5.20 Polyimides

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5.20.1 Introduction

Aromatic polyimides (PIs) have been well known as one of the most important classes of high-performance polymers with a combination of exceptional mechanical, thermal, electrical, and optical properties along with chemical and solvent resistance.[1–11] The excellent combination of properties makes them suitable for a wide range of applications, from engineering plastics in aerospace industries to membranes for fuel-cell applications and gas or solvent separation. PIs exhibit high solubility, high optical transparency, low dielectric constant, low refractive index, low water absorption, and low coefficient of thermal expansion (CTE), which are being explored considerably for use as materials for interlayer dielectrics in electronic devices such as integrated circuits and in such optical devices as lenses, optical waveguides, antireflective coatings, and membranes for gas separation.[12–31] The first commercial PI was Kapton® (DuPont), made from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline possessing a high T_g (390 °C) and excellent mechanical properties, and it is still widely used in a variety of applications such as electrical insulating materials and as interlayer/intermetal dielectrics. The annual production in 1984 was about 1600 tons and the growth rate is estimated at 20% per year. There are many papers devoted to the syntheses and applications of PIs. This chapter focuses mainly on the synthesis and development of linear PIs and their extended functions.

5.20.1.1 Polymerization of Tetracarboxylic Dianhydrides and Diamines

5.20.1.1.1 Formation of poly(amic acid)s

As illustrated in Scheme 1, the polycondensation of PMDA (1) with an aromatic diamine (2) is a two-stage reaction leading to poly(amic acid) (PAA; 3) and then to PI (4).[32,33]

5.20.1.1.1(i) PAA formation in aprotic polar solvents

Various solvents can be used to perform the first step of the reaction. Dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and N-methylpyrrolidone (NMP) are the most commonly used. At first, the complexation between the tetracarboxylic dianhydride and the solvent occurs, as was observed in the case of PMDA.[34] Then, the nucleophilic attack of anhydride takes place, leading to PAA.

As would be expected, water has very deleterious effects. First, water can hydrolyze the tetracarboxylic dianhydride function of either the starting monomer or the growing chain. Indeed, it was observed that higher-molecular-weight PAA was obtained when PMDA was added in a solid form to the solution of diamine[35] because solid anhydrides are less sensitive to moisture than dissolved ones. Another effect of water is the hydrolysis of PAA. As a matter of fact, an ortho amide acid such as 2-[(phenylamino)carbonyl]benzoic acid (5) is hydrolyzed 10^5 times faster than the corresponding unsubstituted N-phenylbenzamide (6), by a cooperative effect[36] (Scheme 2).

The reaction temperature is generally room temperature or lower; higher temperatures induce imidization with evolution of water[37] and precipitation of low-molecular-weight PI, thus stopping the chain growth.[38]

When tetracarboxylic dianhydrides react with diamines, the viscosity for the same extent of reaction depends on the nature of the solvent in the following order: in DMSO > in DMAc > in DMF.[39] This observation is in agreement with a complexation of the PAA by the solvent.

5.20.1.1.1(ii) Synthesis of PAAs in other solvents

The adhesion properties of the PAA prepared from benzophenonetetracarboxylic dianhydride (BTDA) (7) and 3,3'-carbonyldianiline (8) are improved if a diglyme solution is used[40] (Scheme 3). In the case of a diamine with a low reactivity, such as 4,4'-sulfonyldianiline (9), the solvent enhances the basicity of the amine by complexation (10), and the obtained polymer exhibits a higher inherent viscosity than the same one prepared in NMP, DMAc, or DMF.[41]

5.20.1.1.2 Cyclization of PAAs

5.20.1.1.2(i) Thermal cyclization of PAAs

This reaction is generally performed by heating a PAA film cast from a low solid content of PAA solution (15–25% solid) in vacuo or in an inert atmosphere. Different thermal cycles have been studied as a function of the nature of the main chain (flexibility) and of the application required. Generally,
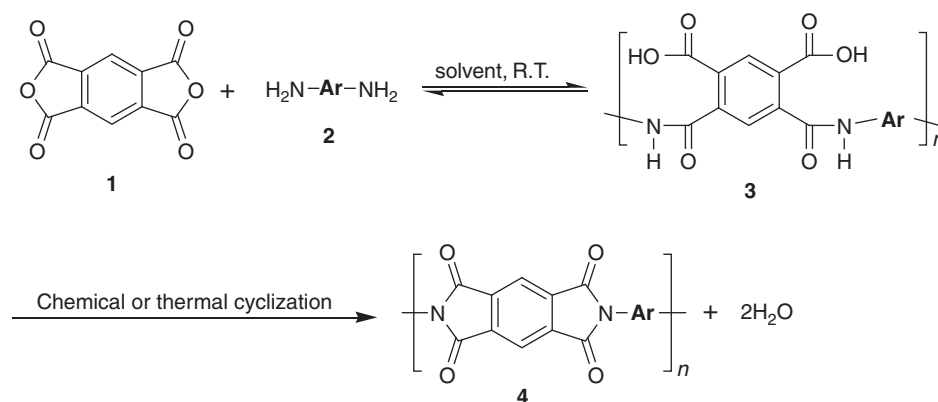
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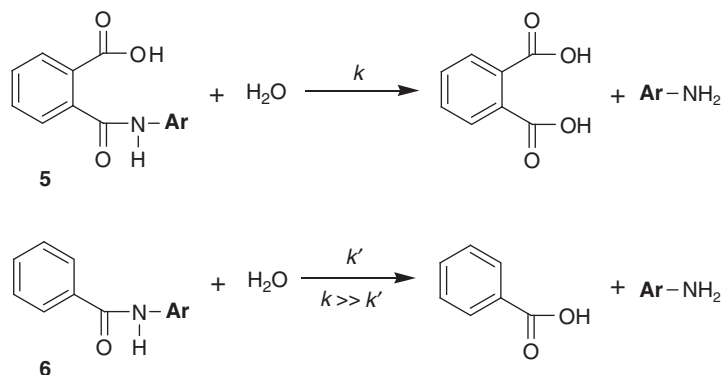
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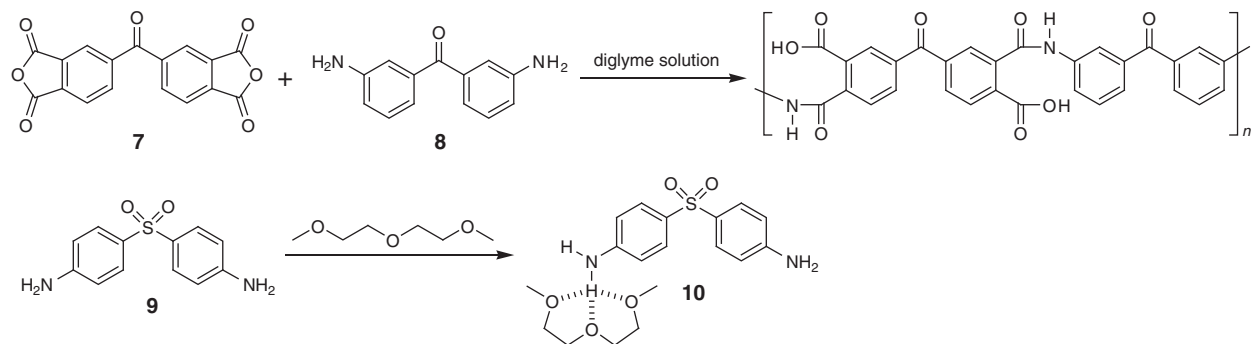
Scheme 3
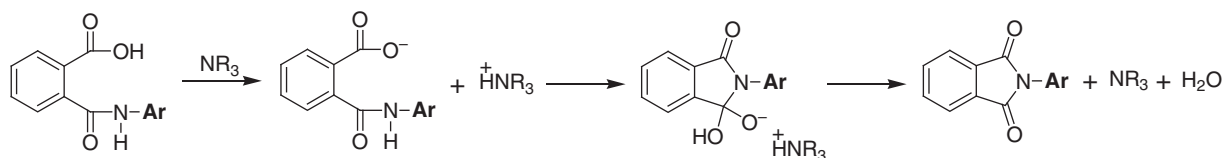
Scheme 4

the solvent is removed at a temperature between 100 and 150 °C, and then the temperature is increased to 300 or 350 °C.[39] The loss of weight observed with PAA by thermogravimetric methods at 170, 185, and 200 °C was interpreted as a two-stage imidization via a complex between PAA and the solvent (DMAc).[42] A process of complexation/decomplexation between amic acid and NMP was also demonstrated by Russian researchers.[43] In the case of PAA derived from PMDA and ODA, the rate of thermal cyclization at 161 °C was increased by adding a tertiary amine,[42] according to Scheme 4. Correlation between the basicity of the starting diamine and the rate of cyclization has been mentioned by Soviet workers;[44] the higher the pK_a of the diamine, the higher the rate constant of ring closure.

Competition between cyclization and depolymerization was observed in the case of polymers obtained from condensation of PMDA with 4,4′-, 3,4′-, and 3,3′-carbonyldianilines (11). These polymers provide brittle films between 175 and 225 °C, but the films become flexible at 300 °C.[45] Using Fourier transform infrared (FTIR) spectroscopy, Young and Chang[46] observed the changes in the anhydride C=O stretching band at $1850 \, cm^{-1}$, which reached a maximum intensity between 150 and 200 °C and diminished in intensity at higher temperatures during the cyclization of PMDA-ODA PAA. This phenomenon was also observed for the soluble polymer (12) carrying flexible linkages (Scheme 5). The anhydride band appeared when the film was heated to 152 °C and showed a maximum intensity at 175 °C and then was not detectable

11

12
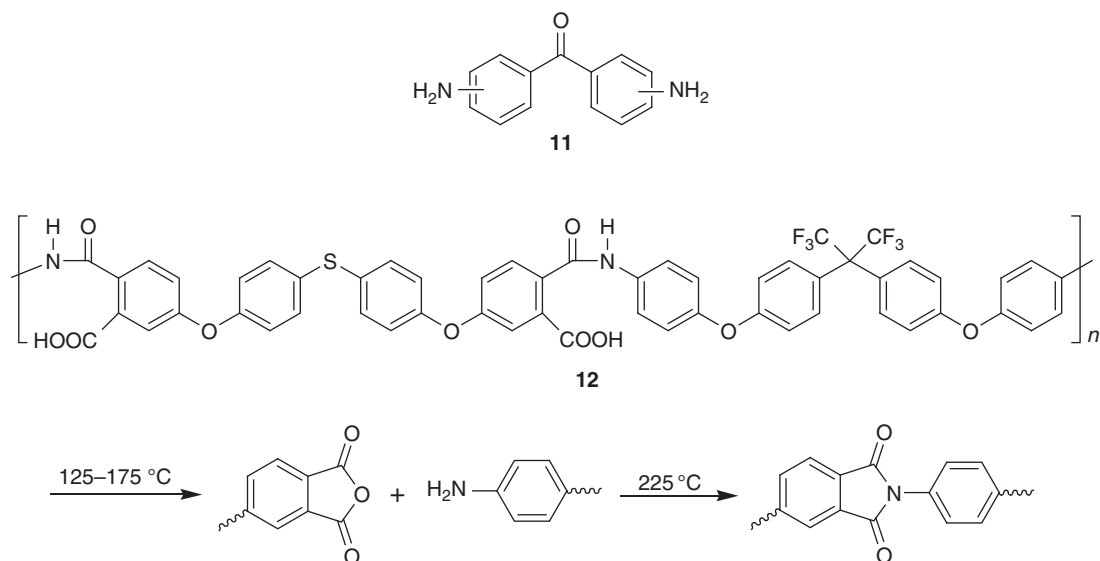
Scheme 5

at 225 °C. The good solubility of these polymers made size-exclusion chromatography and inherent viscosity characterization possible, which agreed with an initial reduction in molecular weight before final solid-state polycondensation.

5.20.1.1.2(ii)   Chemical cyclization of PAAs

PAA can be dehydrated by chemical processes. By using dicyclohexylcarbodiimide (DCC), polyisoimide (13) could be obtained[47] as shown in Scheme 6, and then rearranged into imides by heating or chemical treatment with acetate ions.

Another chemical dehydration extensively studied involves the use of an anhydride in the presence of organic bases such as pyridine or trialkylamine,[48] the mechanism of which was studied on a model compound.[49] When dehydration was performed with acetic anhydride using triethylamine, only imide was obtained, but pyridine gave a mixture of predominantly imide and isoimide; tertiary amine plays a catalytic role. The suggested mechanism is given in Scheme 7. The first step is the formation of a mixed anhydride, and then two independent routes can give imide or isoimide. Isoimide formation is kinetically favored via intramolecular O-acylation through an ion pair in equilibrium with the mixed anhydride. The imide form is thermodynamically favored. In the case of PAA cyclization, viscosity measurements show that no degradation and no cross-linking occur during cyclization. However, chemical cyclization with trifluoroacetic anhydride gives only the isoimide product.

5.20.1.1.3   Polymerization of a tetracarboxylic dianhydride with a diamine without solvent

In microelectronics, PIs are used as dielectric coatings by the process of spin coating of the PAA solutions, solvent removal, and thermal imidization. To avoid problems due to solvent evaporation, PMDA and ODA are coevaporated at 200 °C under a vacuum on a substrate. The diffusion rate of each reactant could be controlled in order to keep the stoichiometric balance. The substrate is kept at 25–50 °C, and the resulting deposited film contains 30–50% of unreacted product and PAA. Final polymerization could be accomplished by heating at 175 and 300 °C for 30 min in nitrogen, respectively, but only lower-molecular-weight PIs could be obtained (M_w = 13 000). Thermal properties of the PI obtained by the vapor deposition method are very similar to the corresponding PI by conventional two-step methods, but the dielectric properties are better (ε = 2.9, tan δ = 0.008 for the former vs. ε = 3.2, tan δ = 0.01 for the latter).[50]

5.20.1.1.4   Polymerization of a tetracarboxylic dianhydride with a diamine in phenolic solvents: Poly(ether imide)s

Tetracarboxylic dianhydrides containing diaromatic ethers were prepared by the aromatic nucleophilic substitution of nitroimide (14) by phenoxide dianions (15),[51] followed by alkaline hydrolysis and cyclodehydration to tetracarboxylic dianhydrides (16) (Scheme 8). The reaction between the tetracarboxylic dianhydride and the diamines was conducted in phenol, cresol, or chlorinated solvents, in combination with inert diluents such as toluene or chlorobenzene. The reaction mixture was heated to 160–180 °C and the water was removed azeotropically; the polymer was recovered by precipitation in methanol. The scope of the reaction for formation of aromatic polymers via nitro group displacement has been reviewed by Takekoshi.[52]

5.20.1.2   Polymerization of Tetracarboxylic Dianhydrides with Diisocyanates

In 1967, it was observed that aromatic and aliphatic diisocyanates react with PMDA to yield PIs.[53] Moldable PIs were obtained by the reaction of a mixture of diisocyanates with a tetracarboxylic dianhydride.[54] The reaction could be activated by water,[55] metallic alkoxides,[56] and alkali-metal lactamates.[57] The catalytic effect of water is interpreted as arising from a
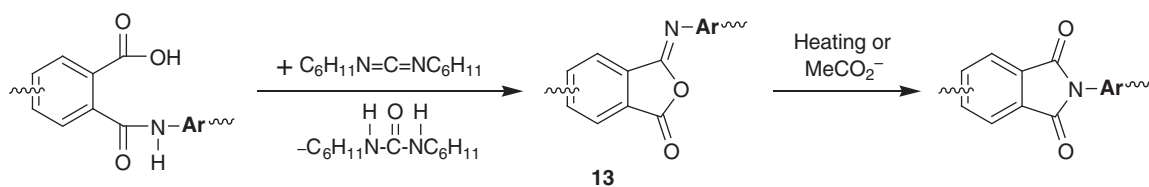
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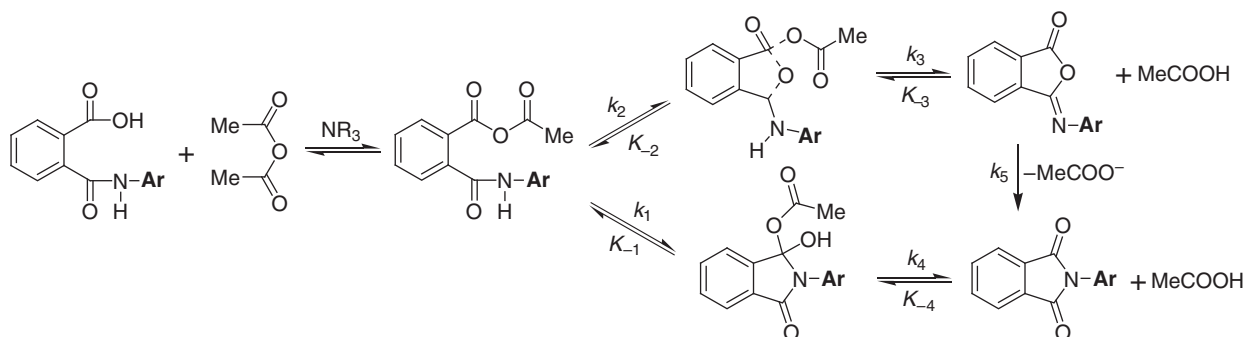
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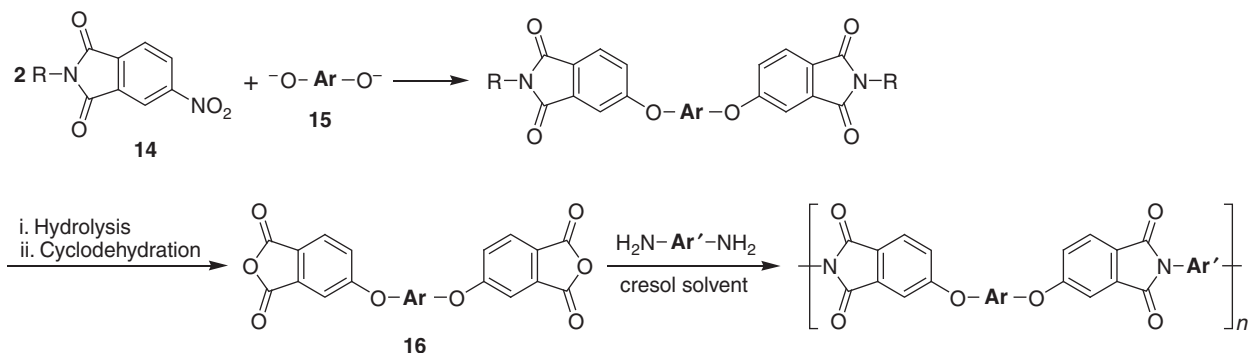
Scheme 8
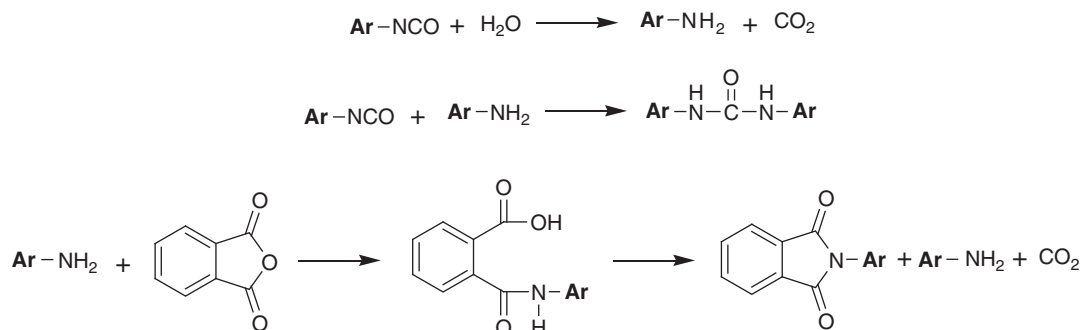
Scheme 9

partial hydrolysis of the isocyanate,[58] followed by reaction of the aromatic amine with the anhydride (**Scheme 9**).

Meyers[59] isolated a soluble seven-membered ring intermediate (**18**) from PI (**19**) in the reaction of PMDA with diisocyanate monomer (**17**) in DMF at 130 °C (**Scheme 10**), and then the intermediate could release carbon dioxide by further heating. This mechanism was supported by IR spectra and increasing yield of the seven-membered intermediates when the reaction was carried out in CO_2 pressure.

Although the synthesis from isocyanates could afford PIs with only lower molecular weight, the reaction is used industrially to produce PI-2080 (Upjohn). The polycondensation of trimellitic anhydrides with diisocyanates was an early patent[60]

and has been said to give soluble poly(amide imide)s (PAIs) with high molecular weight in N-methyl-2-pyrrolidinone (NMP).[61] The PAI prepared by this process is used for wire insulation.

5.20.1.3   Polymerization of Tetracarboxylic Dianhydrides with Silylated Diamines

Silylated diamines (**20**) were obtained by reaction of trimethyl-chlorosilane with diamines. The resulting silylated diamines could be used to react with the tetracarboxylic dianhydride in solvents such as tetrahydrofuran at room temperature, giving a poly(amide trimethylsilylester) (**21**) by a transfer of the silyl
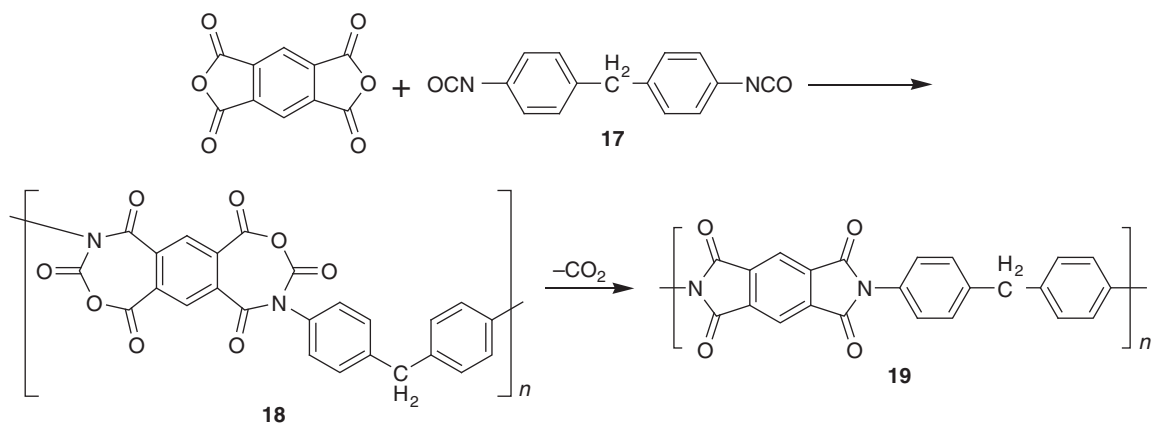
Scheme 10
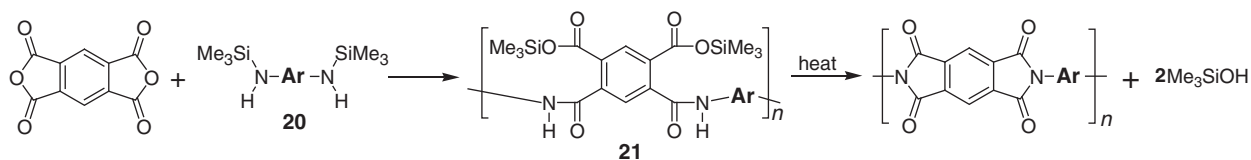
Scheme 11

protective group to the carboxylic group which was subsequently cyclized to PIs with elimination of trimethylsilanol by heating at 150 °C for 30 min (Scheme 11). It was also reported that the diamines fully substituted by trimethylsilyl groups could react with anhydrides to form an imide ring by giving disiloxane as a by-product.[62]

5.20.1.4   Polymerization of Diester Diacids with Diamines

Many applications, such as adhesives or matrices for composites and coatings in electronics, need high solid content solutions. The reactivity of diester diacids is lower than that of the corresponding tetracarboxylic dianhydrides, so it is possible to obtain soluble low-molecular-weight chain-extendable PIs by reaction with diamines.

