Progress in Polymer Science 37 (2012) 907–974

Contents lists available at SciVerse ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Advanced polyimide materials: Syntheses, physical properties and applications

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ARTICLE INFO

Article history:
Received 25 May 2011
Received in revised form 16 February 2012
Accepted 24 February 2012
Available online 1 March 2012

Keywords:
Polyimide
Synthesis
Physical properties
Applications

ABSTRACT

Polyimides rank among the most heat-resistant polymers and are widely used in high temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials, membrane materials for separation, and Langmuir–Blodgett (LB) films, among others. Additionally, polyimides are used in a diverse range of applications, including the fields of aerospace, defense, and opto-electronics; they are also used in liquid crystal alignments, composites, electroluminescent devices, electrochromic materials, polymer electrolyte fuel cells, polymer memories, fiber optics, etc. Polyimides derived from monomers with noncoplanar (kink, spiro, and cardo structures), cyclic aliphatic, bulky, fluorinated, hetero, carbazole, perylene, chiral, non-linear optical and unsymmetrical structures have been described. The syntheses of various monomers, including diamines and dianhydrides that have been used to make novel polyimides with unique properties, are reported in this review. Polyimides, with tailored functional groups and dendritic structures have allowed researchers to tune the properties and applications of this important family of high-temperature polymers. The synthesis, physical properties and applications of advanced polyimide materials are described.

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doi:10.1016/j.progpolymsci.2012.02.005

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1. Introduction

Marston Bogert first produced aromatic polyimides in 1908 [1]. In 1955, high molecular weight aromatic polyimides were synthesized by a two-stage polycondensation of pyromellitic dianhydride with diamines [2]. Since then, interest in this class of polymers has been growing steadily because of their thermo-oxidative stability, unique electrical properties, high radiation and solvent resistance, and high mechanical strength. However, these polymers often have low solubility in common solvents and have high softening temperatures, thus making their processing either difficult or too expensive to be commercially viable. The most common technique used to fabricate polyimides uses a soluble poly(amic acid) as a precursor. Films are cast, and then they are thermally dehydrated to produce the final imide form. Nevertheless, this process has other problems, such as inefficient cyclizations. In addition, it is difficult to remove water and prevent the formation of microvoids in the final material.

Fully aromatic polyimides have rigid chains and strong interchain interactions, which result in the polymers having poor solubility and non-melting characteristics. These characteristics are a result of the highly symmetrical and highly polar groups. Strong interactions originate from intra- and interchain charge transfer complex (CTC) formation and electronic polarization. The CTC formation and electronic polarization are supported by the strong electron acceptor characteristics of imides and the electron donor characteristics of amine segments.

Polyimides have been reviewed from different perspectives [3–5]. For example, Hasegawa [6] and Hrdlovic [7] examined the charge transfer (CT) interactions in fully aromatic polyimides; Negi et al. [8] reported on photosensitive polyimides, and Ding [9] reported on chiral polyimides and polyimides generated from isomeric diamines and dianhydrides. However, currently there are very limited reviews on the design and synthesis of organo-soluble polyimides and their applications.

In the last few decades, many studies have been conducted to modify the molecular interactions of polyimides to allow processing by conventional techniques, such as melt processing or solvent casting, while maintaining the thermo-oxidative stability of the polymer. These studies have involved three major structural modifications: incorporation of thermally stable but flexible or unsymmetrical linkages in the backbone, introduction of large polar or non-polar pendant substituents to the polymer chain, and disruption of symmetry and recurrence of regularity through copolymerization. For instance, the incorporation of flexible linkages, such as –O–, $-CH_2-$, $-SO_2-$ and hexafluoroisopropylidene groups into the backbone, introduces "kinks" in the main chain that decrease the rigidity of the polymer backbone and inhibit close packing of the chains, which reduces the interchain interactions and leads to enhanced solubility. Ultem® (polyetherimide, PEI) (General Electric Co.) is a good example of a polymer that is readily processed, has desirable mechanical properties and retains decent thermal properties.

Ding had concluded general rules for the relation between glass transition temperature and structure of isomeric polyimides based on the experimental results [9]. T_g for polyimides of comparable molecular weight (or inherent viscosity) based on isomeric dianhydride with a given diamine increase in the order 4,4′- < 3,4′- < 3,3′-dianhydride. The behavior is attributed to the suppressed rotation around the bond between the phthalimide and the bridge atom in the 3-substituted phthalimide unit. The T_g difference between the isomeric polyimides generally depends on the rigidity of the polymer chains. However, the T_g of the polyimides derived from isomeric bis(ether anhydride)s based on 3,3′-dianhydride is higher than that on 4,4′-dianhydride (for a given diamine); because of the flexible structure of bis(ether anhydride), the difference of the glass transition temperatures between two isomeric polymers is not so large. On the other hand, the polyimides from *p,p′*-diamines (and a given dianhydride) usually have the higher T_gs than those from *m,m′*-diamines. This may be due to the substitution, which impedes the chain mobility

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but, at the same time, the bent chains decrease the packing of the macromolecular chain, hence tend to decrease interactions between the macromolecular chains.

For general polyimides, bulky substituents can cause a significant increase in both T_g and the thermo-oxidative stability as well as increase the solubility of the polyimide, especially for polyimides with unsymmetrical or flexible groups in the backbone. Bulky and asymmetric substituents decrease the crystallinity and packing efficiency by distorting the backbone symmetry and restricting its segmental mobility. The extent of these effects depends on the number, size, and polarity of the substituents. These strategies generally suffer from a trade-off between the thermal properties and the solubility of a polyimide because the same structural features that enhance one characteristic will decrease the other. Therefore, to create more easily processed materials, a balance between these properties must be maintained without sacrificing the inherent high temperature resistance characteristics of these polyimides.

Introducing aromatic structures and non-aromatic but thermally stable cardo, and spiro, fluorine-containing structures or multicyclic structures (such as adamantine), into the polymer backbone is a promising method of modifying the properties of the polyimide. These modifications can affect the color, dielectric constant (k), degradation temperature, glass transition temperature (T_g), and LCD alignment properties of polyimides. The introduction of certain specialized groups or species into the polyimides, which include both amine and anhydride components, can generate polyimides with special functionalities. In this report, we review and integrate the relevant literatures on polyimides from the viewpoint of monomer and polymer design, and we focus on polyimides with special functionalities and applications.

2. Synthesis

Polyimides are a class of thermally stable polymers; this thermal stability is a consequence of their stiff aromatic backbones. The chemistry of polyimides is itself a vast field, and it includes a large variety of available monomers and different synthetic methodologies. However, there has been considerable debate about the various reaction mechanisms involved in the different synthetic methods. The properties of polyimides can be dramatically altered by minor variations in structure. Subtle changes in the structures of the dianhydride and/or diamine components will have significant effects on the properties of the final polyimide. The important fundamentals regarding the selection of monomers for polyimide synthesis and the basics for understanding these structure–property relationships are discussed below.

2.1. Monomer synthesis

The applicability of polyimides is frequently limited by their infusible and insoluble nature. To overcome this drawback, extensive structural modifications have been attempted, such as the incorporation of flexible or unsymmetrical linkages in the backbone [1,10] and the introduction of kink, spiro, bulky, cardo or pendant substituents [8,9] that do not sacrifice the thermal stability of the polyimide. That is, the selection of the monomers plays a key role in tailoring the basic traits of polyimides. Many papers [1] have reviewed the synthesis and properties of modified polyimides. Herein, we will introduce certain moieties such as noncoplanar components, which possess special thermal stability characteristics and increase solubility. These noncoplanar moieties include both in amine and anhydride components, which we expect will help expand the application of polyimides.

2.1.1. Noncoplanar structures (kink, spiro, and cardo structures)

2.1.1.1. Kink. The kink structure is a crank and twisted noncoplanar structure. The introduction of kink structures into polymer chains might prevent chains' alignment and disrupt the formation of efficient charge transfer-complexes (CTC). The kink structure can also result in the formation of colorless polymer films with high transmittance [1]. Some commercial diamines contain kink structures, which improve the solubility and decrease the crystallinity of the obtained polyimides; these diamines are shown in Scheme 1. The incorporation of substituted methylene and propylidene linkages can result in kink structures. However, the chain flexibility of the propylidene groups can decrease the thermal stability of the polyimide [10].

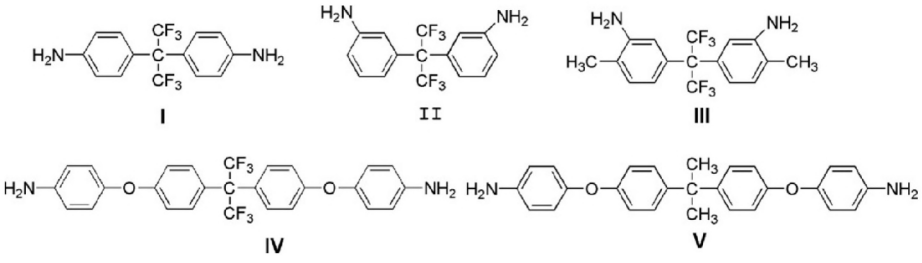
Some of the diamines and dianhydrides with kink structures that have been synthesized for the preparation of polyimides are shown in Scheme 2 [10–15]. Liaw et al. reported the synthesis of a kink bisphenol, bis(4-hydroxyphenyl)diphenylmethane (**BHPP**), which was used in the synthesis of diamines and dianhydrides [10,14,15]. In general, kink bisphenols can be prepared by the acid-catalyzed condensation of ketones with excess phenol in the presence of hydrogen chloride. However, the reaction of benzophenone and phenol under the same conditions does not afford the desired phenol **BHPP** (Scheme 3). This result can be explained by the steric hindrance of the bulky phenyl substituents. **BHPP** was successfully prepared by refluxing dichlorodiphenylmethane and phenol (molar ratio 1:2) in xylene (Scheme 3). Because the phenyl substituents are bulkier than the methyl or trifluoromethyl substituents on isopropylidene, polyimides with a kink diphenylmethylene linkage exhibit good solubility and amorphous structure and have a higher thermal stability than polyimides with an isopropylidene linkage [10,14,15].

In general, bis(ether dianhydride)s are prepared through the nucleophilic nitro displacement reaction of a bisphenol with 4-nitrophthalonitrile to form bis(ether nitrile)s. The nitriles are hydrolyzed to obtain the corresponding bis(ether diacid)s. Finally, cyclodehydration generates the bis(ether dianhydride)s, as shown in Scheme 4.

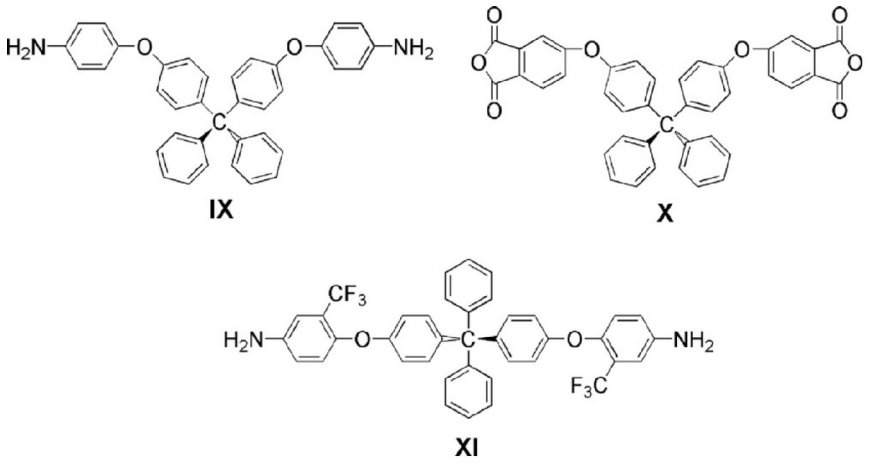
Liaw et al. synthesized reactive polyimides using a novel functional dianhydride (**BHTDA**) with a hydroxyl group [16] (Scheme 5); this polyimide was further modified for application on photoresist by Sekiguchi et al. [17].

Cheng and Jian [12] prepared a new noncoplanar heterocyclic diamine with an unsymmetrical kink,

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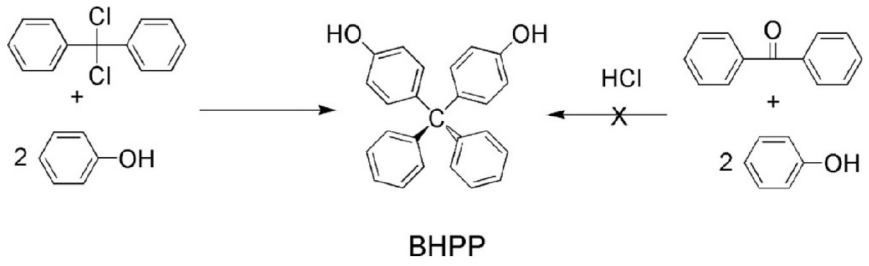
Scheme 1. Some commercial diamines with kink structures.



Scheme 2. Some structures of novel kink diamines and dianhydrides.

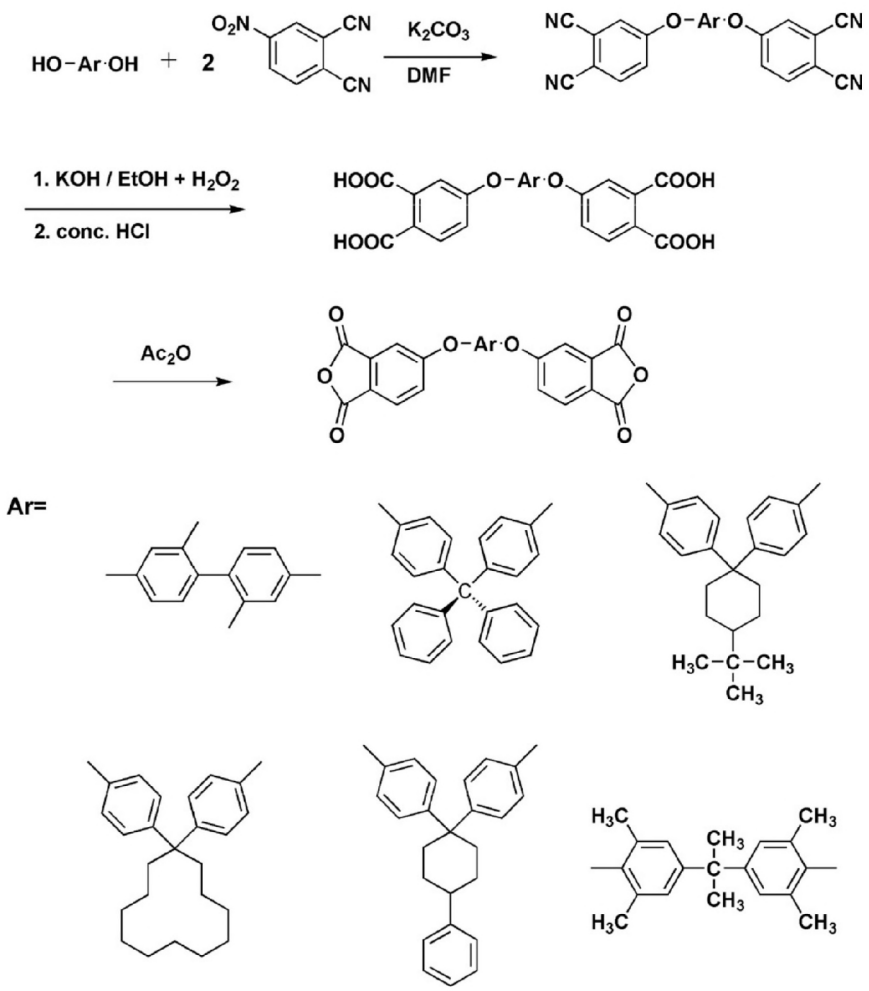
1,2-dihydro-2-(4-aminophenyl)-4-[4-(3-phenyl-4-aminophenoxy) phenyl]-(2*H*) phthalazin-1-one, from a readily available, bisphenol-like unsymmetrical phthalazinone. The glass transition temperatures of the obtained polyimides were in the range of 315–340 °C, and the temperatures for 5% weight loss in nitrogen were in the range of 487–512 °C. The polyimides derived from this kink diamine exhibit good solubility.

2.1.1.2. Spiro. A spiro structure (called a spiro center) consists of two rings connected orthogonally through a particular tetrahedral bonding atom. Usually, a carbon atom serves as the spirocenter. Spiro diamines and dianhydrides have been synthesized in different ways, and their structures are shown in Scheme 6 [18–34]. The spirobifluorene monomer consists of two identical fluorene moieties connected through a common tetracoordinated carbon atom [18–21]. The monomers (diamines and dianhydrides) that contain spirocenters are summarized in Scheme 6. The resulting polyimides containing spiro structures are expected to have a polymer backbone that is periodically twisted at 90° angles at each spirocenter. This structural feature restricts the close packing of the polymer chains and reduces the probability of interchain interactions. Because of the less favorable molecular packing and lower crystallinity, the polymer should be more soluble



Scheme 3. Synthesis of **BHPP**.

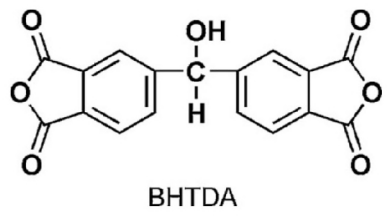
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Scheme 4. Preparation of bis(ether anhydride)s.

and have a significantly increased T_g and thermal stability.

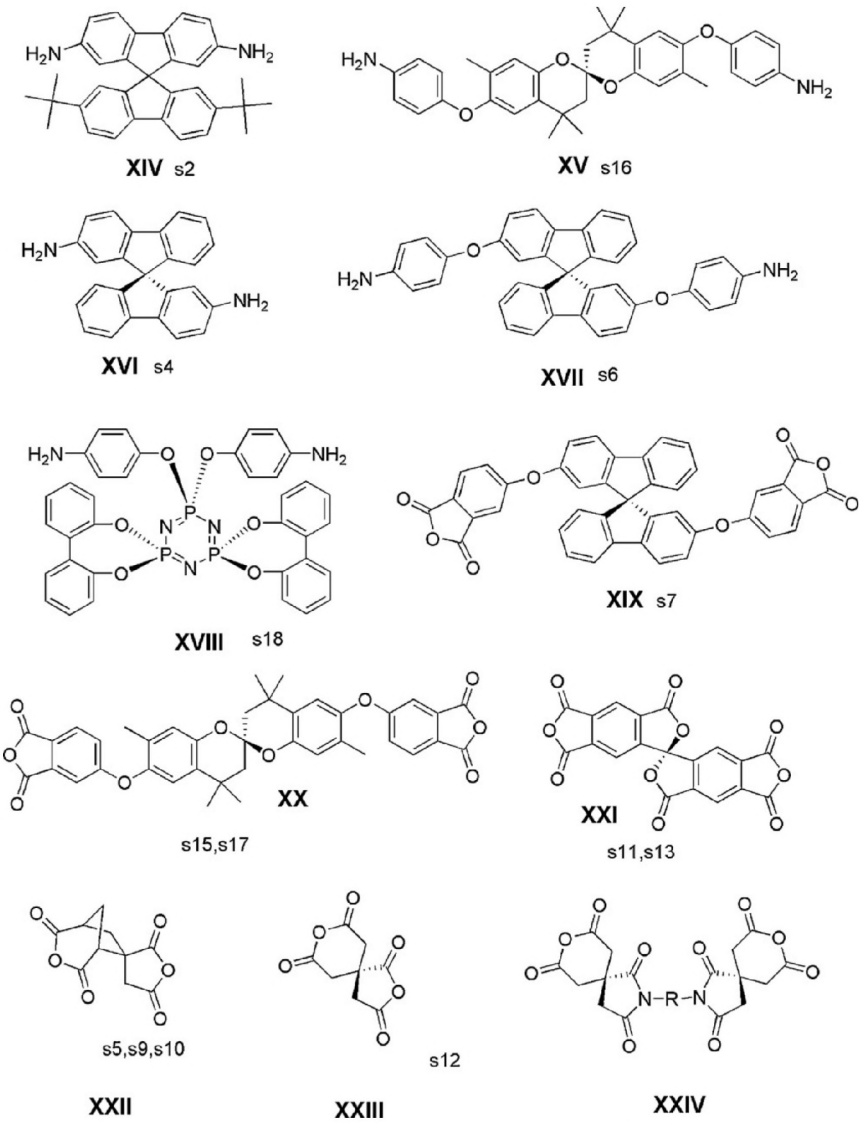
In addition, the new polyimides derived from 2,7-bis-amino-2′,7′-di-*tert*-butyl-9,9′-spirobifluorene (Scheme 6, **XIV**) exhibit high oxygen permeability ($P(O_2)$ 18–121 barrier) and desirable O_2/N_2 gas separation properties ($P(O_2)/P(N_2)$ 2.2–9) [18].



Scheme 5. Functional dianhydride (**BHTDA**) with a hydroxyl group.

Shu et al. synthesized polyimides derived from several spiro diamines and dianhydrides, as shown in Scheme 6 (**XVI**, **XVII**, **XIX**). These polyimides have excellent solubility, good optical transparency, and high thermal stability characteristics, which can be attributed to the presence of spiro-fused orthogonal bifluorene segments along the polymer chain [19–21]. Hsiao et al. reported the synthesis of spirobichromans that contain either a diamine (**XV**) [22] or a dianhydride (**XX**) [23]. Polyimides derived from these monomers are soluble in various solvents and can be cast into transparent, flexible, and tough films. Kumar et al. synthesized a novel diamine containing bis(arylenedioxy)spiro-cyclotriphosphazene (**XVIII**) with two spirocenters (phosphorus atoms) [25]. The polyimides derived from the spiro-diamines give rise to colorless or light-yellow films due to the bulky bis-spiro-substituted pendants. The polyimides also show good thermal stability and are noteworthy for their high char yield in air. Han et al. [24,25] reported that polyimides from a

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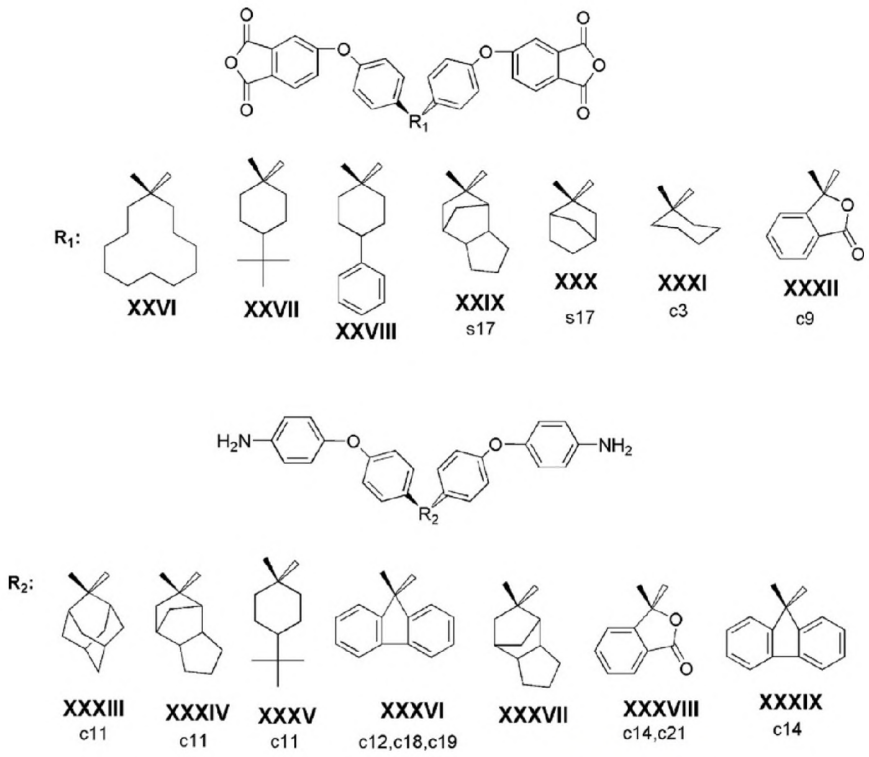


Scheme 6. Chemical structures of novel spiro diamines and dianhydrides.

novel spirodilactone dianhydride (**XXI**) showed a high T_g (above 400 °C). Furthermore, polyimides containing the spirodilactone unit (**XXI**) are capable of crosslinking via lactamization, which enhances their thermal properties [25]. Some novel dianhydrides containing aliphatic spiro units have been prepared by Shiraishi et al. [20–33]. Polyimides containing aliphatic spiro structures derived from **XXII** [26,27] and **XXIII** and **XXIV** [28,29] showed excellent solubility and formed colorless films due to their unsymmetrical spiro and aliphatic structures. A series of copolyimides was prepared from two alicyclic dianhydride isomers, a spiro compound **XXII** and a non-spiro compound **XXII**, with *p*-phenylenediamine by the conventional two-step procedure. By increasing the fraction of **XXII** in the backbones, the copolyimides showed better film formation, enhanced solubility, increased glass transition temperatures and birefringences and decreased average refractive indices. These properties are most likely the result of the unsymmetrical spiroalicyclic structure of **XXII** [28].

2.1.1.3. Cardo and alicyclic. "Cardo" means "hinge" or "loop" in Latin. Therefore, polymers that contain loop shaped moieties in their main chains are called "cardo polymers". The cardo structure is very similar to the spiro structure but has only one ring attached to a cardo

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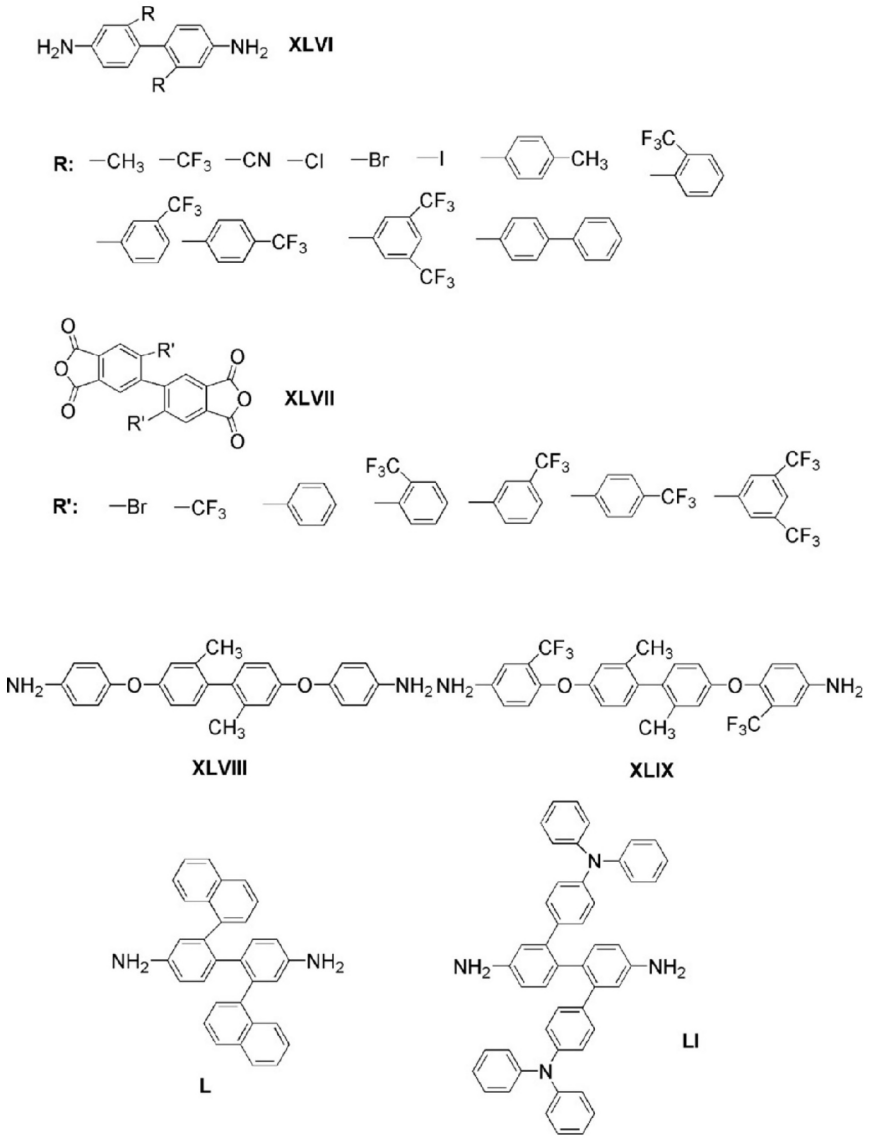
Scheme 7. Chemical structures of novel cardo monomers [23,30–34,36,78,79,448].

center, while two rings are attached to a spirocenter. A series of polymers containing bis(phenyl)fluorenes or bis(phenyl)phtarides as cardo moieties have been synthesized, and their physical properties have been reported. Liaw's group and others have reported many aromatic and alicyclic cardo diamines and dianhydrides, as summarized in Scheme 7. The phenylfluorene-based cardo polymers have good thermal stability, solubility, transparency, and refraction indices, among other favorable properties. Thus, polyimides that have a cyclic cardo group, such as cyclododecylidene, adamantane, or tricycle decane, exhibit high solubility and have outstanding thermal properties. The high solubility enables the preparation of an ultrathin active layer, which can act as an asymmetric or composite membrane. In addition, alicyclic cardo-containing polyimides exhibit a lighter color than the corresponding aromatic cardo-containing polyimides.

2.1.1.4. Other noncoplanar structures. Harris et al. [35,36] reported the incorporation of 2,2′-disubstituted biphenylylene (Scheme 8) in a *para*-linked polymer chain. The substitution at the 2- and 2′-positions of the biphenyl moiety forces the rings to adopt a noncoplanar conformation. The resulting twist in the backbones of the polymers prepared from these monomers hinders chain packing and thus reduces the crystallinity and intermolecular interactions, enhancing solubility. Liaw et al. [37] also synthesized and studied 2,2′-dimethyl biphenylylene-containing noncoplanar ether diamines, which have flexible aryl ethers and bulky 2,2′-disubstituted moieties. The aryl ether linkages in the main aromatic chains (**XLVIII–XLIX**) significantly decrease the energy required for internal rotations, This decrease not only results in lower glass transition and crystalline melting temperatures but also leads to significantly improved solubility and other process characteristics of the polymers without greatly sacrificing thermal stability.

Kakimoto et al. [38,39] reported the synthesis of crank and twisted noncoplanar structure diamines (**LII** and **LIII**) and dianhydrides (**LIV** and **LV**) (Scheme 9). The two diamines (**LII** and **LIII**) were successfully synthesized using, respectively, biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl as starting materials. After *p*-fluoronitrobenzene was reacted with bisphenols, the intermediate product was subjected to catalytic reduction to obtain the final product. The two ether-containing dianhydrides (**LIV** and **LV**) were first synthesized by a nitro substitution reaction of 4-nitrophthalonitrile with the bisphenols to obtain a tetranitrile. The synthesis of aromatic ether-containing tetranitriles by nucleophilic displacement of activated aromatic nitro groups with aryloxy anions was also reported by Takekoshi et al. [40] in 1980. The tetranitrile compounds were hydrolyzed with aqueous potassium hydroxide to produce the corresponding tetracarboxylic acid. This compound was then converted to

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Scheme 8. Monomers with noncoplanar structure.

