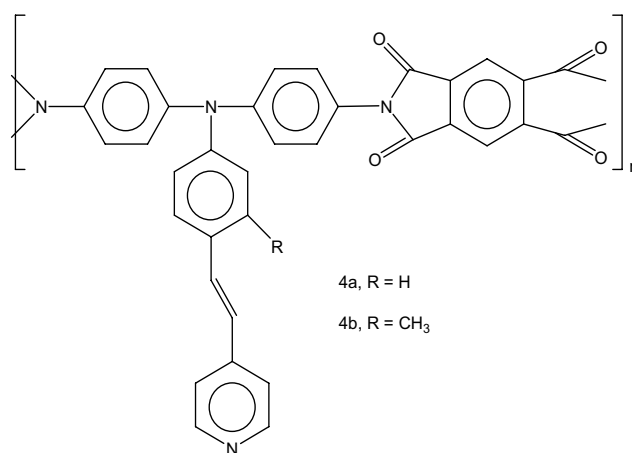
Scheme XVIII. Polyimides containing styrylpyridine.

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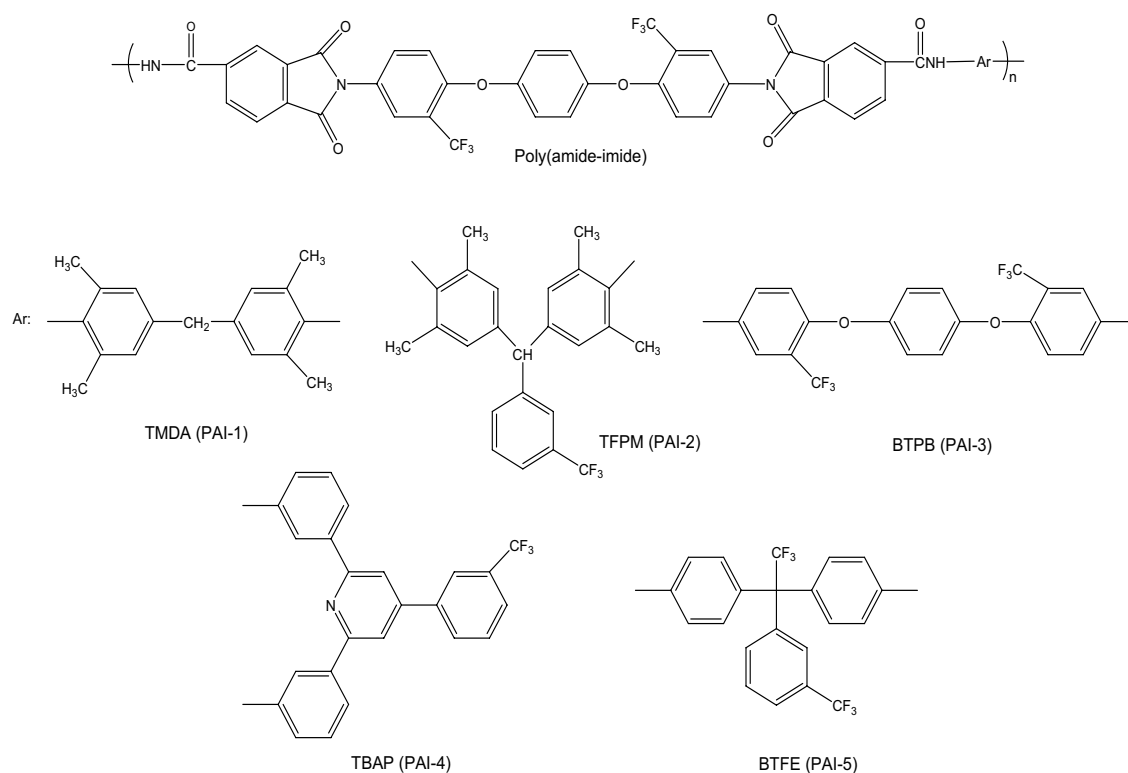
Scheme XIX. Structure of fluorinated poly(amide imide)s (PAIs).

are considered to be due to the presence of fluorinated substituents and hydrophobic methyl groups. In comparison with other structures, PAI-4 has shown relatively lower solubility. However, it has been dissolved in THF and *m*-cresol and has been partially soluble in acetone only after heating at 60°C. The lower solubility of PAI-4 in respect to other polymers of these series may be due to the effect of the hydrophilic and rigid pyridine segment and lack of alkyl units in the polymer chain. Obviously, the effect of fluoromethyl bulky group on the solubility of polyimides is higher than that of pyridine ring. Solubility

behaviours of these polymers are shown in Table 8.