Aliphatic PIs were prepared in 1955 from dialkyl tetracarboxylates (22) and aliphatic diamines by a two-stage melt condensation of the resulting organic salts (23) at 110–140 °C, then at 250–300 °C (Scheme 12).[63]

In the case of aromatic diamines, formation of the diesters of PAA by heating the reactants at 150 °C has been claimed.[64] The formation of an intermediate salt between the diester diacid and the aromatic diamine was observed before polycondensation.[65]

Reactions of more acidic alcohols, such as chloro- or fluoropropanols or ethyl glycolate with anhydrides, give ester acids with better leaving groups than the case of alkyl ester acids.[66] Reactivity with aromatic amines could be greatly enhanced due to the fast elimination of alcohol followed by reaction of the amine with anhydride (Scheme 13).

5.20.1.5   Formation of PIs via Nucleophilic Nitro Group Displacement Reactions

The application of aromatic nucleophilic substitution reaction to polymer synthesis has been well documented. Industrial polymers such as polysulfone, poly(phenylene sulfide), and poly(ether ketone) are produced by this synthetic route.[67] As mentioned, nitro groups activated by the imide function react very smoothly with phenolate anions. This reaction has been extended to prepare poly(ether imide)s and poly(sulfide imide)s from arylenebis(nitroisoindoledione) (24) with bisphenol and bisphenylthiol salts, respectively (Scheme 14).[68,69]
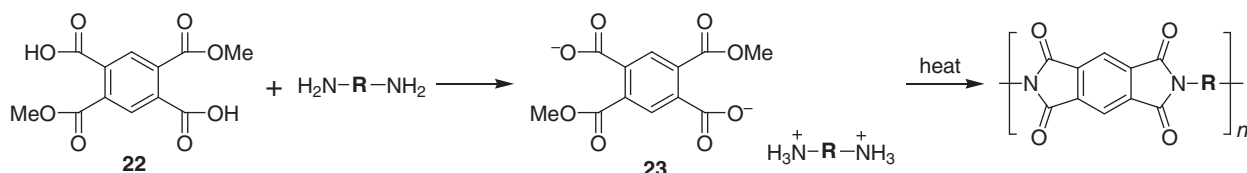
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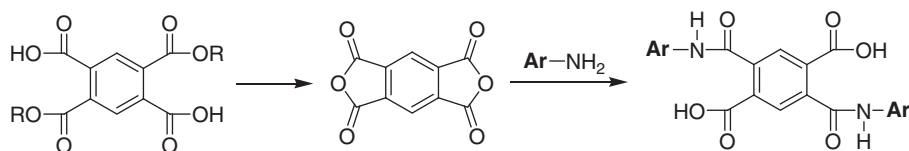
Scheme 13
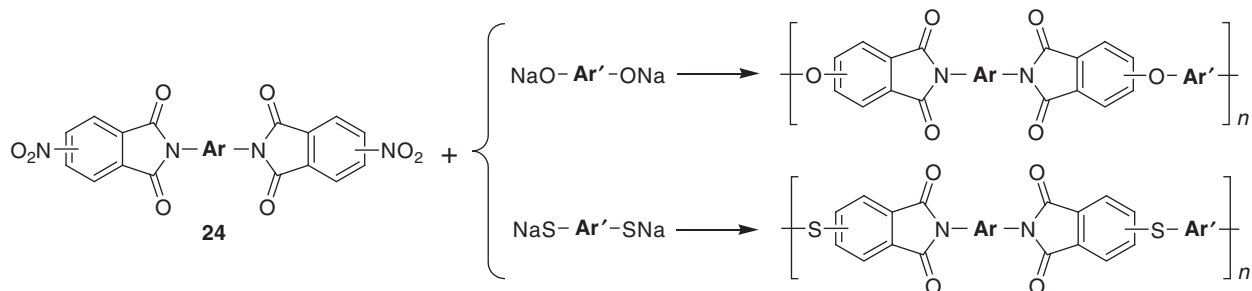
Scheme 14

5.20.1.6 Linear Polymerization of Bismaleimides by Michael Addition

The maleimide carbon–carbon double bond is strongly electrophilic and can react with nucleophilic reagents such as amines and thiols as shown in Scheme 15.[70] The addition with thiols has to be carried out in protic solvents in order to avoid the side reactions of intermediate anionic maleimido species with maleimide, resulting in cross-linking.

Polymerization of maleimide with aromatic diamines took place in *m*-cresol solution and polymers with high molecular weights could be obtained. However, in the case of aliphatic diamines such as 1,2-ethanediamine and 1,3-propanediamine (26), could react with 1,3-bismaleimidobenzene (25) by a ring-opening reaction to yield the corresponding polymaleamide (27) (Scheme 16).

5.20.1.7 Palladium-Catalyzed Carbonylation Polymerization for the Formation of PIs

A synthetic method for the formation of PI from the reactions of bis(*o*-diiodobenzene)[71] or bis(*o*-iodoesterbenzene)[72] compounds with diamines was carried out in the presence of CO, a palladium catalyst and a base in a dipolar aprotic solvent. A goal of isolating the intermediate amide esters from the *o*-iodo esterbenzene was not realized. Even though all the examined conditions indicated that the intermediate amide esters were not observed, this reaction for preparing PIs was found in model compound approach to be an efficient route to cyclic imides (Scheme 17).[71–73]

5.20.2 Conventional PI

5.20.2.1 Poly(ether imide)s

Aromatic PIs are well-known high-performance polymers that have excellent thermal, mechanical, and electrical properties. However, the problems for most aromatic PIs are their poor processability caused by limited solubility in organic solvents and high melting and softening temperatures. Therefore, much effort has been spent on preparing tractable aromatic PIs by changing the chemical nature of the molecular structures to some degree while maintaining their desired properties. One

of the strategies to increasing solubility and lowering melting/softening temperature is the introduction of flexible bonds in the polymer backbone. The ether group is the most popularly flexible linkage introduced into the polymer backbone. It has been generally recognized that aryl-ether linkage imparts properties such as better solubility and melt-processing characteristics. On the other hand, introduction of bulky substituents, noncoplanar structures, and spiro skeletons into the polymer backbone could also increase the solubility due to the decreased packing and crystallinity. Recent studies demonstrated the PIs derived from ether-bridged diamines with trifluoromethyl (CF_3) groups are thermally stable and organosoluble polymeric materials with low moisture uptake, low dielectric constant, and high optical transparency.[74] Therefore, we summarize the recently reported poly(ether imide)s and divide them into two parts which are as follows.

5.20.2.1.1 Organosoluble poly(ether imide)s

Many efforts on the modification of the backbone structure of PIs to obtain soluble and/or thermoplastic PIs without sacrificing their excellent thermal and mechanical properties have been devoted to extend the utility of PIs by incorporation of bulky groups such as pyridine with pendant phenyl (28), fluorenyl (29), and triphenylamine (TPA) (30) groups (Scheme 18).[75–77]

Chern *et al.*[78–80] synthesized new PIs derived from asymmetric diamines and aromatic tetracarboxylic dianhydrides (Scheme 19). Due to the introduction of the asymmetric di-*tert*-butyl groups into diamine monomer, the resulting PIs exhibit excellent solubility and retain other desirable properties such as low dielectric constant and high thermal stability.

Yang and Hsiao[81–86] reported several types of poly(ether imide)s with light color and good physical properties from the bis(ether–anhydride)s and various aromatic diamines via a conventional two-stage procedure that included a ring-opening polyaddition to yield PAAs, followed by chemical or thermal imidization to the poly(ether imide)s (Scheme 20). These poly(ether imide)s could be cast into light-colored and tough films with low dielectric constants. They also exhibited moderately high T_g and good thermal stability. Thus, these poly(ether imide)s demonstrated a good combination of properties and
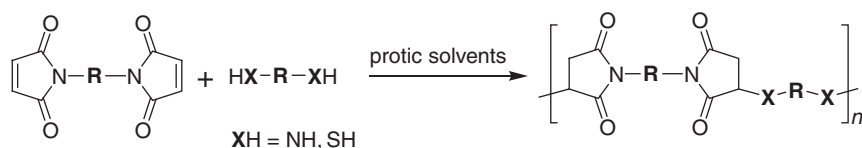
Scheme 15
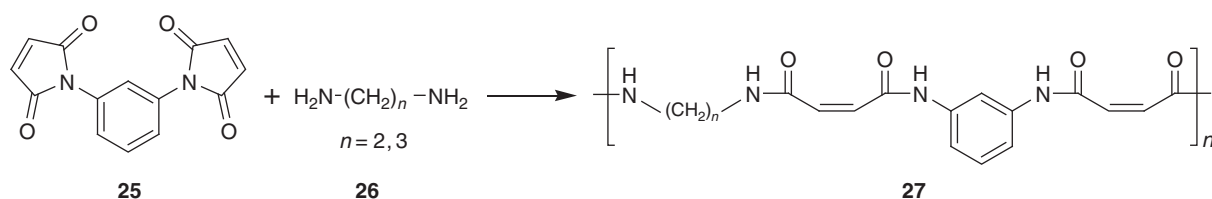
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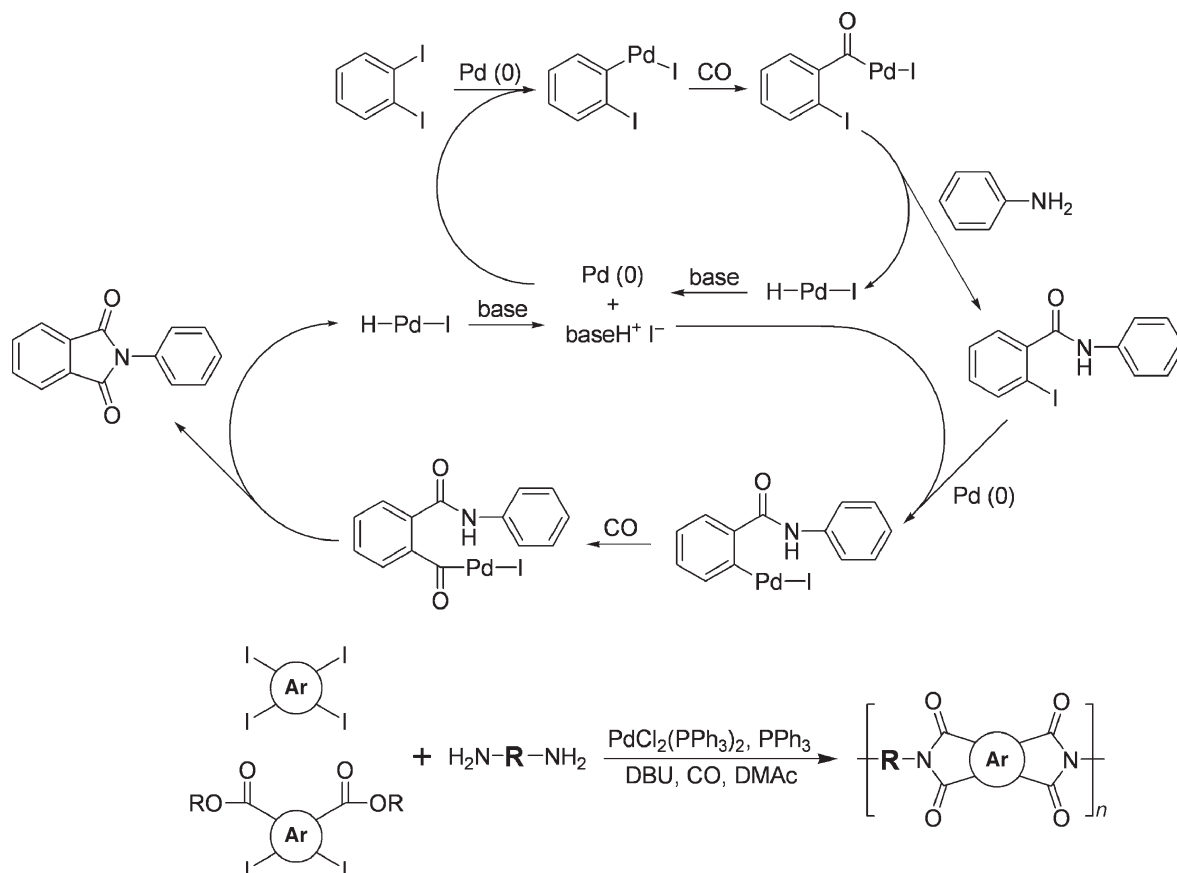
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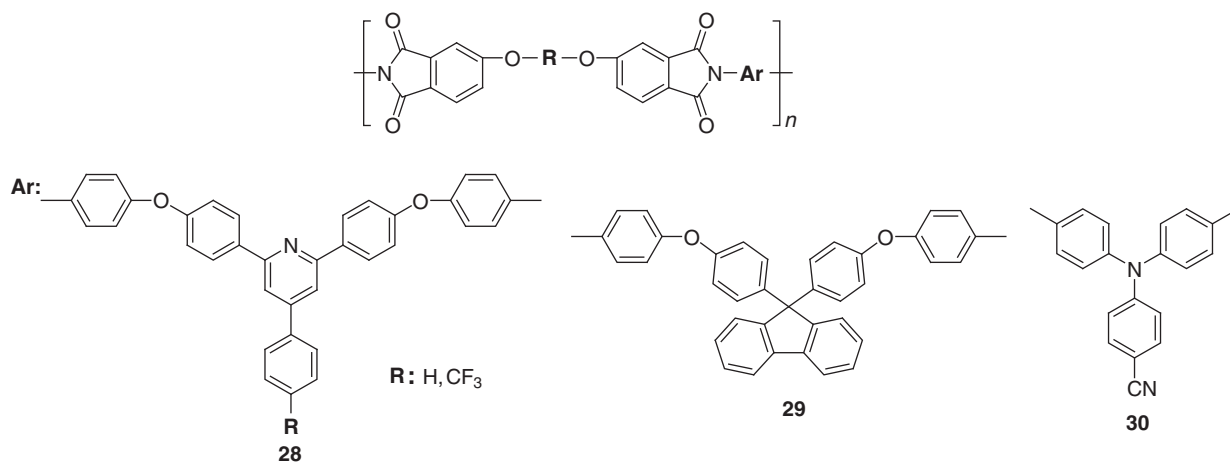
Scheme 18

may be of interest for microelectronic and optoelectronic applications.

5.20.2.1.2 Fluorinated poly(ether imide)s

Banerjee et al.[87–89] took a different strategy to impart solubility while retaining good thermal properties in the PIs (Scheme 21). They reported the synthesis of semifluorinated PIs based on rigid monomers containing indane (31), phthalimide (32), and anthracene (33) moieties. All the obtained

polymers exhibited excellent solubility in various solvents including dichloromethane with a very low boiling point. The resulting poly(ether imide)s were amorphous and revealed good thermal stability with good mechanical strength. Besides, these poly(ether imide)s could be solution cast into light-colored films with good optical transparency and low moisture uptake. Hence they are promising materials for optoelectronic applications and as gas separation membranes.

Scheme 19

Ar:

Scheme 20

Ar:
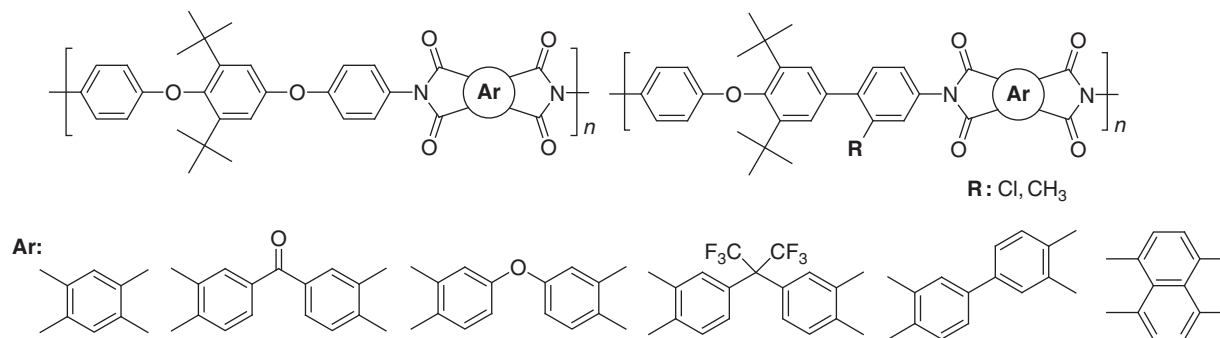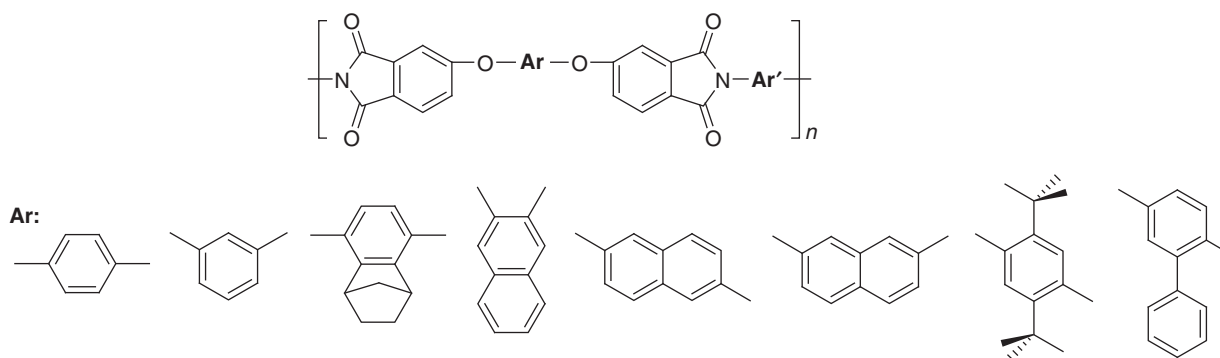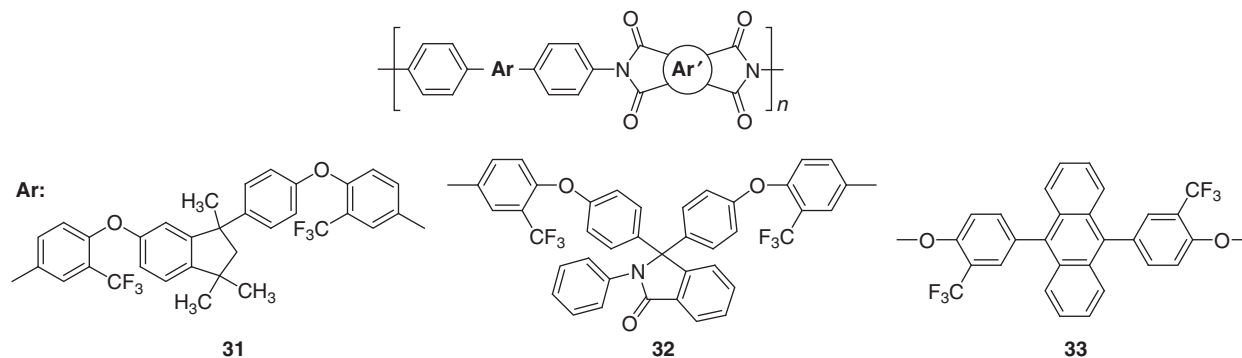
Scheme 21

Yang and Hsiao[82–85,90–92] reported the synthesis of soluble and light-colored fluorinated poly(ether imide)s using bis(ether–anhydride)s and various fluorinated aromatic diamines by a conventional chemical imidization (Scheme 22). All polymers made from fluorinated diamines showed light color, high optical transparency, good solubility, low dielectric constant, and low water absorption.

New family of fluorinated PIs with moderate to high molecular weights have been synthesized from the newly synthesized bis(ether-amine), 1,5-bis(4-amino-2-trifluoro-methylphenoxy)naphthalene (**34**), 1,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (**35**), and various aromatic tetracarboxylic dianhydrides by two-step thermal or chemical imidization method (Scheme 23).[93,94] Because

of the presence of CF_3 and aryl ether groups along the polymer backbone together with the asymmetric structure of the repeat unit, the obtained PIs exhibited good solubility in many organic solvents and could be solution cast into transparent, flexible, and tough films. The PIs also showed high thermal stability, high optical transparency, and low dielectric constants.