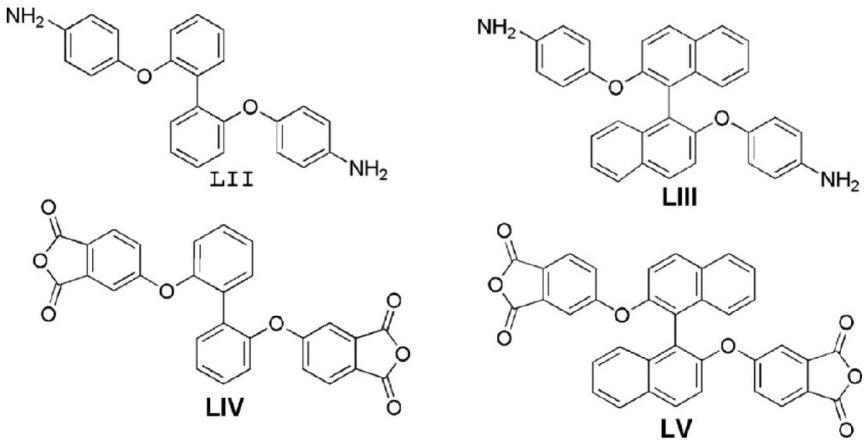
the aromatic ether that contains the tetracarboxylic dianhydride moiety [38,41].

Mikroyannidis [42] developed the synthesis of rigid-rod noncoplanar and twisted diamines using pyrylium salts, as shown in Scheme 10.

2.1.1.5. Unsymmetrical monomers. The introduction of geometrically or molecularly unsymmetrical diamines (**LVI–LXI**) [12,43–47] and dianhydrides (**LXII–LXVI**) [48–52] into the main chain has led to new polyimides with improved solubility, melt processability and other desirable properties. The advantages of this method are two-fold: (1) close chain packing and intermolecular interactions of the resulting polyimide are restricted, resulting in a relatively high solubility, and (2) the main chain rigidity of the polyimides can be maintained, allowing the polyimides to have a high T_g and other excellent thermal properties. Some unsymmetrical diamines and dianhydrides are shown in Scheme 11.

Polyimides based on an unsymmetrical dianhydride **(LXIV)** (**aBPDA**) were prepared, and their properties were compared with those of corresponding symmetrical dianhydrides (**sBPDA**) by Hergenrother et al. [51]. Polyimides derived from **aBPDA** had higher T_g values, a higher optical

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Scheme 9. Crank and twisted noncoplannar structure diamines or dianhydrides.

transparency, and generally lower tensile properties (in thin films) than polyimides from **sBPDA**.

Liaw et al. [53,54] synthesized a series of novel triphenylamine-containing diamines and polyimides, as shown in Scheme 12. The triphenyl-containing polyimides showed good solubility and excellent thermal and electrochromic properties.

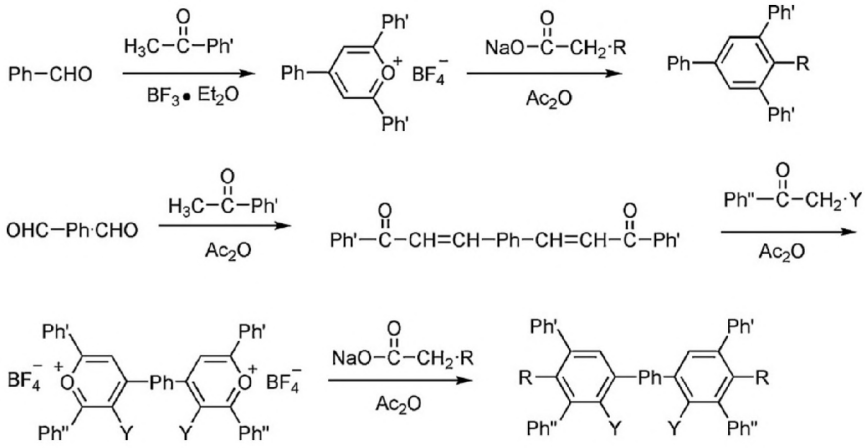
Liaw et al. synthesized an unsymmetrical 2,2′-dinaphthylbiphenyl-4,4′-diamine (**4**) (Scheme 13). First, the biphenyl was nitrated with nitric acid and sulfuric acid at 0 °C to give 4,4′-dinitrobiphenyl (**1**). The dinitro compound (**1**) was then iodinated using Marvel's reaction condition, which involves electrophilic aromatic substitution by an iodine cation, to give the 2,2′-diiodo-4,4′-dinitrobiphenyl (**2**) compound. Next, the diiodo-dinitro compound (**2**) was treated with 1-naphthylboronic acid in a Suzuki coupling reaction to afford the 2,2′-dinaphthyl-4,4′-dinitrobiphenyl (**3**). Finally, the nitrobiphenyl group was converted to the diamine compound (**4**) with ammonium formate and 10% Pd/C in a DMF solution at 80 °C.

Normally, bisphenols containing cardo structure are prepared from ketones and phenols [55]. In addition, Liaw et al. [55] reported a synthetic route of bisphenols that, according to a procedure by Schmidt, involves the rearrangement of a dihydrochloride, as shown in Scheme 14.

Unsymmetrical ether-containing diamines can be prepared from the novel bisphenols via nucleophilic substitution and reduction, as shown in Scheme 15.

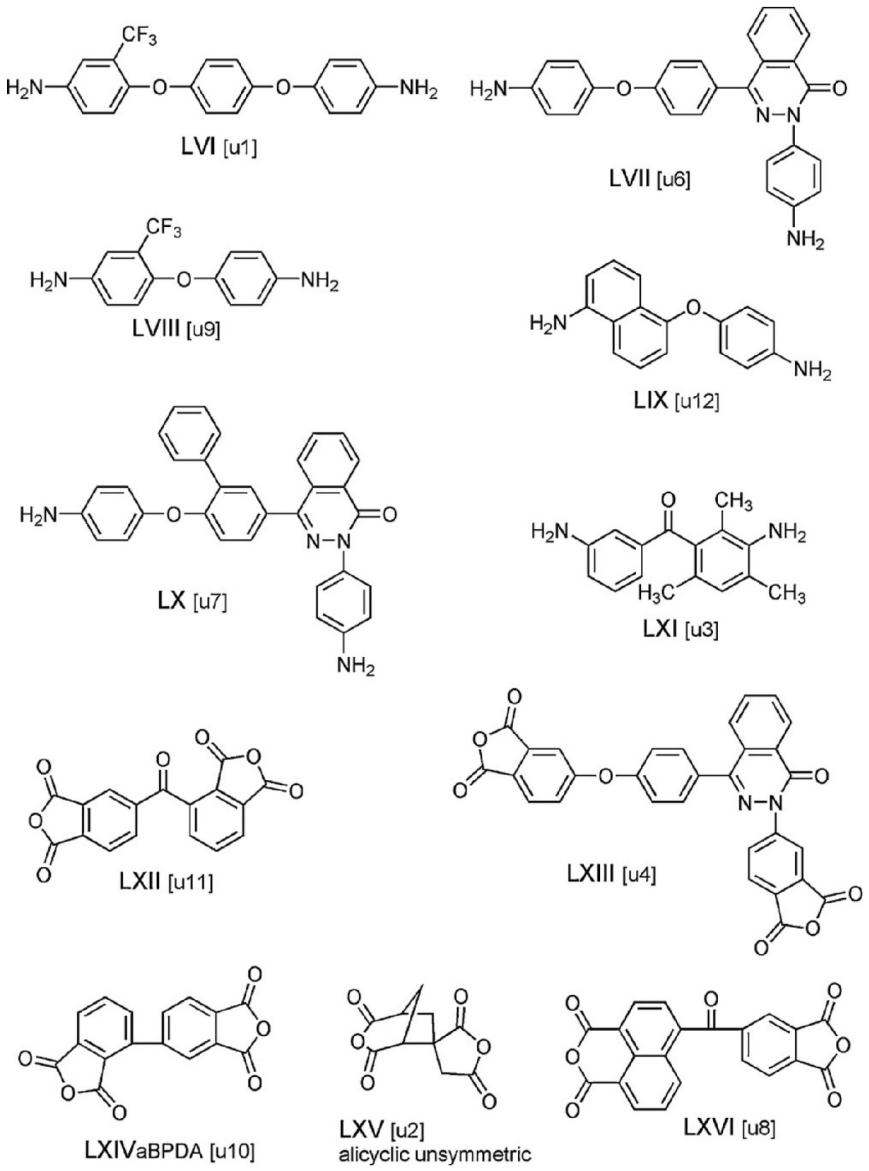
2.1.2. *Alicyclic units in main chains*

In recent years, polyimides with high optical transparencies and low dielectric constants have been in demand for optoelectronic and microelectronic applications. Alicyclic polyimides are candidates for applications in optoelectronics and interlayer dielectrics due to their higher transparency and low dielectric constants when compared to aromatic polyimides [56–61]. These properties result from their low molecular density, low polarity, and low probability of undergoing inter- or intramolecular charge transfer [62–67]. Numerous fully



Scheme 10. Synthesis of rigid-rod noncoplanar and twisted diamines using pyrylium salts.

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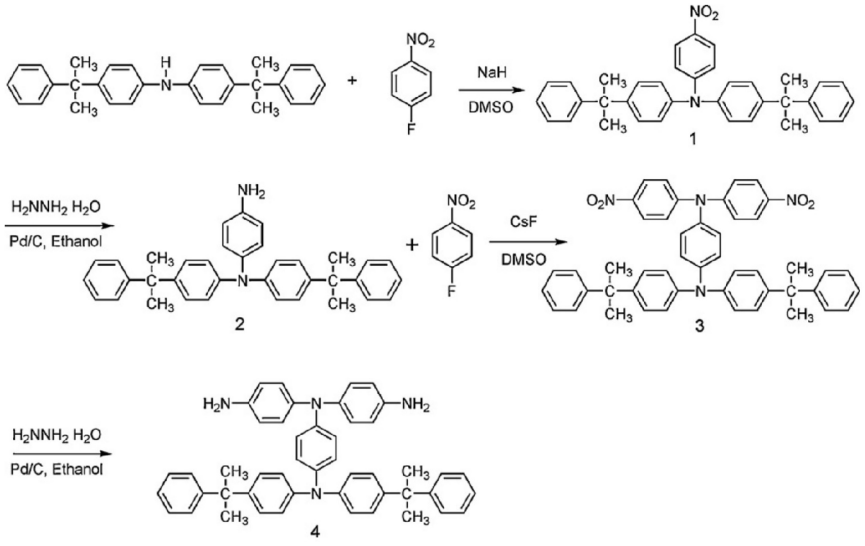
Scheme 11. Chemical structures of unsymmetric monomers.

alicyclic polyimides [68,69] and partially alicyclic polyimides [33,48,67,70] have been studied. These alicyclic polyimides all show excellent transparency and good solubility and thermal properties.

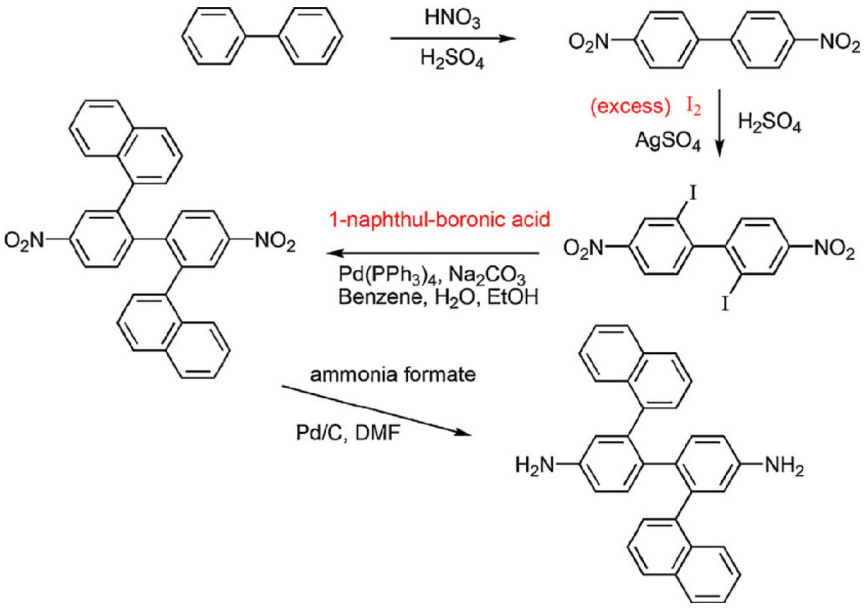
The incorporation of adamantane (tricycle[3.3.3.1.1] decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations, can enhance the thermal stability and optical properties of a polyimide without sacrificing the its high transparency, solubility, low dielectric constant, and low coefficient of thermal expansion [68,69]. Typical examples of the alicyclic monomers including diamines and dianhydrides are shown in Scheme 16 [71,72] (**LXVII**). In addition, some alicyclic dianhydrides have been reported and used as alignment films for color LCD applications. The alicyclic monomers are summarized in Scheme 16.

Schenk et al. [73] prepared *cis*-cyclobutane-l,2,3,4-tetracarboxylic dianhydride by irradiating a solution of maleic anhydride in dioxane with a high pressure mercury lamp. Suzuki et al. reported the synthesis of substituted 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and performed the light-induced dimerization of a

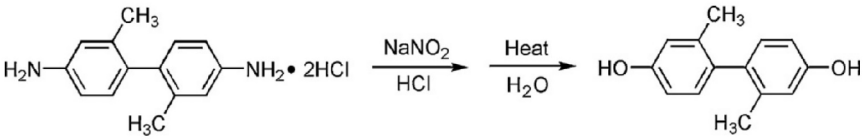
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Exhibit 1024 - Page 10



Scheme 12. Synthesis triphenylamine-containing diamines [53,54].

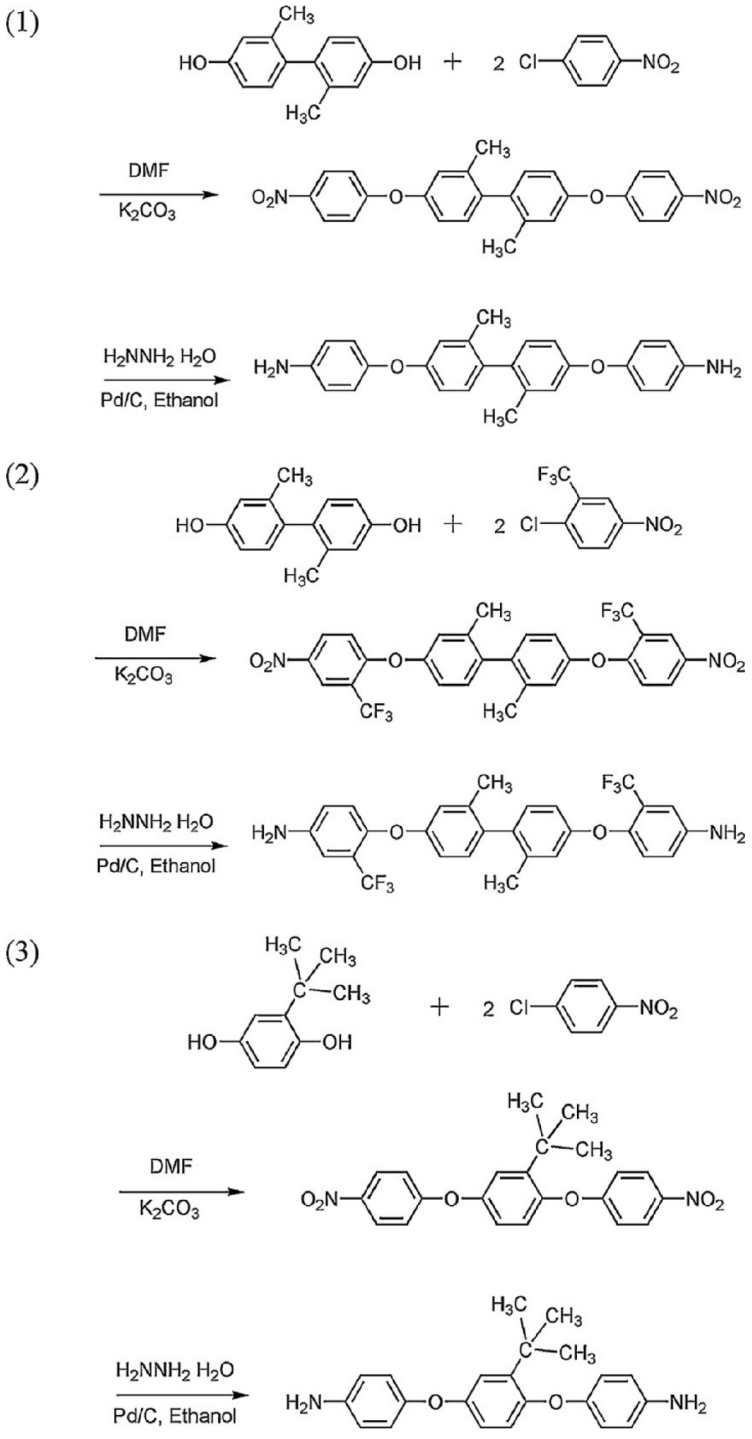


Scheme 13. Synthesis of biphenyl dinathalene diamine.



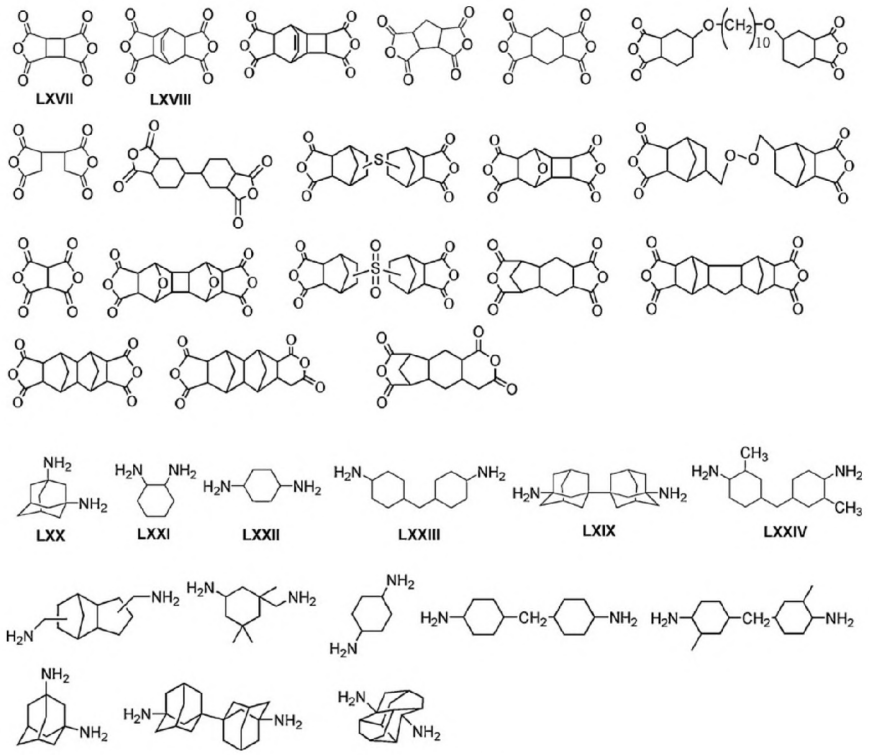
Scheme 14. Synthesis route for bisphenol through rearrangement from dihydrochloride.

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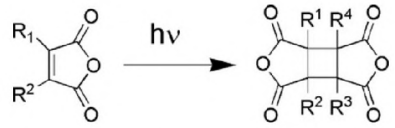


Scheme 15. Unsymmetrical ether-containing diamines.

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Scheme 16. Chemical structures of alicyclic monomers.



Scheme 17. Preparation of *cis*-cyclobutane-l,2,3,4-tetracarboxylic dianhydrides.

maleic anhydride compound from −10 to 50 °C in the range of 300–600 nm wavelength (Scheme 17). The R1, R2, R3, and R4 groups can be either hydrogen atoms, alkyl groups (1–10C), phenyl groups, or halogens [74].

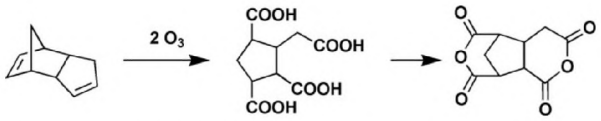
The l,2,3,4-cyclopentanetetracarboxylic acid [75–77] was obtained by oxidizing a Diels–Alder adduct of cyclopentadiene and maleic anhydride with nitric acid, followed by neutralization with an aqueous solution containing sodium hydroxide or ammonia to afford the l,2,3,4-tetrasodium salt of cyclopentanetetracarboxylic acid or the l,2,3,4-tetra-ammonium salt of cyclopentanetetracarboxylic acid, respectively. The 1,2,4-tricarboxyl-3-methylcarboxyl cyclopentane dianhydride was obtained by dehydrating the cyclopentanetetracarboxylic acid (Scheme 18).

2.1.3. *Fluorinated monomers*

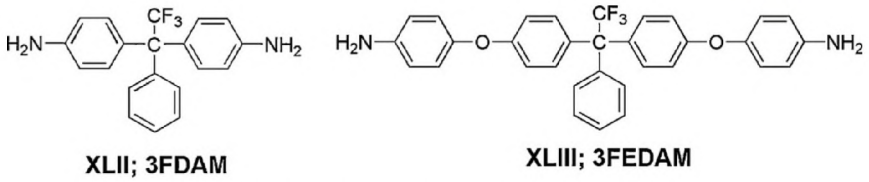
Because of the need for high integration and high signal-propagation in miniaturized electronic devices and components, speed is of utmost importance in the microelectronics industry. A reduced dielectric constant in insulation materials allows higher signal-propagation speeds. Fluorine-containing polymers are of special interest because of their low dielectric constants, high optical transparency, low refractive indices and remarkably low water absorption. In addition, the 6F (1,3-ditrifluoromethyl-2-isopropyl) groups in the polymer backbone enhance polymer solubility (a characteristic known as the "fluorine effect") without reducing the thermal stability. The bulky trifluoromethyl group ($-CF_3$) also serves to increase the free volume of the polymer, thereby improving gas permeability and electrical insulating properties.

McGrath et al. [36] reported a fluorinated diamine monomer based on trifluoroacetophenone; this monomer was synthesized *via* a straightforward, high yielding two-step procedure. Trifluoroacetophenone was reacted with 4-nitrophenyl phenyl ether to yield the 3F-dinitro compound, which was subsequently reduced to afford the fluorinated diamine, 1,1-bis[4-(4-aminophenoxy)phenyl]-l-phenyl-2,2,2-trifluoro-ethane (3FEDAM) (Scheme 19). Yang's group also reported the synthesis of a '9F' fluorinated diamine [78] and dianhydride [79] using similar synthetic procedures (Scheme 20). The triarylfluoroethane derivative, 3′,5′-bis(trifluoromethyl)-2,2,2-tifluoroacetophenone (9FAP), was obtained by a Grignard reaction between anhydrous lithium trifluoroacetic acid, 1-bromo-3,5-bis(trifluoromethyl)benzene

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Scheme 18. Preparation of 1,2,4-tricarboxyl-3-methylcarboxyl cyclopentane dianhydride [75–77].



XLII; 3FDAM **XLIII; 3FEDAM**

Scheme 19. Chemical structures of **XLII** (3FDAM) and **XLIII** (3FEDAM).

and magnesium. The dinitro and tetramethyl intermediates were subsequently synthesized by a coupling reaction of 9FAP with 4-nitrophenyl phenyl ether and *o*-xylene, respectively, in the presence of trifuoromethanesulfonic acid, which acted as a catalyst. The diamine was derived *via* reduction of the dinitro group, and the dianhydride was derived *via* oxidation of the methyl group and subsequent dehydration reaction.

Liaw and Yang recently reported a number of monomers and polyimides that contain trifluoromethyl ether linkages [64,80–86]. The CF_3-containing diamines were prepared *via* a conventional two-step procedure. The intermediate dinitro compound was synthesized by a nucleophilic halogen displacement reaction of 2-halogen (F or Cl)-5-nitrobenzotrifluoride with a bisphenol in the presence of potassium carbonate in NMP, DMF or DMAc. The diamine monomers were obtained in good yields upon catalytic reduction of the dinitro compounds with hydrazine hydrate (or hydrogen gas) and Pd/C catalysts in ethanol under reflux. Banerjee and his group [87,88] have also reported the synthesis of diamines containing ether linkages and different rigid units with pendant trifluoromethyl in the same procedures. Some of the fluorine-containing diamines are summarized in Scheme 21.

Another approach to obtaining trifluoromethyl-containing diamines is through nucleophilic displacement of activated fluorine atoms of intermediate trifluoromethyl-containing difluoro compounds by 4-aminophenol. These reactions are performed in the presence of excess potassium carbonate, which acts as a base, in NMP with the concomitant azeotropic removal of water formed in the acid–base reaction between phenol and base, under well-established reaction conditions, as shown in Scheme 22 [88].

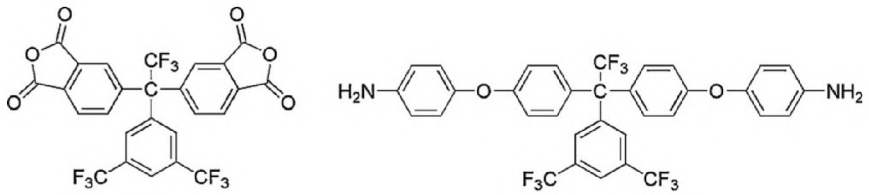
Yoon et al. [89,90] reported the synthesis of 3,5-bis(trifluoromethyl)phenyl containing diamines, as shown in Scheme 23. The resulting polyimides derived from the diamines exhibit good thermal stability and have desirable adhesive properties, low dielectric constants, and low refractive indices and birefringence properties.

The fluorine-containing dianhydrides, **6FPPMDA** [91] and **12FPPMDA** [92], which contain multi-fluorine groups, were prepared as shown in Schemes 24 and 25. The compound **6FBB** was prepared from 3,5-bis(trifluoromethyl) bromobenzene *via* a Grignard reaction with trimethylborate. **6FBB** was then reacted with **B4MB** (or **2B4MB**) to obtain **6FP4MB** (or **12F4MB**) in a Suzuki cross-coupling reaction. The 3,5-bis(trifluoromethyl)phenyl-containing dianhydrides were successfully prepared by oxidizing **6FP4MB** and **12F4MB**, followed by cyclodehydration. The polyimides based on the two diamines had high T_g values, low dielectric constants and low coefficients of thermal expansion (CTE) [91,92].

Some triarylfluoroethane-containing diamines and dianhydrides with kink structures were introduced in Section 2.1.1.1.

2.1.4. Miscellaneous structures

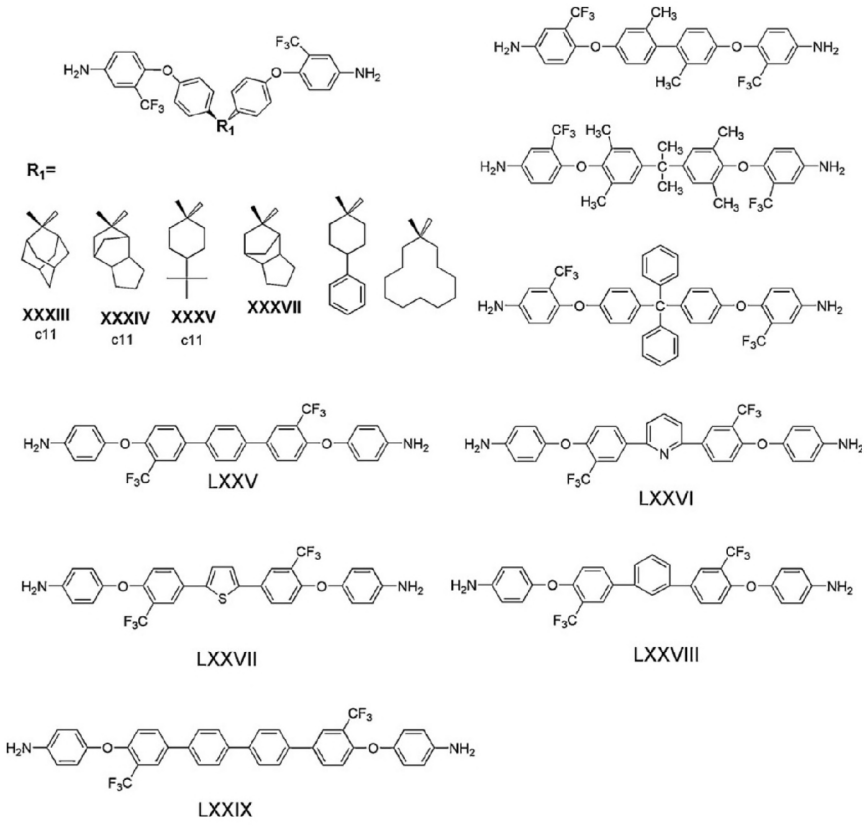
Apart from the popular aromatic, noncoplanar, aliphatic, acyclic and fluorinated monomers described above, specialized monomers for specific applications are also an interesting area of research. Silicon atoms, carbazoles, heterocyclic rings, perylene, and chiral functionalities have also been incorporated into polyimide



XLIV **XLV**

Scheme 20. Triarylfluoroethanes-containing dianhydride (**XLIV**) and diamine (**XLV**).

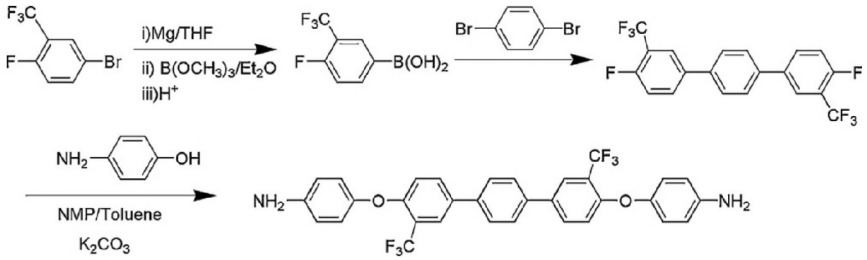
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Scheme 21. Diamines containing trifluoromethyl with different linkages [87].