Hariharan et al. [64] have synthesized a new series of polyimides from 2,6-diaminopyridine and different dianhydrides. They found that the incorporation of the pyridine group in the main chain would increase the chemical, mechanical, and thermal stability of polymers. The char yield at 800°C in nitrogen atmosphere was in the range of 60-48% confirming that incorporation of the pyridine group in the main chain has indeed enhanced the thermal stability of the polymers.

New soluble and thermally stable poly(ester-imide)s from a diimide-dicarboxylic acid having

Table 8. Solubility behaviour of PAIs.

Polymer	Organic solvents								
	NMP	DMAc	DMF	DMSO	Cyelopentanone	THF	*m*-Cresol	Acetone	CHCl$_3$
PAI-1	++	++	++	++	++	++	++	++	-
PAI-2	++	++	++	++	++	++	++	++	-
PAI-3	++	++	++	++	++	++	++	++	-
PAI-4	++	++	++	++	++	+	+	+ -	-
PAI-5	++	++	++	++	++	++	++	++	-

Soluble at room temperature: ++; Soluble with heating at 60ºC: +; Partially soluble with heating at 60ºC: +-; Insoluble: -

biphenylene pendant groups have been reported (Scheme XX) [65], in which the crystallinity of poly(ester-imide)s has been examined by means of WAXD patterns. These polymers have shown an amorphous nature, because biphenylene pendant groups significantly increases the disorderliness in chains and impedes the chain packing effectively. The solubility behaviour of all poly(ester-imide)s are summarized in Table 9. Almost all polymers are shown to be soluble in both polar aprotic solvents, such as NMP, DMAc, DMF, and DMSO, and less polar solvents, including Py, chloroform, THF, and *m*-cresol. In general, the flexible ester groups affect the solubility of a polyimide to a great extent due to the solvation effect.

In addition to the solvation effects related to an enthalpy factor and presence of pyridine unit, the good solubility of these polymers are also caused by a favoured entropy resulting from the bulky biphenylene pendant group in the polymer backbone which leads to expansion of the macromolecular chains in their solution state. This means that the organosoluble behaviour of the poly(ester-imide)s could also be attributed to the introduction of this bulky group that inhibited the close packing of the polymer chains.

Copper is the most important metal in packaging and chips industry because it has high conductivity and exhibits low electromigration. Polyimide-based flexible copper clad laminates (FCCLs) are important for high-density packages. The FCCLs used in the
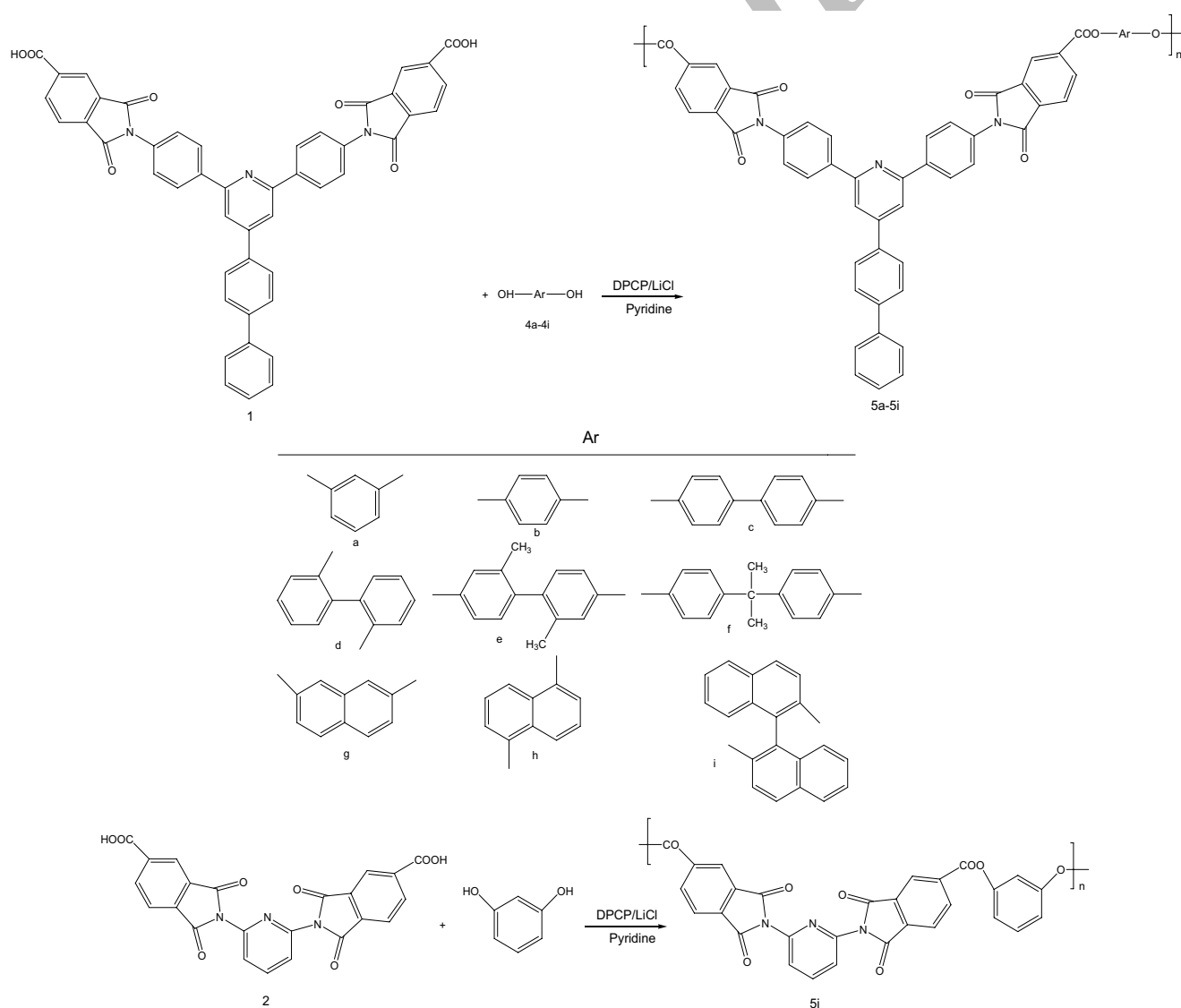
Scheme XX. Synthesis of poly(ester-imide)s with biphenylene pendant group.