In 2009, fluorinated polynaphthalimides were successfully synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and trifluoromethyl-substituted aromatic bis (ether–amine)s by high-temperature solution polycondensation in m-cresol (Scheme 24).[95] The obtained polynaphthalimides exhibited good solubility in many organic solvents and could afford flexible and ductile films with
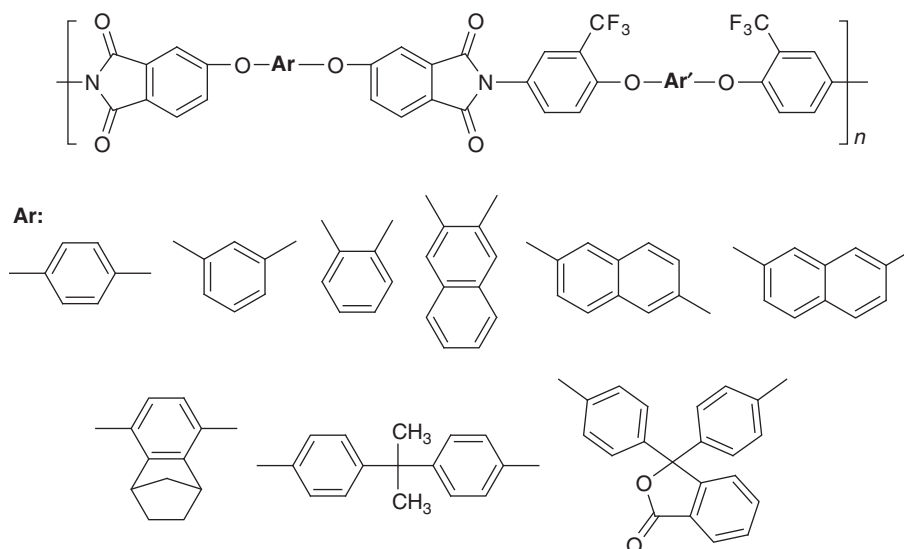
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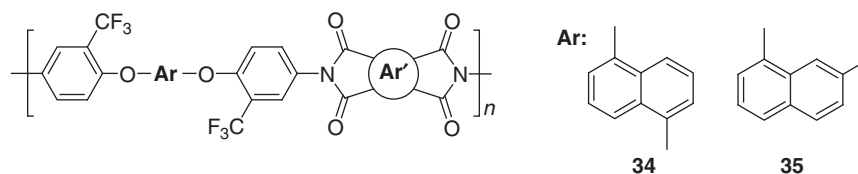
Scheme 23
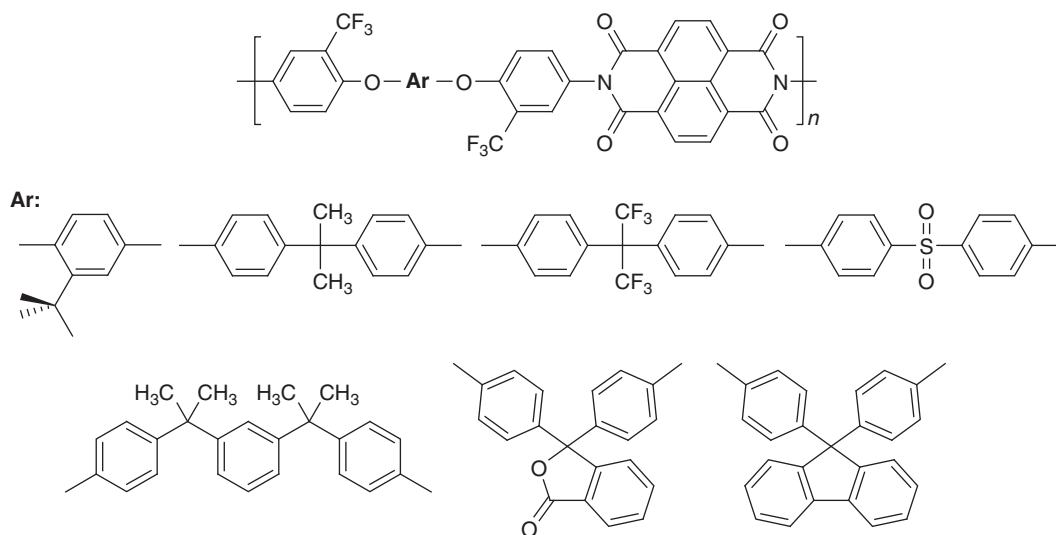
Scheme 24

excellent mechanical properties and high thermal stability. These properties suggest the potential usefulness of these novel polynaphthalimides in high-tech applications.

5.20.2.2   Poly(amine imide)s

Poly(amine imide)s were first prepared in 1992 from 4,4'-diaminotriphenylamine (**36**) and various tetracarboxylic dianhydrides by Imai et al.[96] (**Scheme 25**). In the past, new arylamines, such as p-anisidine (**37**), hydroxy-aniline (**38**), naphthylamine (**39**), 1,4-phenylenediamine (**40**), and benzidine (**41**), were used to prepare poly(amine imide)s (**Scheme 26**).[97–102]

Recently, Liou et al.[103–105] reported the synthesis of high-performance poly(amine imide)s carrying the TPA (**42**), N-phenylcarbazole (**43**), and methoxy-substituted TPA (**44, 45**) as
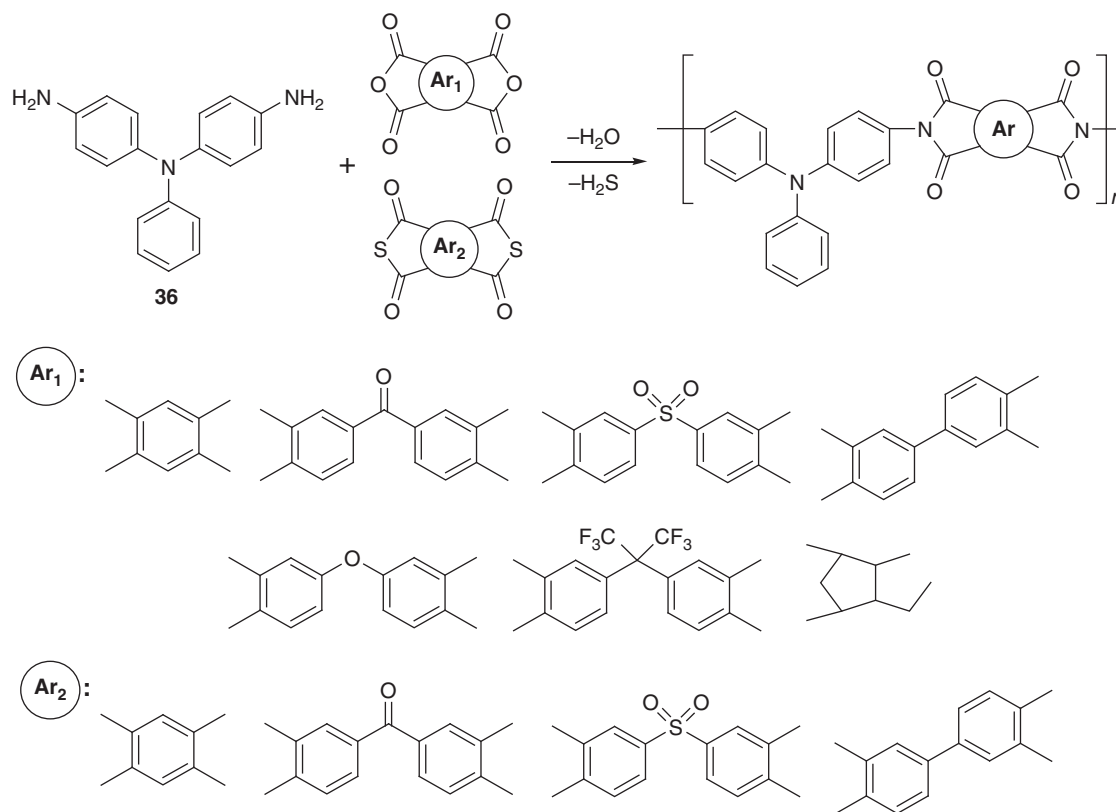
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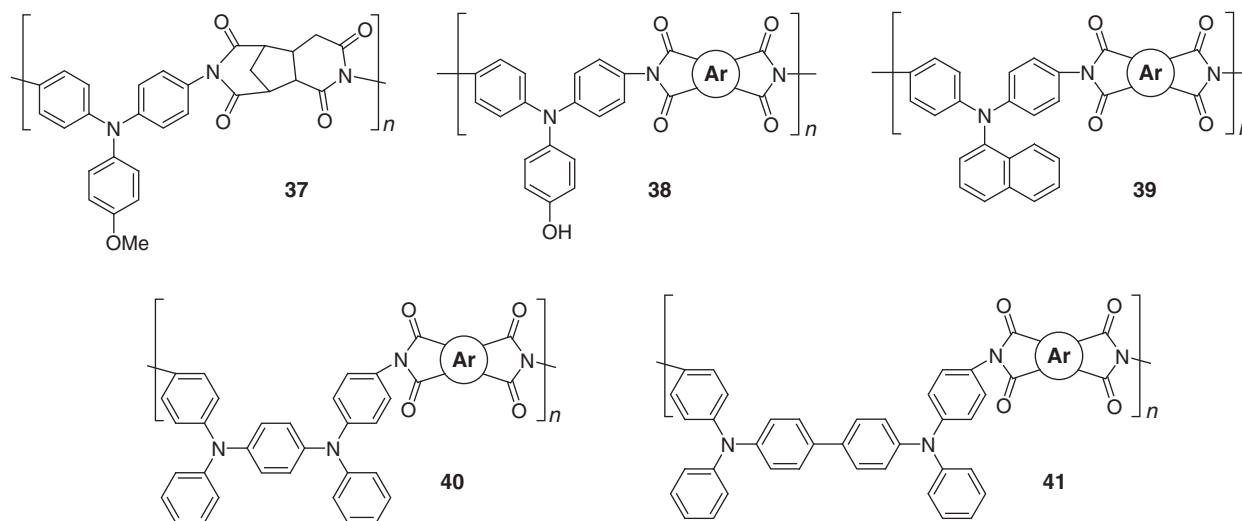
Scheme 26

electroactive functional moieties (Scheme 27). All the nitrogen-containing PIs revealed high thermal stability, organosolubility, good film-forming ability, high electrochemical reversibility, and good electrochromic behavior.

5.20.2.3   Poly(sulfide imide)s

Conventional sulfur-containing polymers afford high transparency, high refractive indices, and good adhesion, although the

thermal stability of the polymers was often limited owing to their intrinsic thermally less stable structures. Recently, high refractive index PI coatings with high thermal stability have been proposed for optoelectronic applications, such as charge-coupled device (CCD) image sensors and complementary metal oxide semiconductor (CMOS) image sensors. Ueda et al.[106–117] reported new poly(sulfide imide)s prepared from sulfur-containing diamine or tetracarboxylic dianhydrides by a two-step polycondensation procedure to develop optical
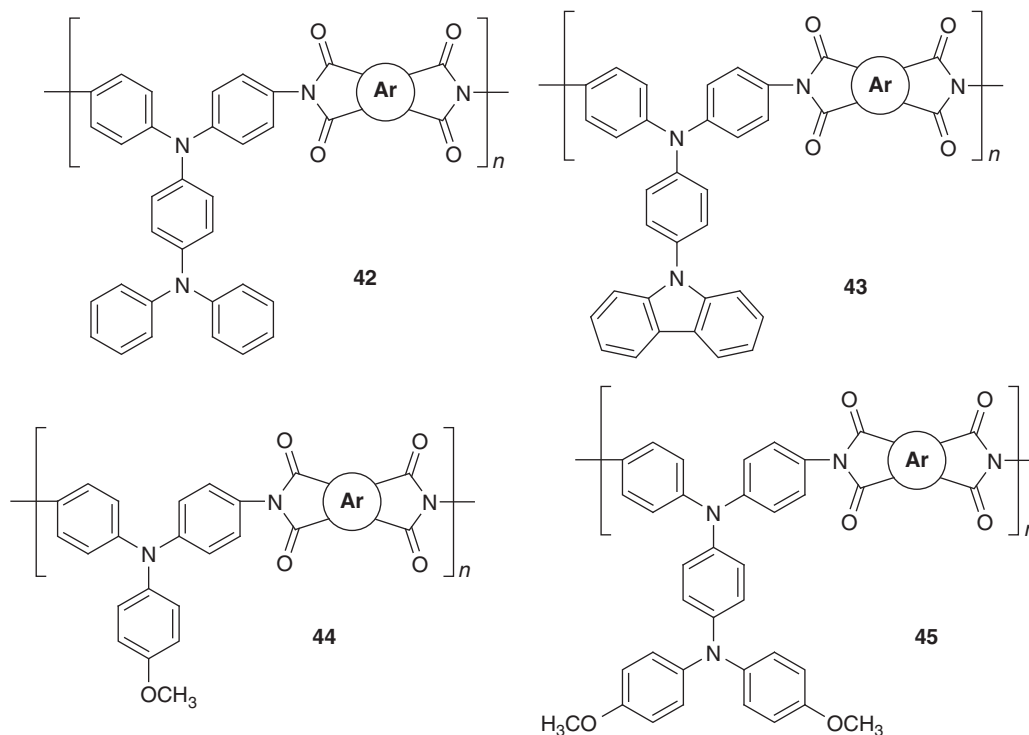
Scheme 27

polymers exhibiting high refractive indices, combined with low birefringence, high thermal stability, and high optical transparency. The diamines or tetracarboxylic dianhydrides with sulfur atoms were used to prepare PIs containing *p*-phenylenedisulfanyl, *p/m*-sulfonylbis(phenylenesulfanyl), dibenzothiophene, fluorene, thianthrene, tetrathiaanthracene, thiophene, selenophene, pyridazine, and pyrimidine moieties (**Scheme 28**). These PIs exhibited good transparency in the visible region with a transmittance >80% at 500 nm, high refractive indices higher than 1.7200, and low birefringence lower than 0.0200. All these properties are desired for advanced optical materials.

5.20.2.4   Phosphorus-Containing PIs

Phosphorus (P)-containing polymers have been known for many years to exhibit the primary advantage of flame retardancy, and

they are increasingly gaining popularity over their halogen counterparts because they generally generate less toxic combustion products. The incorporation of organophosphorus functionality either within the main chain or as groups appended to it has led to the production of inherently fire-retardant polymers.

In 2001, Liou and Hsiao[118] prepared two series of phosphorus-containing aromatic poly(ester amide imide)s via low-temperature solution polycondensation from phosphorus-containing aromatic di(ester-amine)s (**46**) with three imide ring-preformed diacid chlorides (**47**) (**Scheme 29**). All the polymers had good solubility in many polar aprotic solvents and could be cast into transparent, tough, and flexible films. Good solubility, moderate T_g or T_s values suitable for molding, reasonable thermal stability, and good flame-retardant properties make these phosphorus-containing poly(ester amide imide)s as promising high-performance polymeric materials.
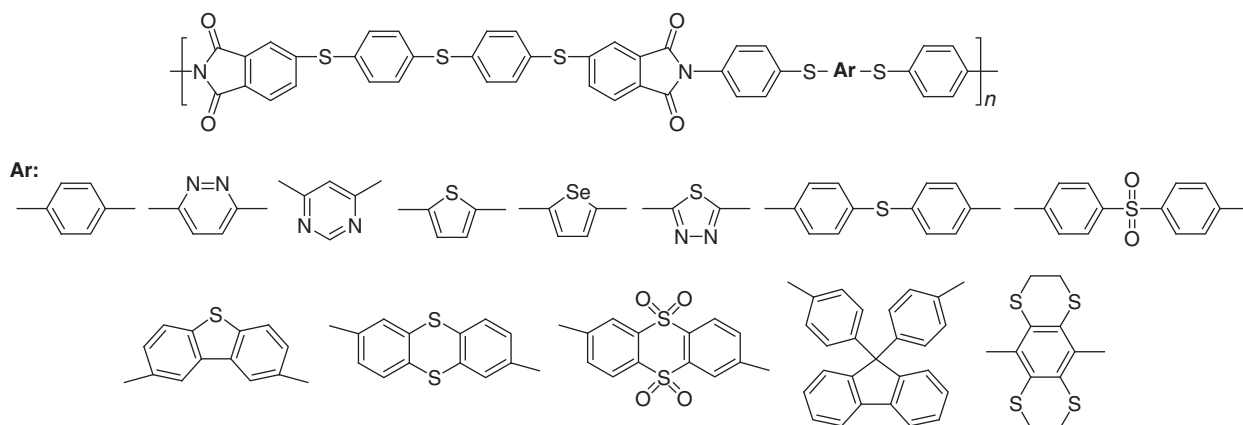
Scheme 28
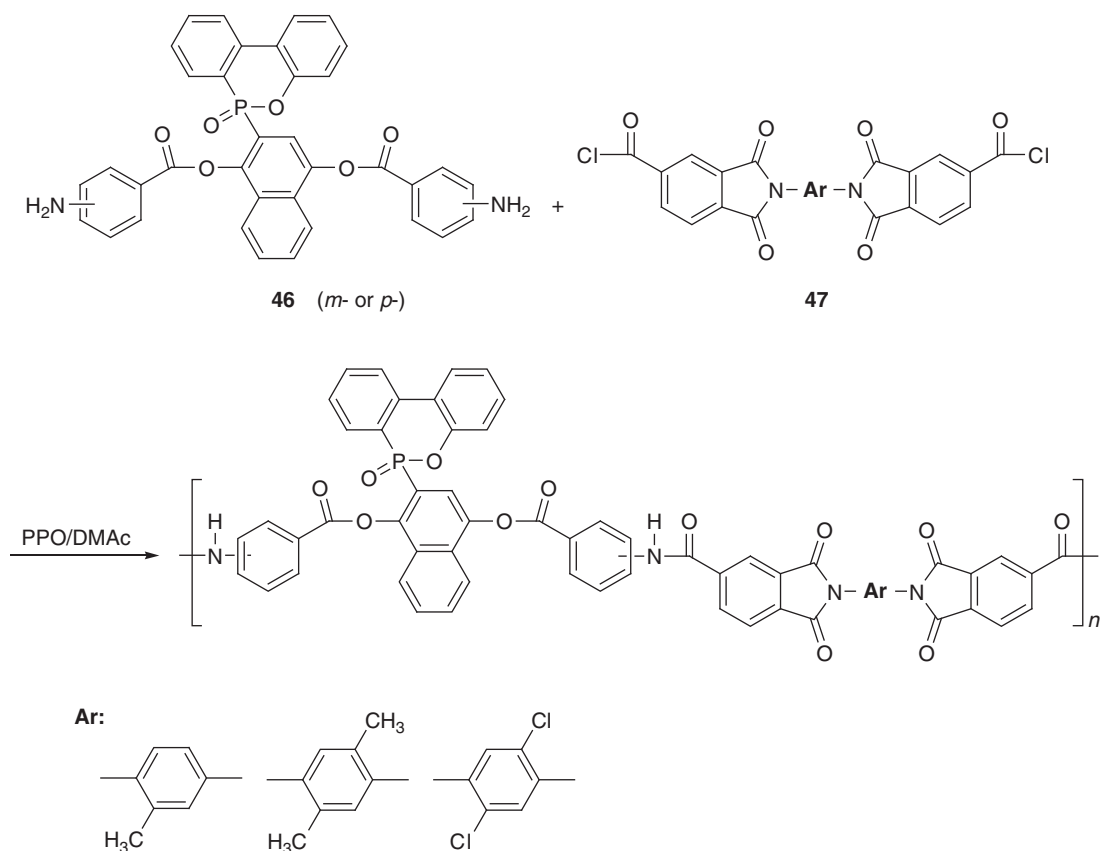
Scheme 29

Since 2007, Lin *et al.*[119,120] reported phosphorus-containing aromatic diamines and its derived PIs ((**Schemes 30** and **31**). The bulky biphenylene phosphinate pendant is responsible not only for the improved solubility but also for the suppressed coloration. The combination of flexibility, high glass transition temperature, high antioxidative stability, excellent flame retardancy, and improved organosolubility makes the phosphorus-containing PIs as promising polymers for electronic applications, especially in the field of halogen-free flexible printed circuit (FPC) boards, in which flame retardancy and high T_g are essential.

The phosphorus-containing PI/SiO$_2$ nanocomposites were prepared from the imidization of PAA of PMDA/ODA/triethoxysilane (**Scheme 32**).[121] In addition to the microstructure and
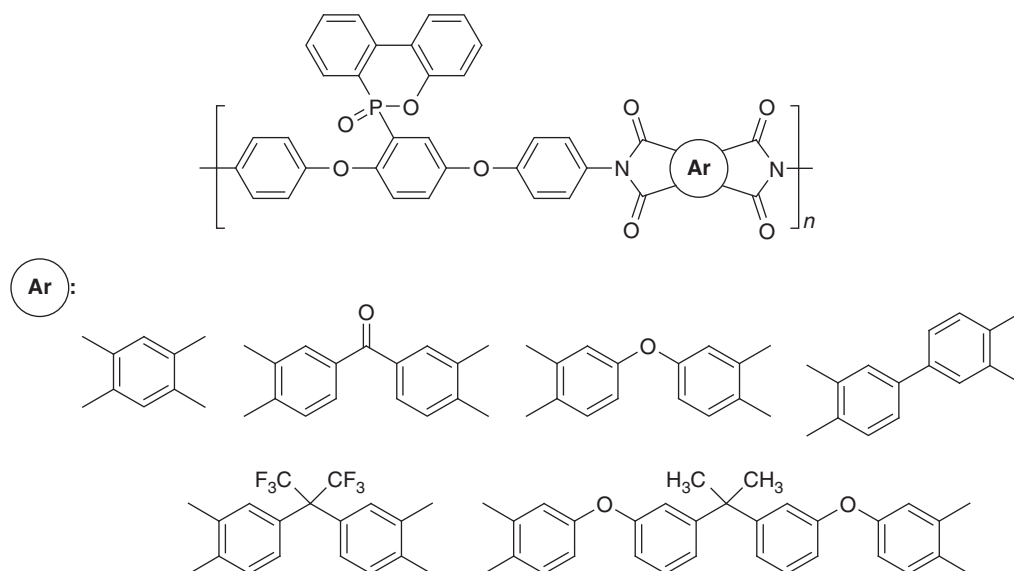
Scheme 30
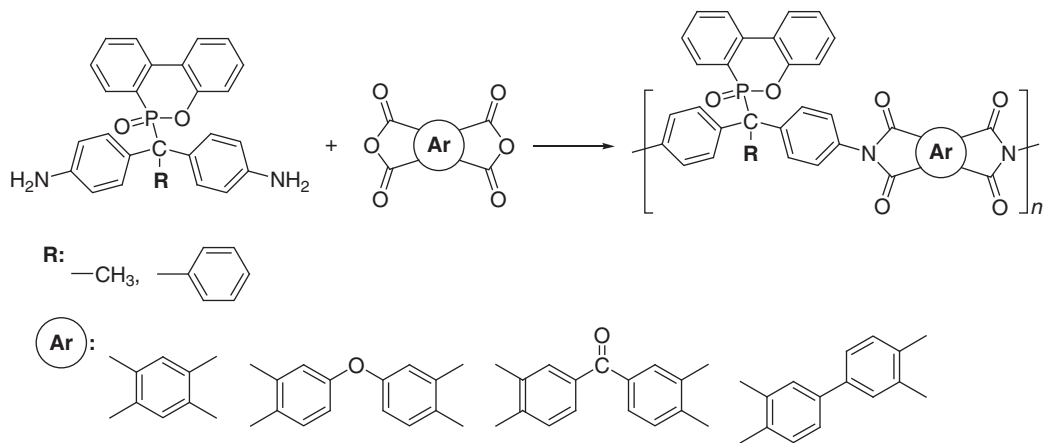
Scheme 31
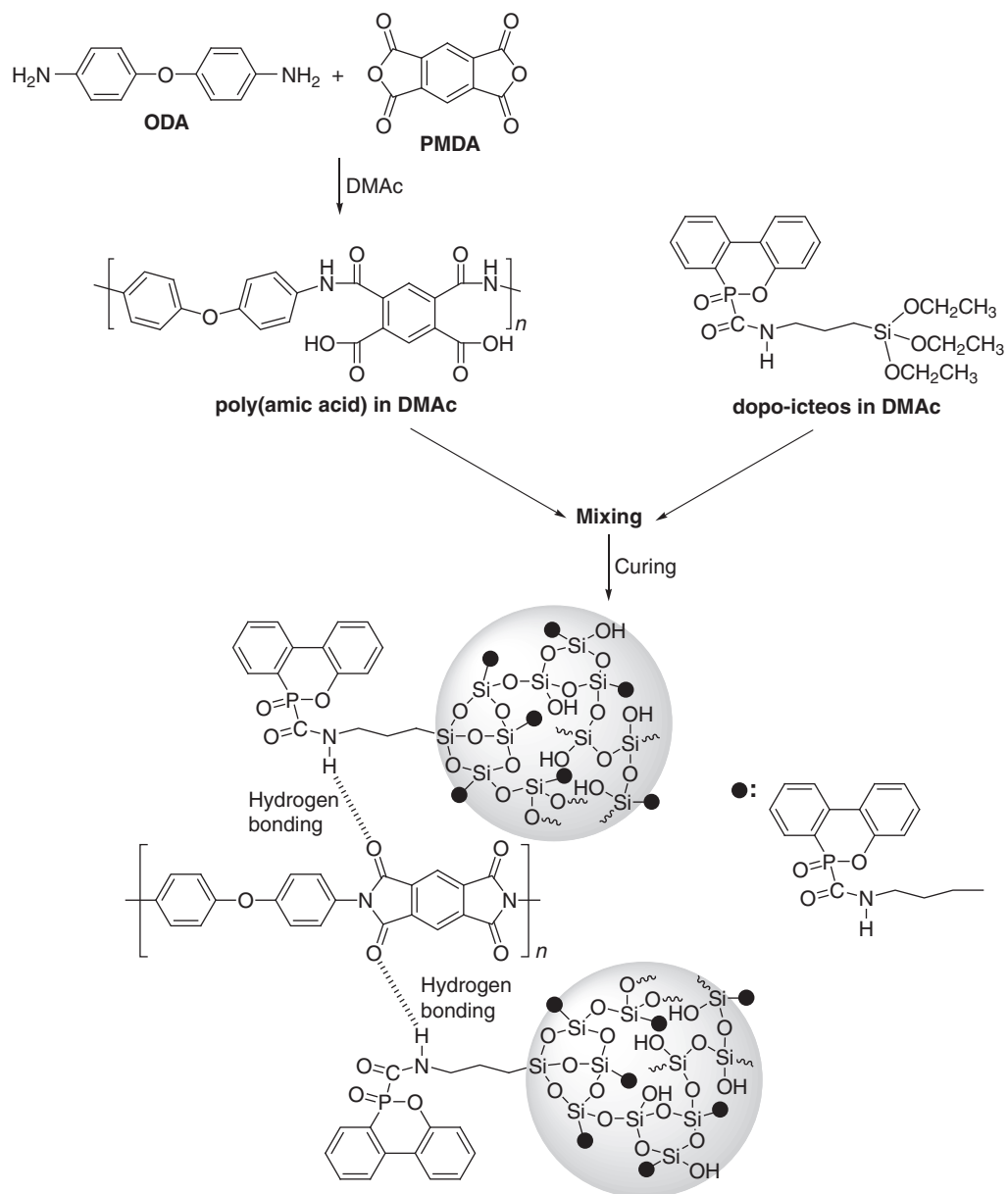
Scheme 32