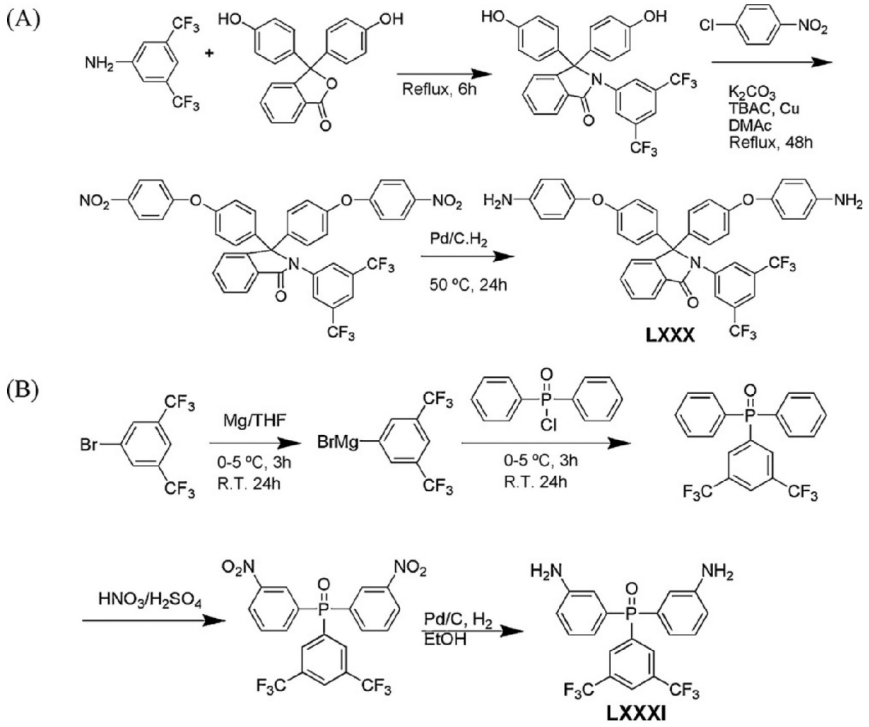
monomers to obtain polymers with properties that are desirable for specific applications.

2.1.4.1. Silicon-containing monomers. Silicon-containing aromatic polyimides have attracted considerable scientific and technological interest because of their potential applications in optoelectronic materials. Silicon, when placed next to aromatic groups, provides σ–π conjugation and thus supports the transport of electrons along macromolecular chains [93,94]. Polyhedral oligomeric silsesquioxane (POSS) is a cube-octameric molecule with an inner inorganic and oxygen framework that is externally covered by organic substituents. The incorporation of POSS into polyimides could lead to the development of high performance materials by combining the properties of inorganic and organic components. Applications of polyimides with POSS side chains and end groups have been reported. Recently, Wei et al. prepared polyimide nanocomposites with tethered polyhedral oligomeric silsesquioxane in their side chains, as shown in Scheme 26 [95–97]. As also shown in Scheme 26, Kakimoto et al. synthesized linear polyimides derived from a double-decker-shaped silsesquinoxane dianhydride (**DDSQDA**) [98], which was prepared from a double-decker-shaped



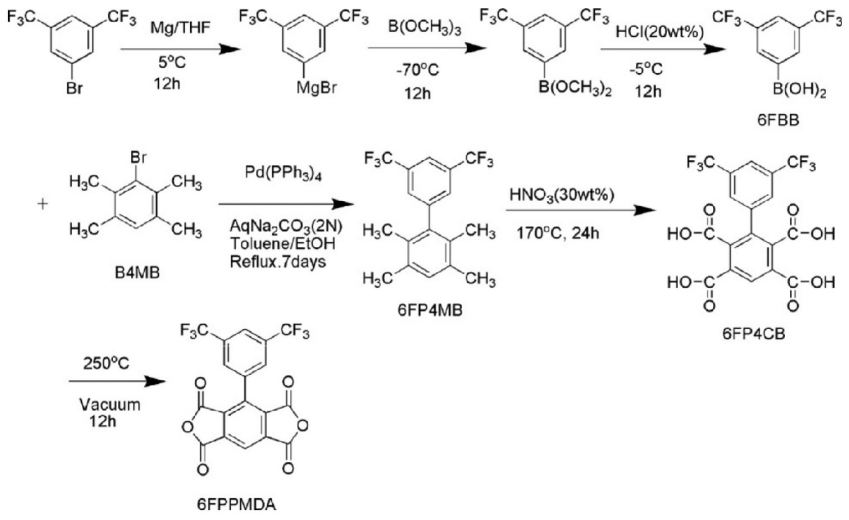
Scheme 22. Synthesis of monomer, **LXXV** [88].

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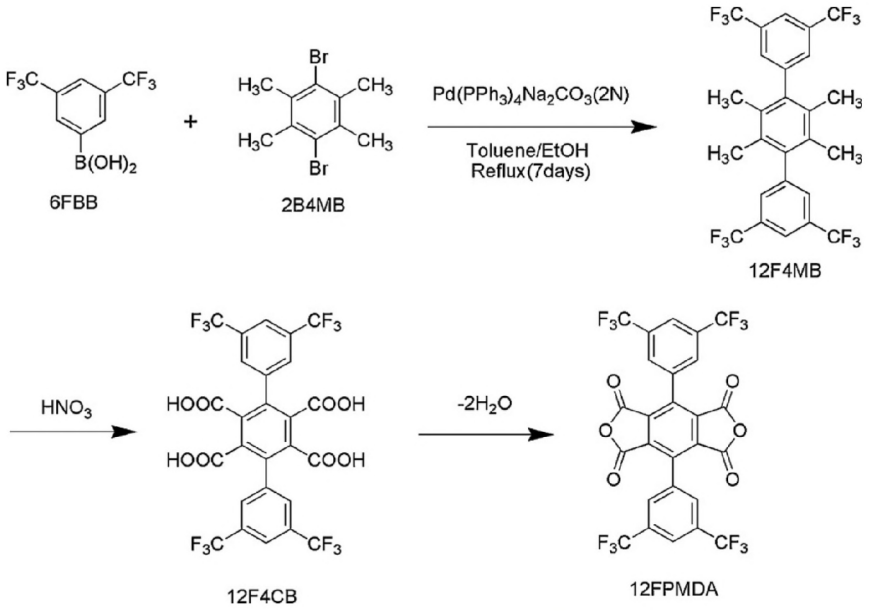
Scheme 23. Synthesis of 3,5-bis(trifluoromethyl)phenyl containing diamines [89,90].

silsesquinoxane (**DDSQ**) [99] containing two reactive hydrosilane groups [100]. The POSS-polyimides exhibit good thermal stability and mechanical properties, low water absorption, good alkali resistance and low dielectric constants. The double-decker-shaped poly(silsesquioxane) (**DDPSQ**) showed excellent transparency and thermal stability. The thermo-optic coefficient of the **DDPSQ** is 3 or 4 times larger than that of conventional polymers [101].



Scheme 24. Synthesis of 3,5-bis(trifluoromethyl)phenyl containing diamines [91].

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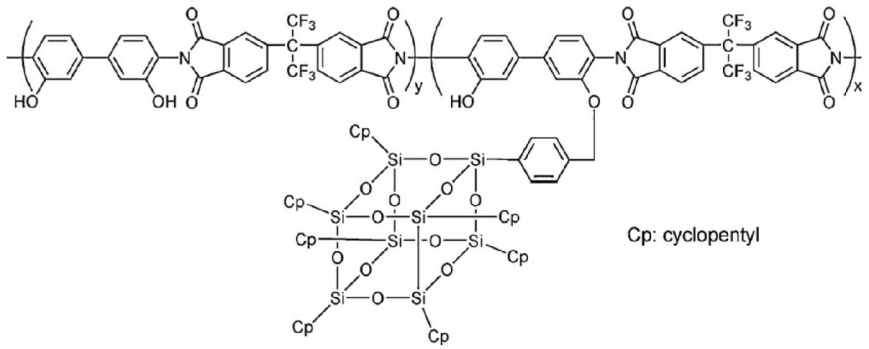
Scheme 25. Synthesis of **12FPPMDA** [92].

2.1.4.2. Heterocycle-containing monomers. The synthesis of new heteroaromatic monomers and corresponding polyimides that have both good processability and thermal stability would be of great interest. Heterocyclic ring-based polyimides are considered to be a unique class of high-temperature polymers. Polyimides with heterocyclic units incorporated into their backbones offer certain advantages, such as higher T_g values, tensile strength and modulus, over polyimides without heterocyclic units. The great variety of known heterocycles has opened the possibility of formulating polyimides with completely different properties [102].

1. The introduction of highly condensed heterocyclic fragments permits an increase in the thermal stability and heat resistance of the polyimides.
2. Heterocycles containing bulky side groups have been introduced to make polyimides soluble in organic solvents.
3. A majority of the aromatic heterocycles is more resistant to hydrolysis and nucleophilic attack than imide rings, and this has made it possible to use high molecular weight heterocyclic monomers, which reduce the content of imide rings per unit molecular weight of the polymer and increase the hydrolytic stability of the polyimides.

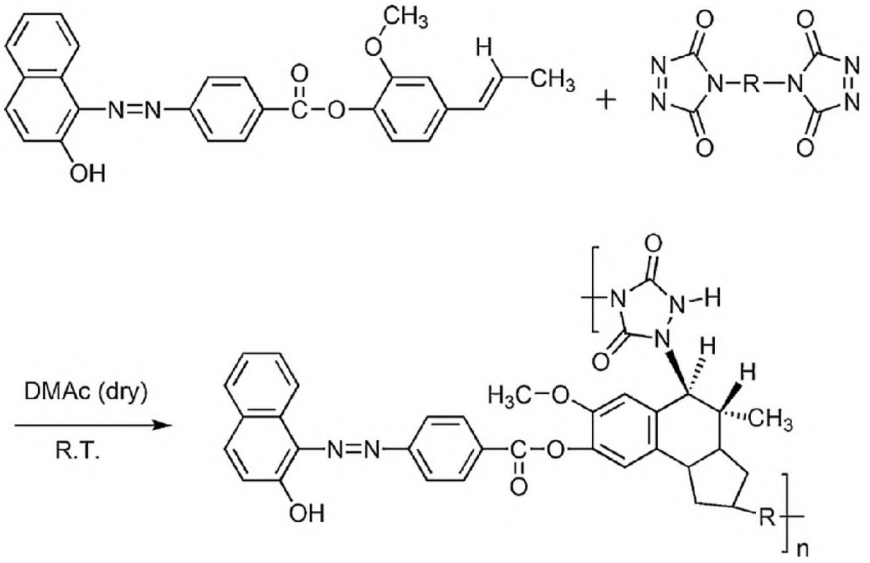
Heterocycles such as phenylquinoxalines [103], benzoxazoles, benzothiazoles [104,105], oxadiazoles [106–108], and triazoles [109,110], among others, have been incorporated into the backbones of polyimides.

New heteroaromatic diamine and dianhydride monomers are expected to play important roles in



Scheme 26. Double-decker-shaped poly(silsesquioxane) (**DDPSQ**).

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Scheme 27. Synthesis of novel heterocyclic polyimides containing the azo-naphthol pendant group via Diels–Alder-ene cycloaddition reactions from an azo-ester.

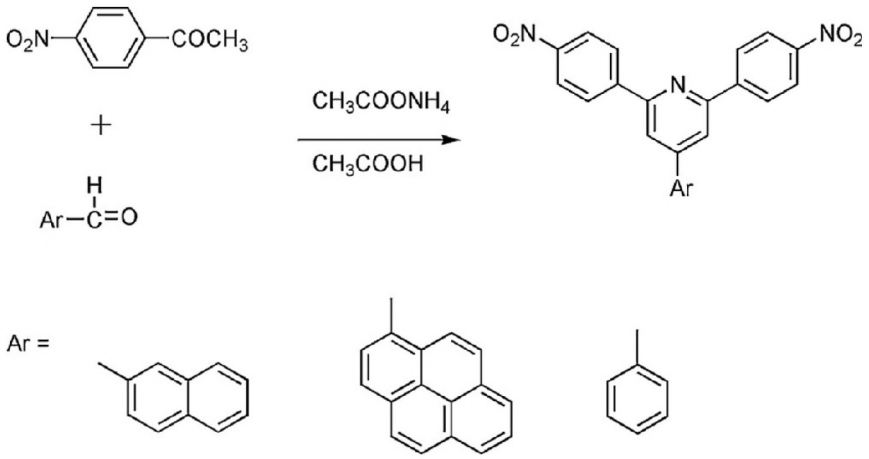
the synthesis of advanced polyimides. Mallakpour et al. [111] reported the synthesis of novel heterocyclic polyimides containing azo-naphthol pendant groups. This polymer was accessed via a Diels–Alder-ene cycloaddition reaction from an azo-ester derivative of isoeugenol and bistriazolinedione at room temperature, as shown in Scheme 27. The reactions are exothermic, fast, and provide novel heterocyclic polyimides in high yield. The polyimides contain OH and NH, as well as C=O functional groups. They can readily undergo hydrogen bonding to form physical networks that contribute to the mechanical properties of the polymers.

In general, the heteroaromatic structures in the main chain of a polymer are expected to impart certain properties to it. Pyridine would provide excellent thermal stability; good electronic, electron-transporting, and electron affinity characteristics; and more resistance to oxidation because of its molecular symmetry and aromaticity as well as the polarizability that result from the nitrogen atom in the pyridine ring. Thus, new heteroaromatic diamines, dianhydrides or other monomers containing pyridine units should be able to contribute to the chemical stability and mechanical properties of the resulting polymers at elevated temperatures and to exhibit unique properties. Consequently, our group [37,112–117] and other researchers [116,117] have focused on adopting monomers containing a pyridine nucleus for the synthesis of novel pyridine-containing polymers that have good thermostability and processability (Scheme 28). Liaw and Wang et al. [112–115] reported that polymers containing pyridine groups also exhibit interesting fluorescent phenomena upon protonation by protonic acids. In the absence of acid, the polymer has UV–vis absorption bands in the wavelength (λ) region of 240–400 nm. The absorption is red-shifted to the 390–500 nm region upon protonation. The protonated polymer exhibits strong orange fluorescence (around 600 nm) in a THF solution. It is proposed that the different absorption spectra of deprotonated and protonated poly(pyridine-imide)s result from a different electronic distribution in the molecule that occurs when the pyridine is protonated. Furthermore, the fluorescent intensity of the protonated polymer was influenced by the concentration of the acids [37].

The dinitro compounds containing pyridine heterocycles and pendant chromophore groups were synthesized with the modified Chichibabin reaction (Scheme 29), which is a facile method for the preparation of substituted pyridines [112–115]. The condensation of chromophore-containing aldehydes with 4-nitroacetophenone in the presence of ammonium acetate affords dinitro compounds in one step. The coplanar conformation and polar nitro group resulted in poor solubility of the dinitro compounds. Reduction of the dinitro derivatives in ethanol with hydrazine monohydrate in the presence of a catalytic amount of palladium on activated carbon at 90 °C produced new diamine compounds [118].

2.1.4.3. Carbazole-containing monomers. Carbazole is a conjugated moiety that has interesting optical and electronic properties, such as photoconductivity and photorefractivity [119]. In the field of electroluminescence, carbazole derivatives are often used as functional moieties for hole transporting and in light-emitting layers because of their high charge mobility, thermal stability, and blue electroluminescence. The electroluminescence is a result of the large band gap that arises from the improved planarity that the bridging nitrogen atom gives the biphenyl unit [120]. From a structural point of view, carbazole is a planar structure, whereas diphenylamine is a kink structure. The thermal stability of the polymer with incorporated

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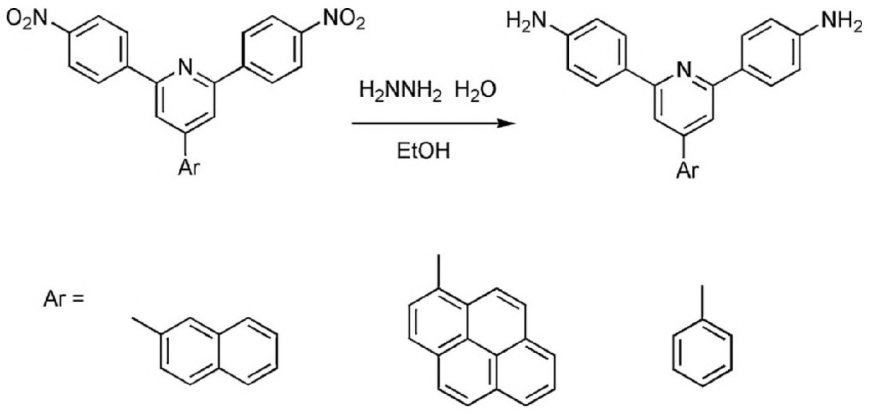


Scheme 28. Synthesis of pyridine-containing dinitro derived by Chichibabin.

carbazolyl units is therefore improved. In addition, carbazole can be readily functionalized at the (3,6) [121,122] (2,7) [123] or N-positions [124–126] and then covalently linked into polymeric systems. Carbazole can be incorporated both in the main-chain as a building block and in the side-chain as a pendant group [127–131]. It is thus worthwhile to explore the feasibility of new carbazole-based aromatic diamines as starting monomers for the preparation of high-performance polyimide systems with novel optoelectronic properties [132].

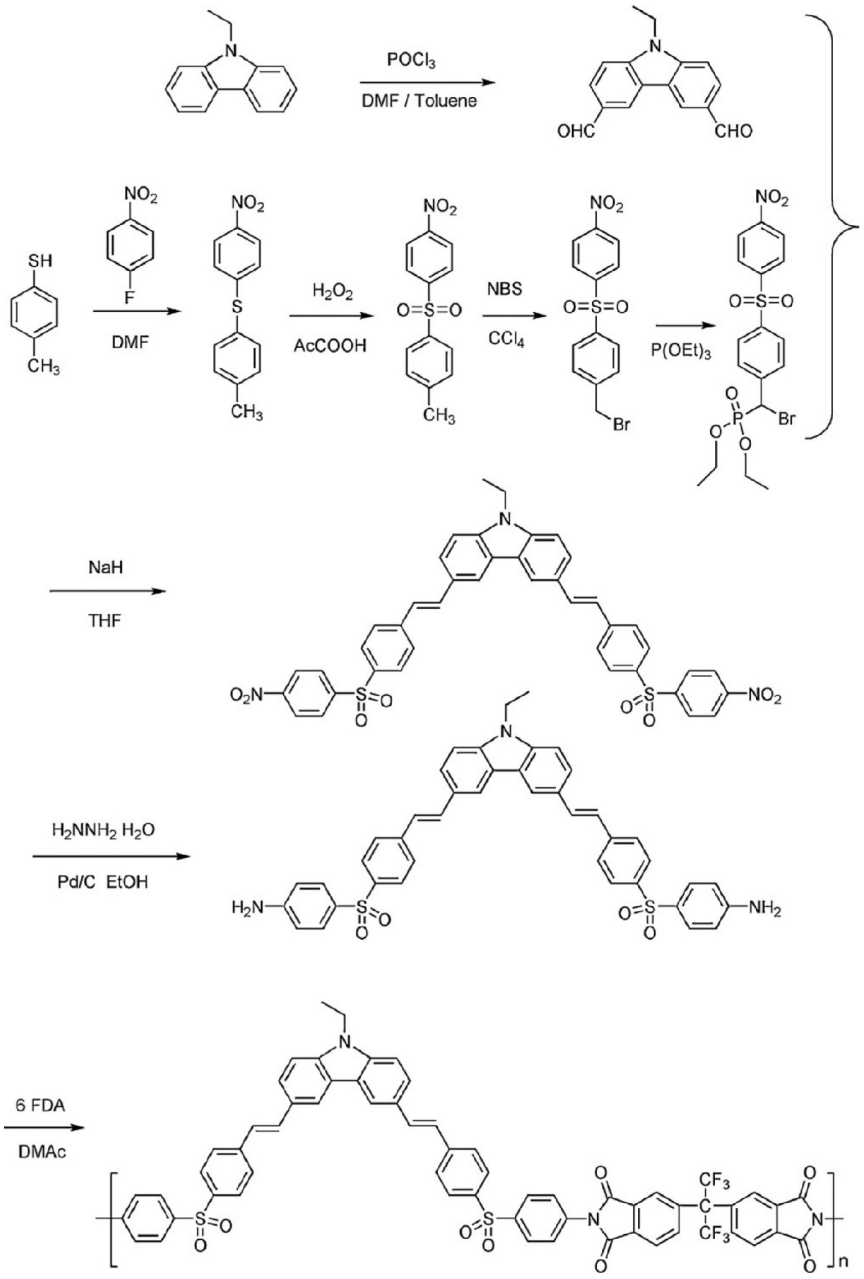
When the carbazole moiety is incorporated into the polyimide backbone, it imparts the polymer with a higher thermal stability, increased solubility, extended glassy state and moderately high oxidation potential [133]. In addition, carbazole is an excellent candidate for nonlinear optically (NLO)-active 2D chromophores, owing to its isoelectronic structures between positions 3 and 6 and its second-order nonlinear optical characteristics and photoconductive properties [134]. Hsiue et al. reported new highly thermally stable polyimides from diamine monomers containing novel lambda-shaped two-dimensional carbazole chromophores [135], as shown in Scheme 30. The polyimides derived from carbazole-containing monomers show good thermal properties and unique electronic characteristics.

2.1.4.4. Perylene containing monomers. Perylene imides represent a class of n-type semiconductors that exhibit a relatively high electron affinity among large-band-gap materials. The perylene-based polymers are of broad interest owing to their wide range of potential applications, including electron-transporting components in optical switching [136,137], electroluminescent [138–140], solar energy conversion [141–144], and liquid crystal color display [145] devices. Derivatization of perylene with highly fluorescent fluorene derivatives in the polymer molecules leads to added advantages in photophysical and photochemical properties [145]. However, the actual application of perylene-containing polyimides has been hampered by their poor solubility and low



Scheme 29. Synthesis of pyridine-containing diamines.

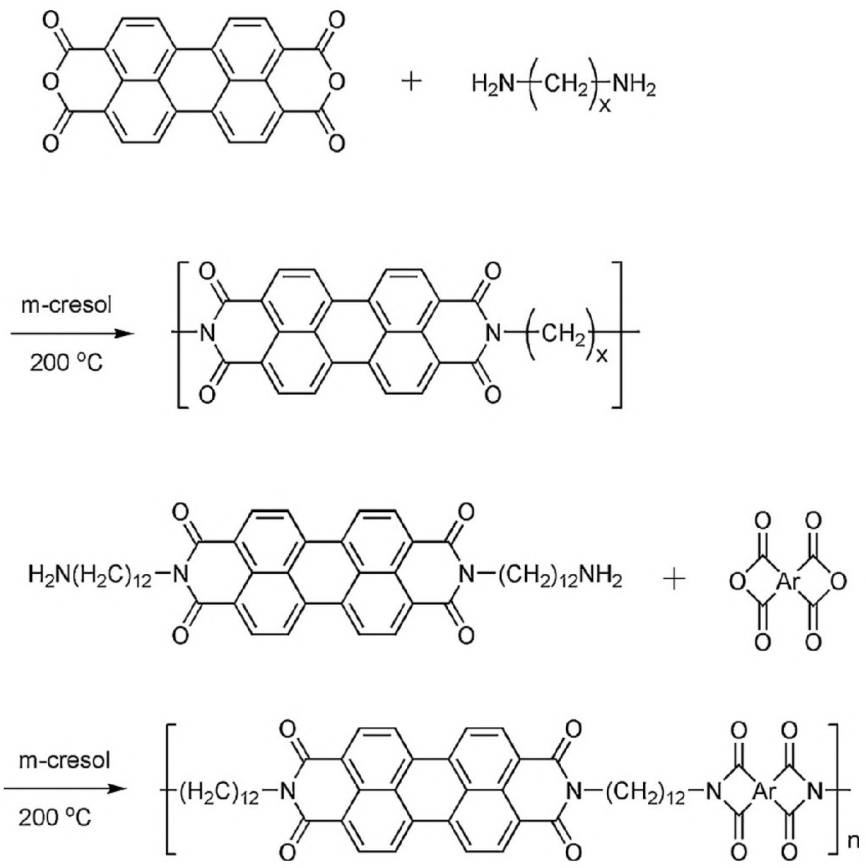
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Scheme 30. Polyimides containing novel lambda-shaped two-dimensional carbarzole chromophore.

solid-state fluorescence quantum efficiency. These undesirable aspects are associated with the rigid perylene group [146]. Most of the perylene bisimides are insoluble; therefore, film preparation of the perylene bisimides requires vapor deposition or dispersion in other polymer matrices, which substantially limits their applications [147,148]. Recently, a number of authors [149–151] have synthesized perylene-containing polyimides that avoid these problems with structural modifications. The two most commonly used approaches to preparing organo-soluble pyrene-containing polyimides are shown in Scheme 31. One approach uses flexible aliphatic diamines and pyrene-containing dianhydrides to form polyimides. The other approach uses

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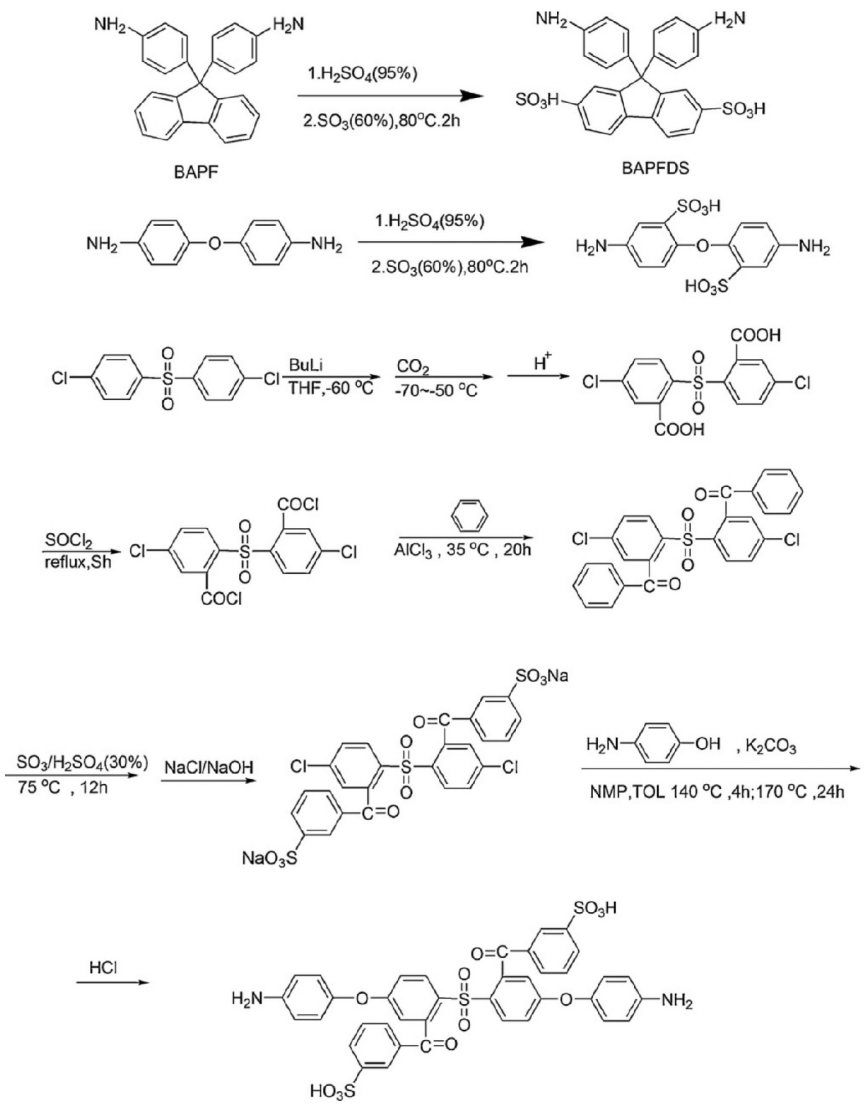
Scheme 31. Two most used approaches to preparing organo-soluble pyrene-containing polyimides.

pyrene-containing dianhydrides and other dianhydrides to form copolyimides. Icil et al. [152] synthesized a photostable polymer based on perylene-3,4,9,10-tetracarboxylic acid-bis-(*N,N′*-dodecylpolyimide). Ghassemi and Hay [153] reported red pigmentary polyimides prepared from *N,N′*-diamino-3,4,9,10-perylene tetracarboxylic acid bisimide. Wang and coworkers [154,155] prepared perylene-containing polyimides and investigated their xerographic electrical and voltage dependent fluorescence properties. Recently, perylenediimides have also been incorporated into conjugated oligomers and polymers as energy- and electron-acceptors [156].

2.1.4.5. Proton-conducting monomers for polyelectrolyte fuel cells (PEFCs). Polyelectrolyte fuel cells (PEFCs) have been identified as promising power sources for transportation vehicles and for other applications that require clean, quiet and portable power. The most important component of a PEFC is the proton-conducting membrane of the polyelectrolyte itself. Proton-conducting polymers have attracted much attention in the past few decades due to their important applications in fuel cell systems. Faure and Mercier's group first synthesized various sulfonated copolyimides from naphthalene-1,4,5,8-tetracaboxylic dianhydride (NTDA), 2,2′-bendizine sulfonic acid (BDSA, a widely used sulfonated diamine), and common nonsulfonated diamine monomers. However, the proton conductivity of these membranes is rather low ($<10^{-2}$ S cm^{-1} at 100% relative humidity) due to the low ion exchange capacity (IEC) [157–160]. The well-studied proton-conducting polymers that have been used in practical applications are sulfonated perfluoropolymers, such as DuPont's Nafion membrane and Dow's membrane, due to their high proton conductivity, high mechanical strength, and excellent thermal and chemical stability. However, there are some shortcomings that could seriously limit the applications of these polymers: they are expensive, have a low conductivity at low humidity or high temperatures, and high methanol permeability. Thus, the development of alternative materials is strongly desired. One major approach has been the attachment of sulfonic acid groups to highly stable aromatic polymers. As such, polyimides are one of the most ideal materials.