Table 9. Solubility behaviour of poly(ester-imide)s[a].

Polymer	NMP	DMSO	DMF	DMAc	Pyridine	Chloroform	THF	*m*-Cresol	EtOH
5a	+	+	++	++	++	++	++	++	-
5b	-	-	+	+	++	++	+	+	-
5c	-	-	-	-	+	+	+	-	-
5d	+	+	+	+	++	++	++	++	-
5e	++	+	++	++	++	++	++	++	-
5f	++	+	++	++	++	++	++	++	-
5g	-	-	+	+	++	++	+	+	-
5h	+	+	+	+	++	++	+	++	-
5i	++	++	++	++	++	++	++	++	-
5j	-	-	-	-	+	+	+	-	-

[a] Concentration: 5 mg/mL. Soluble at room temperature: ++ ; Soluble on heating at 60ºC: + ; Insoluble: -

NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethylsulfoxide; DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; THF: tetrahydrofuran

ultrahigh density packages can only be made by electroplating of copper. Unfortunately, the adhesion of polyimide films to copper is usually poor. Ku et al [66] have proposed that triazole or pyridine-containing polyimides form compheres with copper and these functional groups improve the adhesion forces necessary between the copper and polyimides.

These researchers have mixed 4,4'-oxydianiline (ODA) with 2,6-diaminopyridine (DAP) and 3,5-diamino l,2,4-triazole (DATA), separately, to form co-diamines. A series of polyimides have been obtained in two steps by reacting co-diamines with pyromellitic dianhydride (PMDA). The adhesion strength of the sputter-deposited copper to polyimide films has been found to be proportional to the functional group concentration. At a molar ratio of DAP to ODA of 1/6, the 90°-peel strength of copper/polyimide laminates have reached a maximum of 990 J/m². At a molar ratio of DATA to ODA of 1/6, the 90°-peel strength of copper/polyimide laminates has reached a maximum of 696 J/m². The corresponding polyimide films have exhibited a good balance of thermal, mechanical, and

dielectric properties, as the PMDA-ODA film. The N1s core level spectra of the delaminated copper surface revealed a peak at 398.4 eV in copper/polyimide with DAP/ODA ratio of 1/6 and a peak at 398 eV in copper/polyimide with DATA/ODA ratio of 1/6 perhaps due to the formation of N-Cu charge-transfer complex. This complex substantially promotes the adhesion between sputter-deposited copper and polyimides. Structure of pyridine-containing polyimides is in Scheme XXI.