morphology, dielectric, flame retardant, and thermal properties of the organic–inorganic hybrids were investigated. The results of scanning electron microscopy (SEM) and atomic force microscopy (AFM) surface analysis indicated that the particle size of silica domain in the PI/SiO$_2$ system was nano-scale. The possible hydrogen bonding site of the four carbonyl groups in the repeating unit of PI made the distribution of silica network more homogeneous and the silica domain size in PI/SiO$_2$ hybrids smaller.

5.20.2.5 Hyperbranched PIs

Hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in various fields from coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science (Scheme 33).[122–127] This chapter deals with hyperbranched PIs mainly from a synthetic point of view.

Chen and Yin[128–130] reported a negative-type hyperbranched photosensitive PI based on a triamine, 1,3,5-tris (4-aminophenoxy)benzene (48), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. The photosensitive cinnamate groups were incorporated at the periphery of the polymer by the reaction of cinnamoyl chloride with the terminal phenol groups of the fully imidized hyperbranched PI, which was obtained via the end group modification of the anhydride-terminated hyperbranched PAA (Scheme 34). The polymer showed good thermal stability and excellent solubility even in acetone and 1,1,2-trichloroethane. Photolithographic property
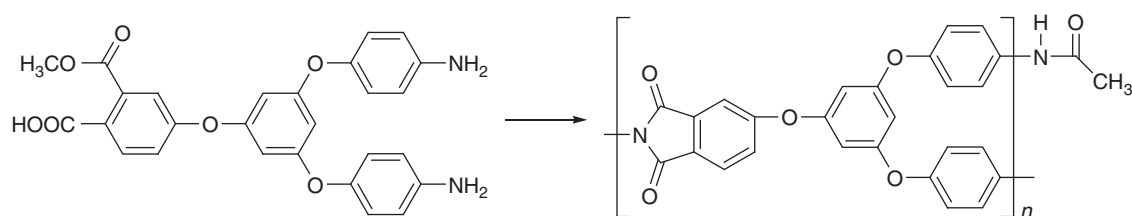
Scheme 33
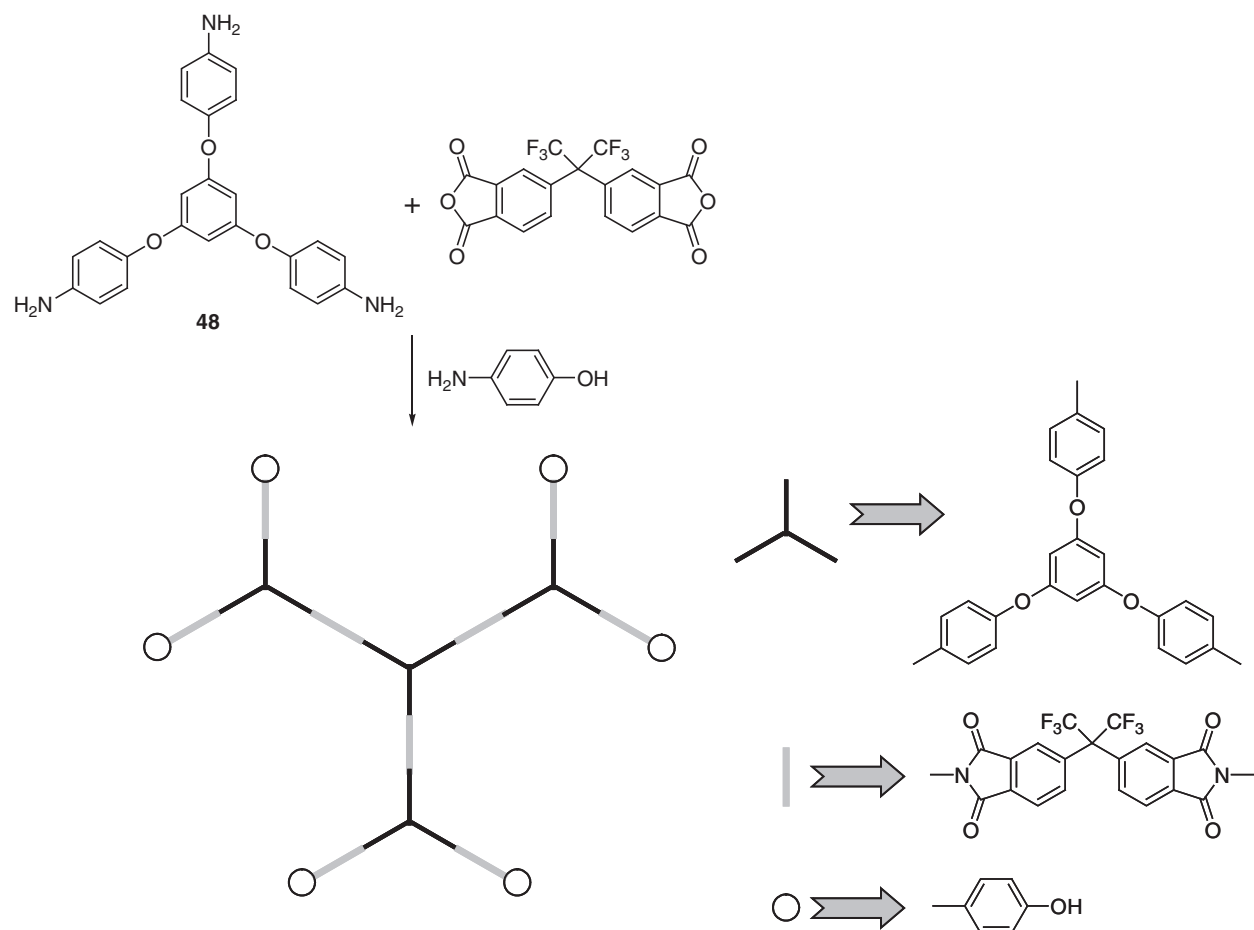
Scheme 34

of the polymer was examined by UV exposure. SEM analysis revealed that highly resolved patterns with a line width of 10 μm were obtained, and a well-defined line as thin as 3 μm in width could be patterned, demonstrating its good photolithographic property.

Okamoto et al.[131,132] prepared two types of hyperbranched PIs (amine terminated and anhydride terminated) by controlling the manner of monomer addition and the monomer molar ratio. The resultant hyperbranched PI membranes were tough enough for gas permeation measurements based on the chemical reaction between the terminal functional groups of the hyperbranched PIs and the cross-linking agents leading to the combination of globular hyperbranched macromolecules. The amine-terminated hyperbranched PI membranes generally displayed higher gas permeability coefficients than the anhydride-terminated ones. The prepared TPA-cross-linked hyperbranched PI membranes displayed better separation performance than that of the linear analogues and many other linear polymeric membranes (Scheme 35).

Kakimoto *et al.*[133,134] designed a AB_2 monomer from a template of the repeating unit of the hyperbranched PIs by nonideal $A_2 + B_3$ polymerization via a multistep synthesis (Scheme 36). Hyperbranched PIs having the same repeating unit as that by nonideal $A_2 + B_3$ polymerization were prepared from this new AB_2 monomer by direct self-polycondensation in the presence of diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate. The results revealed that hyperbranched PIs by nonideal $A_2 + B_3$ polymerization have a certain extent of chain entanglement and intermolecular interaction. A comprehensive analysis finally suggested that hyperbranched PIs by AB_2 self-polymerization have a compact highly branching structure, whereas those by nonideal $A_2 + B_3$ polymerization have a low-branching density topology.

5.20.2.6 Bismaleimide-Type PIs

It is also well known that thermosetting PIs derived from bismaleimides (BMIs) exhibit excellent thermal and mechanical properties, thus making them extremely popular for advanced composites and electronics. BMIs can be self-polymerized through their reactive maleic double bonds to give highly cross-linked, rigid, and brittle PIs. On the other hand, nucleophilic difunctional reagents such as diamines and dithiols could react with the strongly electrophilic maleic double bonds to afford linear and high-molecular-weight PIs. In
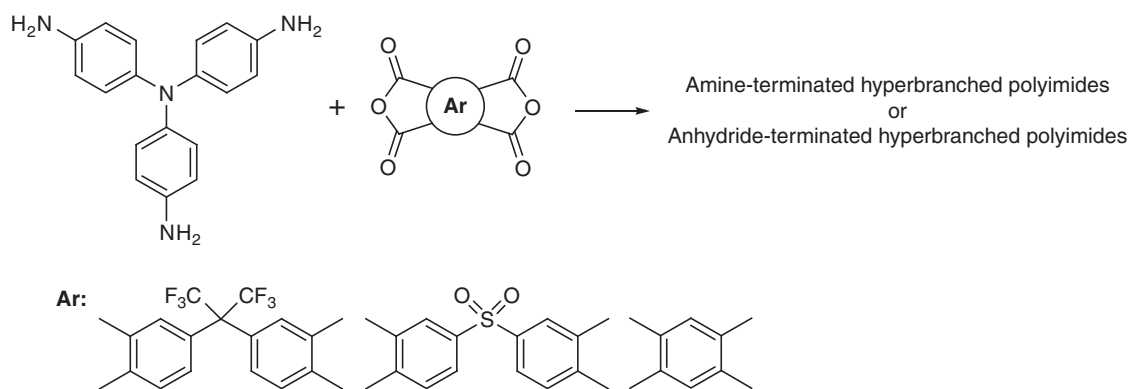
Scheme 35
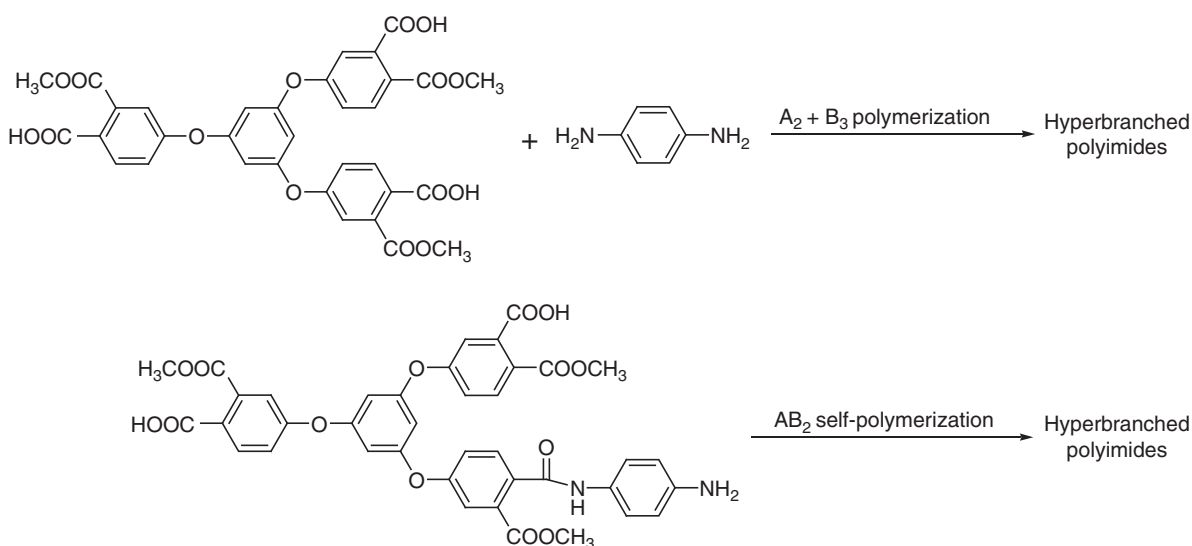
Scheme 36
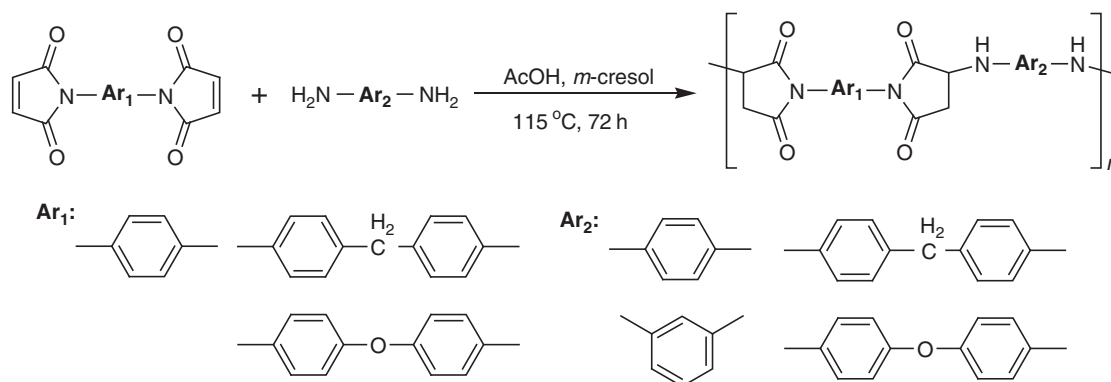
Scheme 37

particular, diamines have been used to extend BMIs, resulting in polyaspartimides and polyimidothioethers (PITEs).

Crivello[135] reported a detailed investigation of the condensation of aromatic amines and maleimide in 1973 (Scheme 37). White and Snider[136] then prepared and compared the reactions of the secondary diamines with BMIs via Michael polyaddition (Scheme 38).

Recently, new linear polyaspartimides were obtained via Michael addition from several functional diamine-based BMIs

with various aromatic diamines in m-cresol (Scheme 39).[137–141] These polymers exhibited an amorphous morphology with good solubility, high T_g values, and good thermal stability, which could be considered to be new processable polymeric materials.

Through the Michael addition, thermally stable nonlinear optical (NLO) hyperbranched systems consisting of azobenzene dyes have been successfully synthesized (Scheme 40).[142] All of the obtained polymers were soluble in DMF, DMAc, and
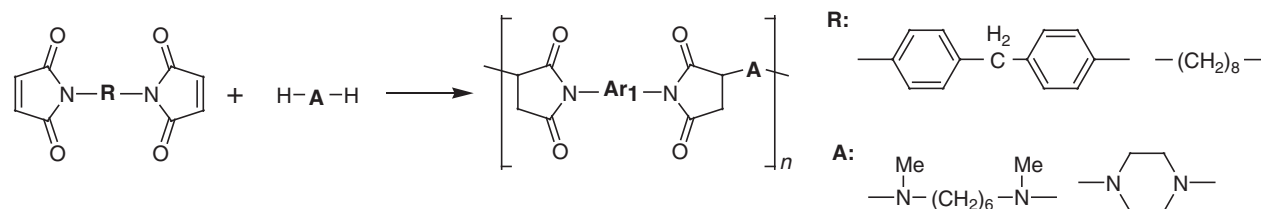
Scheme 38
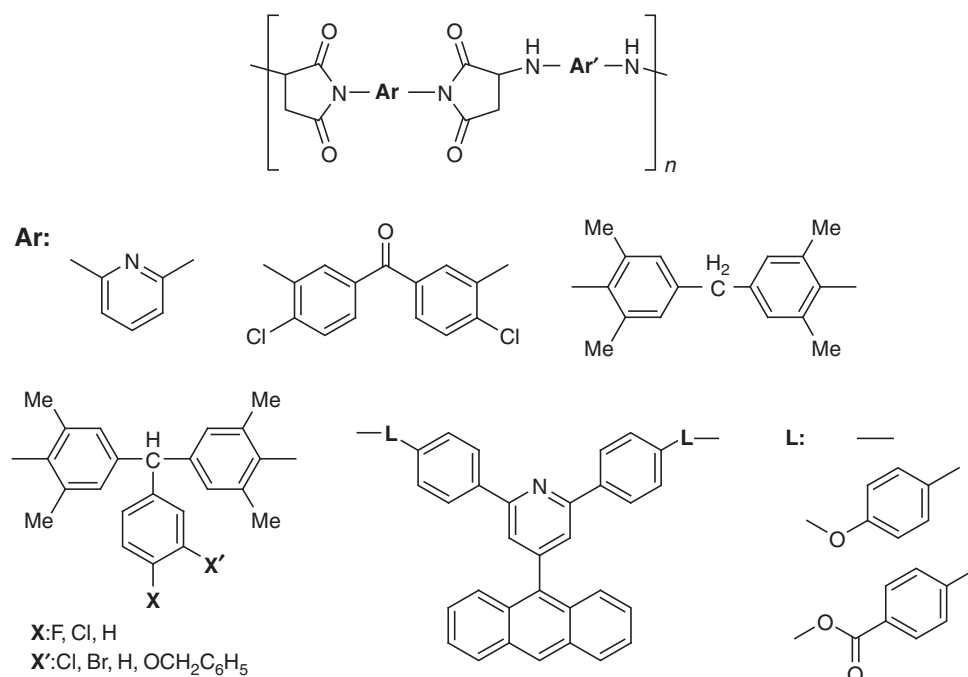
Scheme 39
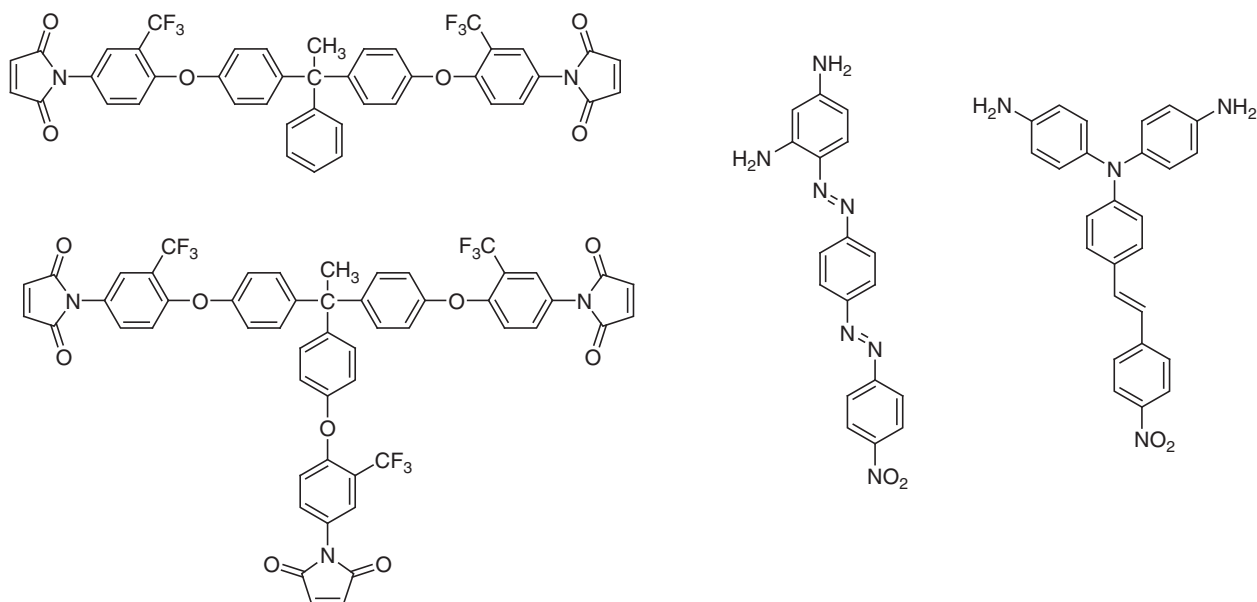
Scheme 40

DMSO. By incorporating the polyaspartimide structure into the NLO-active hyperbranched polymers, thermal stability was greatly enhanced. All the hyperbranched polymers exhibited better NLO properties than their corresponding linear analogues due to the presence of a spherical shape and site isolation effect. Waveguide properties could be also achieved for all the NLO polymers.