The introduction of sulfonic acid groups is achieved either by direct sulfonation of the parent polyimides or by

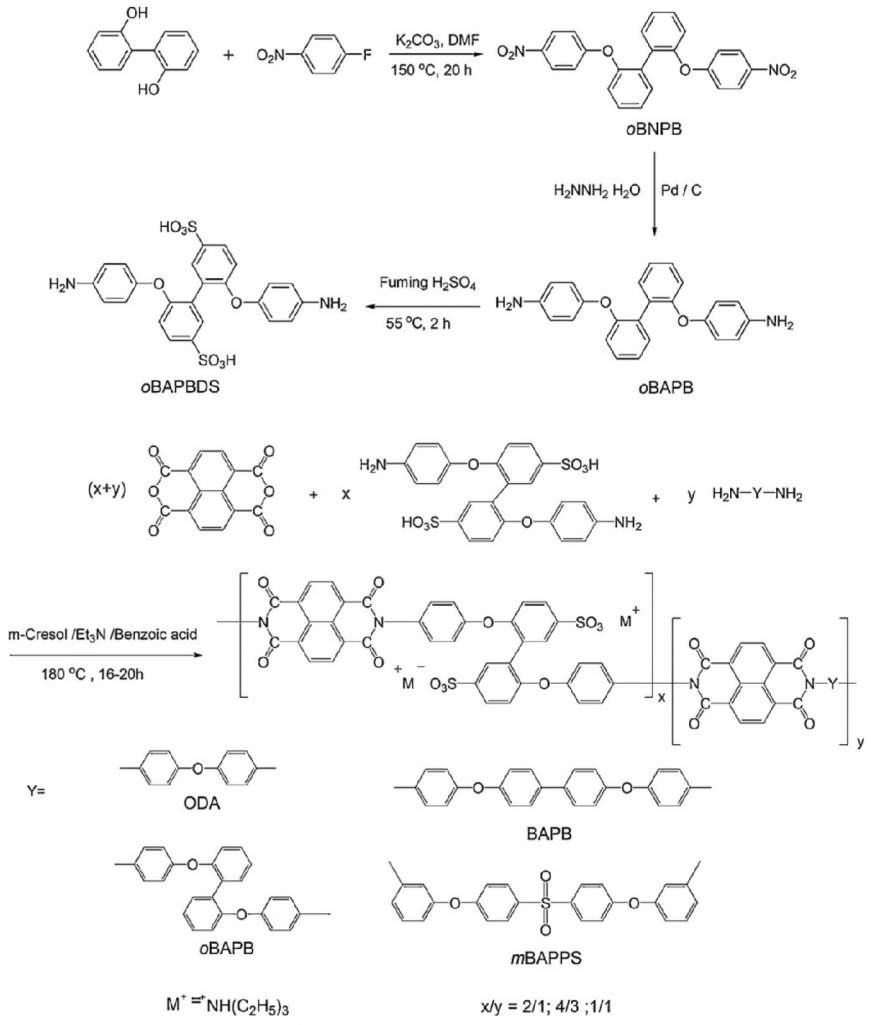
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Scheme 32. Sulfonated diamines derived from sulfonation reaction [161–163].

polymerization of sulfonated monomers. Okamoto et al. reported the synthesis of many new sulfonated diamine monomers, as shown in Scheme 32 [161–163]. The BAPFDS, ODADS, and *o*-BAPBDS monomers were synthesized by direct sulfonation of the corresponding parent diamines. By conducting the sulfonation at different temperatures, the sulfonic acid could be directed to specific positions. For instance, the sulfonation reaction occurred only at the 2,7-positions of the fluorenylidene ring because these two positions are more reactive than the others [161]. However, because the protonated amino group of ODA is a strong electron-withdrawing group, the sulfonation reaction occurred mainly in the position that was *meta* to the amino group [162]. The ODADS-based polyimides display much better stability in water than those derived from the widely used sulfonated diamine (BDSA) because ODADS-based polyimide membranes have a more flexible structure than the corresponding BDSA-based ones. The ODADS-based polyimides retain their mechanical properties and high proton conductivity after being soaked in water at 80 °C for 200 h [161,162]. The homopolyimide NTDA-*o*-BAPBDS membrane (Scheme 33) is soluble in water at room temperature; however, when nonsulfonated diamine moieties are incorporated by copolymerization,

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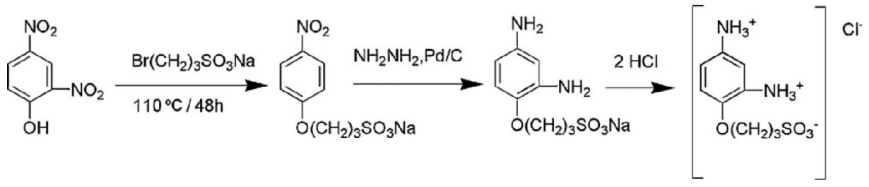
Scheme 33. Homopolyimide NTDA-*o*-BAPBDS.

the polymer is significantly less soluble in water but retains its mechanical strength after being soaked in distilled water at 80 °C for 40–1000 h [163].

Okamoto et al. [164] have also reported the synthesis of a novel sulfonated diamine monomer, 3-(2′,4′-diaminophenoxy)propane sulfonic acid (DAPPS), as shown in Scheme 34. A sulfonated polyimide (SPI) was prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and DAPPS. The SPI membrane displayed proton conductivity of 0.12–0.35 S cm^{-1} in water at temperatures ranging from 35 to 90 °C. The proton conductivity was found to be similar to or higher than that of Nafion® 117 and other sulfonated hydrocarbon polymers. The SPI membrane displayed good stability in water at 80 °C and was thermally stable up to 240 °C. It showed reasonable mechanical strength with a modulus of 1.3 GPa at 90 °C and 90% relative humidity (RH). Its methanol permeability (P_M) was 0.57×10^{-6} cm^2/s at 30 °C with 8.6 wt% methanol in the feed. These properties suggest that the SPI membrane could have potential applications in direct methanol fuel cells.

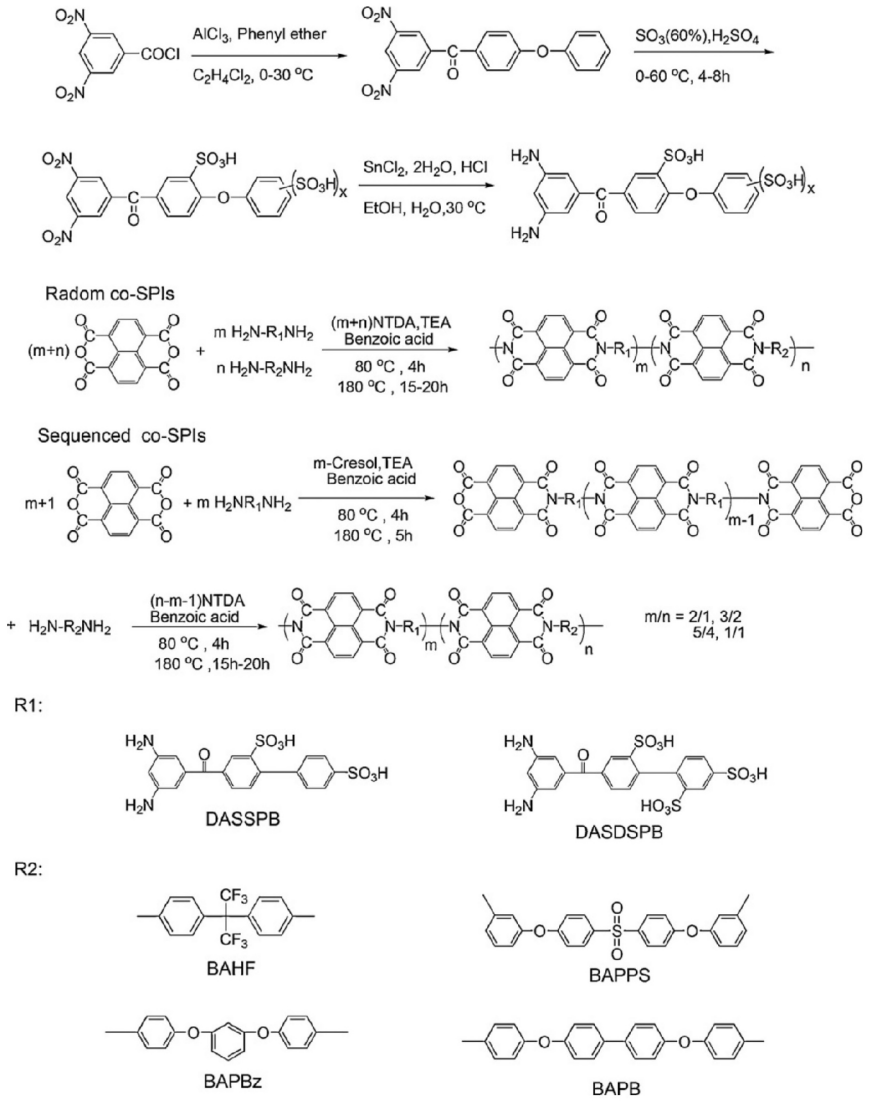
Okamoto et al. synthesized novel diamines bearing sulfonated aromatic pendant groups, namely, 3,5-diamino-3′-sulfo-4′-(4-sulfophenoxy) benzophenone (DASSPB) and 3,5-diamino-3′-sulfo-4′-(2,4-disulfophenoxy) benzophenone (DASDSPB), as shown in Scheme 35 [165]. Novel side-chain-type sulfonated copolyimides (SPIs) have been synthesized from these two diamines, 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and nonsulfonated diamines, such as 4,4′-bis(3-aminophenoxy) phenyl sulfone (BAPPS), in sequenced and random approaches. Tough and transparent membranes of SPIs with ion exchange capacity of 1.5–2.9 mequiv./g were prepared. These membranes showed good solubility and high thermal stability

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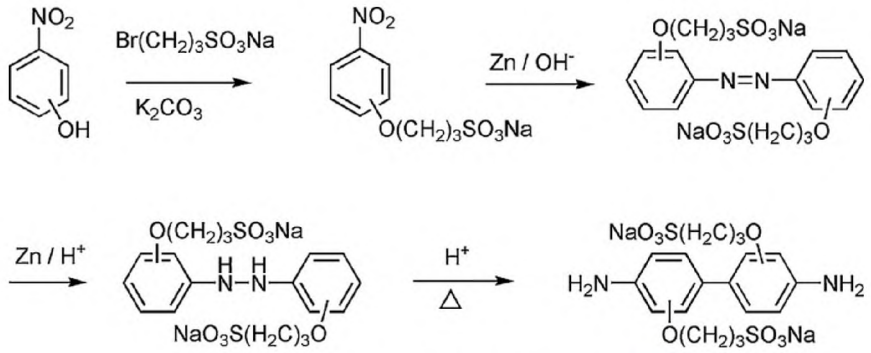
Scheme 34. Synthesis of sulfonated diamine monomer (DAPPS) [164].

up to 300 °C. The membranes showed isotropic swelling in water, unlike the main chain-type and sulfoalkoxy-based side-chain-type SPIs. At low relative RH, the novel SPI membranes showed much higher conductivity than membranes from sulfoalkoxy-based SPIs. The membrane of sequenced NTDA-DASDSPB/BAPPS (1/1) displayed reasonably high proton conductivities of 0.05 and 0.30 S cm^{-1} at 120 °C at an RH of 50 and 100%, respectively.



Scheme 35. Synthesis of diamine monomers with sulfonic acids at side chain [165].

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Scheme 36. Synthesis of sulfonated diamine isomers (BSPB) [166].

Sulfonated diamine isomeric monomers bearing sulfopropoxy groups (BSPB), as shown in Scheme 36, were also prepared by Okamoto's group [166]. The diamine was obtained by rearrangement reactions in hydrochloric acid. The sulfonated polyimides derived from NTDA and BSPB monomers show high proton conductivities and better stability than common sulfonated polyimides in which the sulfonic acid groups are directly bonded to the polymer backbone. The high proton conductivity and stability are likely due to the microphase-separated structure of the membrane, which can be observed by TEM, and the strong basicity of BSPB diamine moieties that result from the electron-donating effect of the propoxy groups.

2.1.4.6. Non-linear optical monomers. Waveguide materials based on polymers with nonlinear optical (NLO) properties have attracted extensive attention because of their potential applications in frequency doubling for data storage, electro-optic modulation for optical telecommunications and optical interconnects, and integrated optics. Inorganic crystals have been used as nonlinear optical materials for several decades. However, the crystals are difficult to grow, are expensive, and are difficult to incorporate into electronic devices. A number of organic chromophores exhibit extremely high and fast nonlinearities that often rival or surpass the performance of inorganic crystals [167]. Though some important issues, including the transparency to efficiency trade-off, centrosymmetric arrangement, and phase matching, continue to challenge material scientists and engineers, highly stable NLO polymers have been prepared by grafting NLO-active chromophores onto aromatic polyimide backbones [168–170].

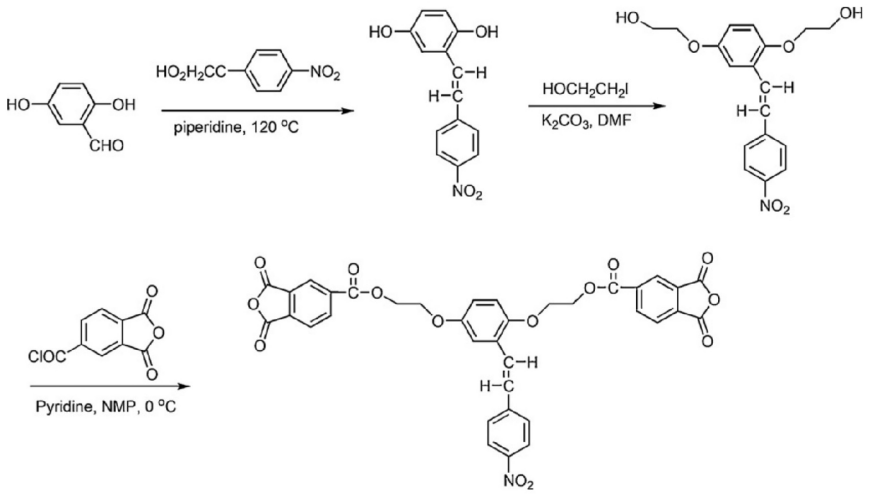
In the development of NLO polymers for electro-optic device applications, stabilization of the electrically induced dipole alignment is an important consideration. Two approaches to minimizing the randomization have been proposed. One is to introduce crosslinking, and the other is to utilize high glass-transition temperature (T_g) polymers. Wang et al. [171] synthesized a series of NLO polyimides by grafting zwitterionic chromophores. The poling and electro-optical (EO) studies revealed a strong dependence of the EO coefficient on the polymer chain mobility or the glass transition temperature. A thermally crosslinkable group was introduced into the NLO polymers to achieve a high thermal stability of the poled NLO polymers [170]. Lee et al. reported novel T-shaped (Scheme 37) [172], Y-shaped (Scheme 38) and Λ-shaped (Scheme 30) [135] chromophore-containing [173] NLO polyimides with high thermal stability that could be used for second harmonic generation. Finally, Shu et al. synthesized a novel main-chain-shaped NLO polyimide, as shown in Scheme 38 [173].

High-T_g aromatic polyimides with pendant dendronized NLO chromophores functionalized on a cardo bisphenol linkage backbone were synthesized and characterized by Jen et al. [170]. The polyimide with dendronized chromophores can achieve high poling efficiency to afford a very large electro-optical (E-O) coefficiency (71 pm/V at 1.3 μm). NLO polyimides containing side chain chromophores were synthesized from functional polyimides and were followed by a Mitsunobu reaction with diol chromophores [104,174–176] or by a post-azo-coupling reaction [177]. The syntheses of novel NLO diamines containing azo groups, shown in Scheme 39, and the NLO properties of polyimides derived from the diamines have been reported [105,178–180].

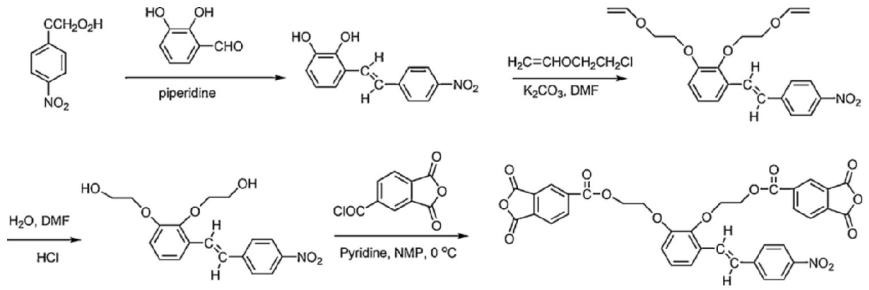
Compare to the NLO polyimides derived from functional polyimides following the Mitsunobu reaction with diol chromophores (Scheme 40(A)) [104,174–176], the two-step process has the following disadvantages: (1) the di(hydroxyalkyl) chromophore must be transformed into a dialkylamino chromophore under Mitsunobu conditions, the resulting reaction mixture is difficult to separate, and the pure materials are obtained in fairly low yields; (2) functionalization of precursor polyimides with a hydroxyalkyl chromophore results in random functionalization and cannot be completely functionalized; and (3) harsh conditions are required to prepare the chromophore monomer; which imposes some limitations on the chromophore structure. Therefore, Samyn et al. [181] have developed a one-step synthesis of NLO polyimides by reacting di(hydroxyalkyl) chromophores and diimides under Mitsunobu conditions (Scheme 40(B)).

2.1.4.7. Others (pendant polyimides using mellitic acid dianhydride). Illingsworth et al. have investigated the

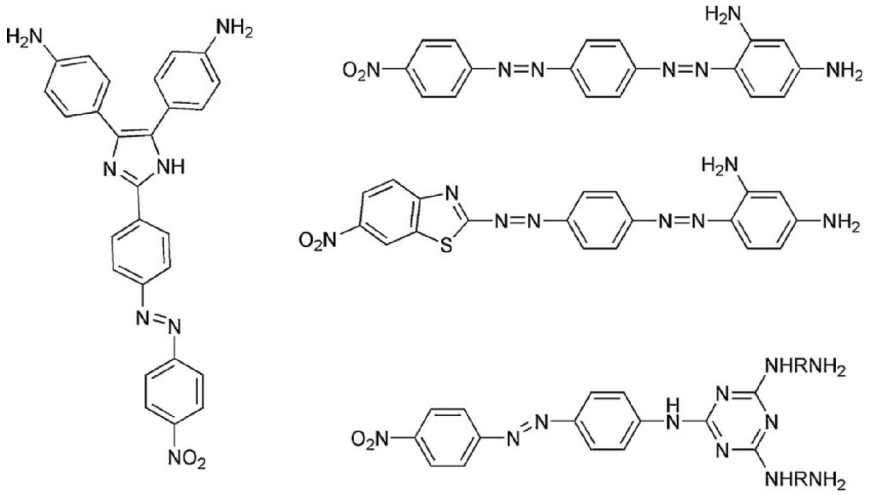
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Scheme 37. Synthesis of T-shaped NLO dianhydride [172].

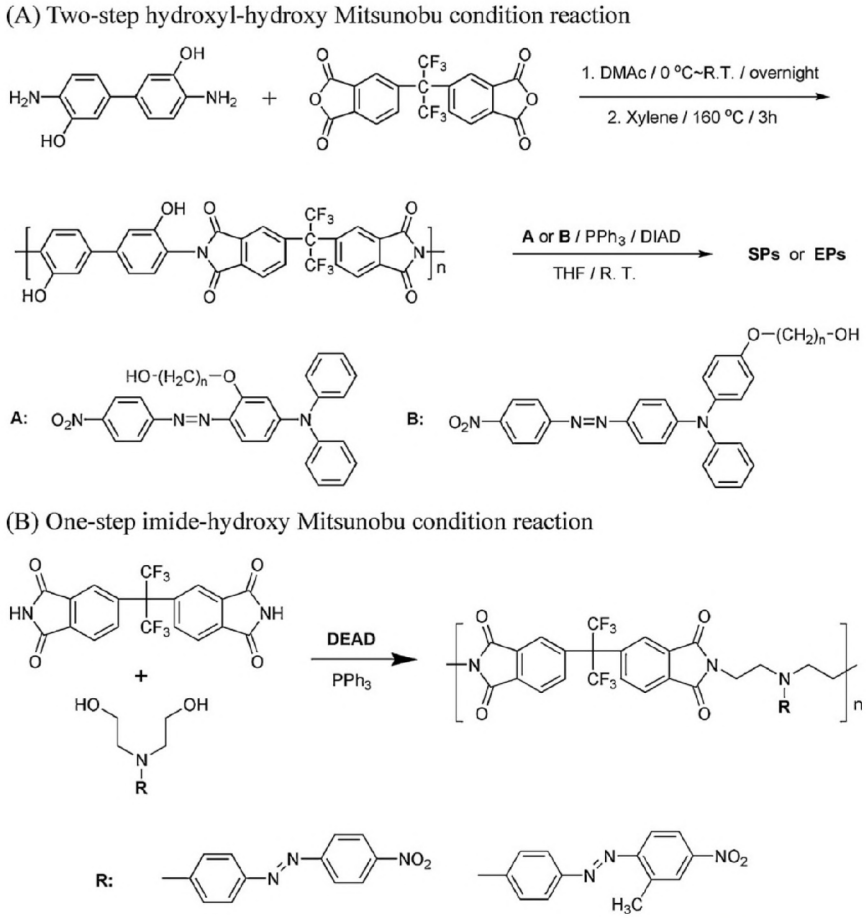


Scheme 38. Synthesis of Y-shaped NLO dianhydride [173].



Scheme 39. NLO diamines containing azo groups [105,178–180]. (A) Two-step hydroxyl-hydroxy Mitsunobu condition reaction and (B) one-step imide-hydroxy Mitsunobu condition reaction.

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Scheme 40. NLO polyimide via (A) two-step and (B) one-step Mitsunobu condition [181].

preparation of Zr-containing pendant copolyimides using mellitic acid dianhydride (co-PIs). Methods are being investigated to increase the Zr concentration and atomic oxygen resistance of these compounds while retaining other desirable film properties. The immediate objectives that must be met to achieve this goal are as follows: (1) addressing the increased tendency of copolyamic acids (co-PAAs) made from MADA diacids (Scheme 41) to undergo gelation during polymerization and upon addition of *N,N′*-dicyclohexylcarbodiimide (DCC) during the Zr-appending reaction; and (2) increasing the number of layers in multilayer films that can be applied prior to crack formation. The highest number of layers that have been incorporated is ten (Scheme 41) [182]. The excellent solvent resistance displayed by these pendant polymers also bodes well for engineered materials applications.

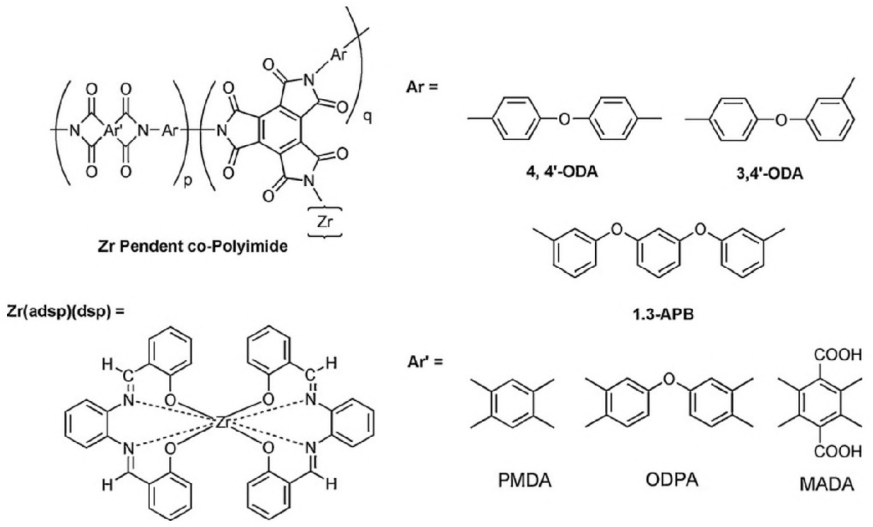
The Toray Company (Japan) [183] synthesized ester and amide groups containing dianhydride with bisphenol and diamine compounds, respectively, in the presence of trimellitic anhydride chloride (Scheme 42).

2.2. Polymerization

2.2.1. General polymerization

The literature on the formation reactions and properties of polyimides is vast. Imai has collected the methods for preparing polyimides in a book review in Japanese [184]. In general, polyimides are prepared from a dianhydride and a diamine. The most developed synthetic method for polyimides is a two-step method. The first step involves a very fast, exothermic, stepwise polymerization at a relatively low temperature to form a poly(amic acid) from a dianhydride and a diamine. Subsequently, the poly(amic acid) is converted into the corresponding polyimide through an intramolecular cyclization (imidization) that releases water condensate. Either chemical or thermal imidizations can be used to convert poly(amic acid)s to polyimides. The solubility of polyimides prepared by different imidization methods differs to some extent. In general, polyimides derived from chemical imidization are more soluble than those from thermal imidization. However, the

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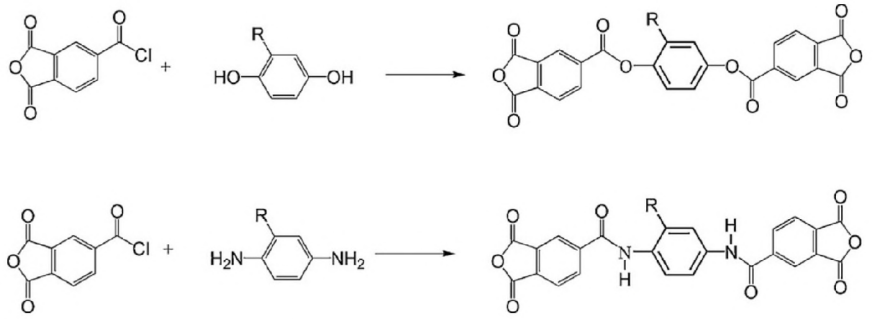
Scheme 41. Structures of dianhydrides, diamines, and pendent group, and structure of polyimide products.

thermal properties of polyimides from thermal imidization, including T_g and decomposition temperatures, are superior to those of polyimides from chemical cyclization. The difference can be ascribed to morphological changes in the polymers, such as increased ordering from molecular aggregation of the polymer chain segments that occurs during thermal imidization [185]. A series of pyridine-containing polyimides [37] has been prepared by the conventional two-step polymerization method from commercial dianhydrides and novel pyridine-containing diamines (described in Section 2.1.4.2) as shown in Scheme 43.

2.2.2. Other approaches to prepare polyimides

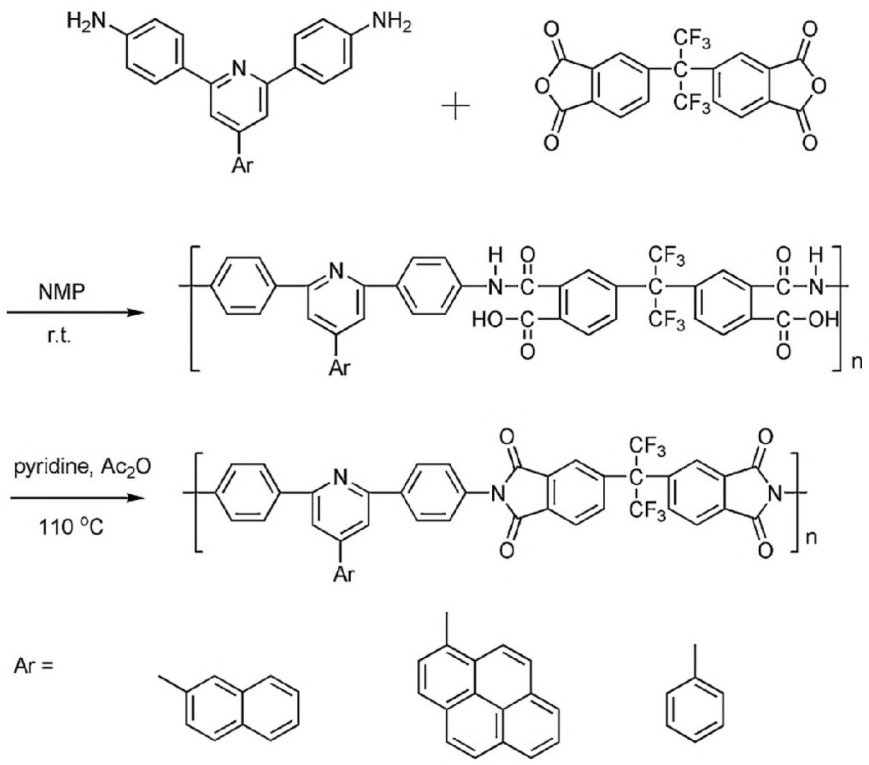
Polyimides can be prepared from diamines and dianhydrides, but they can also be synthesized from the following reactions: (1) diisocynates and dianhydrides [186–188]; (2) diamines and dithioanhydrides [185,189,190]; (3) diamines and bis(maleimide)s (Michael addition reaction) [191]; (4) bisdiene and bidienophiles (Diels–Alder reaction); (5) silylated diamines and dianhydrides; and (6) di(hydroxyalkyl) compounds and diimide compounds (Mitsunobu reaction).

2.2.2.1. From diisocyanates and dianhydrides (Scheme 44). The polymerization of polyimides can be accomplished using diisocyanates in the place of diamines. It has been reported that phthalic anhydride reacts with aromatic or aliphatic isocyanates to form *N*-aryl- or *N*-alkylphthalimides. Based on these reactions, homo- or co-polyimides have been successfully synthesized from diisocyanates and dianhydrides [3,186,192–194]. The polymerization involves hydrolysis of the diisocyanate to form a diamine and then a polyamic acid, which is converted subsequently to a polyimide by general imidization methods [187]. This route is advantageous because the reaction is less sensitive to moisture and diisocyanates are generally more soluble in organic solvents than are diamines. One disadvantage of this method is that there are few diisocyanates to choose from, compared to the numerous diamines available from synthetic or commercial sources. However, the fast reaction between diisocyanates and



Scheme 42. Dianhydrides containing ester or amide groups [183].

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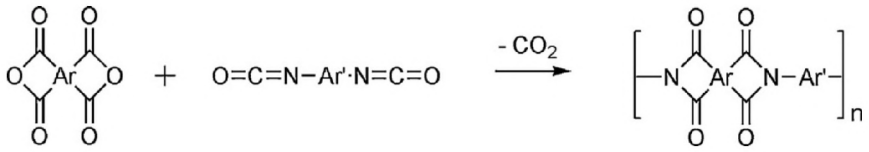


Scheme 43. Synthesized poly(pyridine-imide)s prepared by the conventional two-step polymerization method.

tetracarboxylic acids makes this a viable route for the preparation of polyimides [187]. Yeganeh et al. reported the application of microwave radiation in the direct synthesis of aromatic polyimides from the reaction of aromatic diisocyanates and dianhydrides [188]. The experimental results showed that the polyimides obtained via this method had superior inherent viscosities and higher yields when compared to polyimides obtained via the conventional solution method.

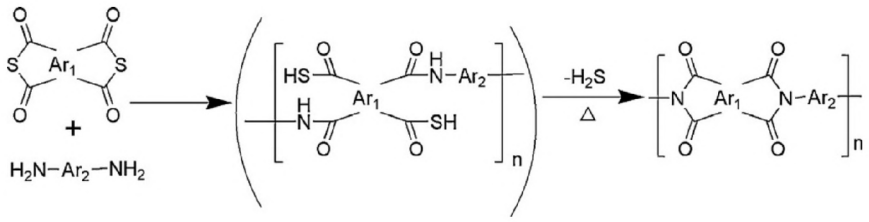
2.2.2.2. From diamines and dithioanhydrides (Scheme 45). In addition to dianhydrides, dithioanhydrides can be used to prepare polyimides. Dithioanhydrides can be prepared by reacting the corresponding aromatic tetracarboxylic acids with sodium sulfide. Imai et al. used dithioanhydrides with diamines to prepare the precursor poly(amide thiocarboxylic acid)s. Polyimides were then obtained after removing the hydrogen sulfide by heating, as shown in Scheme 45 [189]. The poly(amic thiocarboxylic acid) cannot be removed during the reaction due to its high reactivity [190]. Liou et al. compared the preparation of polyimides generated from the one-step diamine and dithioanhydride reaction to those prepared by the traditional two-step method [185]. The inherent viscosities of polyimides derived from dithioanhydrides were comparable to those prepared by the traditional two-step method.

2.2.2.3. From diamines and bis(maleimides) (Michael addition reaction) (Scheme 30). The Michael addition of diamines to bis(maleimides) is another method of preparing polyimides. In contrast to the above methods, the imide ring of polyimides is not formed during the polymerization but arises from the maleimide structure. Bella et al. reported a polyimide synthesis *via* the Michael addition reaction as shown in Scheme 46 [191]. This approach is a general strategy for achieving thin films from insoluble or reactive functional polyimides.