2,2'-Bipyridine is best known as a chelating ligand for a wide range of transition metals. Chen et al [67] have synthesized a series of polyimide copolymers with various compositions from 4,4'-diamino-2,2'-bipyridine, α,α'-bis(4-aminophenyl)- 1,4'-diisopropylbenzene (BAPDIPB), and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride. These polyimides form complexes with nickel malenonitriledithiolate [Ni(mnt)].

The introduction of Ni(mnt) moiety, which would generate a potential NLO active unit as a part of the polymer structures, significantly alters the thermal
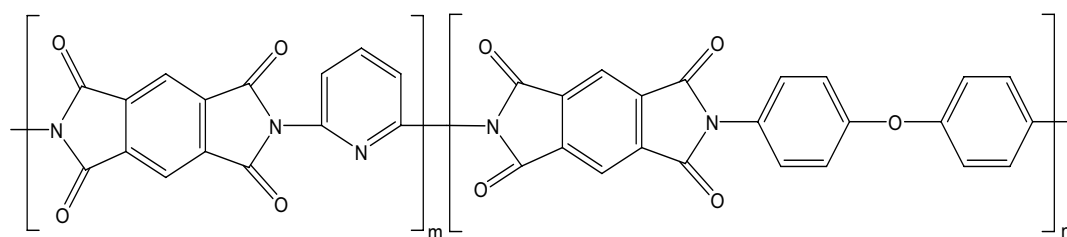
Scheme XXI. Structure of pyridine-containing polyimides (PMDA-ODA-DAP).
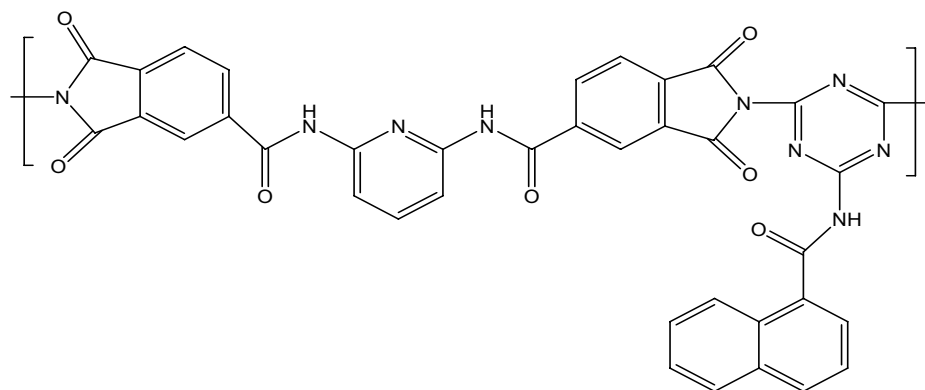
Scheme XXII. Structure of photoreactive polyimide containing naphthalenic pendant group.

properties (T_d and T_g) of the polyimides. Polyimides containing 2,2´-bipyridine units show less thermal stability with the coordination of Ni(mnt) and the T_d value steadily drops with the increasing amount of Ni(mnt) attached to polyimides. The coordination of Ni(mnt) to polyimides containing 2,2´-bipyridine units, however, has demonstrated a positive effect in raising the T_g of the polymers. This can be rationalized by the fact that the coordination of Ni(mnt) to the polymers not only restricts the free rotation of the carbon-carbon single bond connecting two pyridine rings in the solutions but it also imposes a certain chain folding and a less stretched-out conformation of the polymer backbone in the solid state.

Khoee et al have reported a facile method for rapid synthesis of novel photoactive and thermally stable pyridine-based polyimide containing a naphthalenic pendant group with fluorescent property by using a domestic microwave oven [68]. Structure of this photoactive polyimide is in Scheme XXII. Comparing the reaction condition of microwave irradiation technique with that of the solution method has

shown that the internal heat generation by both solvent and monomers under microwave irradiation has been much more effective than the conventional external heating method.

The resulting polymer is thermally stable and shows fluorescence emission phenomena. To investigate the fluorescence behaviour of the polymer, its emission spectra has been recorded in several solvents by fixing the excitation wavelength at maximum absorption wavelengths. The dependency of fluorescence intensity on polymer concentration illustrates the self-quenching phenomenon. By decreasing the polymer concentration to a specific level (ideal concentration), the fluorescence intensity increases and from then, by decreasing the polymer concentration the fluorescence intensity decrease too. The spectra obtained from the polymer systems vary in intensity, shape, and position of the maxima band.