The condensation of maleimide compounds with hydrogen sulfide and bisthiols was studied in several model systems by Crivello[143] in 1976 (**Scheme 41**). BMI compounds undergo rapid, exothermic polymerization with thiol-containing compounds in *m*-cresol and basic catalyst to give linear PITEs with high viscosity. PITE copolymers can readily be prepared by mixing two BMI monomers together in solution and then adding a catalyst and hydrogen sulfide. Random copolymers were obtained in this manner and revealed properties as a combination of those of the two homopolymers; they exhibited only one glass transition temperature and one melting point.

Yen and Liou,[144] therefore, used this facile approach to prepare a series of thermoplastic PITEs (**Scheme 42**). These polymers were highly soluble in various organic solvents and

showed useful thermal stability associated with high glass transition temperatures. These optically isotropic thermoplastic PITEs exhibiting well-balanced optical properties are promising candidates for optical waveguide or encapsulant materials in advanced optical applications for both solution casting and injection molding techniques.

5.20.2.7 PI Copolymers

The intractable characteristics of aromatic PIs are major problems as a result of high melting points and insolubility. To overcome this drawback, copolymerization is an effective approach and various copolyimides have been developed. For example, poly(ester imide)s, **PAIs**, poly(pyrrolone imide)s (**PPIs**), poly(benzimidazole imide)s (**PBIIs**), poly(benzoxazole imide)s (**PBOIs**), and poly(benzothiazole imide)s (**PBTIs**) have been developed as an alternative material offering a compromise between excellent thermal stability and processability. Some of the representative copolyimides were selected and summarized as follows.
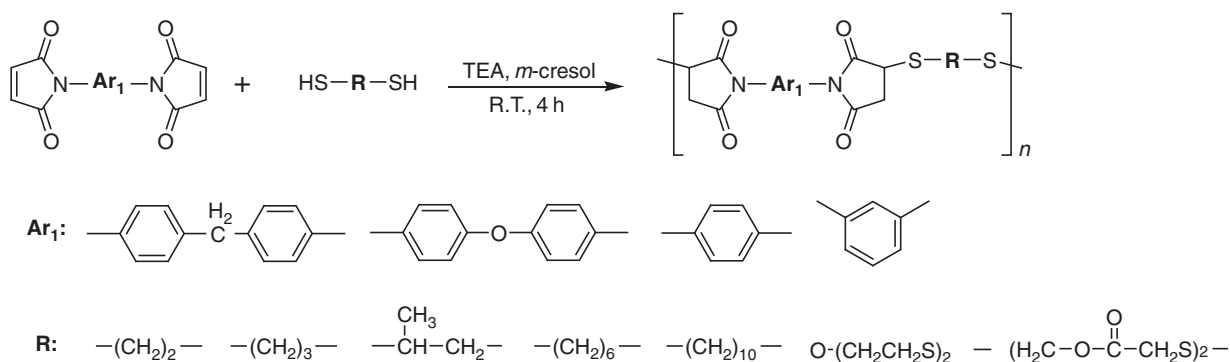
Scheme 41
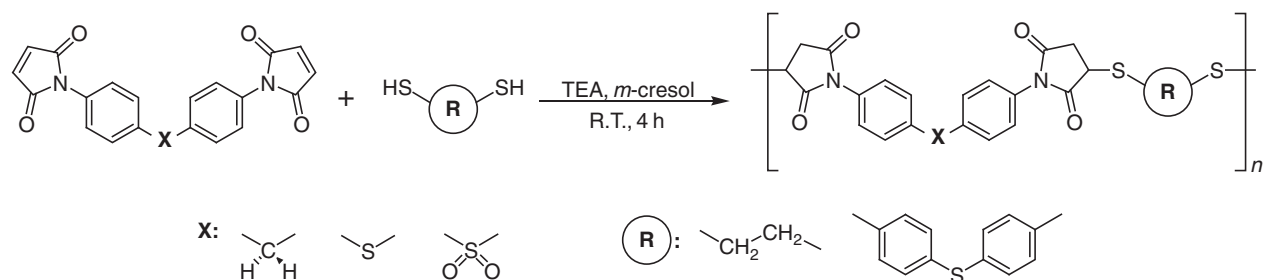
Scheme 42

5.20.2.7.1 Poly(ester imide)s

One of the applications in the greatest demand of PIs is a use as dielectric layers (base film materials) in copper clad laminates (CCLs), from which FPC boards, tape-automated bonding, and chip-on-film assembly systems are fabricated. Thermo-dimensional stability of PI films is one key parameter for realizing higher density assembly in FPC. For this purpose, to use PI films possessing lower in-plane CTE (simply called CTE) is the most effective approach. Particularly in the two-layered CCL, CTE values of the PI base films must be precisely controlled to practically the same value as that of the copper layer ($17.7 \, ppm \, K^{-1}$); otherwise the CCL undergoes curling. In this regard, many PI systems are not applicable because of their much higher CTE values (40–$70 \, ppm \, K^{-1}$). Therefore, considerable efforts have been made for reducing CTE of PI films. Schematic investigations on the structure–CTE relationships revealed that PI systems possessing linear and stiff backbone structures tend to show low CTE characteristics.[145,146]

Hasegawa et al.[147–149] reported the investigations of various poly(ester imide)s for FPC applications. Ester-containing tetracarboxylic dianhydrides and diamines were used to obtain a low CTE and low water absorption (Scheme 43). The resultant poly(ester imide)s showed high dimensional stability, high T_g, low CTE, high
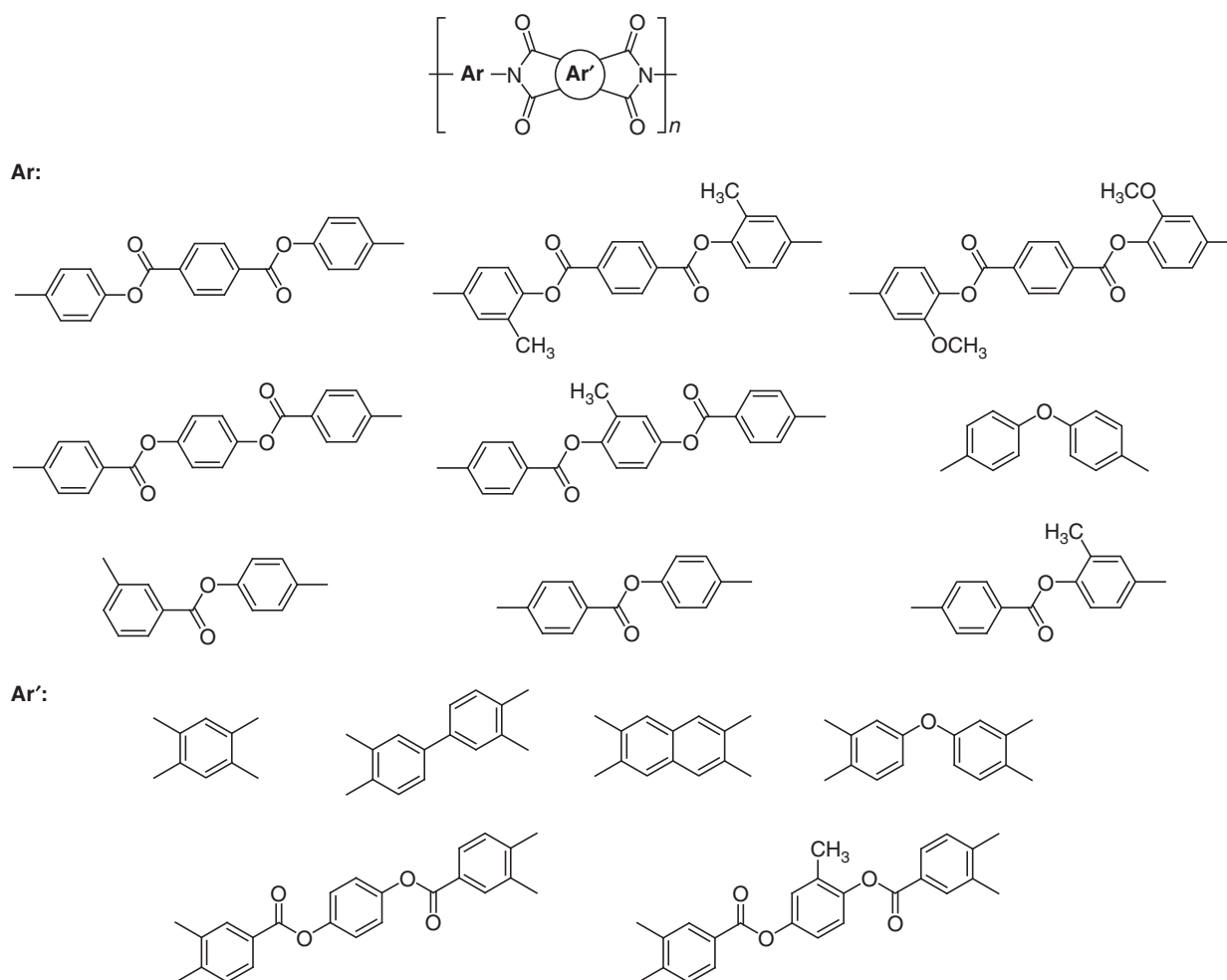
Scheme 43

modulus, low water absorption, and lower coefficients of humidity expansion (CHEs) at the same time. The results revealed that the *para*-aromatic ester units contribute very effectively to the acquisition of low CTE and low water absorption. Moreover, the copolymer system achieved excellent combined properties: a very high T_g at 410 °C, a slightly lower CTE (10.0 ppm K^{-1}) than that of copper foil, suppressed water absorption (0.35%), an extremely low CHE (3.4 ppm per RH%), and good film toughness. Thus, these poly(ether imide)s can be promising candidates as the next generation of FPC-based film materials.

Yang *et al.*[150,151] synthesized high-molecular-weight aromatic poly(ester imide)s from bis(trimellitimide)-diacids and various bisphenols by direct polycondensation using diphenyl chlorophosphate and pyridine as condensing agents (Scheme 44). Hsiao *et al.*[152–154] also reported the synthesis of

soluble and light-colored poly(ester imide)s using naphthalene ring-containing bis(ester-amine)s and various tetracarboxylic dianhydrides by conventional polycondensation (Scheme 44). All polymers showed good thermal stability, high optical transparency, low dielectric constant, and low water absorption. Some of the polymers exhibited good solubility in organic solvents and could be cast into tough and flexible films, which could be considered as new candidates for processable high-performance polymeric materials.

5.20.2.7.2 Poly(amide imide)s

Liou *et al.*[155–157] reported aromatic poly(amine-amide-imide)s having *para*-methoxy substituent, pendant TPA and *N*-carbazolylphenyl units from the phosphorylation polyamidation of the synthesized diamine with imide ring-preformed dicarboxylic acids (Scheme 45).
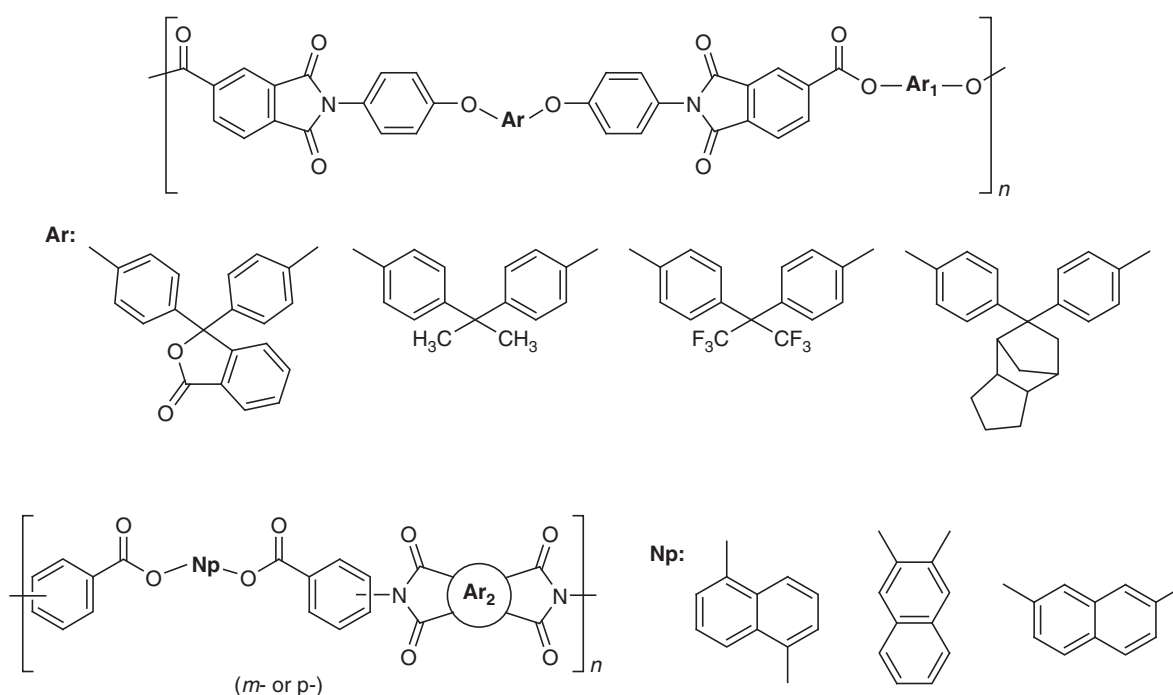
Scheme 44
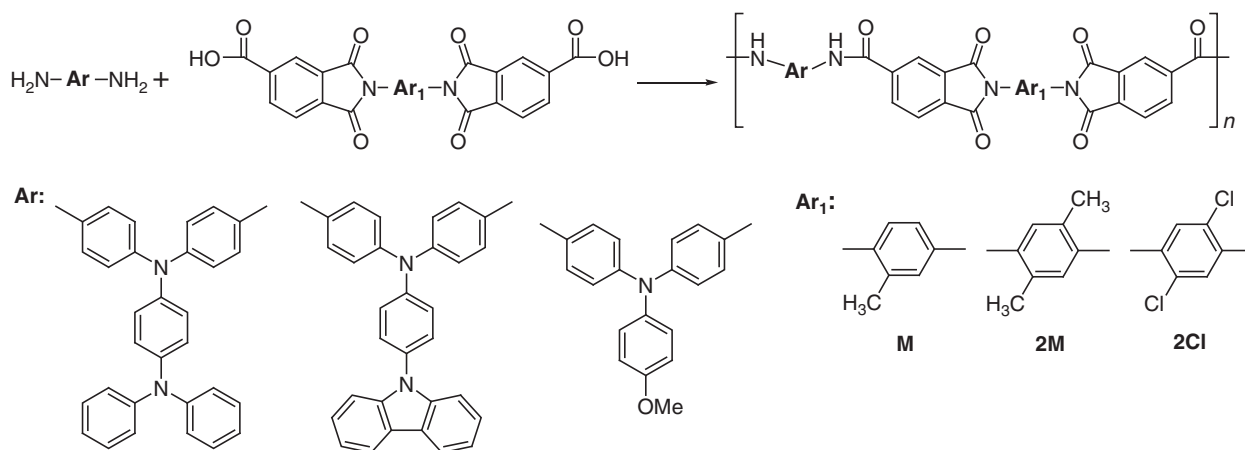
Scheme 45

All polymers are highly soluble in polar organic solvents. Flexible, amorphous, and deep reddish films of poly(amine-amide-imide)s can be obtained by solution casting and showed useful levels of thermal stability associated with high glass transition temperatures and degradation temperatures. The poly(amine-amide-imide) films exhibited reversible electrochemical oxidation redox couples, good electrochromic stability, and high contrast of optical transmittance change.

5.20.2.7.3 Poly(pyrrolone imide)s

The copolymer consisting of pyrrolone and imide units exhibited enhanced solubility without sacrificing thermal and mechanical properties.

Yang *et al.*[158] prepared **PPI** matrix resin by using PMR (*in situ* polymerization of monomer reactants) process in anhydrous ethyl alcohol and NMP (Scheme 46). The homogeneous matrix resin solution (40–50% solid) was stable for a storage period of 2 weeks and showed good adhesion with carbon fibers which ensured production of prepregs. Thermosetting **PPI** as well as short carbon fiber-reinforced polymer composites could be accomplished at optimal thermal curing conditions. The resulting copolymer showed excellent thermal stability with a high initial decomposition temperature and good mechanical properties.

Burns and Koros[159] examined PPI copolymers 6FDA-TAB/DAM for the application of O_2/N_2, CO_2/CH_4, and C_3H_6/C_3H_8 separation by controlling the TAB/DAM ratio to quantitatively alter the structure of the polymer matrix (Scheme 47). Combining these two classes of polymers could also be used to design to provide rigidity and desirable mechanical properties in addition to high-quality gas transport properties.

Choi *et al.*[160] reported poly(benzoxazole-*co*-pyrrolone) copolymers in various compositions by thermal rearrangements from their precursors of hydroxyl-containing PPIs (Scheme 48). All the copolymers showed higher gas permeability as well as gas selectivity than their corresponding polybenzoxazole or polypyrrolone homopolymers.

5.20.2.7.4 Poly(benzimidazole imide)s

The thermal and mechanical properties of PBII copolymers could be further increased comparing to the corresponding PIs. The route to obtaining these copolymers involved the synthesis of benzimidazole-based diamine compounds, which react with aromatic tetracarboxylic anhydrides to yield benzimidazole-imide copolymers (Scheme 49).[161]

The benzimidazole-containing aromatic PIs prepared from synthesized 5,4′-diamino-2-phenyl benzimidazole (**49**) and commercial tetracarboxylic dianhydrides by the conventional two-step polymerization were amorphous and could afford flexible, transparent, and tough films with outstanding thermal and mechanical properties (Scheme 50).[162] In addition, they showed high levels of tensile strength of up to 234 MPa and modulus of up to 5.6 GPa, although the values of the elongation at the break were rather low. Excellent properties of these copolyimides are attributed to the rigid-rod structure and interchain hydrogen bonding.

Acid–base blend membranes prepared by a combination of polymeric nitrogen-containing bases (N bases) and polymeric sulfonic acids are new class of interesting materials that exhibit improved thermal stability and good resistance to swelling. In a similar manner, polymers bearing both sulfonic acid groups and N bases should possess the improved hydrolytic stability.

Molding resin powder, PAI

PMR-type poly(pyrrolone–imide) (PPI) matrix resins

Scheme 46

Scheme 47

250 °C, 1 h
300 °C, 1 h

450 °C, 1 h

Scheme 48

R:

−(CH₂)₂− −(CH₂)₄− −(CH₂)₈−

R₁:
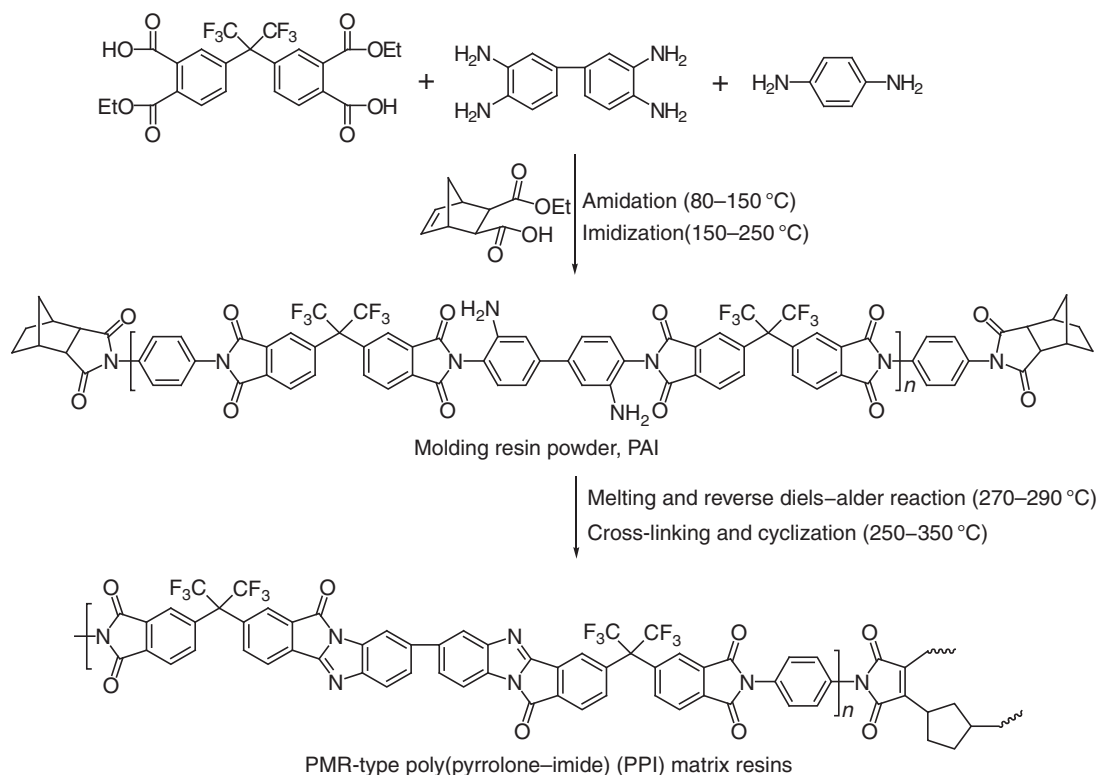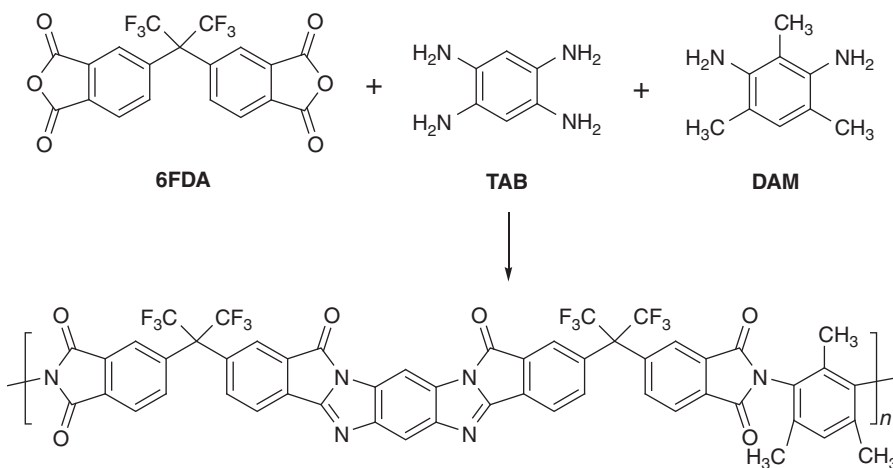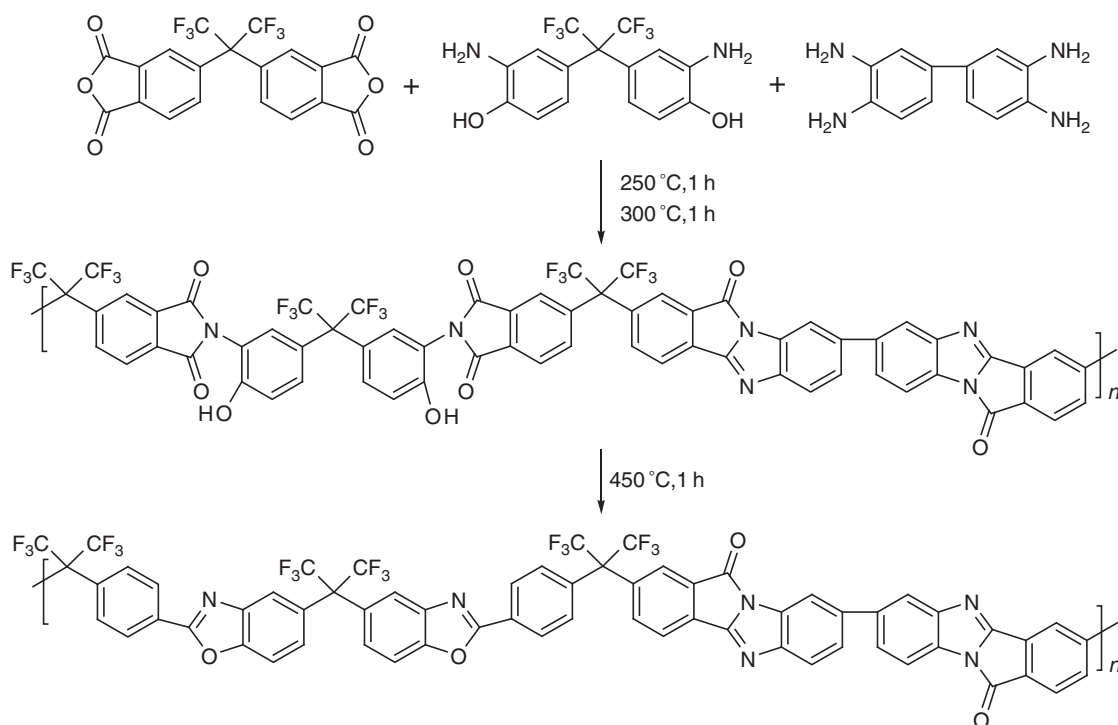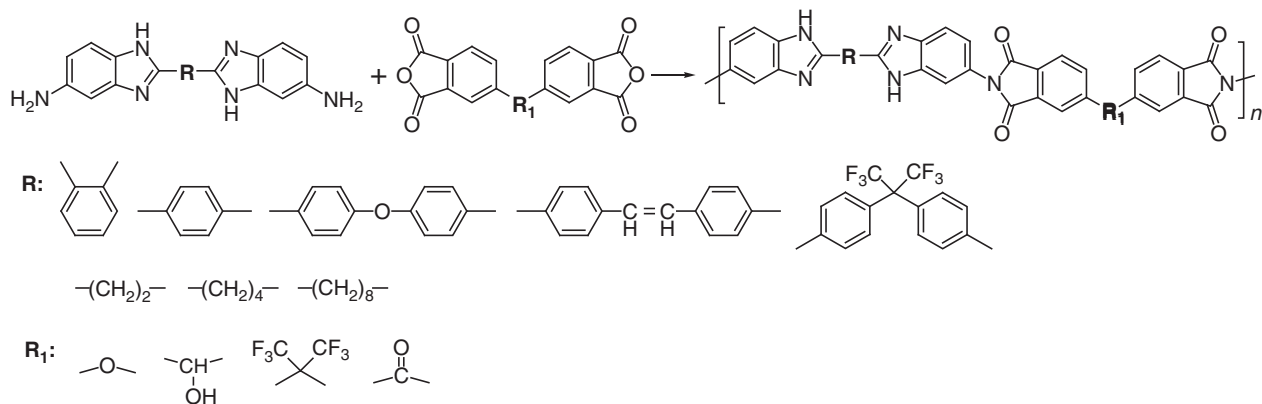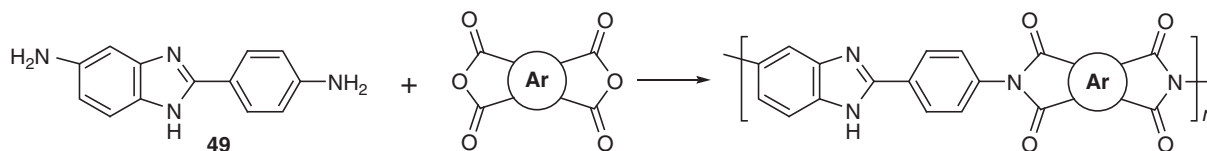
Scheme 49

Scheme 50

In view of this consideration, efforts have been made to develop membrane materials based on sulfonated PIs (SPI) containing benzimidazole groups (Scheme 51).[163–166] SPI membranes incorporated with basic benzimidazole groups showed enhanced thermal and hydrolytic stability at the expense of some proton conductivity. Furthermore, the low methanol permeation rate was also achieved by introducing the benzimidazole into the SPI backbone.
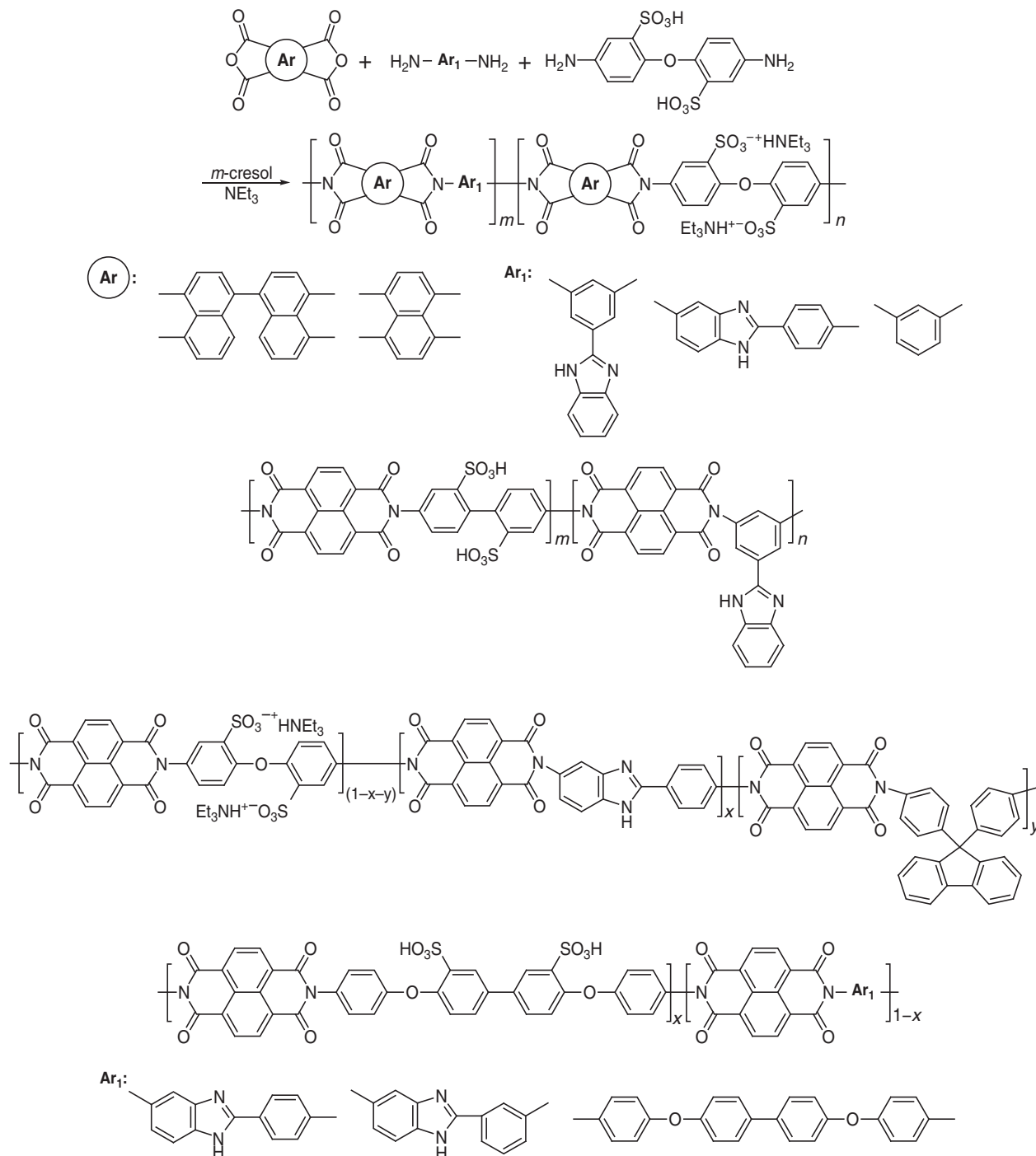
Scheme 51

5.20.2.7.5 Poly(benzoxazole imide)s

Aromatic polybenzoxazoles (PBOs) possess superior thermal and chemical properties to other engineering plastics such as polysulfone and polyetheretherketone (PEEK). The preparation of PBOIs has been developed by using benzoxazole-preformed diamines and tetracarboxylic dianhydrides or thermal conversion of hydroxyl-containing PIs to polybenzoxazole imides (Schemes 52 and 53).[167,168]

The synthesis of poly(o-hydroxy-amide-imide)s with high molecular weights by low-temperature solution polycondensation from imide-preformed diacid chlorides having chloro- or methyl-substituted p-phenylene units and three bis(o-amino phenol)s has been reported by Liou[169,170] (Scheme 54). Subsequent thermal cyclodehydration of the poly(o-hydroxy-amide-imide)s afforded novel PBOIs. These intrinsic alternating copolymers exhibited high glass transition temperatures over 300 °C and were stable up to 500 °C in air or nitrogen.

Hsu et al.[171] reported a novel positive-working and alkali-developable photosensitive PBOI precursor based on
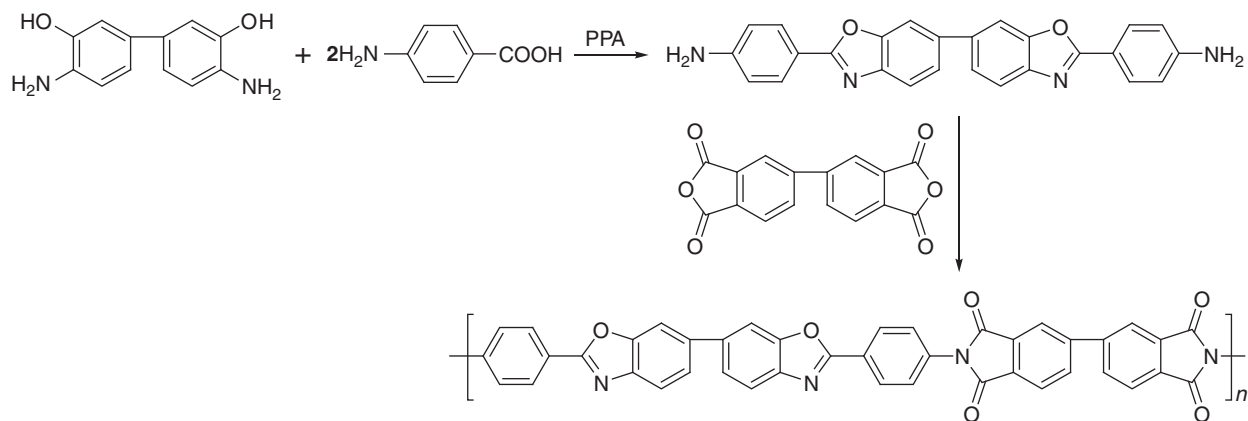
Scheme 52
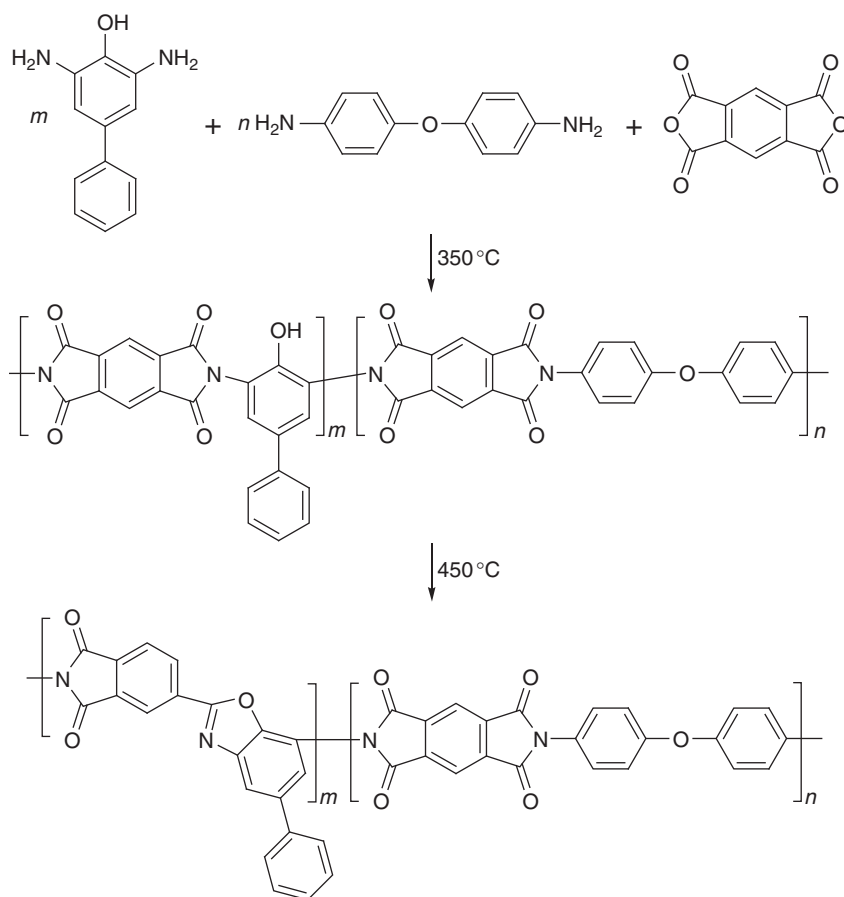
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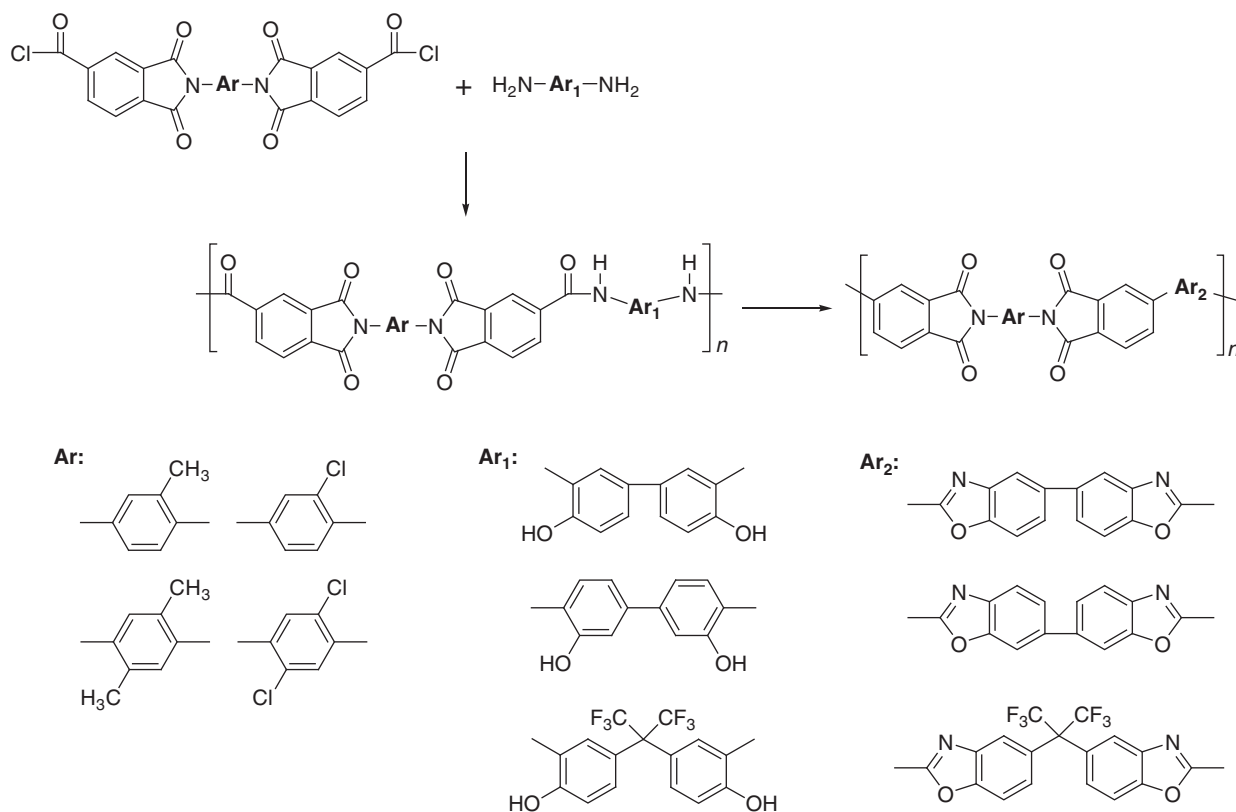
Scheme 54
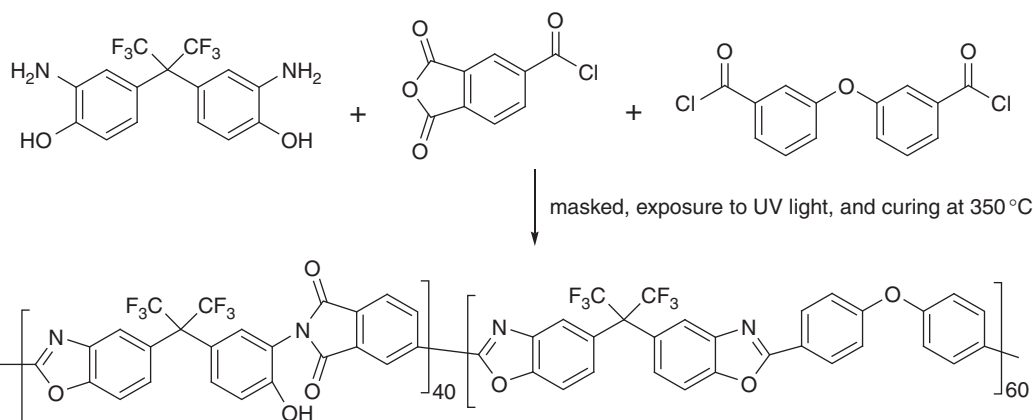
Scheme 55

a poly(amic acid hydroxyamide) bearing phenolic hydroxyl groups and carboxylic acid groups (Scheme 55). By using the photosensitive compound diazonaphthoquinone and 0.6 wt.% tetramethylammonium hydroxide as the developer, the resulting patterns with a resolution of 5 μm were achieved.

5.20.2.7.6   Poly(benzothiazole imide)s

Rigid-rod and extended chain-containing poly(benzothiazoles)s (PBTs) have very high moduli, low CTEs, exceptional thermal stability, and many other desirable properties. The high degree of molecular rigidity in these

systems dominates the morphology and subsequent mechanical properties. The poly(benzothiazoles)s are generally processed from nematic liquid crystalline solutions in polyphosphoric acid into highly ordered or semicrystalline fibers. A drawback of these rigid-rod polymers is their limited solubility and intractability, precluding their uses in many applications. The PBTIs prepared from benzothiazole-preformed diamines and tetracarboxylic dianhydride could enhance solubility without sacrificing thermal stability (Scheme 56).[172]

PI-based second-order NLO materials were usually synthesized from poly(hydroxy imide)s, followed by the Mitsunobu
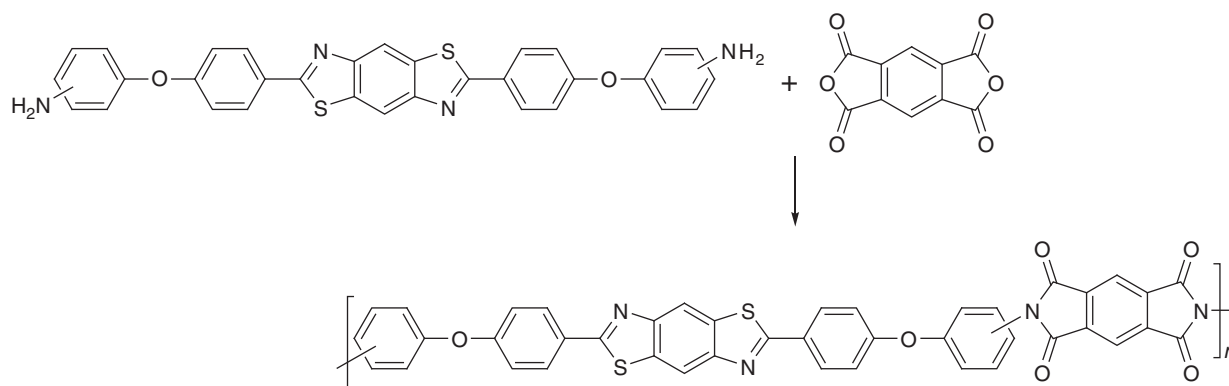
Scheme 56
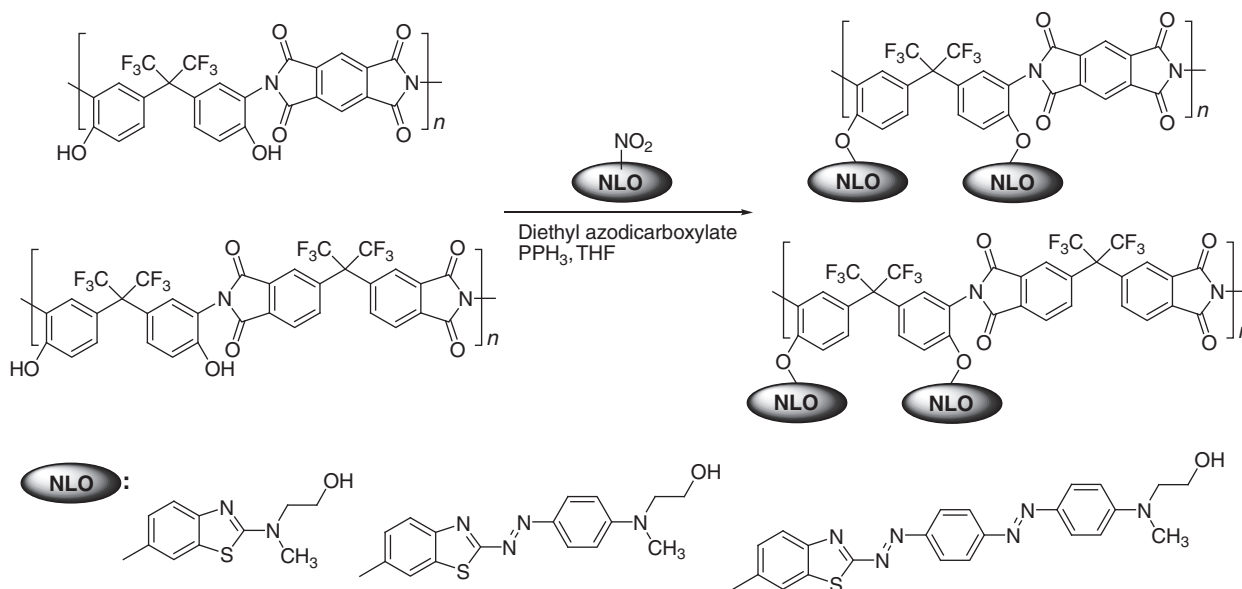
Scheme 57

reaction with NLO chromophores (Scheme 57).[173] In addition, benzothiazole-based diamines with nitro group were also used to prepare the NLO PIs (Schemes 58 and 59).[174,175] These benzothiazole chromophores containing an electron-withdrawing nitro end group have been developed as donor–π-bridge–acceptor NLO units. The resulting copolyimides with side-chain benzothiazole groups showed good solubility in aprotic polar solvents such as DMF, DMAc, and NMP. It was also found that the stability of the NLO chromophore increased with increasing the glass transition temperatures of the PBTIs. The versatility of the reaction scheme and the ease of processing ensure this series of materials for further use.