Scheme 44. Synthesis of polyimides from diisocynates and dianhydrides.

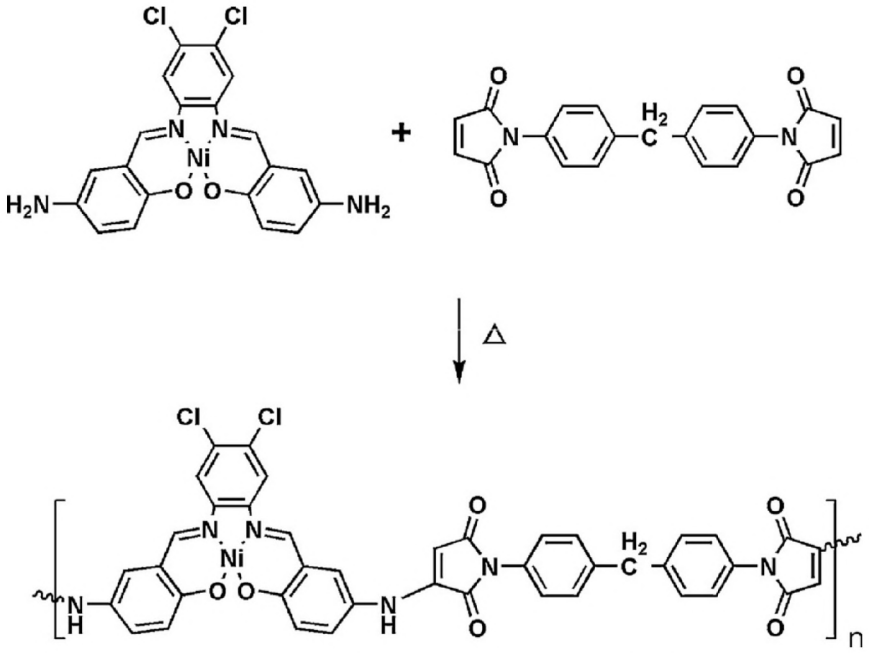
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Scheme 45. Synthesis of polyimides from diamine and dithioanhydride.

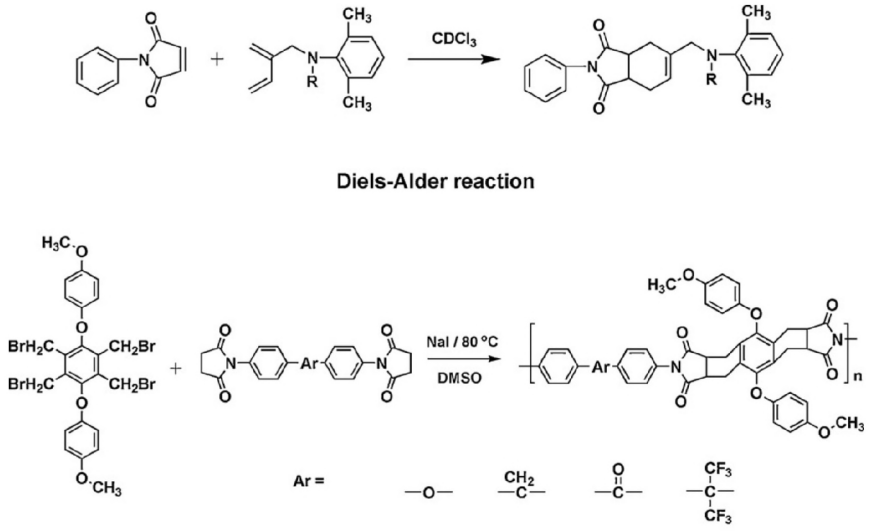
2.2.2.4. From bisdiene and bidienophiles (Diels–Alder reaction) (Scheme 47). The Diels–Alder reaction is a thermally driven [4+2] cycloaddition reaction between a dienophile and a conjugated 1,3-diene. The Diels–Alder reaction provides a simple, efficient, and clean procedure to generate new bonds by inter- or intramolecular coupling, and it represents one of the most useful synthetic methods in organic chemistry. In this reaction, a dienophile is added to a conjugated diene to give a cyclic product called an adduct. The furan ring is one of the most important heterocyclic dienes used in Diels–Alder reactions [195]. Chi et al. [196] prepared polyimides at 80 °C in the presence of NaI in DMSO by the *in situ* Diels–Alder polymerization of 1,4-bis[4-(methyloxy)phenyloxy]-2,3,6,7-tetrakis-(bromomethyl)benzene (MPBB) with four arylenebismaleimides (AMIs), as shown in Scheme 47. DSC and wide-angle X-ray diffractometry studies indicated that all APIs appeared completely amorphous, and UV–vis spectroscopy confirmed that DPAI and APIs were transparent at wavelengths longer than 375 nm.

2.2.2.5. From silylated diamines and dianhydrides (Scheme 48). The first synthesis of aromatic polyimides using silylated diamines was disclosed by Boldebuck and Klebe [197] in the patent literature in 1967. The use of silylated amines has several disadvantages, such as the need to synthesize and purify activated monomers, which are difficult to isolate because of their sensitivity to moisture. Silylated amines are also more expensive than diamines. Kaneda et al. [198] circumvented these problems by using *in situ* silylated diamines that were generated by adding chloro(trimethyl)silane (CTMS) or other silylating agents to the diamine solutions. *In situ* silylation of aromatic diamines with CTMS in the presence of a base, such as pyridine, has proved to be a facile and convenient method to obtain high molecular weight polyimides [199]. When sterically hindered amines or amines with strong electron-withdrawing groups are used, silylation can improve the low reactivity of the diamines [199].



Scheme 46. Synthesis of polyimides from diamine and bis(maleimide).

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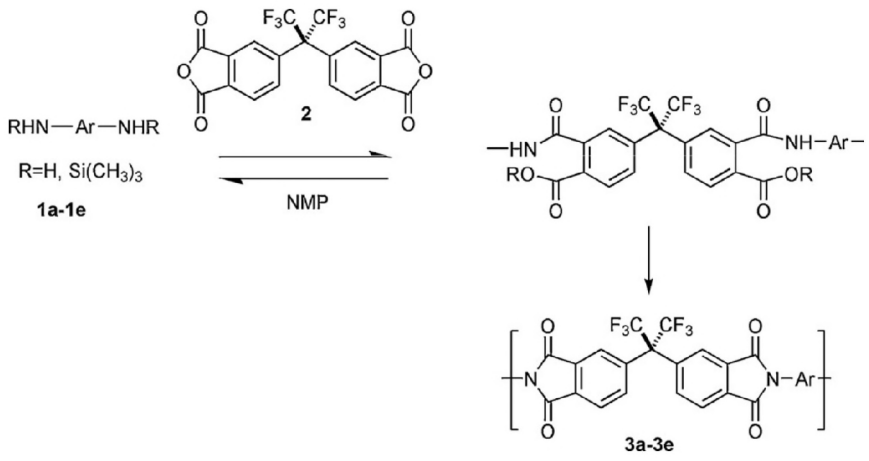


Scheme 47. Synthesis polyimide by Diels–Alder reaction.

2.2.2.6. Di(hydroxyalkyl) compounds and diimide compounds (Mitsunobu reaction). The reaction of di(hydroxyalkyl) compounds and diimides under Mitsunobu conditions gives rise to the direct formation of polyimides in a single step. These reaction conditions offer an alternative and convenient method for the design of NLO-functionalized polyimides [181,200,201] (Scheme 40(B)).

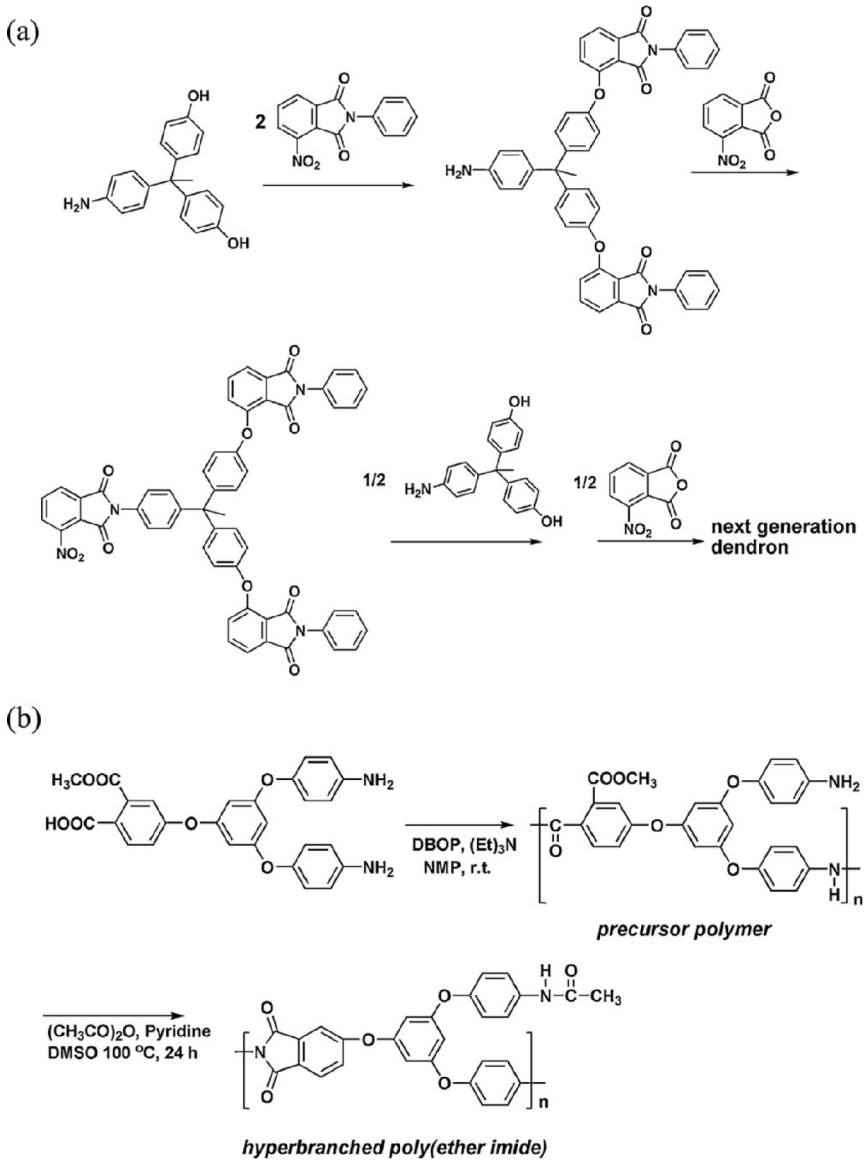
2.2.3. Dendritic and hyperbranched polyimides

Dendritic and hyperbranched polyimides are a new type of polymer that has unique properties, such as the presence of multi-functional end groups and good solubility. Jikei et al. [202] reviewed dendritic aromatic polyimides, including dendrimers and hyperbranched polyimides. In addition to conventional stepwise reactions for dendrimer synthesis, an orthogonal/double-stage convergent approach and dendrimer syntheses with unprotected building blocks are described as new synthetic strategies for dendritic polyamides. Besides the self-polycondensation of AB_2-type monomers, hyperbranched polyimides have been formed in new polymerization systems with AB_4, AB_8, A_2+B_3, and $A+BB'_2$ monomers. As examples, the general procedures of dendritic polyimides including dendrimers and hyperbranched polyimides are shown in Scheme 49.



Scheme 48. Synthesis of polyimides from silylated diamines and dianhydrides.

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Scheme 49. (A) Preparation of dendritic poly(ether imide)s by stepwise reaction and (B) preparation of hyperbranched polyimides via poly(amic acid) precursors.

3. Physical properties

Because polyimides possess many desirable properties, this class of materials has found applications in many technologies, ranging from microelectronics to high temperature adhesives to high-performance membranes. For quite some time, there have been active R&D programs focused on synthesizing new polyimides and/or modifying existing materials. There are many reports that address the aspects and new developments in polyimides. Many factors affect the properties of polyimides. Generally speaking, amorphous polyimides show better solubility but have lower mechanical and thermal properties than polymers that exhibit crystalline morphology. Herein, the reported physical properties of polyimides are summarized based on their chemical structures.

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3.1. Solubility

The solubility of polyimides depends strongly on the chemical structure of the polymer. The two key factors in designing soluble and processable polyimides are (1) reducing the rigidity or regularity of the backbone, and (2) minimizing the density of imide rings along the backbone. Progress has been made in addressing these issues by using fluorine-containing dianhydrides, such as 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), or by incorporating "hinges", such as oxygen atoms, into the diamine (*e.g.*, oxydianiline). In addition, aliphatic side chains have been incorporated into diamines to reduce the interaction between polyimide chains and increase the solubility [203]. A large number of structural modifications have been attempted in previous decades, including incorporating thermally stable, flexible, or nonsymmetrical linkages in the backbone and introducing bulky substituents [8,9]. Polyimides containing bulky, propeller-shaped triphenylamine units along the polymer backbone are amorphous and exhibit good solubility in many aprotic solvents, excellent film-forming capabilities, and high thermal stabilities [132]. The incorporation of pendant cardo groups, such as cyclododecylidene, adamantane, tricyclo[5.2.1.0] decane and triphenylamine, into the backbone of polyimides improves their solubility, processability and thermal stability. Furthermore, the *tert*-butylcyclohexylidene group, which can be considered an alicyclic cardo group, has been incorporated into polymer backbones to improve the polymer's processability [64].

Most of the polyimides derived from rigid dianhydrides, such as PMDA, BPDA and BTDA, show less solubility in organic solvents. Polyimides derived from diamines containing flexible ether, isopropylidene, bulky pendant, and noncoplanar bisphenylene groups exhibit excellent solubility in organic solvents, including *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethyl acetamide (DMAc), pyridine, cyclohexanone and tetrahydrofuran (THF). In particular, the presence of noncoplanar, unsymmetrical, kink, spiro and cardo structures in the diamine or dianhydride moiety improves the solubility of the polymer without sacrificing its thermal or mechanical properties. The noncoplanar monomers cause twists in the polymer backbones and hinder chain packing; these modifications reduce crystallinity and intermolecular interactions and enhance solubility.

Polyimides prepared via thermal imidization have lower solubility than those prepared via chemical imidization. The lower solubility might be a result of a tight packing or partial intermolecular crosslinks that form during the thermal imidization procedure [117]. Nevertheless, these polyimides often have excellent thermal and mechanical properties.

The polyimide synthesized from pyromellitic dianhydride and 4,4′-oxydianiline is not soluble in organic solvents (Scheme 50(A)). However, the polyimide can soluble in organic solvents only if the dianhydride was changed to be 4,4′-biphthalic anhydride (Scheme 50(B)) [204].

3.2. Thermal properties

Thermogravimetric (TG) analysis reveals good thermal stability for aromatic polyimides. In general, polyimides are stable up to a temperature of 440 °C in a nitrogen atmosphere. Polyimides containing heteroaromatic units, noncoplanar or rigid aromatic units show high heat resistances and high glass transition temperatures. However, polyimides that contain flexible linkages, such as ether units, show lower glass transition temperatures because of their relatively flexible polymer backbones. Pyridine rings increase the symmetry and aromaticity of the polymer and increase the thermal and chemical stability. In addition, pyridine rings help the polymer retain its mechanical properties at elevated temperatures [37,112–117].

3.3. Mechanical properties

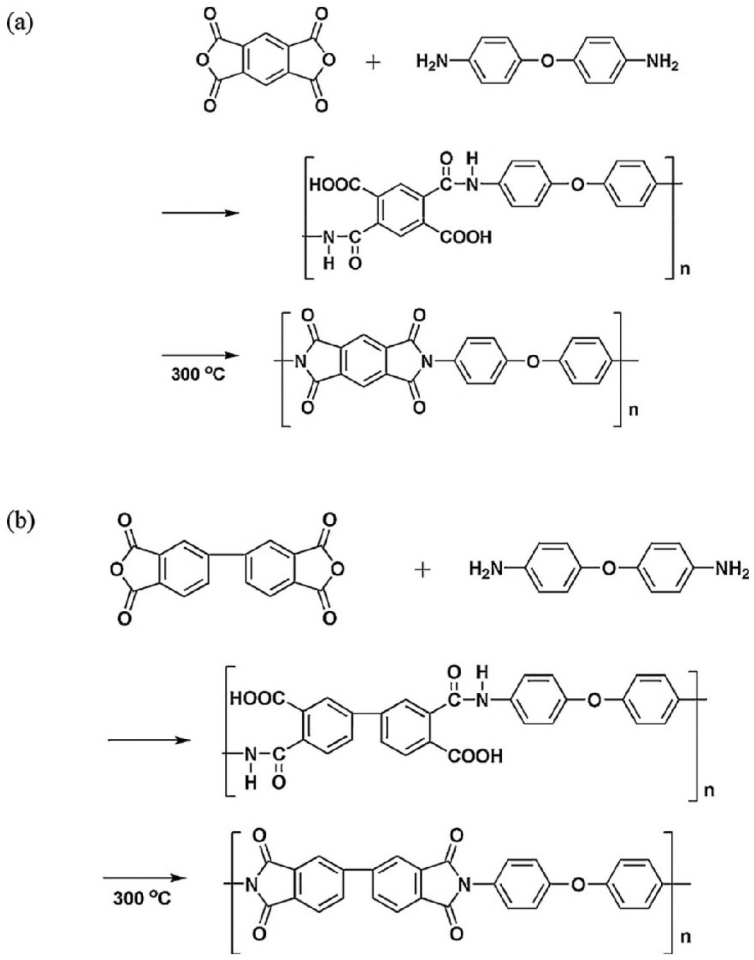
The mechanical properties of polyimides are influenced by many factors, such as the chemical structure, viscosity, molecular weight, preparation procedure, heating history, sample preparation and the method of property determination. Therefore, there is no clear rule can be discerned for the mechanical properties of the polyimides. Thus it is likely that differences in mechanical properties are concealed by large experimental uncertainties. In general, polyimides exhibit modulus values of 1.5–3.0 GPa and tensile strengths of 70–100 MPa. However, the elongation at breakage ranges from 2 to 15%, depending on the chemical structure. Polyimides containing flexible linkage units, such as ether linkages and isopropylidene [4], in the main chain exhibit more elongation. In addition, noncoplanar, asymmetrical and amorphous polyimides also usually show higher elongation. It is a general rule but not absolute: the polymers with high mechanical modulus show lower elongation.

Yokota and coworkers reported the dynamic tensile properties of asymmetric polyimides derived from an asymmetric dianhydride [205–207] or diamine [208] using dynamic mechanical analysis. Yokota group discussed dynamic tensile properties of two Kapton-type polyimides [208]. A symmetrical (PI(PMDA/ODA)) and an asymmetrical polyimides (PI(PMDA/*p*-ODA)) derived from symmetrical 4,4′-diaminidiphenyl ether (ODA) and asymmetrical 2-phenyl-4,4′-diaminidiphenyl ether (*p*-ODA) diamines, respectively, with pyromellitic dianhydrides (PMDA). The symmetrical polyimide and the asymmetrical polyimide films showed very tough but different dynamic mechanical properties above T_g. The symmetrical polyimides showed higher glass transition temperatures and without obvious drop in the E', however, the asymmetrical polyimide showed a significant drop in the E' from 10^9 to 10^7 Pa above the T_g, which results from the rotational inflexibility of the ether linkage of *p*-ODA and restricted the conformational change of the PI(PMDA/*p*-ODA) backbone structure.

3.4. Optical and electrical properties

Polyimides generally exhibit brown coloration due to charge transfer (CT) between the diamine donor

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Scheme 50. (A) Synthesis of insoluble polyimide derived from 4,4′-oxydianiline and (B) synthesis of soluble polyimide derived from 4,4′-biphthalic anhydride.

moieties and dianhydride acceptor moieties. The color of the polyimide can be changed by incorporating strong electron-withdrawing CF_3 groups in the dianhydride moiety or by using aliphatic diamines and/or dianhydrides. These modifications reduce CT interactions. Less colored or colorless polyimides can be obtained by using dianhydrides with lower electron-acceptor capabilities and diamines with lower electron-donating capabilities. When these monomers are used, the intra- and intermolecular CT interactions are weakened. Soluble and colorless polyimides can be obtained by using alicyclic dianhydrides or diamine monomers. However, the polymers are less stable at high temperature because they have less-stable aliphatic segments [209]. Polyimides that contain adamantane (tricycle[3.3.3.1.1] decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations, produce light-colored films with high transmittance in the visible region and good thermal stability [68,69]. The incorporation of bulky CF_3 groups into polyimides is another approach to obtain light-color polyimide films. Polyimide backbones containing CF_3 units have increased solubility and optical transparency, in addition to lower dielectric constants. These polymer characteristics have been attributed to the low polarizability of the C–F bond and increases in the free volume of polymer.

The optical and electrical properties of polyimides can be tailored by incorporating chromophores such as triphenylamine, carbazole, perylene groups, etc. Carbazole is a conjugated unit that has desirable photoconductivity and photorefractivity properties. In the field of electroluminescence, carbazole derivatives are often used as materials for hole-transport and in light-emitting layers because of their high charge mobility and thermal stability. Carbazole-containing polymers exhibit blue electroluminescence. Because the nitrogen atom improves the planarity of the biphenyl unit, the carbazole unit has a large band gap, and this leads to the observed electroluminescence [132].

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Polyimides that contain electron-donor and electron-acceptor units enhance the CT interactions in the polymer, and these polymers exhibit interesting memory switching behavior [210,211]. The application on memory materials based on polyimides will be described in Section 4.9.

4. Applications

Aromatic polyimides have excellent thermal stabilities and good mechanical properties, and they have been widely used in photoresists, liquid crystal alignments, gas separation membranes, composites, LB films, blending applications, vapor phase depositions, electroluminescent devices, polyelectrolytes, fuel cells, electrochromic materials, nanomaterials and polymer memory materials. The applications of polyimides are discussed in detail in the following section.

4.1. Photoresists

Photosensitive polyimides (PSPIs) are widely used in interconnects, multichip modules, protection layers, optical interconnects and resists because of their excellent thermal and chemical stabilities, low dissipation factors, and reasonably low dielectric constants. Because polyimides are insoluble in most common solvents, they are usually processed in the form of their precursor poly(amic acid)s and are then thermally converted to their corresponding imide structures. Kerwin and Goldrick first reported on the use of polyimides as photoresists, which include poly(amic acid). Sodium dichromate is used as a photoreactive additive [212]. The application of these materials in electronic devices has been difficult because of the instability of the polymer solution and the persistent contamination of residual chromic ions. The first report of a material applicable to microelectronics devices was made by Rubner et al. [213,214]. They described negative-type photosensitive polyimide precursors in which the poly(amic acid) side chain carboxyl groups were esterified with photoreactive methacryloyl groups. In the application of polyimides to electronic devices, the formation of holes and/or bonding pads is usually accomplished by an etching process in which a photoresist is used as an etch mask. When a photosensitive polyimide is utilized, the patterning process is simplified, and the pattern can be formed directly without the use of photoresists [215]. Recently, researchers have reported that polyimides can be functionalized by incorporating new functional monomers in the polymer reaction [60,216,217] or by chemical modification of functional polyimides [218]. These new-generation photosensitive polyimides have improved resolution, solubility, stability and mechanical properties.

Yamashita et al. have developed a convenient fabrication method that utilizes a PSPI resin to produce a core–cladding structure for a self-written waveguide [219]. The PSPI resin shows a photo-bleaching effect in which the refractive index of the exposed portion becomes large compared to that of the unexposed portion [220]. By using the PSPI resin, an all-solid core–cladding structure was realized through exposure and thermosetting processes. This all-solid self-written waveguide has some additional features that make it practical in the low-cost fabrication of optical devices. The resin acts as a glue for the optical components and can be used as plastic packaging for the optical modules.

Photosensitive polyimide insulation layers have been introduced for fabricating superconducting integrated circuits. PI Research & Development Company and the National Institute of Advanced Industrial Science and Technology (AIST) have proposed a new fine-resolution photosensitive polyimide, synthesized using aliphatic materials, as a KrF photoresist [221]. This photosensitive polyimide is synthesized via a single-step polycondensation reaction, and the polyimide has the attractive feature of not requiring thermal curing; these properties might allow for a low-temperature process to produce the polymer. Because the photosensitive polyimide is used as the insulation layer instead of a conventional inorganic insulation film, there is no need for an etching process, which simplifies the fabrication process.

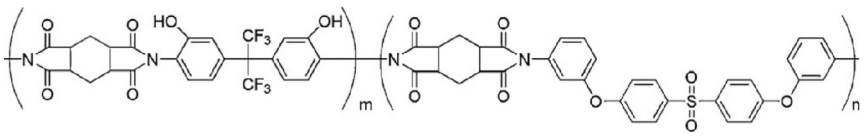
In the microelectronics industry, polyimides are used as passivation or insulation materials. Photosensitive polyimides (PSPIs) have significantly enhanced the development of microelectronic devices because they eliminate the need for a photoresist. Negi et al. have reviewed the synthesis, characterization and applications of photosensitive polyimides [8]; some recent PSPI will be discussed here. Two common photoresists exist: positive acting resists [222–230] and negative acting resists [231–235]. Positive acting resists exhibit enhanced solubility after exposure to radiation, whereas resists that become insoluble after exposure to radiation are termed negative resists. In general, positive type PSPIs are a combination of hydroxyl-containing polyimides and a photosensitive compound that contains diazonaphthoquinone (DNQ) groups. However, it is important that the PSPIs are colorless and transparent. Therefore, diamines and/or dianhydrides containing hexafluoropropane groups are used to prepare PSPIs.

Ishii et al. [222–224] reported two positive type polyimides based on soluble block copolyimides (Bco-PI)s that have excellent transparency characteristics. These polyimides have hydroxyl groups and utilize diazonaphthoquinone as a photoreactive compound. The structures of the (Bco-PI)s are shown in Scheme 51. The hydroxyl groups in the polyimide backbone allow Bco-PIs to be alkaline. The ester of 2,3,4-trihydroxybenzophenone with 1,2-naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC5) or 1,2-naphthoquinonediazide-5-sulfonic acid (NT200) as the photoreactive compound were added to the Bco-PI. The polyimide films have low dielectric constants because of the aliphatic cyclic dianhydrides and/or fluoro-containing diamines. The structures and reactions of PC5 and NT200 under exposing and developing conditions are shown in Scheme 52.

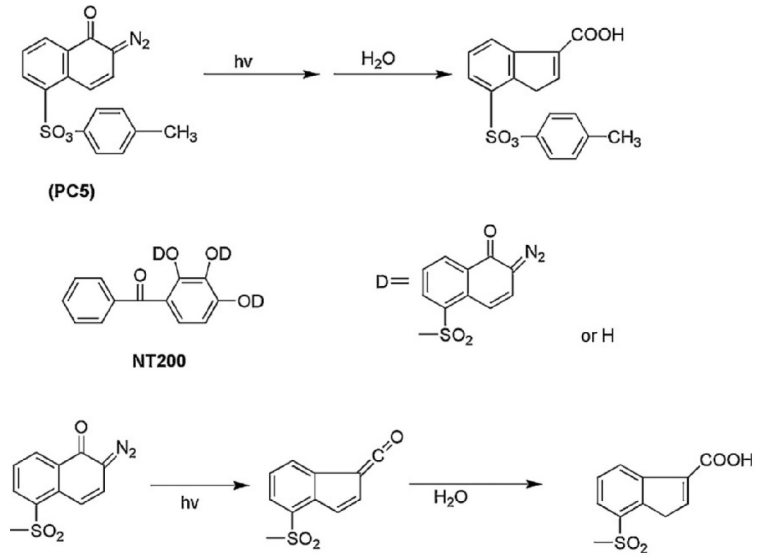
Hsu et al. [225,229] and Ueda et al. [226,230] also reported novel positive working and photosensitive polyimides that can be developed in aqueous base. These polymers included 20–25 wt% of DNQ or DNQ derivatives as photosensitive compounds.

Polyimides that contain an *o*-nitrobenzyl carboxylate or phenoxide groups have been shown to undergo a photorearrangement reaction upon UV

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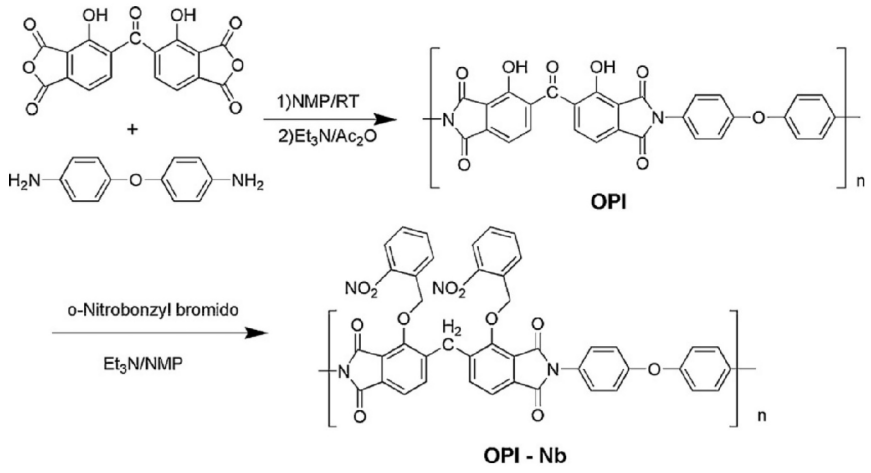


Scheme 51. Structure of Bco-PI.



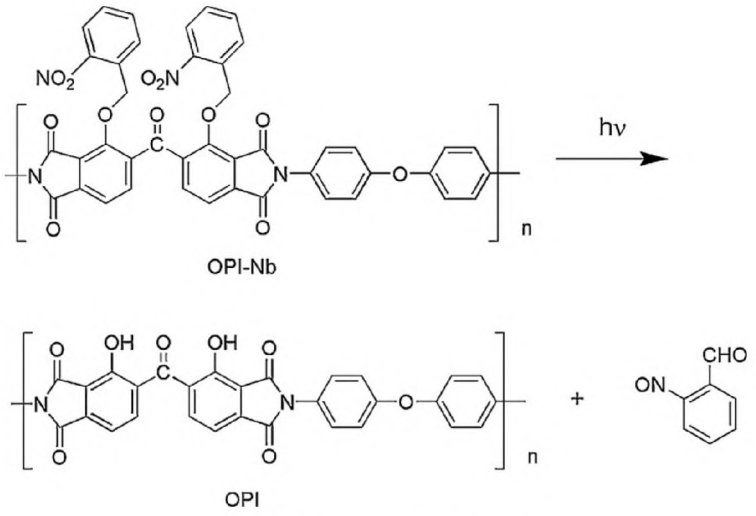
Scheme 52. Structures and reactions of photoreactive compounds under exposing and developing.

irradiation. These photochemical reactions generate an *o*-nitrosobenzaldehyde and a carboxylic acid group [236] or a phenol group [237]. This transformation makes the polyimides soluble in an aqueous base. Shin et al. synthesized a novel positive-working photosensitive polyimide [237], poly[1,4-phenyleneoxy-1,4-phenylene-2,2′-di(2-nitrobenzyloxy)-benzophenone-3,3′,4,4′-tetracarboxdiimide] (OPI-Nb), that can be developed with an aqueous base. The polymer was synthesized using *o*-nitrobenzylation of a



Scheme 53. Synthetic route to photosensitive OPI-Nb.