Another poly (pyridine-imide) that shows fluorescent emission is shown in Scheme XXIII. The bulky pendant pyrene group in the pyridine unit and trifluoromethyl group in the dianhydride unit reduces pack-
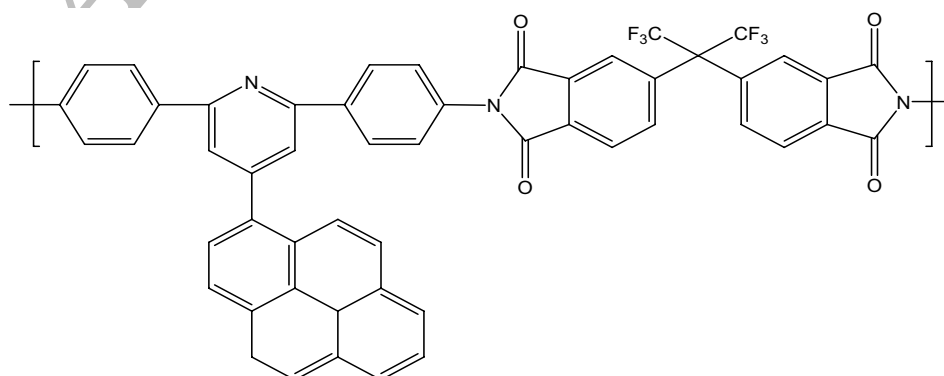
Scheme XXIII. Poly(pyridine imide) with fluorescent property.

PMDA-PDA/3 (n/m=3)

BPDA-PDA/3 (n/m=3)

PMDA-PDA/6 (n/m=6)

BPDA-PDA/6 (n/m=6)
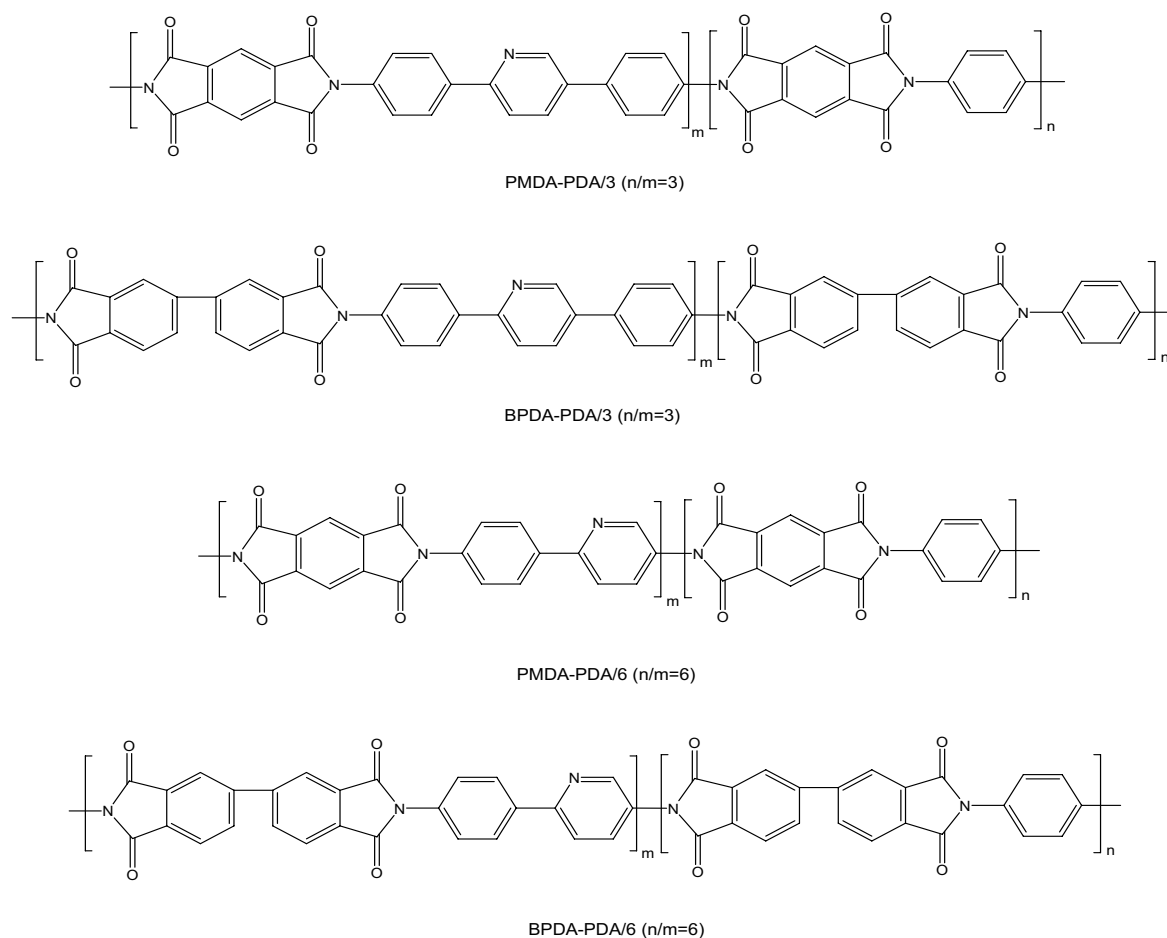
Scheme XXIV. Chemical structures of polyimides (n/m: molar ratio).