In 2008, a series of PI/benzothiazole silica NLO hybrid materials were synthesized from PMDA, 2,2-bis (3-amino-4-hydroxyphenyl)hexafluoropropane, and an NLO benzothiazole molecule via a sol–gel process; the tetraethoxysilane content in the hybrid films varied from 0% to 22.5% (Scheme 60).[176] The NLO experimental results suggest that the hybrid thin films have potential applications as passive films for optical devices.

5.20.3   Functional PI

5.20.3.1   Electrochromic PI

Since 2005, the first electrochromic aromatic poly(amine imide)s with pendant TPA units were reported by Liou et al.[103] from the newly synthesized diamine, N,N-bis(4-aminophenyl)-N',N'-diphenyl-1,4-phenylenediamine,   and various tetracarboxylic dianhydrides by either a one-step or a conventional two-step polymerization process (Scheme 61). All the poly(amine imide)s were amorphous showing high solubility in many organic solvents and could be solution cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with relatively high glass transition temperatures. The poly(amine imide) films exhibited two reversible oxidation redox couples and revealed good stability of electrochromic characteristics with a drastic color change from pale yellowish to green and blue when oxidized.

In the following years, organosoluble aromatic PIs and poly (amine-amide-imide)s bearing pendant N-carbazolylphenyl,
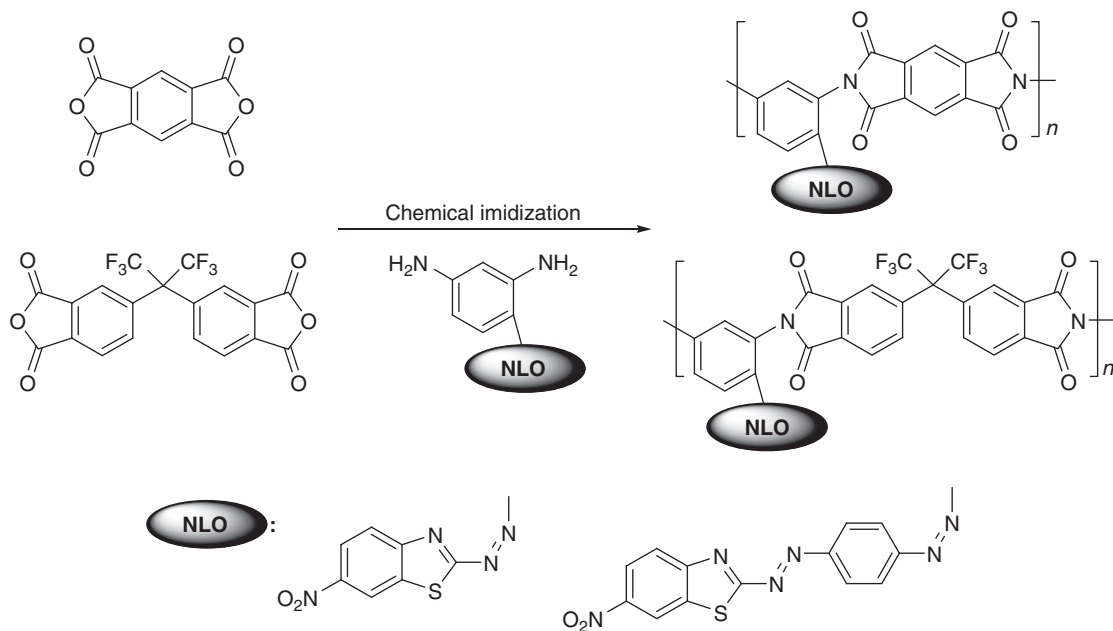
Scheme 58
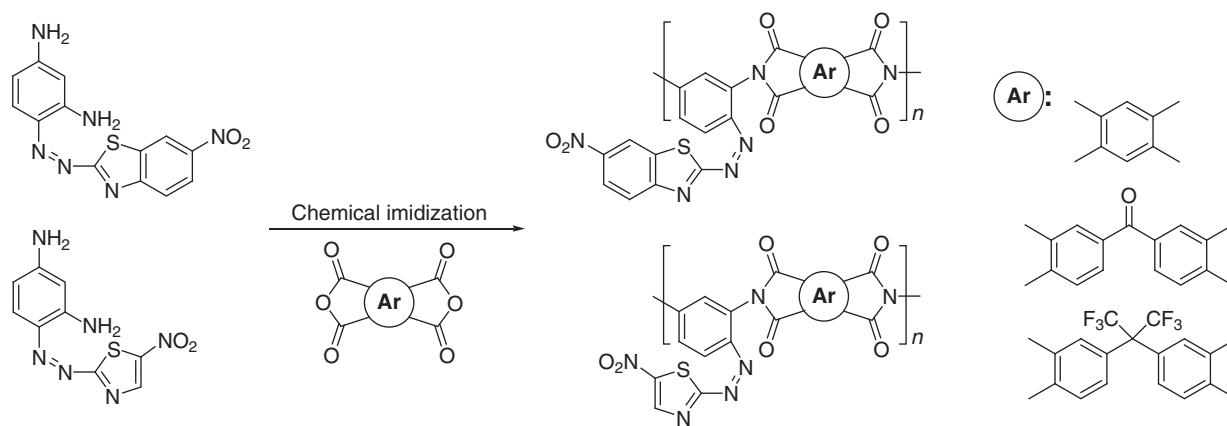
Scheme 59
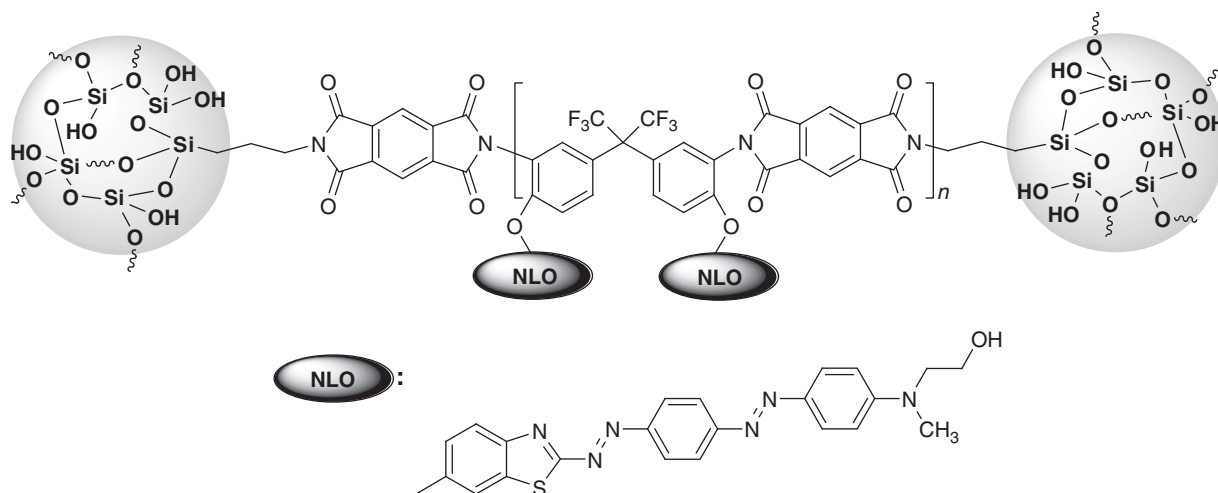
Scheme 60
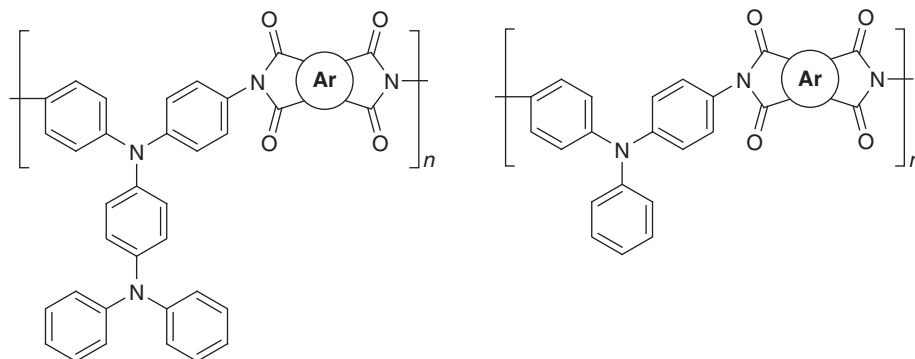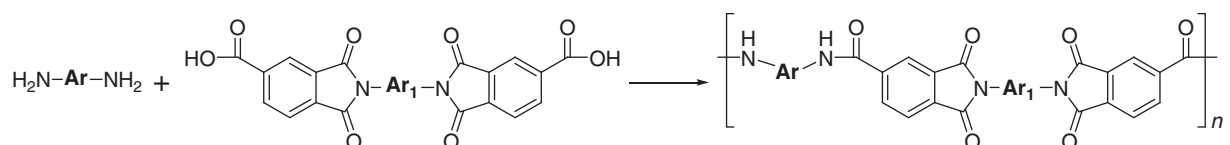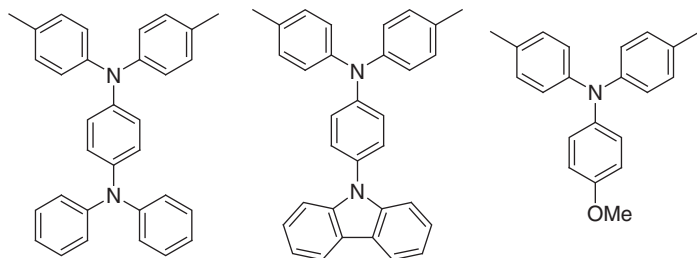
Scheme 61
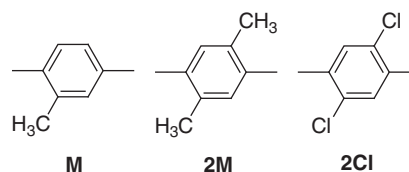
Scheme 62

TPA and methoxy-substituted TPA moieties were also developed from the corresponding diamines (Scheme 62).[155–157] All the PIs were highly solution processable and exhibited excellent thermal stability with high T_s. The PI films showed good adhesion with indium tin oxide (ITO)-coated glass electrode and good electrochemical stability and also revealed electrochromic characteristics changing color from the original pale yellowish to green or blue when scanning potentials positively. Thus, the TPA-based PIs could be good candidates as anodic electrochromic materials because of their proper oxidation potentials, electrochemical stability, and thin film formability.

Gas transport properties of the PIs for CO_2, CH_4, O_2, and N_2 were also investigated (Scheme 63).[105] It was shown that the introduction of the bulky TPA unit into aromatic PIs can improve gas transport properties by increasing permeability at the slight expense of a decrease in permselectivity. The combination of electrochromic and gas permeability properties along with excellent thermal stability makes these new PIs as newly processable high-performance polymers with multifunction.
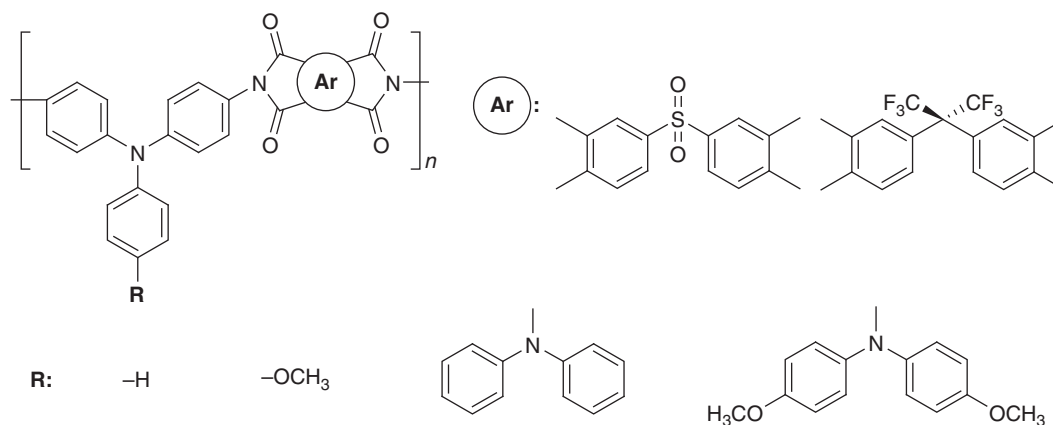
Scheme 63

5.20.3.2 Photoluminescent PI

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity. In the field of electroluminescence, carbazole derivatives are often used as the materials for hole-transporting and light-emitting layers because of their high charge mobility and thermal stability, and show blue electroluminescence due to the large bandgap of the improved planar biphenyl unit by the bridging nitrogen atom. Poly(amine imide)s bearing pendant *N*-phenylcarbazole units were prepared by the two-step method starting from the diamine, 4,4′-diamino-4″-*N*-carbazolyltriphenylamine, and various tetracarboxylic dianhydrides (**Scheme 64**).[104] All the poly(amine imide)s were amorphous with high T_g, excellent thermal stability, and useful mechanical properties (e.g., flexibility). The semiaromatic poly(amine imide) (**50**) showed light color and high optical transparency and exhibited violet–blue photoluminescence both in film state and in NMP solution with about a quantum yield of

4.54%. The poly(amine imide) films showed good adhesion with ITO and were found to be electroactive. The polymer films exhibited multicolor behavior, that is, pale yellow, green, and blue in color when various potentials were applied. All the obtained poly(amine imide)s revealed good stability of electrochromic characteristics for the first oxidation state, changing color from the yellowish neutral form to the green oxidized forms when scanning potentials positively. The poly(amine imide)s can be used as potential candidates in the development of dynamic electrochromic and electroluminescent devices due to their suitable highest occupied molecular orbital (HOMO) levels, excellent thermal stability, and reversible electrochemical behavior.

Ando *et al.*[177] examined the UV/vis absorption and fluorescent properties of imide compounds and PIs having a hydroxy group at the terminal anhydride moiety extensively, and a new molecular design concept for controlling the emission colors of fluorescent PIs was established (**Scheme 65**). The synthesized PIs (**51–54**) showed high transparency in the visible region. The
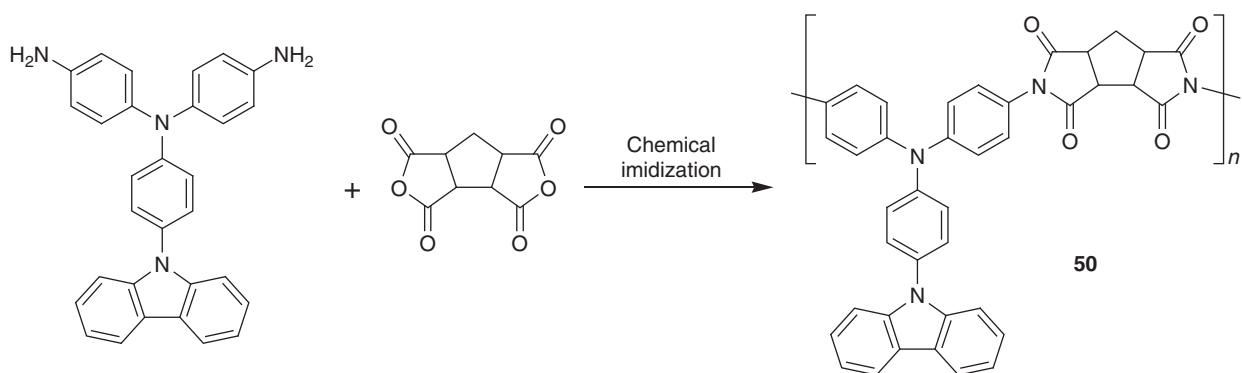
Scheme 64
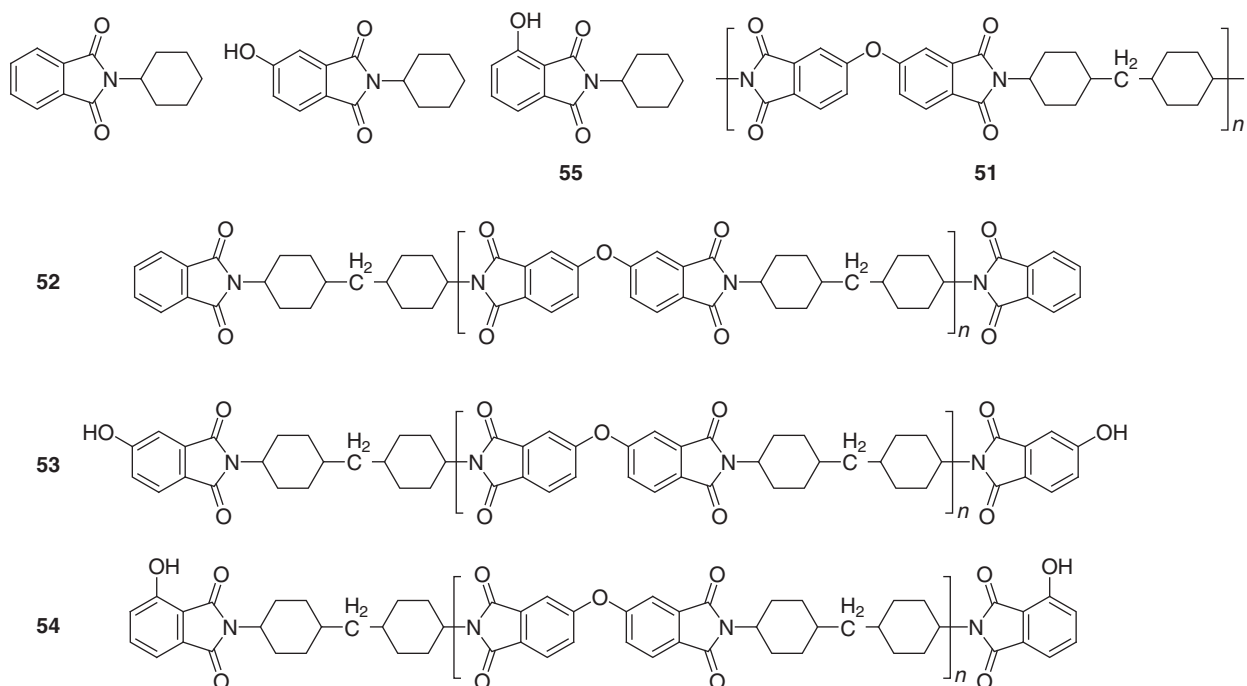
Scheme 65

fluorescence lifetime of imide moieties in the main chain decreased with increasing the (55) terminal group, indicating that the intra- and/or interchain energy transfer should occur from the PI main chain to the terminal group. As a result, the emission color of 54 was successfully controlled from blue to light green by varying the amount of terminal groups while maintaining the inherent high transparency of the PIs. The molecular design concept established in this study should be beneficial for developing a new class of superengineering plastics for advanced optical and electronic applications.

5.20.3.3   PI for Memory Device

Resistive switching behavior has been primarily studied in amorphous silicon-based materials for the past 30 years. It was found that the digital data could be stored by applying or discharging electrical charges through a simple device configuration consisting of two electrode layers sandwiching the storage medium. As compared to the traditional inorganic semiconductor-based memories, polymeric memory devices are extensively attractive today because of the advantages of structural flexibility, low cost, solution processability, and three-dimensional stacking capability. The recently studied polymer systems exhibit memory switching characteristics, including conjugated polymers, functional PIs, polymers with specific pendant chromophores, and polymer nanocomposites (metal nanoparticle and fullerene embedded). The electrical switching phenomena in polymers and the corresponding polymer electronic memories as an emerging area in organic electronics have been reviewed by Kang et al.[178] recently.

Organic and polymer materials are promising candidates for future molecular-scale memory applications. Their attractive features include good processability, miniaturized dimensions, and the possibility for molecular design through chemical synthesis. Among all the studied polymer systems, PIs are promising candidates for memory device applications because of their excellent physical and chemical properties in addition to the electrical switching behavior. Functional PIs containing both electron donor and acceptor moieties within a repeating unit contribute to electronic transition between the ground and excited states, which could be manipulated by the induced charge transfer (CT) from donor (D) to acceptor (A) under applied electric fields. Among the studied functional PIs, the

TPA-based PIs prepared by Liou et al.[103] since 2005 attracted significant attention. For example, the memory device of a TPA-functionalized PI (56)[179] exhibited dynamic random access memory (DRAM) behavior, whereas a device based on 57[180] showed the improved DRAM performance as reported by Kang and coworkers. And an oxadiazole-containing PI (58)[181] was found to reveal a static random access memory (SRAM) behavior (Scheme 66).