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Scheme 54. Photochemical reaction of OPI-Nb.

polyimide, poly(1,4-phenyleneoxy-1,4-phenylene-2,2′-dihydroxybenzophenone-3,3′,4,4′-tetracarboxdiimide) (OPI), as shown in Scheme 53. The aromatic OPI was completely soluble in dilute aqueous NaOH and tetramethylammonium hydroxide (TMAH), whereas OPI-Nb did not swell in these solutions. In the micropatterning process, OPI-Nb showed a line-width resolution of 0.4-lm and a sensitivity of 5.4 J/cm^2 when the thin film was irradiated with 365-nm light and developed with a 2.38% aqueous TMAH solution at room temperature for 90 s. The photosensitivity of OPI-Nb is poor in comparison to that of other commercial systems. The low sensitivity might arise from absorption of UV light by the aromatic backbone in the 240–270 nm range and absorption in the 350–370 nm range by the intramolecular charge transfer transition of OPI-Nb (Scheme 54). This phenomenon is referred to as a "matrix effect" and has been observed in many PSPIs.

Negative type PSPIs usually contain side-chain methacryloyl or acryloyl crosslinking groups and also have a photosensitizer. Yin et al. reported [231] a negative photoinitiator-free PSPI that incorporated the photosensitive 4,4-bis[(4-amino)thiophenyl] benzophenone (BATPB) into its backbone and methacryloyl or acryloyl groups into its side chains. Upon UV irradiation, the BAPTB structure in the polyimide chain undergoes photolysis to produce several types of radicals that can initiate polymerization of the methacryloyl or acryloyl groups to form the crosslinked system shown in Scheme 55.

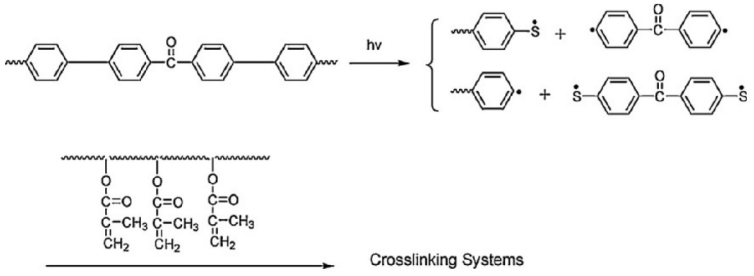
As shown in Scheme 56, Tomoi et al. [233] prepared polyimides with pendant carboxyl groups, which were blocked with photopolymerizable acrylamides or acrylates through ionic bonding. The ionic-bonded photosensitive polyimide films contain Michler's ketone (MK) as a photosensitizer and ethylene glycol dimethacrylate (EGDMA) as an external multifunctional crosslinker. These films exhibit negative-tone behavior upon near-UV irradiation after they have been developed with a 10% aqueous NaOH solution at 25 °C. The length of alkylene groups attached to the nitrogen in aminoalkyl acrylates might affect the sensitivity of ionic bonded negative PSPIs. The more hydrophobic the substituents, the more sensitive the PSPI is. When acrylamides are employed as pendant photopolymerizable groups in PSPIs, the resulting patterns are better than from PSPIs that employ acrylates (Scheme 56).

A negative hyperbranched PSPI was prepared by Yin et al. [234]. This polymer was based on a novel triamine (TAPOB) and 6FDA. The photosensitive cinnamate groups were incorporated at the periphery of the polymer by derivatizing the terminal phenol groups with cinnamoyl chloride. The fully imidized hyperbranched polyimide was obtained via end group modification of an anhydride-terminated hyperbranched poly(amic acid) precursor. In the photolithography process, 5 wt% of Michler's ketone relative to the hyperbranched PSPI was used as the photosensitizer.

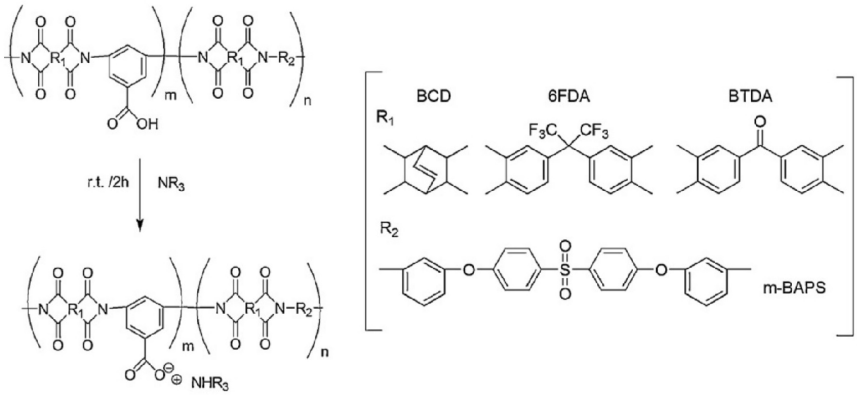
A group of fully imidized, soluble polyimides based on 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and ortho-alkylsubstituted diamines has been shown to be highly sensitive negative-resist materials. Such polyimides are sensitive to 365 nm (i-line) radiation without added sensitizers, and the obtained images do not suffer from thickness loss at high temperatures [235]. The photo-crosslinking of polyimides containing benzophenone units and alkyl moieties, such as the polyimide synthesized from DAI and BTDA, is caused by a recombination of radicals. These radicals are generated when the excited triplet state of benzophenone abstracts a hydrogen from the alkyl moiety as shown in Scheme 57.

Two types of PSPIs have been developing. In general, positive type PSPIs are a combination of hydroxyl-containing polyimides and a photosensitive compound; negative type of PSPIs should contain photosensitizers and crosslinkers. Novel photosensitive groups and compounds with high sensitivity undergo a chemical reaction upon UV irradiation are important for development of positive type PSPIs. Novel crosslinkers and crosslinking approaches are

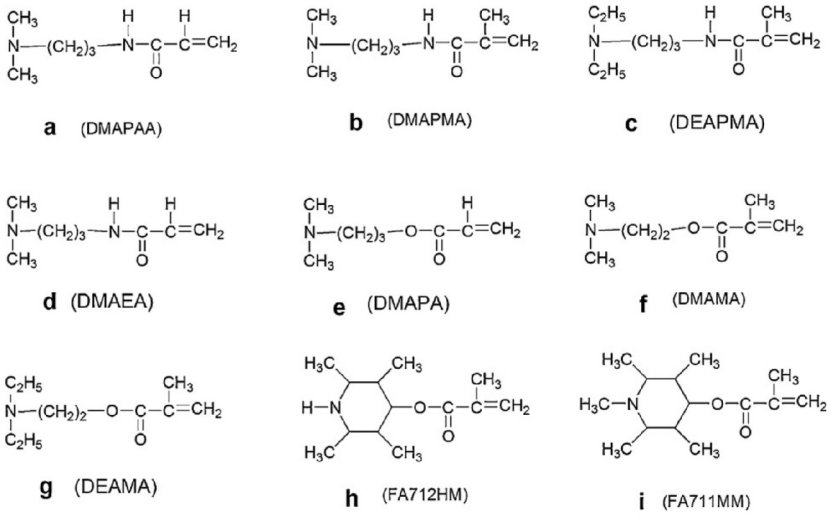
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Scheme 55. The crosslinking reactions in negative photoresist [231].

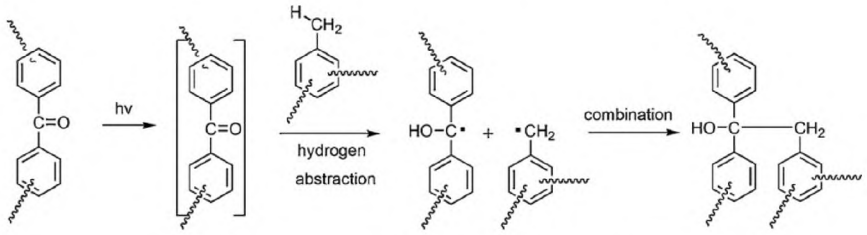


NR_3 (functional amine):



Scheme 56. Ionic bonded negative PSPI.

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Scheme 57. Photocrosslinking of a benzophenone unit and alkyl moiety.

necessary for negative type PSPIs. Different polyimide or copolyimide structures carrying out novel chemical reactions for positive or negative under photo-radiation are candidates for application in PSPIs. It is also important to consider colorless and transparent of the PSPIs.

4.2. Liquid crystal alignment

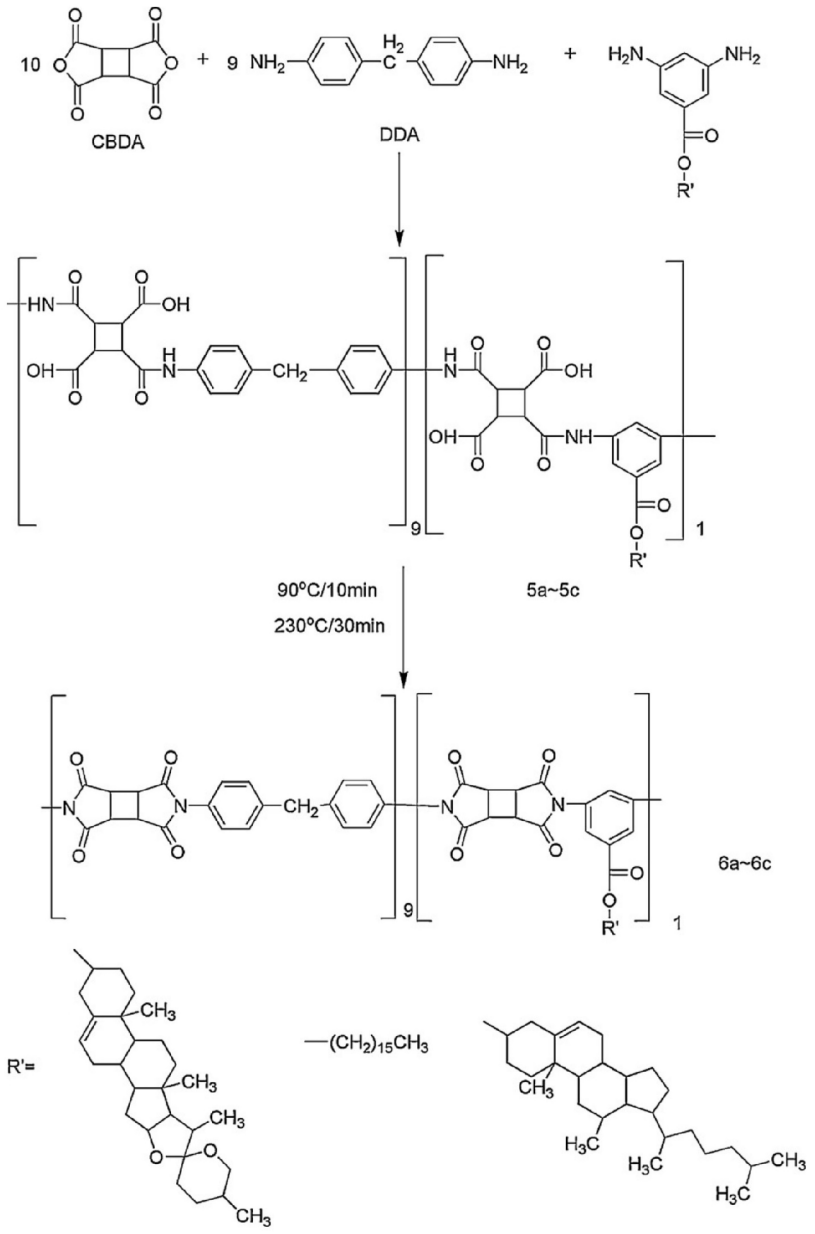
Liquid crystal display devices are composed of a liquid crystal, a color filter and a liquid crystal alignment layer. The liquid crystal alignment layer must uniformly align the liquid crystal molecules. The rubbing processes rub an organic-polymer-coated substrate with a rotating drum that is covered with a rayon velvet fabric cloth. Different mechanisms have been proposed for the alignment of liquid crystals on rubbed polymer surfaces. One theory suggests that the mechanical rubbing creates microgrooves or scratches on the polymer surfaces. The LC aligns along the grooves to minimize the energy of elastic distortion [238]. Alternatively, the rubbing process aligns surface polymer chains, which in turn, align the liquid crystals through intermolecular interaction [239]. The rubbing method is simple, convenient and inexpensive. However, the process generates dust, has electrostatic problems, and it is difficult to control the rubbing strength and uniformity after the production of TFT-LCDs has begun [240]. The rubbing process mechanism has been studied and some alternative methods have been proposed, including photoalignment [241–245] and the use of microgrooved surfaces and Langmuir–Blodgett membranes [246,247]. Several processes to produce microgrooved structures have been proposed, including reactive ion-etching on glass surfaces with chromium masks [248,249], pattern formation by laser-induced periodic structures on a polymer surface (LIPSS) [250], holographic light exposure or exposure of photocurable polymer films to UV through masks with a grating pattern [251]. The photoalignment technique involves the generation of an anisotropic distribution of alignment material molecules by using the molecules' dependence on the polarization direction of absorbed light [241–245,252]. There are three main types of materials that are used as photoalignment layers. They can be categorized according to the photochemical reaction responsible for the photoalignment: (i) azo-containing polymers (photoalignment by reversible *cis–trans* isomerization), (ii) crosslinkable materials (photoalignment by photo-dimerization), and (iii) polyimides (photoalignment by photodegradation) [253,254].

A vertical alignment method has been used to improve the alignment of liquid crystals (LCs) with negative dielectric anisotropies. These LCs achieve faster response times and have higher contrast ratios than do twisted nematic liquid crystal displays [255]. In the negative dielectric anisotropy LC display, a polyimide layer was used as the liquid crystal alignment layer, and after a rubbing process, the liquid crystals were vertically aligned in the field-off state at a pretilt angle above 89°. Yi et al. synthesized a series of poly(amic acid)s from CBDA, DDA and functional diamines, which have side chain groups of different flexibility (Scheme 58). The authors researched the effects that the polyimide side chain structure has on the pretilt angle of liquid crystal cells [56]. For the full-color, TFT-LCD organo-soluble polyimide alignment, unsymmetrical bulky structures and high voltage-resistances are required. In addition, non-polar and non-conjugated polyimides are also necessary (Scheme 58) [256].

Ueda et al. [257] reported novel siloxane-containing liquid crystalline (LC) polyimides with methyl, chloro, and fluoro substituents on mesogenic units (Scheme 59). These polyimides were developed from siloxane-containing diamines with pyromellitic dianhydride (PMDA) or 3,3′,4,4′-tetracarboxybiphenyl dianhydride (BPDA), and their thermotropic LC behavior was examined. Among these polyimides, the chloro and fluoro substituents effectively form LC phases, particularly when the substituents are substituted away from the center of the mesogenic unit. The isotropization temperature is significantly affected, but the crystal–LC transition temperatures are significantly decreased. The methyl substituent, however, tends to interrupt liquid crystallization. Thus, the fluoro-substituted polyimide derived from BPDA exhibits the lowest crystalline–LC transition temperature (T_{cr-lc} = 134 °C) among all polyimides and maintains its liquid crystal form up to 238 °C. X-ray diffraction measurements of the mesogenic phases of fibrous polyimides were found to form SmA and SmC as high- and low-temperature mesophases, respectively.

Many photoalignment approaches are developed as described above, such as microgrooved structure, pattern formation by laser-induced periodic structures, photocurable polymer through masks with a grating pattern, etc. As a liquid crystal alignment layer to uniformly align the liquid crystal molecules, more efficient and novel photoalignment techniques or photoalignment reactions should be developing in the future.

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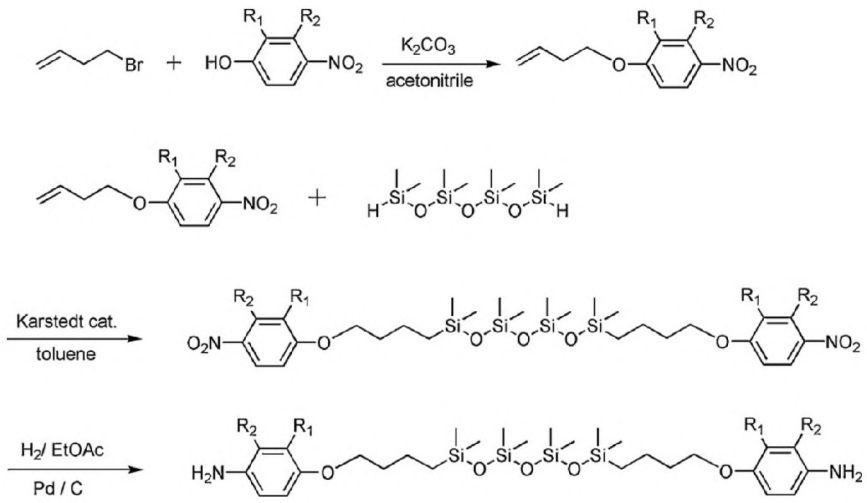


Scheme 58. Synthesis of the (polyamic acid)s and the polyimides from CBDA and DDA [256].

4.3. Gas separation membrane

DuPont (USA) and Ube Industries (Japan) have been pioneers in the commercial application of polyimides in separation processes. DuPont began developing membranes for industrial separations in 1962 and initially sought to separate helium from natural gas (Scheme 60). In 1981, Ube Industries developed and launched the production of Upilex-R, a polyimide material that exhibits high thermal resistance and is stable to various organic solvents and vapors, hydrogen sulfide, and ammonia vapor [1]. An important objective in the development of new gas separation polymer membranes is to combine a high gas permeability with a high selectivity [258]. Over the past

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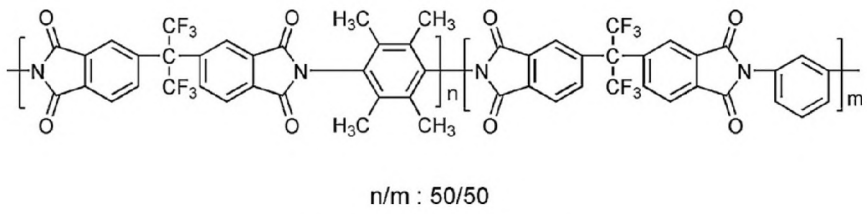
Scheme 59. Novel siloxane-containing liquid crystalline (LC) polyimides [257].

two decades, there has been increasing interest in polyimides as membrane materials for gas separation purposes [1,259–265].

Many new polyimide structures have been proposed for gas separation applications, including hyperbranched polyimides [266–269], indan structures [270–272], brominated polyimides [273–276], noncoplanar structures [18,277,278], and polyimides with bulky groups [258,279,280], among others, to improve the performance (separation factors) of these applications. Mixed matrix composite membranes (MMCMs) [281–289] and carbon molecular sieve membranes (CMSMs) [290–299] have also been examined for gas separation in recent years. The MMCMs fabricated by encapsulating zeolites or molecular sieves into polymer matrices have been recognized as a promising alternative to conventional membranes [300–304].

Carbonization of polymeric membranes has been studied in the past few years as a method to improve the permeation properties and thermal resistance of polymeric membranes. Carbonization offers a promising alternative to both inorganic and polymeric membranes. CMSMs are rigid and highly porous materials, and the selectivity phenomenon of CMSMs involves a size-sieving mechanism. CMSMs possess a distribution of small, selective pores, which are similar in size to diffusing gas molecules (3–6 Å) [305–307]. CMSMs are responsible for the high permselectivity of small gas pairs, such as O_2/N_2, H_2/N_2, CO_2/N_2 and He/N_2. Thus, the high gas separating-ability is dependent on an effective size-sieving mechanism in these materials. Koresh and Soffer [308] proposed the first modification methods of CMSM. They showed that the permeability of CMSMs increased in oxidized membranes, whereas lower permeability was observed in sintered membranes. Carbonization of polymer precursors has been adopted as a useful method for preparing CMSMs. Many studies have reported that CMSMs with tailored microstructures could be obtained by controlling the pyrolysis conditions [305,306,309–314] or the post-/pre-treatment conditions [308,315–320]. A number of researchers, including Koros [299], Haraya [312,319], Kusakabe [320–322], Centeno [323,324], Okamoto [315], Tsotsis [309], Chung [325], and Lee [326], have described the preparation and characterization of CMSMs by carbonization of polyimides.

One way of achieving good gas transport performance is to fabricate an asymmetric polyimide membrane that consists of a defect-free (surface defects of less than 1 μm) skin layer and has a high gas permeability and good gas selectivity [327]. Koros et al. [305] reported the fabrication of defect-free polyimide hollow fiber membranes using a dry-jet, wet quench process. In addition, many other groups [299,305,328–333] have reported the preparation



n/m : 50/50

Scheme 60. Polyimide for gas separations.

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of defect-free polyimide hollow fiber membranes. These groups have also characterized and fabricated other polyimide hollow fiber membranes for gas separations.

Many new polyimide structures have been proposed for gas separation applications as describe above. The high gas separating-ability is dependent on an effective size-sieving mechanism in the polymers. The important factors affecting the separation efficiency are the physical space and chemical selective. Therefore, the polymer morphology and chemical structures are important for the performance of the separation membrane. Of course, the thermal properties of the membranes are also important issue for the membrane application.

A novel combination of modified Stöber sol–gel techniques has been used to prepare silsesquioxane nanoparticles. An aqueous synthesis technique for polyimide resins has been used to prepare polyimide–silsesquioxane nanocomposites. Silica nanoparticles are strongly associated with the polyimide and appear to be attached to the surface of the polymer [334].

Chen et al. [335] prepared a series of new polymer–silica hybrid materials through the intrachain coupling of 3-aminopropyl trimethoxysilane (APrTEOS) and interchain hydrogen bonding with γ-glycidyloxypropyltrimethoxysilanes (GOTMS) (Scheme 61). The prepared hybrid films were homogeneous and thermally stable. The thermal properties of the organo-soluble polyimides were significantly enhanced by hybridizing 6.30–7.99 wt% of silica. It was found that the intrachain chemical bonding could effectively enhance the glass transition temperature or CTE in comparison to interchain interactions. The prepared hybrid films had low dielectric constants, tunable refractive indices and a high optical transparency, which suggests that these films could have potential applications in optoelectronic devices.

4.4. LB film

The ultrathin mono- and multilayer films of polyimides have been successfully prepared using Langmuir–Blodgett (LB) techniques in conjunction with a precursor method. Electrically insulating ultrathin LB films of polyimides (0.4 nm) have been successfully prepared on solid substrates [336,337]. The polyimide LB film between two metal electrodes showed excellent electrical insulating properties, had a resistance higher than $10^{15}\ \Omega$ cm and had an electrical breakdown strength higher than 10^7 V/cm.

Electrostatic phenomena that occur at the metal/polymer interface are interesting to the fields of organic and molecular electronics. Many investigations have been performed to clarify the contact potential formed at the metal/polymer interface. Various models, such as the surface states model, the molecular-ion state model and the local (intrinsic) model have been proposed [338–340].

Polyimide LB films were found to work well as tunneling barriers in tunnel junctions. Furthermore, the Nb/Au/PI/Pb-Bi junctions had an *I–V* curve that is characteristic of a superconductor–insulator–superconductor (SIS) transition. Iwamoto and coworkers [341] reported the fabrication of this Josephson junction as shown in Fig. 1. The

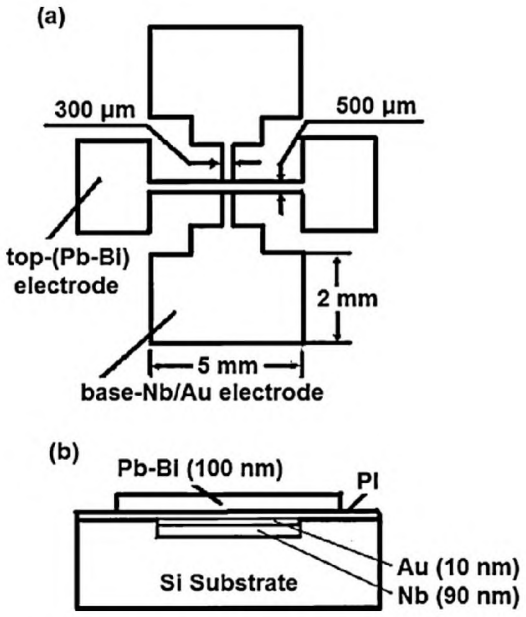


Fig. 1. Josephson junction (A) top view and (B) side view.

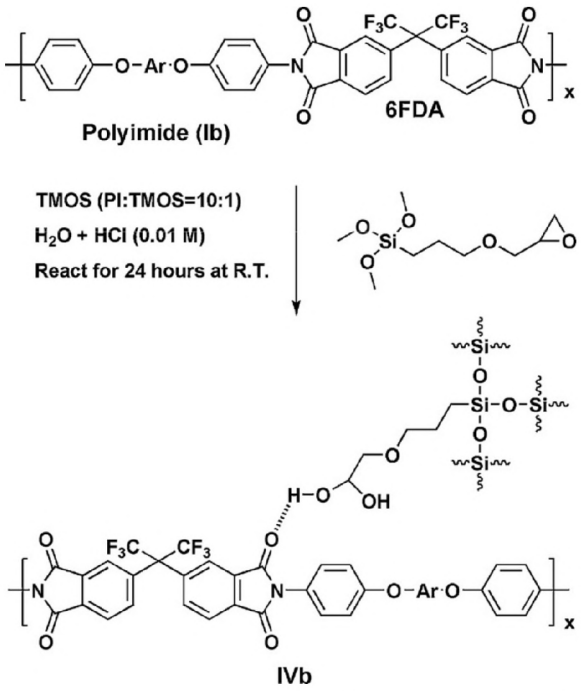
Josephson junction was very effective in the detection of microwaves.

Sakai and coworkers [342,343] showed reproducible memory switching effects between a high-impedance state (OFF state) and a high-conductance state (ON state) in a metal/polyimide or squarylium dye (SQ) LB films/metal device. This device also utilized a noble-metal base electrode. The device fabrication process is shown in Fig. 2. The switching elements have also been applied in scanning tunneling microscope (STM) probes.

Iwamoto et al. reported the preparation of polyimide LB films and their groups' investigations of interfacial phenomena, such as surface potential, spatial distribution of charge, potential changes with photo-irradiation, and charge storage phenomena. The presence of electron-acceptor and donor states was revealed, and excessive electronic charges were discovered to transfer from metals to the LB films. It was found that a high density of electronic states (10^{25}–$10^{26}\ m^{-3}$) and a very high electric field (10^8–10^9 V/m) exist in the interfacial space charge layer within a range of 10 nm [344]. Thus, it is obvious that the interfacial space charge makes a significant contribution to the device operation.

Kakimoto and Imai et al. [345] reported polyimide LB multilayer films that have different chemical structures. These films were constructed from polyimides that have a triphenylamine unit as an electron donor (D), a tetraphenylporphyrin as a sensitizer (S), and an aromatic polyimide as an electron acceptor (A) (Scheme 62). Two types of photodiodes with E/D/S/A and E/A/S/D systems were prepared on a semi-transparent gold electrode (E). The dependence of the number of D, S, and A layers on the photocurrent behavior was examined as a way to study

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Scheme 61. Prepared series of new polymer–silica hybrid materials through the intrachain bonding by γ-glycidyloxypropyltrimethoxysilanes (GOTMS) [335].

the electron transfer in each layer. In the photodiode system, the hole mobility in the D layer was high, whereas the electron mobility in the S and A layers was relatively low.

Langmuir–Blodgett techniques can be used in many applications due to the ordered structures and layer controllable properties. Doubtlessly, more applications using LB techniques to afford ordered and controlled layer structures will be reported in the near future.

4.5. Electroluminescent polyimides

In recent years, research in organic electroluminescence (EL) and polymeric light emitting diodes (PLEDs) has intensified. Currently, π-conjugated polymers, such as poly(*p*-phenylene vinylene), poly(thiophene) and poly(*p*-phenylene), are the most studied electroactive polymers for light-emitting components in PLEDs, and they have been demonstrated in large-area display applications [346–348]. Although aromatic polyimides have been extensively studied as high-performance polymers for their unique properties, few attempts have been made to use them for the light-emitting layer in EL devices [349–351]. Their applications have been limited to transporting layers [352–354] or as dye doped matrices in EL devices [355–357].

Kakimoto et al. fabricated a PLED device using a polyimide-based Langmuir–Blodgett film with indium tin oxide (ITO) as an anode and Mg–Ag as a cathode [350]. The device emits orange-red light at a forward bias voltage above 7 V. The EL intensity depended linearly on the applied current density, which indicates that the light emission results from the recombination of injected charges in the polyimide layer.

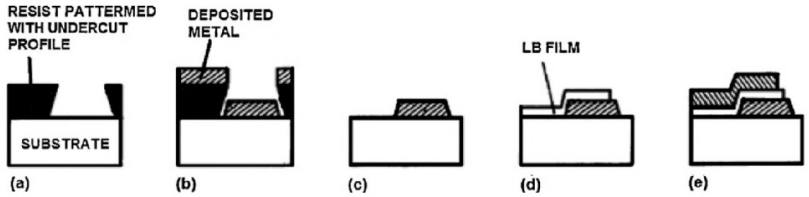
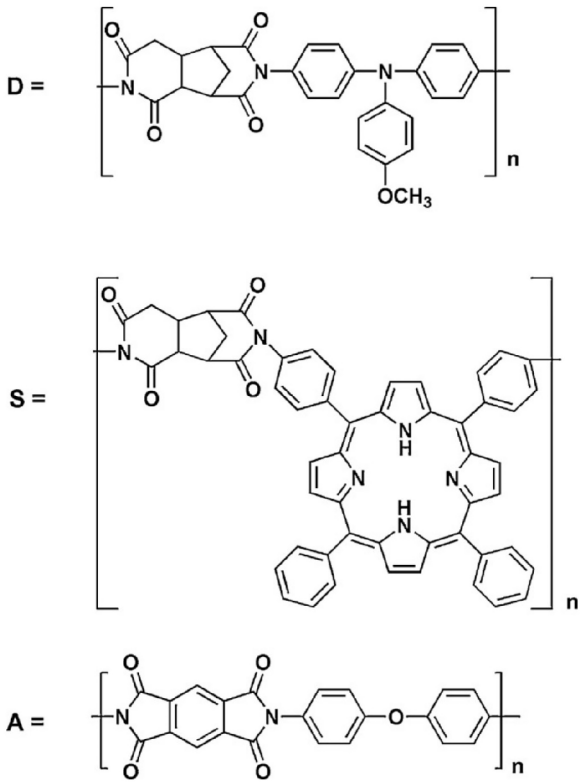


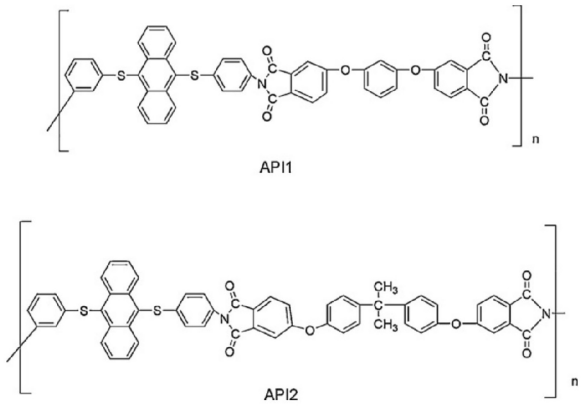
Fig. 2. Fabrication process of switching elements. (A) The resist is patterned with an undercut profile. (B) The base-electrode metal is deposited. (C) The excess metal is lifted off when the resist is removed, leaving behind a patterned deposit on the substrate surface. (D) The LB film is deposited. (E) The top-electrode metal is deposited and patterned using a conventional wet etching after the resist process.