ing force and therefore, this polymer exhibits excellent solubility in various solvents. The poly(pyridine-imide) can be cast into a film from DMAc solution and the film is in light colour, optically transparent, flexible, and tough [69].

A series of novel homo- and co-polyimides containing pyridine units are reported to have been prepared from the heteroaromatic diamines, 2,5-bis(4-aminophenyl) pyridine and 2-(4-aminophenyl)-5-aminopyridine, and 1,4-phenylenediamine (PDA), with pyromellitic dianhydride (PMDA), and 3,3', 4,4'-biphenyl tetracarboxylic dianhydride (BPDA) via a conventional two-step thermal imidization method. Structures of these polymers are shown in Scheme XXIV.

The polyimide films show excellent thermal stability and mechanical properties. These characteristics are considered to be due to the introduction of the aromatic and rigid structure containing pyridine into the polymer backbone. The films are insoluble in common organic solvents and exhibit high chemical resistance. The crystallinity of the prepared polyimides has been evaluated by WAXD scans. All the polyimides have revealed a strong peak reflection at 2θ values of about 20°. This indicates that these polyimides have a high packing density. These results have shown good confirmation of the rigid structure of the polyimides; also have offered an explanation for their poor solubility and high T_g values. BPDA-based polyimides have shown, however, two glass transition temperatures that may be attributed to the flexible BPDA moiety that can rotate around the main chain of polymers. As shown in Scheme XXV, the kinked (cis) conformation of BPDA could be transformed into the extended (trans) conformation by rotation around the central single bond during the thermal process at elevated temperature [70].

A new kind of diamine monomer, i.e., 2,6-bis(3-
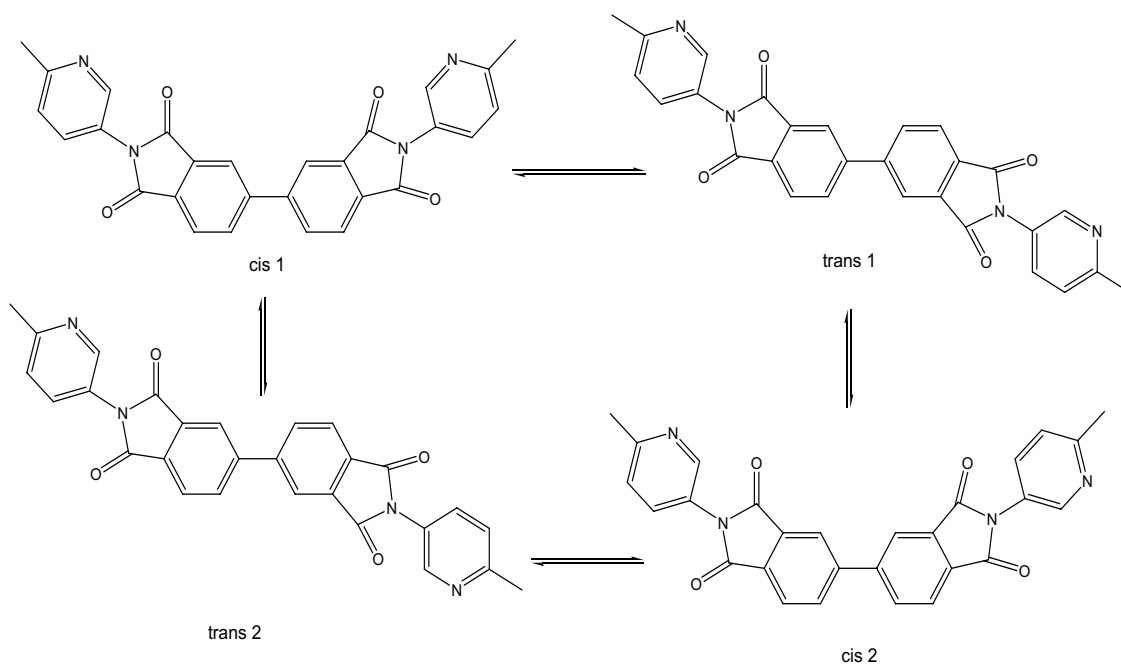
Scheme XXV. The transformations of different conformations of polyimides based on BPDA.

aminobenzoyl) pyridine(BABP), is successfully prepared in high purity and reacted with various aromatic dianhydrides to form a series of aromatic polyimides by two-step thermal or chemical imidization methods (Scheme XXVI). The solubility of these

polyimides has been tested qualitatively, and the results are summarized in Table 10. There are some cross-linkages in polyimides obtained by thermal imidization, therefore, PI (1–3) series obtained via thermal imidization are reported to be insoluble in all
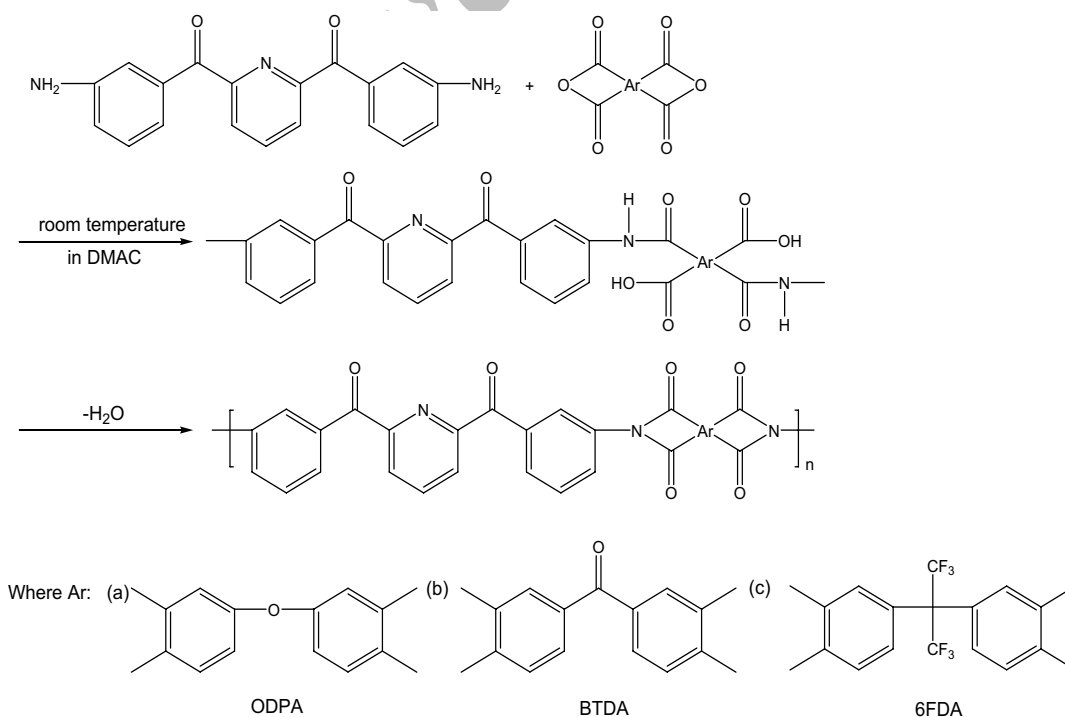
Scheme XXVI. Preparation of pyridine containing polyimides .

Table 10. solubility of polyimides.[a]

No.	Polyimide	Solvent[b]				
		NMP	DMAc	DMF	DMSO	H$_2$SO$_4$
1	BABP-BTDA	--	--	--	--	--
2	BABP-ODPA	--	--	--	--	--
3	BABP-6FDA	--	--	--	--	--
4[c]	BABP-BTDA	+	--	--	--	++
5[c]	BABP-ODPA	+	+	+	--	++
6[c]	BABP-6FDA	++	++	+	--	++

(++) Soluble at room temperature; (+) soluble on heating; (--) insoluble even on heating. [a] Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent. [b] NMP: *N*-methylpyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylfor-mamide; DMSO: dimethyl sulfoxide. [c] Measured by chemical cyclization from the corresponding poly(amic acid)s.

test solvents. While, PI (4–6) series prepared via chemical imidization have shown better solubility than those prepared thermally. The T$_g$ values of these PIs are determined to be in the range of 284-310°C. The T$_5$ and T$_{10}$ values of the polyimides are also found to be in the range 496-549°C and 526–580°C in air, respectively, while in nitrogen atmosphere these values are reported to be within the range of 522–555°C and 558-561°C. According to wide-angle X-ray diffraction data, these polymers show little crystalline morphology which maybe related to the rigidity and planar structure of the polymer chains