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Scheme 62. Structures using triphenylamine unit as an electron donor (D), tetraphenylporphyrin as a sensitizer (S), and aromatic polyimide as an electron acceptor (A).

Mal'tsev et al. also reported the fabrication and operational characteristics of polyimide electroluminescent devices [356,358]. The photoluminescence of anthracene-containing aromatic polyimides (APIs) has a strong and pronounced exciplex character that arises from interchain donor–acceptor interactions between the excited anthracene groups and the diimide fragments. The LEDs with uni-layer sandwich structures (ITO/API/Mg:Ag) have a maximum brightness greater than 100 cd/m^2 at 15 V [359]. The aromatic polyimides shown in Scheme 63 [356,358] contain sulfur atoms in the polymer backbone and were studied as electron-hole transporting and light-emitting materials. These polyimides were used in combination with tris(8-hydroxyquinoline)-aluminium in multilayer



Scheme 63. Molecular structures of APIs [356,358].

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organic electroluminescent devices. When operating under a forward bias with ITO as the positive electrode, bright emission was observed in the visible range. A maximum luminance of 15,000 cd/m^2 was reached at 14 V.

Chan et al. [351] described the fabrication of single-layered light-emitting devices with polyimides functionalized with $[Ru(tpy)2]^{2+}$ complexes (Scheme 64). Red light was emitted, and a maximum luminance of 120 cd/m^2 was observed.

Yang et al. [360] synthesized a novel diphenylfluorene-based cardo copolyimide containing perylene (PFB5) (Scheme 65). This polymer was synthesized by through a polycondensation of a diamine, 4,4-(9H-fluoren-9-ylidene)bisphenylamine, with perylene dianhydride and another dianhydride. The reaction was carried out in *m*-cresol with an isoquinoline catalyst at 200 °C. Because of the bulky diphenylfluorene units in the backbone, PFB5 has a high thermal stability and good solubility in common solvents. The high solubility of PFB5 in low boiling solvents allows direct spin coating of the polymer films, which exhibit intense photo- and electroluminescence (EL) in the visible range. This non-conjugated polymer could be used in emitting and electron–hole transporting layers in polymer electroluminescent devices (PLEDs).

Moreau and coworkers [361] described the electroluminescence characteristics of a phenylene–ethynylene-based polyimide that combines a C2 chiral structure with a confined chromophore (Scheme 66). The C2 symmetry of the chiral unit induces secondary structures that reduce intra- and interchain interactions and π-stacking. A monolayer electroluminescent polymeric diode exhibits high performance (1500 Cd/m^2 at 10.5 V with a turn-on voltage of 5.5 V).

Electroluminescent devices using polyimides as active layers in the PLED were reported. In general, the polyimides are prepared by incorporating chromophores with high efficiency. The organo-soluble and high thermal properties are required for the developing of active-layer polymers in PLED. The relationship between solubility, thermal properties and chemical structures should be considered in the designing of polyimide-based PLED.

4.6. Polyelectrolytes

The idea of using an organic cation exchange membrane as a solid electrolyte in electrochemical cells was first described in a fuel cell in 1959. At present, the polymer electrolyte fuel cell (PEFC) is the most promising alternative of all the fuel cell systems in terms of its mode of operation and applications. The Nafion® series have been almost the only advanced membranes that have been used in practical systems. Unfortunately, these membranes have some demerits, including a high cost, low conductivity at low humidity or high temperatures, and high methanol permeability. Rikukawa et al. presented an overview on proton-conducting polymer electrolyte membranes based on hydrocarbon polymers for fuel cell applications [362].

The perfluorinated ionomer membranes are highly proton conductive (10^{-2} S cm^{-1} in its fully hydrated state) and chemically and physically stable at moderate temperatures. However, these desirable properties deteriorate above their glass transition temperature (T_g) of ca. 110 °C [363,364]. High gas permeability, high cost, and environmental inadaptability of the fluorinated materials are also serious drawbacks for their practical applications in fuel cells.

In the past decade, some proton conductive materials have been proposed as alternative membranes [365–368]. These materials include a variety of nonfluorinated hydrocarbon proton-conducting materials [369] that are inexpensive and perform well. Several research groups have proposed that sulfonated polyimide (SPI) membranes used for PEFCs have a higher proton conductivity than perfluorinated materials [362,370,371].

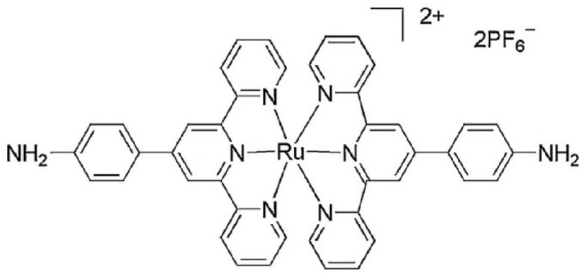
Mercier and coworkers first synthesized a series of sulfonated copolyimides from naphthalene-1,4,5,8-tetracaboxylic dianhydride (NTDA), 2,2′-bendizine sulfonic acid (BDSA) and common nonsulfonated diamine monomers [160,372] (Scheme 67). The proton conductivity of these membranes is rather low (<10^{-2} S cm^{-1} at 100% relative humidity) due to a low ion exchange capacity (IEC), which is essential for maintaining hydrolysis stability. These sulfonated copolyimide membranes have been practically tested in fuel cell systems and exhibit fairly good performance.

Litt's group has also used BDSA as a sulfonated diamine monomer in the preparation of various random and sequenced copolyimides [373]. They reported that some copolyimide membranes containing bulky and/or angled comonomers had higher conductivities than Nafion® at all humidities. However, the poor hydrolytic stability of their membranes remains a problem.

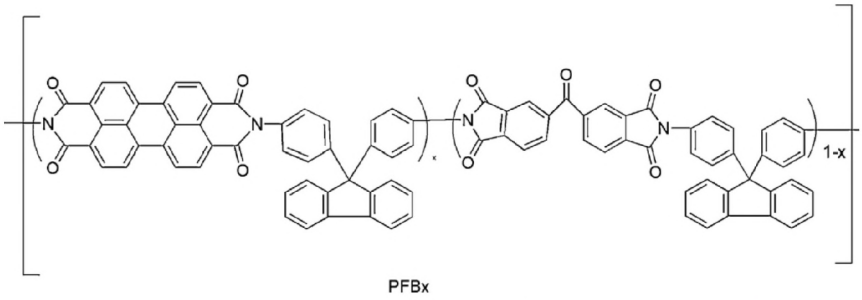
Okamoto's group synthesized a series of main-chain type, side-chain type, branched/crosslinked (B/C) and sulfonated polyimides (SPIs) from sulfonated diamines [161] (Scheme 32). The main-chain type copolyimide containing fluorine disulfonic acid and the side-chain type polyimide containing either propane sulfonic acids or sulfopropoxy groups displayed similar or higher proton conductivities than commercial Nafion® 117 [163–166,168,369,374,375] (Schemes 33–36, 68 and 69). The branched/crosslinked structure SPIs also exhibited high mechanical strengths and fuel cell performance comparable to that of Nafion® 112 in a single H_2/O_2 PEFC system. At 120 °C, the B/C SPIs membranes showed conductivity values of approximately 0.02–0.3 S cm^{-1} at 50–100% RH [369,376], and they exhibited fuel cell performance comparable to that of Nafion® 112 in a single H_2/O_2 PEFC system [376]. In addition,

Watanabe's group has also reported the synthesis and characterization of sulfonated polyimides (SPIs). The fluorenyl containing SPIs exhibited proton conductivity up to 1.67 S cm^{-1} (at 120 °C and 100% RH) when the bulky fluorenyl groups were incorporated at a level of 30–60 mol% into the polymer [377]. Branching was introduced with melamine and cross-linking was introduced by electron beam irradiation; these modifications produced a positive effect on the oxidative stability and mechanical strength while maintaining many of the desirable conductivity properties [378]. The introduction of 30 mol% of bis(trifluoromethyl)biphenylene groups into sulfonated copolyimides resulted in a balance of oxidative stability, proton conductivity and mechanical properties. Direct

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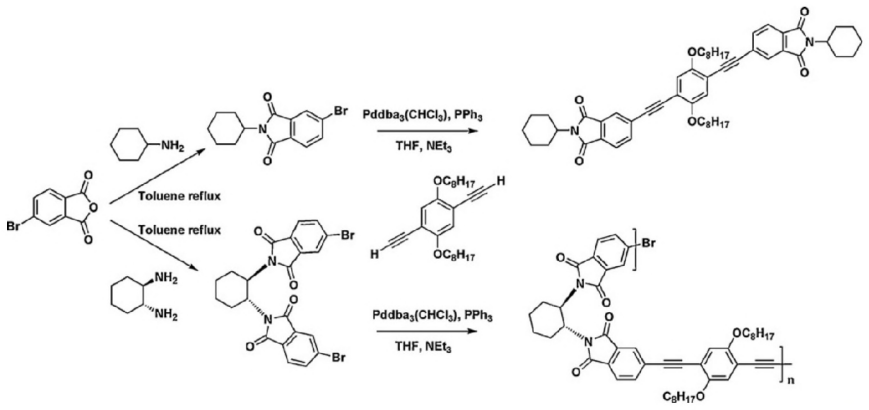
Scheme 64. Structure of the $[Ru(tpy)2]^{2+}$.



Scheme 65. Novel diphenylfluorene-based cardo copolyimide containing perylene (PFB5) [360].

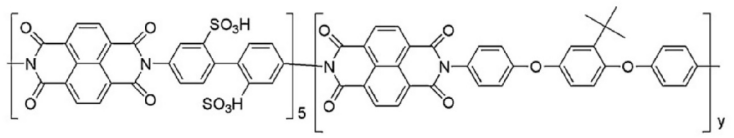
methanol fuel cell (DMFC) experiments revealed that the methanol crossover through the FSPIH-30 membrane was only 30% of that of Nafion® 112. The lower methanol crossover would be a great advantage over the perfluorinated ionomers when taking the efficiency of fuel cells into account [379]. The introduction of aliphatic groups in the main chain and/or side chains could significantly improve the hydrolytic stability of sulfonated polyimides, which could possibly make these polymers better than Nafion® 112 [380,381]. Side-chain sulfonated polyimide membranes have been evaluated as electrolyte membranes in DMFCs. The performance was compared with that of Nafion® 112 under various operation conditions. The methanol crossover in the cell based on SPI was a half of that of Nafion® 112 and resulted in improved cell efficiency. The advantage of using SPI over Nafion® 112 became even clearer when the DMFC was operated at a higher temperature (T_{cell}) or a higher concentration of methanol (C_{MeOH}) [382].

Liu et al. [383] prepared a series of SPIs that contain ether and ketone linkages through a copolymerization method, as shown in Scheme 70. At 80 °C, the proton conductivities of several samples, including SPI-KK-X and SPI-K-X, were higher than 0.10 S cm^{-1}; these values are comparable to that of Nafion®. Methanol permeabilities of the obtained polymer electrolyte membranes (PEMs) were in the range of 1.43–2.03 × 10^{-7} cm^2/s, which is several times lower than that of Nafion® 117. It is

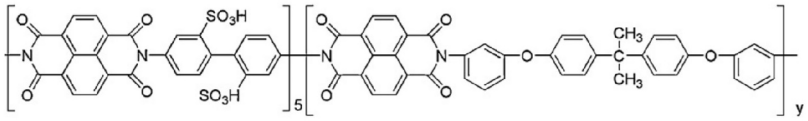


Scheme 66. Phenyleneethynylene-based polyimide which combines the C2 chiral structure with a confined chromophore [361].

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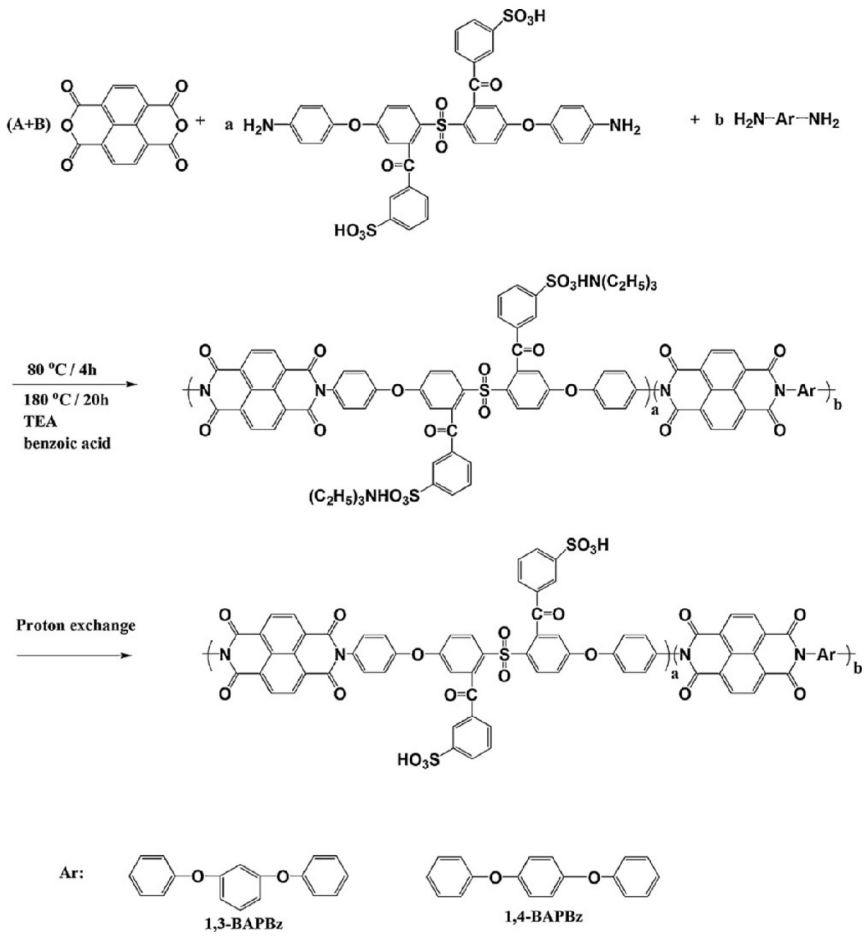


BDSA/NTDA/ATB



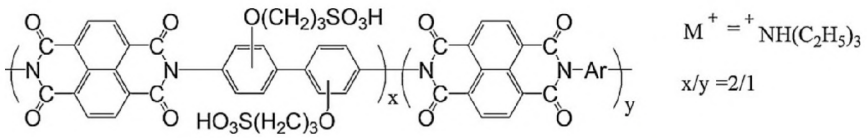
BDSA/NTDA/mAPI

Scheme 67. Structures of BDSA/NTDA/mAPI and BDSA/NTDA/ATB [160].



Scheme 68. Synthesis of BAPSBPS-based polyimides [168].

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Scheme 69. Copolyimides bearing pendant sulfonic acid groups [375].

interesting to note that the SPI-KK-X series, which has a more rigid phenyl–ketone–phenyl–ketone–phenyl moiety, had a lower dimensional swelling ratio and a lower methanol permeability in comparison to the corresponding SPI-K-X series at the same ion exchange capacity (IEC).

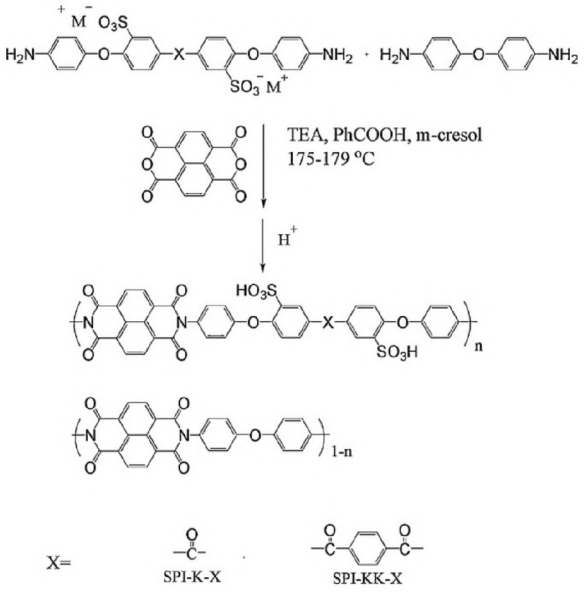
Sotzing et al. [384] described the template polymerization of EDOT with sulfonated poly(amic acid) (SPAA) that resulted in a stable conducting polymer aqueous dispersion, PEDOT-SPAA, with a particle size of ca. 63 nm. In films of PEDOT-SPAA, the sulfonated poly(amic acid) template undergoes imidization within 10 min at temperatures greater than 150 °C and results in a PEDOT-sulfonated poly(imide) (PEDOT-SPI) with a 10-fold conductivity enhancement. This material is highly thermally stable as compared to PEDOT-PSS (Scheme 71). Thermal stability is necessary for many processing applications of conducting polymers. Isothermal TGA experiments were run at 300 °C for PEDOT-PSS and PEDOT-SPAA and revealed that PEDOT-SPAA had a smaller slope for degradation. Annealing the films at 300 °C for 10 min caused the conductivity of the PEDOT-PSS films to be unmeasurable ($<1 \times 10^{-5}$ S cm^{-1}), while those of PEDOT-SPAA increased 6-fold. Secondary doping of the PEDOT-SPAA system with additives commonly used for PEDOT-PSS was also investigated.

Commercial perfluorinated polymer electrolyte membranes have been extensively used as polymer electrolytes for fuel cells; however, they are expensive. Several research groups have proposed that sulfonated polyimide (SPI) or copolyimide membranes used for PEFCs have higher proton conductivity than perfluorinated materials. The polyimides have great variety with regard to chemical structure and can be modified chemically at very low cost. However, the poor hydrolytic stability of their membranes remains a problem. Therefore, low-cost new proton-conducting polymer electrolytes with long-term stability and mechanical properties are necessary for the developing of polyelectrolytes.

4.7. Electrochromic polyimides

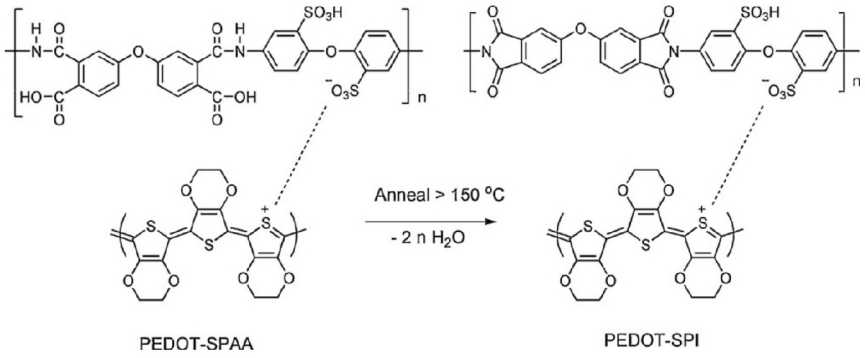
Electrochromism occurs when color can be alternated by applying a potential [385–387]. This interesting property has led to many technological applications, such as smart windows, automatic antiglazing mirrors, large-scale electrochromic screens, and chameleon materials [388–392]. The electrochromic behavior of polymers is based on the redox behavior of the polymers.

Most hole-transport layer (HTL) materials are based on ternary aromatic amines, such as *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)(1,1′-biphenyl)-4,4′-diamine

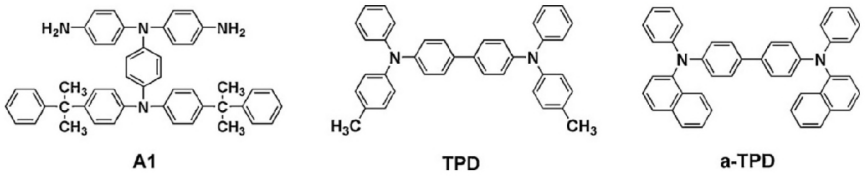


Scheme 70. SPIs containing ether and ketone linkages through a copolymerization method [383].

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Scheme 71. PEDOT-SPI derived from PEDOT-SPAA [384].

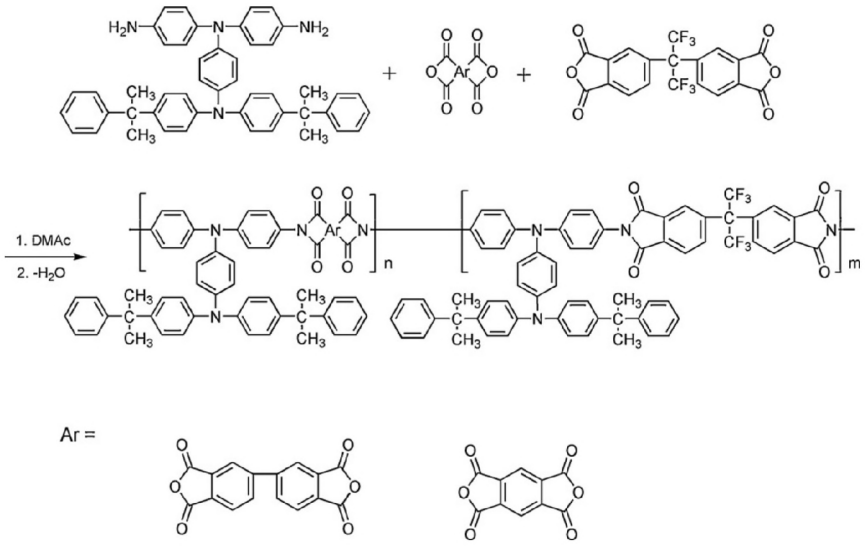


Scheme 72. Triphenylamine-containing monomers A1, TPD and a-TPD.

(TPD) and *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (a-NPD); these are shown in Scheme 72 and are known for their high hole mobility [357,393–398]. Recently, Liaw's group has reported many triarylenylamine-based electrochromic polyimides from novel diamines (A1), as shown in Scheme 73.

Electrochromic polyimides with high molecular weights based on triphenylamine derivatives are synthesized from the diamine and various aromatic dianhydride *via* a direct polycondensation, as shown in the Table 1 [54].

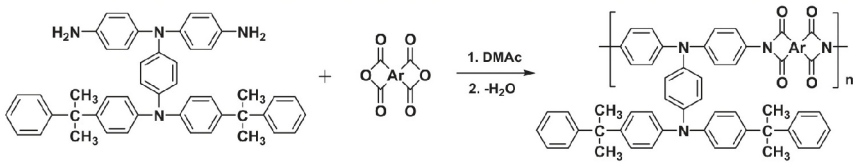
In Table 2, polyimide **Ib** shows a better solubility profile and shorter switching and bleaching times but a lower thermal stability than polyimide **P1** and **P2** are results of the pendant 2-phenyl-2-isopropyl groups. Polyimide **Ib** and **P1** films changed from their original pale green-yellowish color to green and then to Prussian blue. This color change correlates with the oxidized form. However, the polyimide



Scheme 73. Copolyimides with propeller-shaped triarylamine unit prepared from the diamine and various aromatic dianhydride *via* direct polycondensation [54].

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Table 1
Properties of electrochromic polyimides [54].



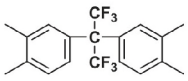
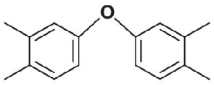
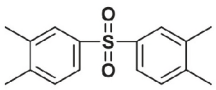
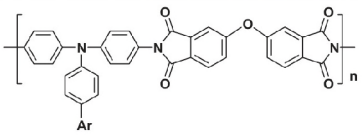
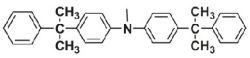
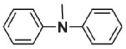
	Ia	Ib	Ic
Ar			
Color			
Switching voltage	First: 0.97 V Second: 1.30 V	First: 0.93 V Second: 1.32 V	First: 0.94 V Second: 1.32 V
T_g (°C)	266	241	267
T_{d10} in N_2 (°C)	528	519	504
T_{d10} in air (°C)	466	424	446

Table 2
The triphenylamine containing polyimide synthesized by Liaw's and Liou's group [54,447]. (For interpretation of the references to color in this table, the reader is referred to the web version of the article.)



Code		Ib	P1		P2
Ar					H
Switching (oxidation) voltage	1st	0.93 V	0.78 V		1.25 V
	2nd	1.32 V	1.13 V		
Switching time (s)		4.5	20		–[a]
Bleaching time (s)		1.9	3		–[a]
Color changing	0 V (Yellow)		0 V (Yellow) 	0 V (Yellow)	
	1.2 V (Green)		0.98 V (Green) 	1.3 V (Blue)	
	1.5 V (Blue)		1.35 V (Blue) 		
T_g (°C)		241	264		295
T_{d10} in N_2 (°C)		519	610		608
T_{d10} in air (°C)		424	600		611
Solubility in organic solvent	NMP	S	S		+h
	DMAc	S	S		+h
	DMF	S	P		I
	DMSO	+h	+h		+h
	m-Cresol	+h	+h		+h
	THF	S	P		I
	$CHCl_3$	S	S		I

S: soluble at room temperature; +h: soluble on heating to 70 °C; P: partially soluble on heating 70 °C; I: insoluble.
[a] Not reported.

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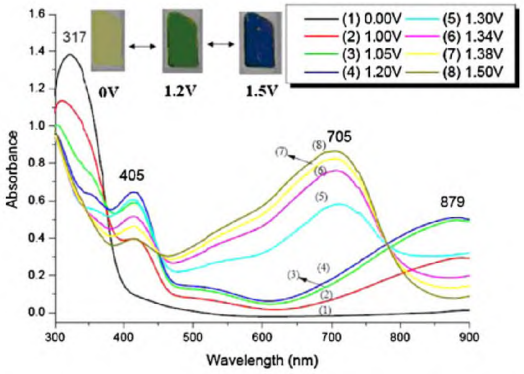


Fig. 3. Electrochromic behavior of polyimide **Ib** film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte).

P2 film only changed from pale green-yellowish to Prussian blue color because the polyimide **P2** had only one triarylenylamine group in a unit.

The polyimide from diphenyl-3,3′,4,4′-tetracarboxylic dianhydride and pyromellitic dianhydride is insoluble. However, the solubility can be improved by copolymerization to obtain a strong and tough film (Table 1) [54].

The electrochromism of these polymer thin films was examined by an optically transparent thin-layer electrode coupled with UV–vis spectroscopy. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic spectra of polyimide **Ib** is shown in Fig. 3. The color switching time was estimated by applying a potential step, and the absorbance profiles were followed (Fig. 4). The switching time was defined as the time required for reaching 90% of the full change in absorbance after switching the potential.

All theoretical calculations in this study were performed using the quantum mechanical package of Gaussian 03 [399,400]. The equilibrium structure of basic unit **M3** was determined using DFT with the B3LYP functional and 6-31G(d) basis set. The atomic charge was determined using Mulliken population analysis.

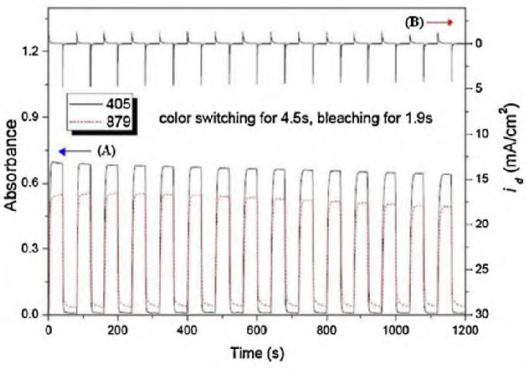


Fig. 4. (A) Potential step absorptometry and (B) current consumption of polyimide **Ib** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step 0–1.20 V.

The sketch map of the polyimide **Ib** structure was determined by DFT(B3LYP/6-31G(d)). The main atomic charge difference was located on the 1N, 9C, 29C, and 32N atoms (Scheme 74). In the first oxidation (loss of the first electron), the 1N, 9C, 29C and 32N atoms contribute 3.6%, 2.0%, 3.8% and 4.3% of an electron, respectively. For the second oxidation (loss of the second electron), the 1N, 9C, 29C and 32N atoms contribute 2.1%, 1.5%, 1.5% and 1.6% electron, respectively. The electron density contour of the ground state and first oxidation state are plotted by Gauss View and is shown in Scheme 74. This plot suggests that the nitrogen lone pairs have a strong coupling with the π electrons. The electron density distribution of the first oxidation state is broader than that of the ground state, but the main distribution was located on the *N*,*N*,*N*′,*N*′-tetraphenyl phenylene diamine in both cases.

A new oxidation mechanism based on molecular orbital theory was proposed by Liaw's group. In other words, all of the atoms in the HOMO (first oxidation) or SOMO (second oxidation) contributed to the oxidation of the molecule; the oxidation was not dictated only by the nitrogen atoms (Scheme 74).

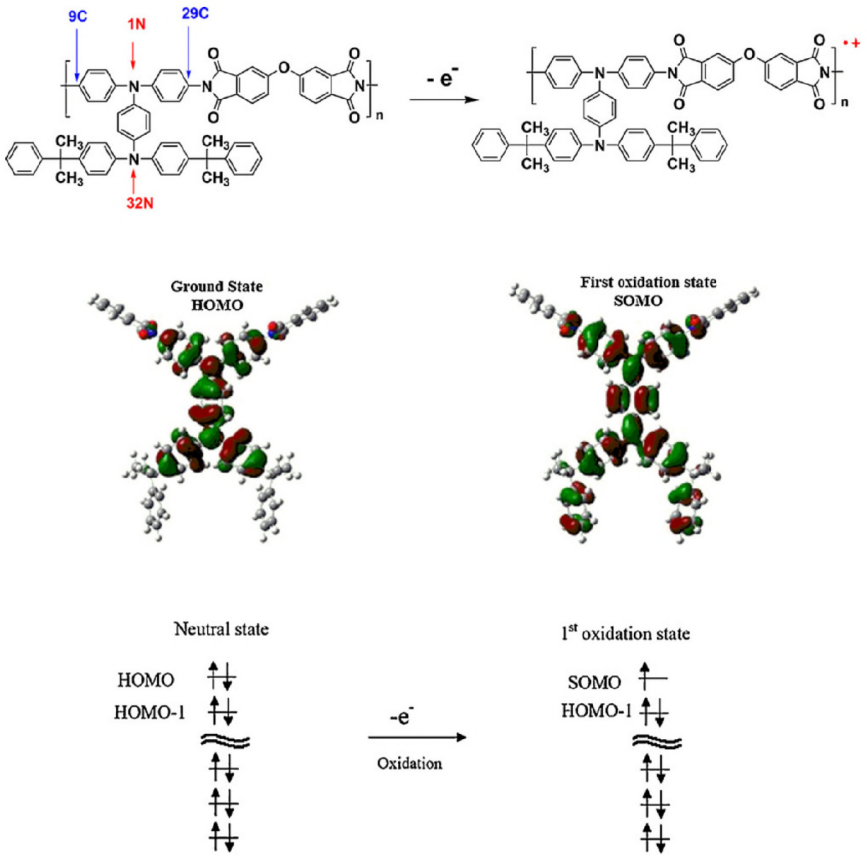
Polyimide-based polymers are great candidates for the electrochromic materials due to their unique thermal properties. Triphenylamine-containing polyimides are major structure developed for electrochromic polymers in the literatures. Electrochromic polyimides containing different electrochromophores and exhibits long-term stability should be developed for electrochromic application.