(a)

(b)

(c)
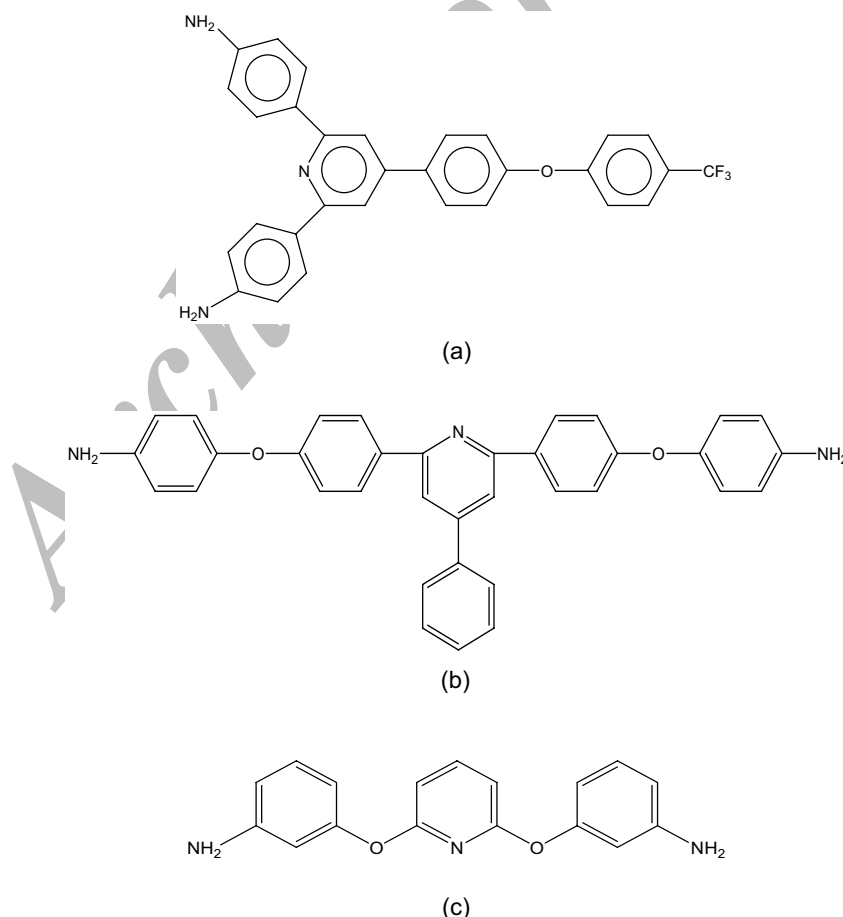
Scheme XXVII. Some new pyridine containing diamines for the preparation of polyimides.

[71]. Liu et al. have prepared new liquid-crystal align-
ment agents based on fluorinated polyimides using
following pyridine-based diamine (Scheme XXVIIa)
[72]:

4-Phenyl-2,6-bis[4-(4-aminophenoxy)phenyl]-
pyridine has been synthesized for the preparation of
new types of soluble pyridine-containing polyimides
(Scheme XXVIIb) [73]. A novel pyridine diamine has
been also used for the preparation of new semi-inter-
penetrating polymeric networks from linear poly-
imides and thermosetting bismaleimides (Scheme
XXVIIc) [74]:

CONCLUSION

The following results may be concluded.

- This review has been devoted to the synthetic
methods and structure/property relationships of poly-
imides and copolyimides specially those containing
pyridine rings in their backbone.

- Polyimides with improved properties have been
prepared by the incorporation of various functional
moieties into the polymer backbone to enhance
processability and solubility of these polymers with-
out much sacrificing their thermal stability.
Modification of the properties of pyridine-based poly-
imides by incorporation of amide, ester, and ether
groups has been studied. Order of increasing thermal
stability of these functions is found as follows:
imide > amide > ester > ether.

- Rigidity and thermal stability of pyridine is sim-
ilar to benzene, but, because of the presence of nitro-
gen atom in pyridine and its interaction with dipolar
solvents, solubility of polymers containing pyridine is
higher than those containing benzene.

- Introduction of bulky pendant groups in poly-
imide backbone decreases chain to chain interactions
and close packing of the polymer chains, thereby
leading to enhancements in solubility and decreasing
crystallinity.

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