4.8. Nanomaterials

Recently, carbon nanotubes (CNTs) have attracted much attention because their nanocomposite material is expected to enhance mechanical properties and improve load transfer and tear resistance. In addition, they may be able to achieve certain levels of electric conductivity through a percolation network for charge mitigation and electromagnetic shielding [401–413]. The combination of carbon nanotubes and polyimides is expected to play an important role in the development of novel high-performance nanocomposites [414]. There are two common processing techniques for fabricating the composites. One is to mix CNTs with the resin matrix in the melt state to form composites. The other technique involves dispersing the CNTs into a polymer solution, performing solution casting, and removing the solvent to obtain the composite.

Park and coworkers have reported a process that effectively disperses single wall carbon nanotube (SWNT) bundles into an aromatic polyimide matrix at a nanoscale level [407]. The resultant SWNT–polyimide nanocomposite films are electrically conductive (antistatic) and optically transparent. A sharp increase in conductivity was observed between 0.02 and 0.1 vol.% of SWNT (Fig. 5); during this process, the nanocomposite was converted from a capacitor to a conductor. Incorporation of 0.1 vol.% SWNT increased the conductivity by 10 orders of magnitude, which surpasses the antistatic criterion of thin films for space applications (1×10^{-8} S cm^{-1}). The polyimide film

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Scheme 74. Electrochromic mechanism and electronic density contours of polyimide **Ib** structure.

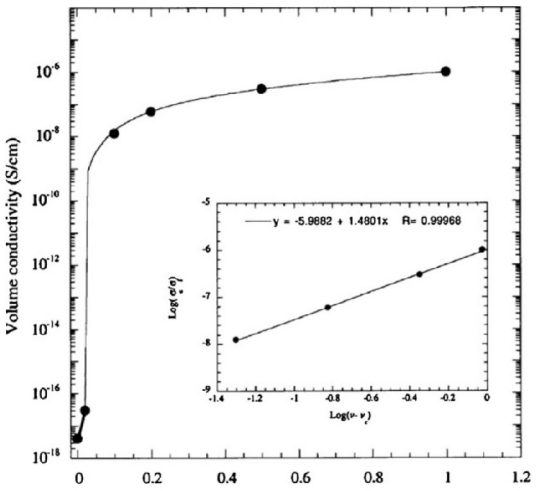


Fig. 5. Volume conductivity of SWNT–CP2 nanocomposites [407]. Copyright 2002, Elsevier Ltd.

that contained 1.0 vol.% SWNT still transmitted 32% of visible light at 500 nm, whereas the film that was prepared by direct mixing transmitted less than 1%. Dynamic mechanical testing data showed that the modulus increased up to 60% at 1.0 vol.% SWNT loading and that the polyimide thermal stability was enhanced in the presence of SWNT.

Connell et al. [408] reported the synthesis of an alkoxysilane terminated poly(amic acid) polymer. The SWNTs were added to a pre-made poly(amic acid) solution, which is in contrast to the previously mentioned *in situ* method. At a loading of 0.05 wt% SWNT, the percolation threshold was reached, as evident by the sharp drop in the surface resistivity of the material. The surface resistivity (1.7×10^8 Ω/square) and volume resistivity (1.7×10^9 Ω cm) results indicate that the SWNT–polyimide composite is conductive. However, the SWNTs in the polyimide had a negligible effect on the T_g and tensile properties of the polymer [408]. Increasing the ionic strength of the polyimide matrix by adding an inorganic salt ($CuSO_4$) resulted in sufficient SWNT network formation to afford conductivity. The addition of 0.014 wt% $CuSO_4$ to a composite containing 0.03 wt% SWNTs resulted in a film that exhibited 4 orders of magnitude reduction

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in surface and volume resistivity [415]. Polyimide films containing SWNTs throughout the bulk of the film had volume resistivities sufficient for electrostatic charge (ESC) mitigation, but the optical properties (solar absorptivity, α and transparency, %T) were negatively affected. It was found that films coated with SWNTs (spray-coating) exhibited surface resistivities of 1×10^7 to 1×10^6 Ω/square and had a high degree of flexibility and robustness, as evidenced by their retention of surface resistivity after harsh manipulation [416]. Polyimides prepared from side chain aliphatic diamines and various aromatic dianhydrides were successful in breaking up SWNT agglomerates and resulted in homogeneous SWNT suspensions in DMAc. Increased electrical conductivity was observed in the nanocomposite films. However, electrical percolation occurred at higher loadings than those typically expected for SWNT–polyimide nanocomposites. Modulus values of the films increased slightly with higher SWNT loading. Electrospun fibers were prepared from the same SWNT–polyimide suspensions used for preparing the films. High resolution SEM images showed that the SWNTs were captured in the interior of the fiber and might have some directionality parallel to the fiber axis [417].

Sun et al. [418] reported the fabrication of functionalized CNTs using amine-terminated polyimides with pendant hydroxyl groups. The resulting polyimide-functionalized CNTs were found to be soluble in the same solvents as the parent polyimide. A significant advantage with this approach is that the functionalized nanotube samples can be used directly to prepare polyimide-CNTs with relatively higher nanotube contents.

Bin et al. [419] prepared polyimide–carbon nanotube composites by performing an *in situ* polymerization in the presence of multi-walled carbon nanotubes (MWNT). The percolation threshold for the electric conductivity of the resultant PI–MWNT composites was about 0.15 vol.%. The electrical conductivity has been increased by more than 11 orders of magnitude to 10^{-4} S cm^{-1} at the percolation threshold and was further increased to 10^{-1} S cm^{-1} when the MWNT concentration was raised to 3.7% in volume.

Nakashima and coworkers reported [414] the synthesis of completely aromatic polyimides that contain the triethylammonium salts of disulfonic acids (Scheme 75). The resulting polyimides are highly capable of solubilizing a large number of individual SWNTs in organic solutions. The major driving force for the solubilization of SWNTs is π–π interactions between the condensed aromatic moieties on the polyimide and the surface of SWNTs. Higher concentrations of SWNTs in polyimide solutions form gels that are composed of individually dissolved SWNTs.

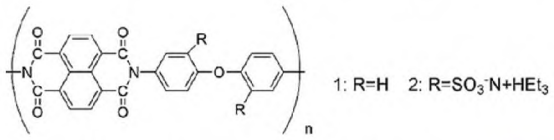
Ando et al. [420] prepared novel nano ZnO/hyperbranched polyimide hybrid (Scheme 76) films *via* the *in situ* sol–gel polymerization technique. The films, which originated from colorless, fluorinated HBPI and homogeneously dispersed ZnO nanoparticles, exhibited good optical transparency. Furthermore, two types of model compounds with and without ZnO and a hyperbranched polyimide (HBPI) film blended with ZnO microparticles were prepared. These materials were used to clarify the fluorescence mechanism in pristine HBPI and *in situ* hybrid films. Efficient energy transfer from the ZnO nanoparticles to the aromatic HBPI main chains was observed in the *in situ* hybrid films, whereas energy transfer occurred only from the locally excited states to the charge-transfer state in the HBPI film. These findings demonstrate that the peripheral termini of HBPI are covalently bonded to ZnO particles *via* the mono-ethanolamine (MEA) functionality; this functionality operates as an effective pathway for energy transfer and results in an intense fluorescent emission.

Liou et al. [421] prepared polyimide–nanocrystalline–titania hybrid optical films with a relatively high titanium content and thickness from soluble polyimides containing hydroxyl groups (Scheme 77). Two series of newly soluble polyimides were synthesized from the hydroxy-substituted diamines with various commercial tetracarboxylic dianhydrides. The hydroxyl groups on the backbone of the polyimides provided organic–inorganic bonding and controlled the mole ratio of titanium butoxide to hydroxyl groups. This resulted in homogeneous hybrid solutions. Flexible hybrid films could be obtained, and an analysis revealed that the films had relatively good surface planarity, thermal dimensional stability, tunable refractive indices, and a high optical transparency. A three-layer antireflection coating based on the hybrid films was prepared and showed a reflectance of less than 0.5% in the visible range; these characteristics suggest that these films could be used in optical applications.

The combination of polyimides and other organic/inorganic compounds is expected to play an important role in the development of novel high-performance nanocomposites to apply in many fields.

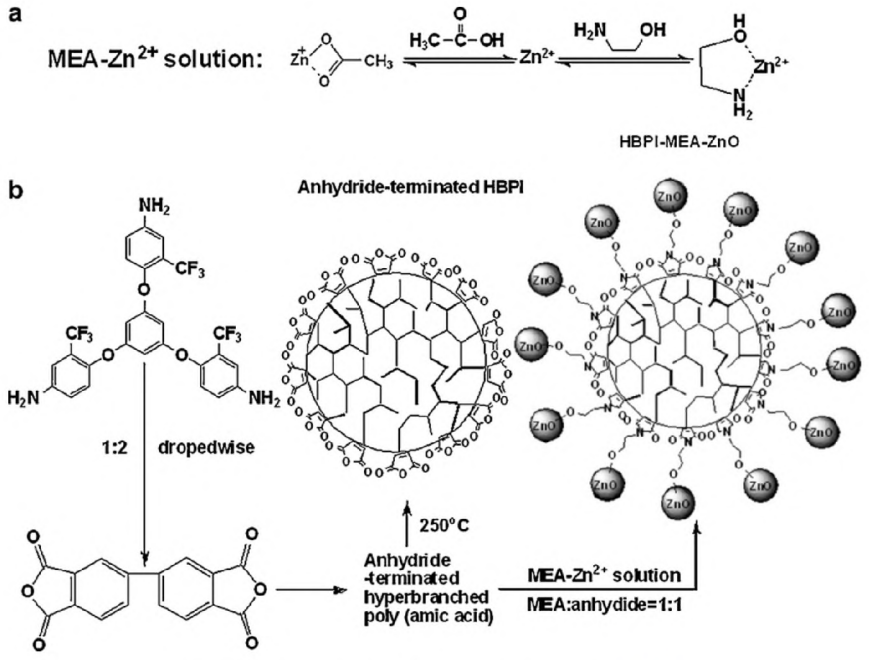
4.9. Polymer memory

Polymer memories have simple structures, good scalability, low cost potential, 3D stacking capability, and a large capacity for data storage. Recently, several types of polymer memory, including nonvolatile flash memory [422–430], write once read many times (WORM) memory [431–436], dynamic random access memory (DRAM) [437,438], and static random access memory (SRAM) [439] have been reported. A polymer memory stores information in a manner entirely different from that of silicon devices. Rather



Scheme 75. Polyimides containing disulfonic acid neutralizated [414].

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Scheme 76. Novel nano ZnO/hyperbranched polyimide hybrid [420].

than encoding "0" and "1" from the number of charges stored in a cell, a polymer memory stores data on the basis of high and low conductivity responses to an applied voltage. Polymer memory cells may be stacked to produce a 3-D architecture, which could translate into memory devices that have several times the storage capacity of conventional semiconductor flash memory devices. Polyimides could be potentially used for these practical applications due to their high mechanical strength and high thermal stability.

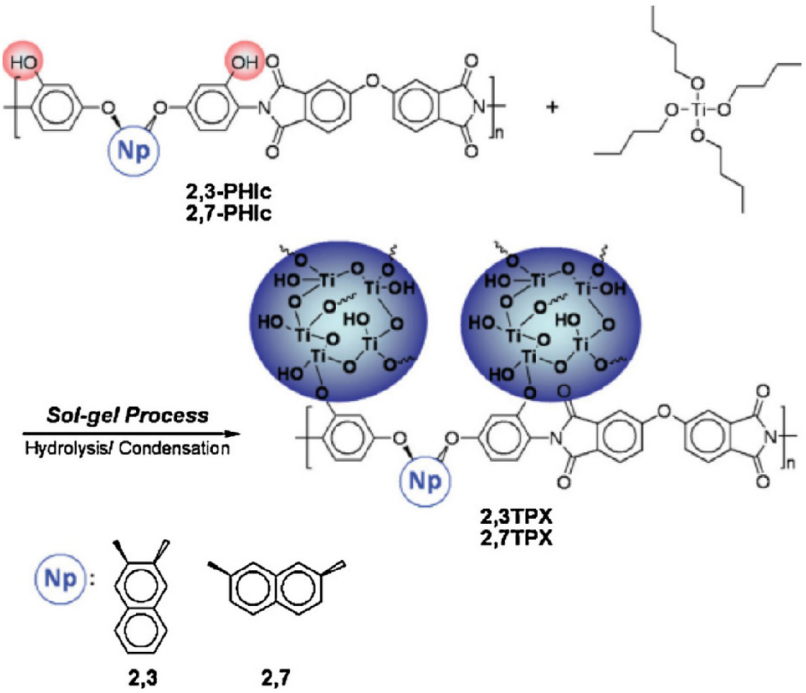
A dynamic random access memory (DRAM) device based on a functional polyimide that contains both electron-donor (D) and electron-acceptor (A) moieties within a single macromolecule has been reported [437]. The polyimide device exhibits an ON/OFF current ratio up to 10^5. Both the ON and OFF states were stable under a constant voltage stress of 1 V and survived up to 10^8 read cycles at 1 V. The molecular structures of the polyimide and single-layer memory device are shown in Scheme 78.

The mechanism of field-induced conductivity is similar to that of photoinduced charge-transfer (CT) in photoconductive polyimides. The incorporation of donors enhances the photocurrent in the polyimide by several orders of magnitude and arises from improved CT complex formation in the polyimide backbone. More comprehensive reviews on the topic of polymer electronic memories are available [210,211].

Wang and Kang's groups [435,436] reported the synthesis and memory behaviors of a series of functional aromatic polyimides (OXTA-PI) containing triphenylamine and 1,3,4-oxadiazole moieties (Scheme 79) and polyimides (AZTA-PI) containing triphenylamine-substituted triazole moieties (Scheme 80). Resistive switching devices based on the sandwich structure of indium-tin oxide/polymer/Al were fabricated, and their memory behavior was tested. The devices exhibit two conductivity states and can be switched from an initial low-conductivity (OFF) state to a high-conductivity (ON) state at threshold voltages of 1.8 V and 2.5 V, respectively, under both positive and negative electrical sweeps, with an ON/OFF state current ratio on the order of 10^5 at −1 V. The devices are able to remain in the ON state even when the power is turned off or if the device is subjected to a reverse bias. The nonvolatile and nonrewritable natures of the ON state indicate that the devices are WORM memory.

Liu et al. [439] synthesized a functional polyimide, P(BPPO)-PI, that contains oxadiazole moieties (electron donors) and phthalimide moieties (electron acceptors), as shown in Scheme 81. A switching device with the polyimide exhibits two accessible conductivity states, and the device can be switched from a low-conductivity (OFF) state to a high-conductivity (ON) state when swept positively or negatively. This device has an ON/OFF current ratio on the order of 10^4. The device exhibits ON state "remanence," in which the ON state persists for a period of about 4 min after the power is removed. The ON state can be electrically sustained either by a refreshing voltage pulse of −1 V or by a continuous bias of −1 V. The "remanent" but volatile nature of the ON state and the ability to write, read, and sustain the electrical states with bias are characteristic features observed in static random access memory (SRAM). The mechanisms associated with the memory effect were elucidated from molecular simulation results and changes

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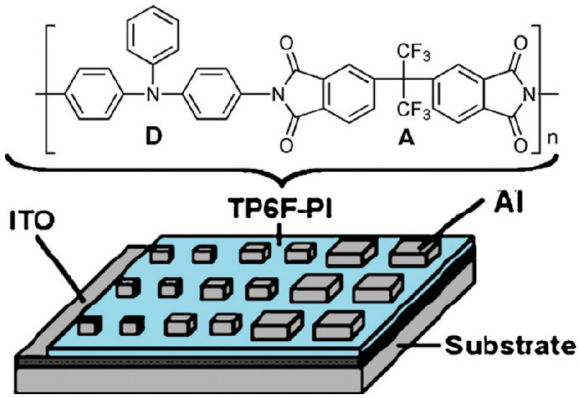


Scheme 77. Polyimide–nanocrystalline–titania hybrid synthesized from the hydroxy-substituted diamines with various commercial tetracarboxylic dianhydrides [421].

in the photoelectronic spectrum of a P(BPPO)-PI film that occurred when the device was switched between the ON and OFF states.

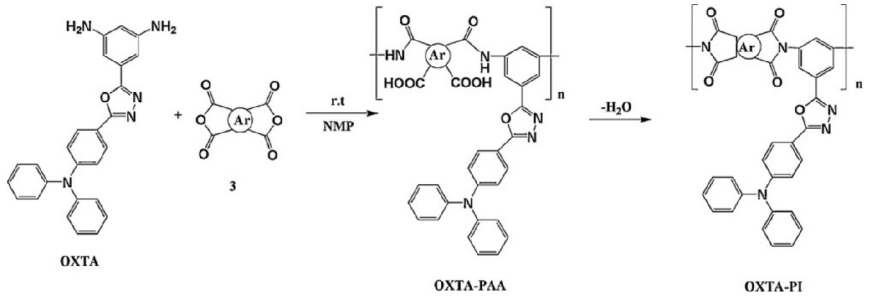
Ueda and Chen's [430] group have successfully synthesized two new sulfur-containing polyimides, APTT-6FDA and 3SDA-6FDA, as shown in Scheme 82, for memory device applications. The memory devices showed nonvolatile memory characteristics with two low turn-on threshold voltages at 1.5 and 2.5 V, respectively. These devices could be repeatedly written, read, and erased. The ON/OFF current ratios of the devices were all around 10^4 in ambient atmosphere. The different turn-on threshold voltages apparently resulted from two different low-lying HOMO energy levels. A theoretical analysis suggests that a charge-transfer mechanism can be used to explain the memory characteristics of the studied polyimides. The higher dipole moment of the sulfur-containing polyimides, compared to the triphenylamine-based polyimide, provides a more stable CT complex that can be used in a flash memory device.

A more stable charge transfer might improve polymer memory devices [210,211]. The memory behaviors of the



Scheme 78. Molecular structure and schematic diagram of the single layer memory device [437].

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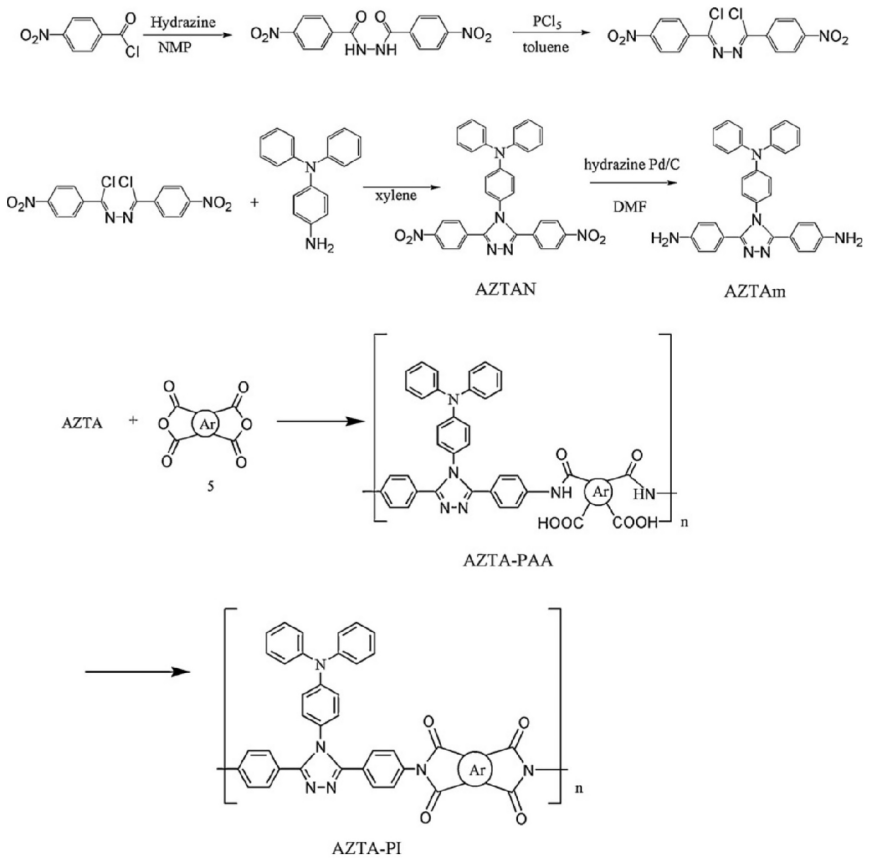


Scheme 79. Aromatic polyimides (OXTA-PI)s containing triphenylamine and 1,3,4-oxadiazole moieties [435].

polyimides depend on the donor–acceptor interactions of the polyimide structures.

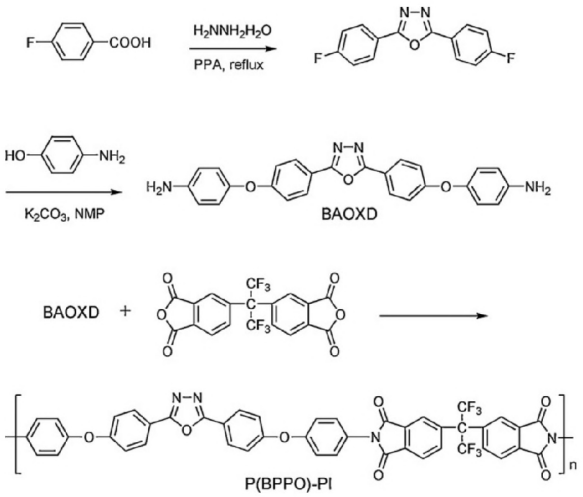
1. If the donor–acceptor interaction of a polyimide has an unstable "ON" state, then the memory can be used as DRAM [437,438].
2. If the stabilized donor–acceptor interaction but erasable, then the memory can be used as flash-rewritable memory [422–430].
3. If a very stable charge-transfer complex and nonerasable "ON" state exists, then the memory can be used as WORM [431–436].
4. If the donor–acceptor state is a temporary interaction due to a coupled conformational change in the ON-state, then the memory can be used as SRAM [439].

Polyimides are potential candidates for new generation memory materials because of their high mechanical,



Scheme 80. Aromatic polyimides containing triphenylamine-substituted triazole moieties [436].

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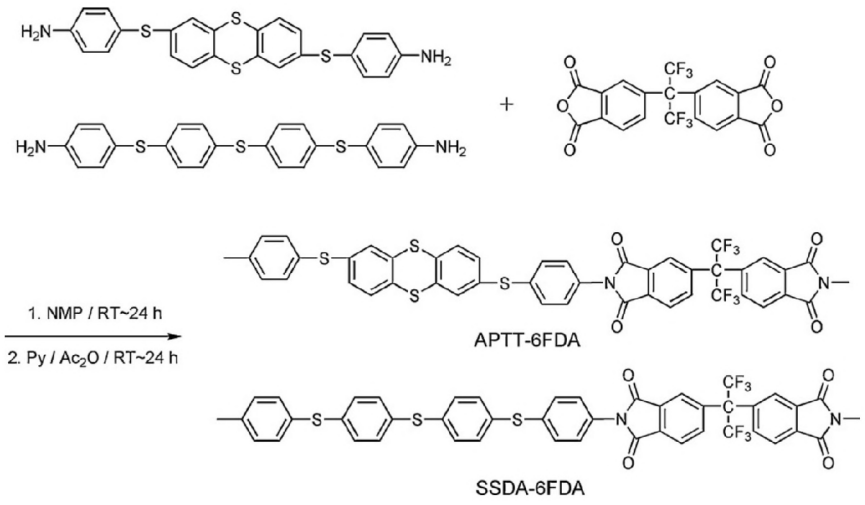


Scheme 81. Synthesis of functional polyimide, P(BPPO)-PI, containing oxadiazole moieties (electron donors) and phthalimide moieties (electron acceptors) [439].

thermal properties and flexibility as flexible devices. The polyimide is suitable for developing polymer memory due to it contains electro-donor diamine moiety and electro-acceptor imide moiety. The D–A interaction in the polyimides plays an important role in the memory effects.

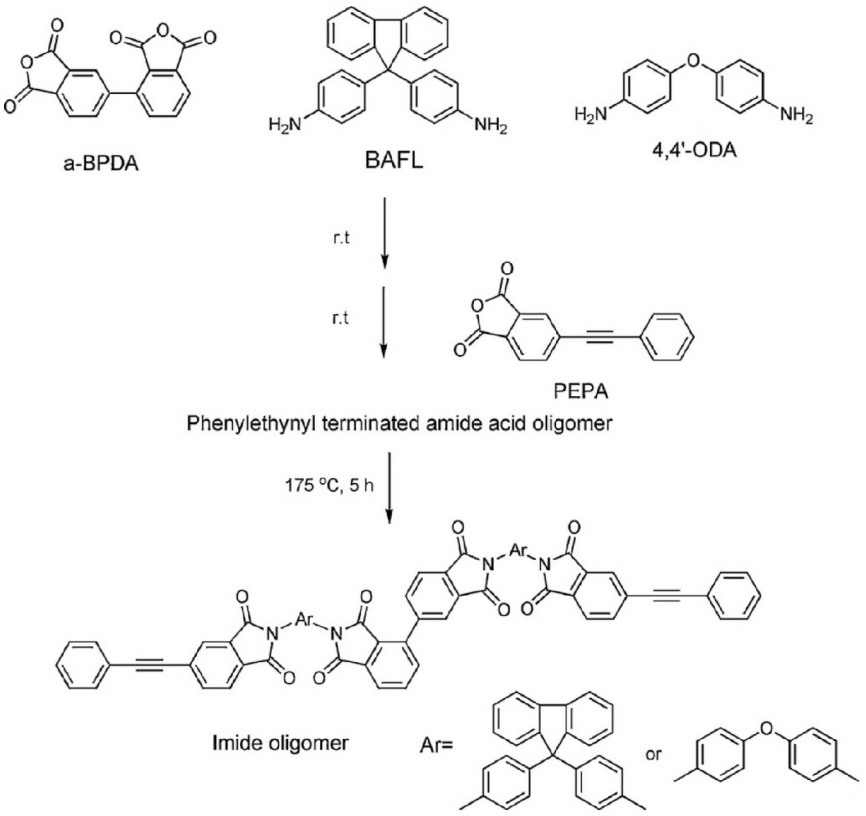
4.10. Fiber reinforced composites

Aromatic polyimides are well-known as high performance polymers due to their excellent thermal stability, mechanical and electronic properties; therefore, they are suitable to be used as a matrix resin in fiber reinforced composites. Usually, composites of carbon fibers and thermosetting polyimides are fabricated by routing an poly(amic acid) solution, because solubility of more than 30% is required to produce a prepreg [9,12]. In this route, water generated as a by-product of imidization in the fabricating process might result in voids in the composites. Therefore, polyimides prepared through a polycondensation reaction require extremely severe processing conditions for molding. For moldable materials and matrices of carbon fiber composites, many addition-type polyimides (*i.e.* imide oligomers terminated with reactive groups) have been developed [440–442]. However, there are drawbacks for the polyimide matrices such as brittle or relatively low T_g [443,444]. Yokota et al. developed imide oligomers containing asymmetric structures as shown in Scheme 83 and they had low melting temperatures and



Scheme 82. Synthesis of two new sulfur-containing polyimides, APTT-6FDA and 3SDA-6FDA [430].

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Scheme 83. Synthesis of the additive imide oligomers by Yokota and coworkers [440].

low viscosity. The cured polymers showed high T_g, high heat resistance, high thermo-oxidative stability and good fracture toughness. The polyimide containing fluorenylidene groups, which have bulky and rigid cardo structures, are good solubility and high heat resistance of polymers. Polyimide/carbon fiber composites were fabricated from the imide solution prepreg in two steps. First, the laid-up prepregs were heated at 300 °C for 30 min on a hot plate to remove the solvent. The prepregs were cured at 370 °C for 1 h under pressure using a hot press. The resultant composites had good quality with high T_g up to 347 °C and the optical micrograph of the composite showed no voids.

The polyimides containing special structures reviewed in Section 2.1.1 such as cardo, spiro and adamantane structures are also good candidates for using in the fiber reinforced composites. Some of the synthesis approaches reviewed in Section 2.2.2 are also useful to avoid generating voids due to the by-product water of imidization in the fabricating process in the composites. More breakthrough innovation using addition reaction rather than condensation reaction to avoid voids in the composites will enlarge the polyimide applications in fiber reinforced composites.

5. Conclusion and outlook

In this review, we have integrated the synthesis and applications of various functional polyimides. Since high molecular weight products were firstly synthesized by a two-stage polycondensation of pyromellitic dianhydride with diamines in 1955, the interest in this class of polymers has been growing steadily. Polyimides possess a number of valuable and unique physico-mechanical, electrical and chemical properties. It is possible to use polyimides for prolonged periods of time at temperatures up to 200 °C, whereas short-term applications are possible at temperatures up to 480 °C. In fact, polyimides exhibit excellent physico-mechanical properties in a broad temperature range and have exceptionally high radiation resistance and superior semiconductor properties. These characteristics allow polyimides to dominate the applications in many fields. This review is devoted to the description of the synthesis, properties and applications of polyimides. The unique advantages and specific functions of polyimides for different purposes and applications have been critically reviewed.

Companies of all sizes are involved in various aspects of polyimide research, and many academic laboratories

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have multidisciplinary efforts dedicated to expanding the applications of these polymers. With their unique features, polyimides will continue to find new industrial applications in the future. Further work will be required to develop polyimide materials with sufficient solubility profiles and processable properties, as well as to further optimize their performance. Novel polyimides with various functions are possible and can be explored using new monomers, polymer design principles, and modifications, such as using Suzuki couplings and alkylations. Polyimides can be used in novel applications in a variety of fields, and the excellent properties of polyimides will be developed and reported in the future.

KYOCERA Chemical Corporation developed a low temperature curing type polyimide precursor (KEMITITE CT4112), which can be cured at a lower curing temperature (180 °C) compared to general polyimide resins [445]. The polyimides are used widely as dielectric layers, insulation layers, as substrates for flexible printed circuits, and other applications. Therefore, the low curing temperature property of KEMITITE CT4112 will be very important in future electronic developments, such as the development of organic field effect transistors (OFETs) [446].

Acknowledgments

The authors are deeply indebted to Prof. En-Tang Kang (National University of Singapore) and Dr. Anu Stella Mathews (Pusan National University) for their variable comments. We also thank our students who collected the literatures for this review. Finally, the authors thank the National Science Council and the Ministry of Education, The Republic of China for the financial support of this work.

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