Meanwhile, Lee et al.[182] also proposed a series of TPA-based PIs for memory characteristics. They found that 59 (two connected TPA rings) showed stable digital nonvolatile write-once-read-many-times (WORM) and volatile DRAM memory characteristics depending on film thickness. Moreover, a flash-type memory of 60[183] bearing two pendant TPA groups and a unipolar WORM memory of 61[184] having an attached hydroxyl group on TPA were also reported recently (Scheme 67).

Ueda and Chen[185,186] prepared sulfur-containing PIs (62 and 63), and found that the relatively high dipole moments of the sulfur-containing PIs provided a stable CT complex for the flash memory device with nonvolatile memory characteristics and low turn-on threshold voltages. They further synthesized two functional PIs (64 and 65) consisting of electron-donating TPA with single and double isolated ether linkage, respectively, and electron-accepting phthalimide moieties. The memory devices with the configuration of 64/Al or ITO/65 exhibited distinct volatile memory characteristics of DRAM and SRAM, respectively. The result provides the strategies for the design of functional PIs for advanced memory device applications (Scheme 68).

5.20.3.4   High Refractive Index PI

5.20.3.4.1   *Sulfur-containing high refractive index PI*

Sulfur-containing linear thioether and sulfone, cyclic thiophene, thiadiazole, and thianthrene are the most commonly used moieties for increasing refractive index of polymers. Recently, systematic work by the Ueda group revealed the influence of sulfur groups on the refractive indices and optical dispersion of polymers. First, a series of sulfur-containing PIs were developed to increase the n values of polymers. The average n values (n_{av}) are all higher than 1.72 and increase with an increase in the sulfur content of the PIs. In addition, the flexible thioether or sulfonyl linkages in PIs endow lower

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58

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Scheme 66

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61

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Scheme 67

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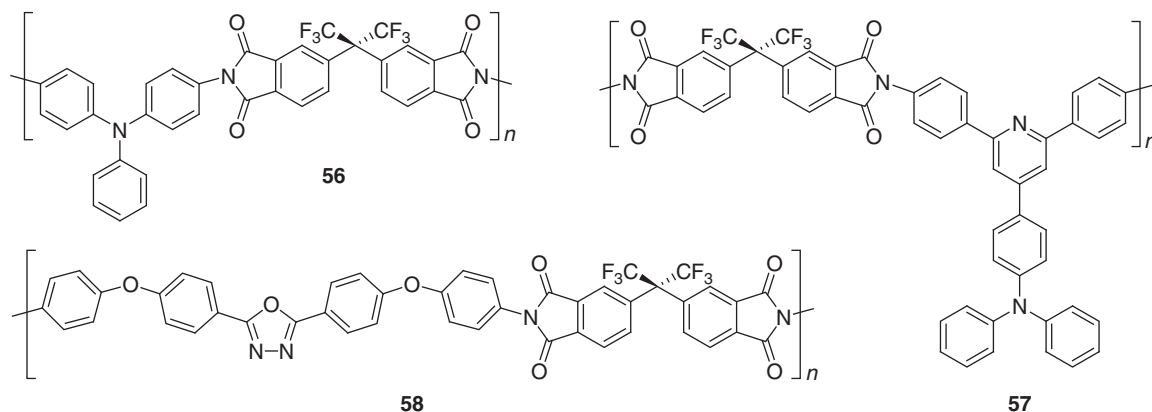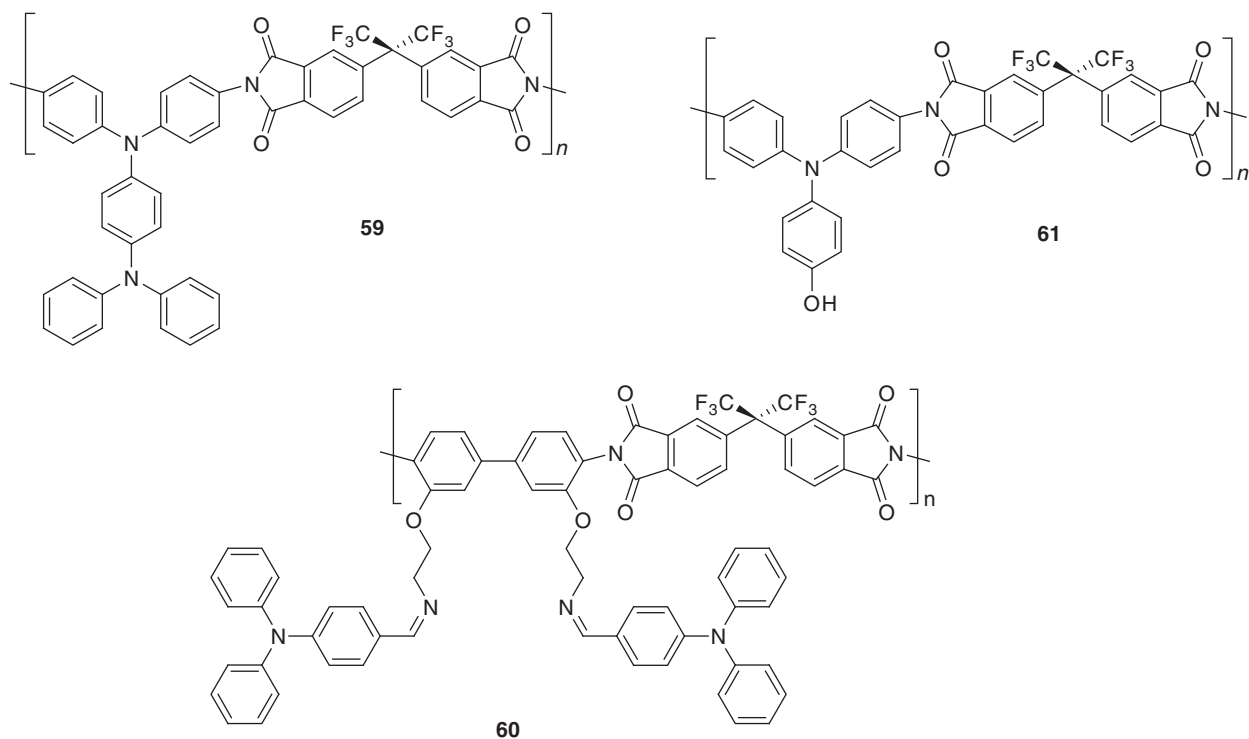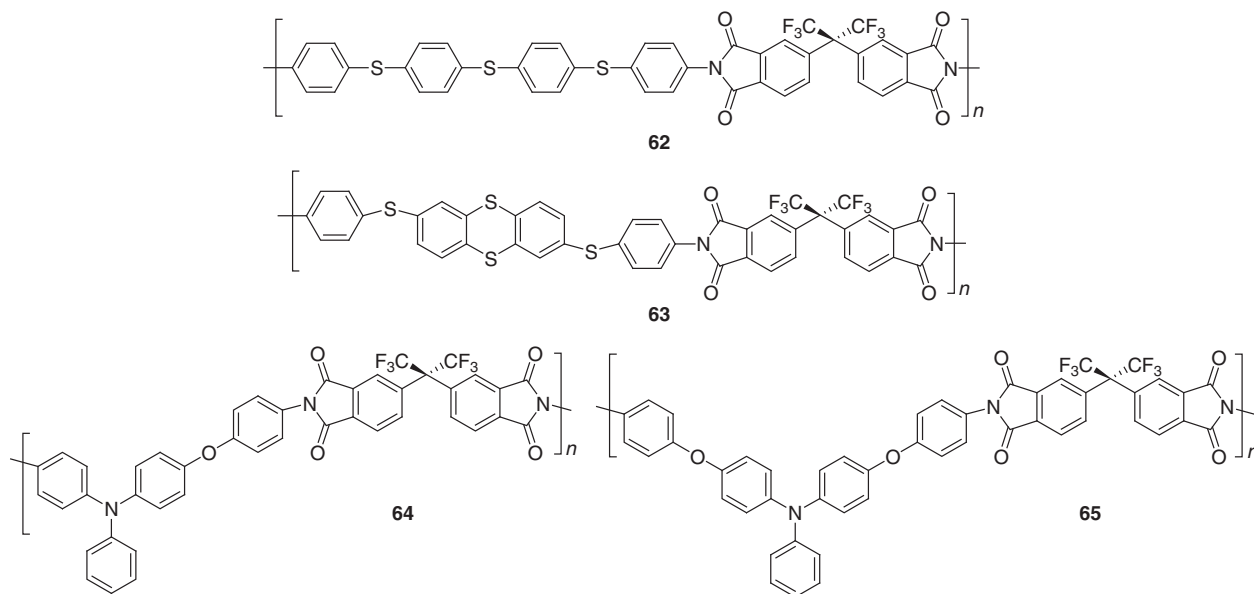
Scheme 68
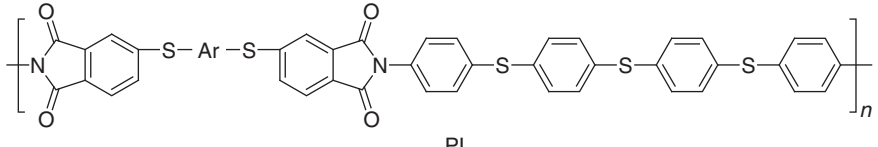
birefringence ($^{\triangle}n$) less than 0.01. PIs containing sulfur-rich thianthrene and tetrathiaanthracene moieties in the repeating units exhibited the highest n_{av} values among previously reported PI systems in the literature.

Optical properties of the PIs prepared from various tetracarboxylic dianhydrides are summarized in Table 1.[114–117] **PI-a** and **PI-d** showed the highest n_{av} and optical transparency, respectively. These results provide the strategies for the design of high refractive PIs for optical applications.

5.20.3.4.2 PI/inorganic hybrid materials
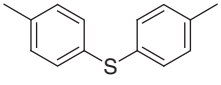
Recently, polymer–inorganic hybrid materials have attracted considerable interest owing to their enhanced mechanical, thermal, magnetic, optical, electronic, and optoelectronic properties when compared to the corresponding individual polymer or inorganic component.[187] Chemical methods based on hybridization approach by *in situ* sol–gel reaction made it possible to manipulate the organic/inorganic interfacial interactions at various molecular and nanometer length scales,

Table 1   Optical properties of PIs

Ar:
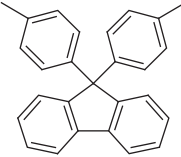
Index	d(μm)	λ_0 (nm)	n_{av}	Δn
		Optical Properties		
PI-a	9.3	402	1.748 2	0.006 8
PI-b	7.4	~380	1.731 9	0.006 5
PI-c	5.4	374	1.730 9	0.005 9
PI-d	6.6	367	1.725 5	0.005 9

resulting in homogeneous structures and thus overcoming the problem of nanoparticle agglomeration. For optical applications, such as high refractive index materials, optical waveguides, and antireflective films, the inorganic domains of these hybrid materials must be less than 40 nm to avoid scattering loss and retain optical transparency.[188] Precise control of the morphology and the phase separation is critical in preparing transparent hybrid films, and the sol–gel reaction was widely used for making transition metal oxide solids with fine-scaled microstructures. Particle sizes less than a couple of nanometers could easily be achieved in the derived gels, and microstructural dimensions could also be maintained when subsequently crystallized at elevated temperatures.

In 1992, Imai et al.[189] prepared the PI–silica hybrid films with ethoxysilyl groups in the polymer backbone. The polyamic acid–silica gel mixtures can be cast onto glass plates, and then be heated to 300 °C to convert the component matrix polymers to PIs (Scheme 69). The PI–silica hybrid films containing 70 wt.% of the silica obtained were self-standing and tough. The silica particles were dispersed homogeneously in the matrix PIs as observed by SEM. The size of the silica particles increased with increasing silica content, and decreased with increasing ethoxysilyl content. Results of the dynamic-mechanical analysis indicate that movement of the PI chain in the matrix is restricted, especially when the PIs contain higher amounts of ethoxysilyl. The report is very beneficial for the designing of PI–inorganic hybrid films.

In 2008, Ueda et al.[190] successfully prepared a PI–TiO$_2$ hybrid film containing 45 wt.% silica-modified anatase-type TiO$_2$ nanoparticles with a refractive index of 1.81 at 632.8 nm (Scheme 70). In addition, Su and Chen[191] developed a new synthetic route to prepare PI–nanocrystalline–titania hybrid materials with a relatively high titania content (up to 90 wt.%) (Scheme 71). This approach demonstrates a new route for preparing high refractive index PI–nanocrystalline–titania hybrid materials for optical applications.

Recently, Liou et al.[192,193] successfully synthesized highly transparent and tunable refractive index PI–titania hybrid optical films from hydroxy-containing organosoluble PIs and titanium butoxide by controlling the organic/inorganic mole ratio (Scheme 72). The hybrid thin films had good surface planarity, high thermal stability, tunable refractive indices, and high optical transparency in the visible range. Moreover, the thick titania hybrid films could be achieved even with a relatively high titania content. The refractive index (up to 1.92) and titania content (50 wt.%) are highest among the highly optical transparent polymer–titania hybrid thick films (20–3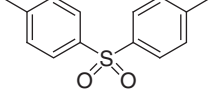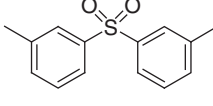0 μm thick). The three-layer antireflective coating based on the hybrid films exhibited a reflectance of less than 1.0% in the visible range. It suggested potential optical applications of the novel PI–titania hybrid optical films.

5.20.3.5 PIs for Fuel-cell Application

Fuel cells have the potential to become an important energy conversion technology. Research efforts directed toward the widespread commercialization of fuel cells have accelerated in light of ongoing efforts to develop a hydrogen-based energy economy to reduce pollution. Proton exchange membrane (also termed 'polymer electrolyte membrane') (PEM) fuel cell employing a solid polymer electrolyte to separate the fuel from the oxidant was first deployed in the Gemini space program in the early 1960s using cells that were extremely expensive and
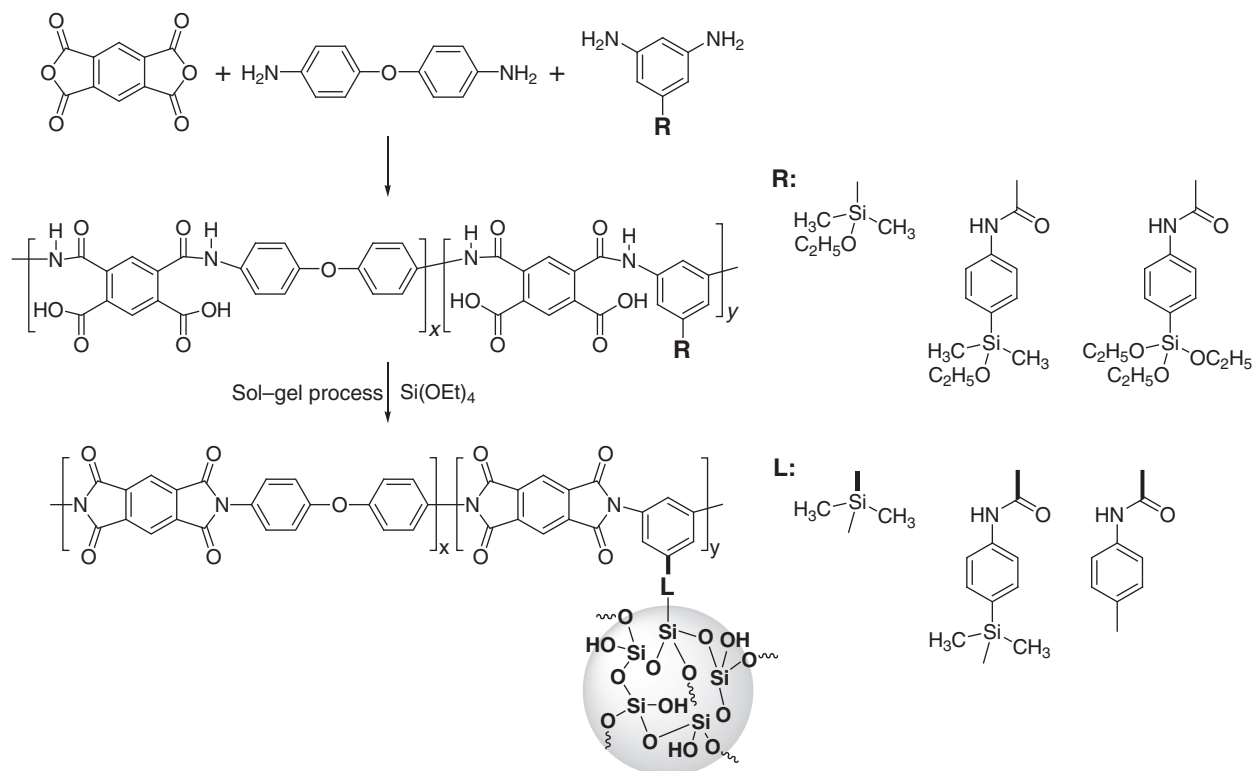
Scheme 69
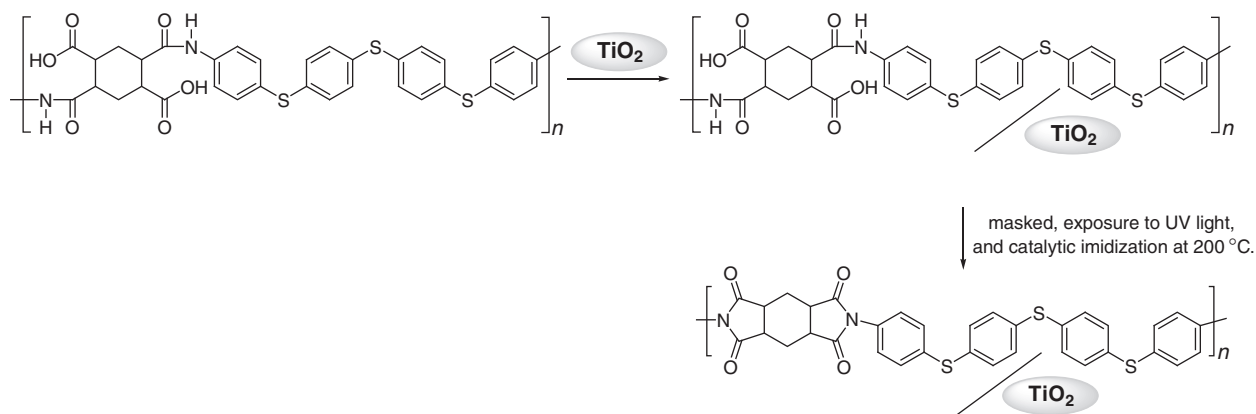
Scheme 70
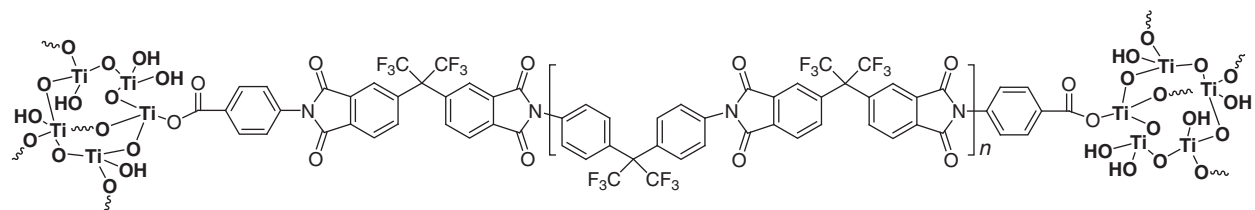
Scheme 71
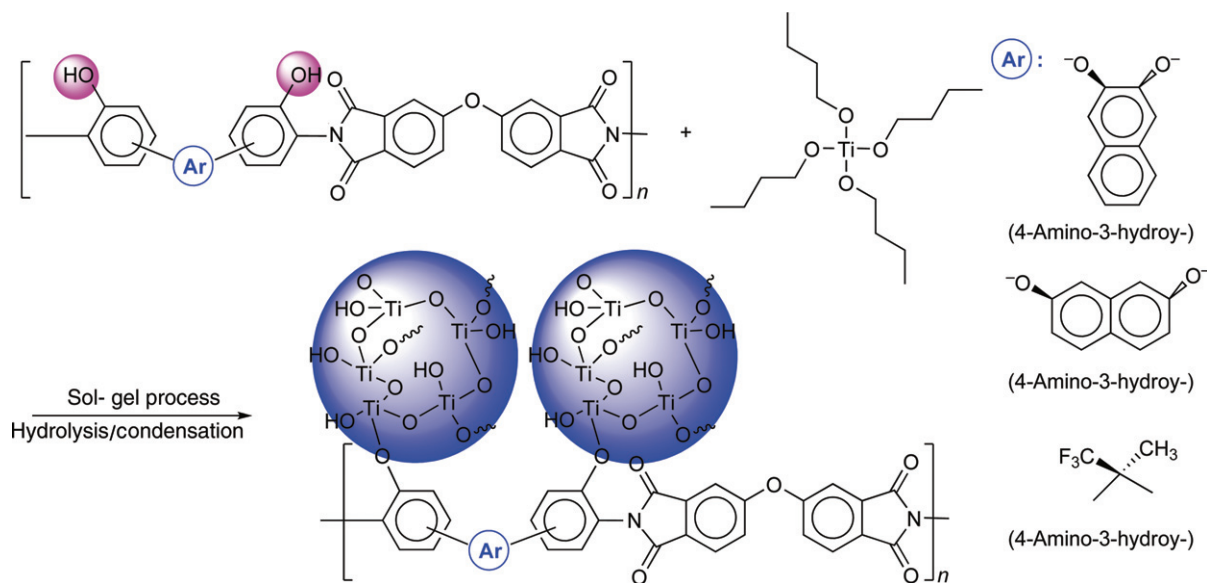
Scheme 72

had short lifetimes due to the oxidative degradation of the sulfonated polystyrene–divinylbenzene copolymer membranes. The commercialization of Nafion by DuPont in the late 1960s helped to demonstrate the potential interest of fuel cells in terrestrial applications.[194]

PEM fuel cells have been developed for three main applications: automotive, stationary, and portable power. Each of these applications has its unique operating conditions and material requirements. Common themes critical to all high-performance proton exchange membranes include (1) high protonic conductivity, (2) low electronic conductivity, (3) low permeability to fuel and oxidant, (4) low water transport through diffusion and electroosmosis, (5) oxidative and hydrolytic stability, (6) good mechanical properties in both a dry and a swollen state, (7) cost, and (8) capability for fabrication into membrane electrode assemblies (MEAs). Most of all the membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce protonic conductivity. Due to the large fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues. Devising systems that can conduct protons with little or no water is perhaps the greatest challenge for new membrane materials. Specifically, for automotive applications the US Department of Energy has currently established a guideline of 120 °C and 50% relative humidity as target operating conditions, and a goal of 0.1 S cm^{-1} for the protonic conductivity of the membrane.[194,195]

Zhang et al.[196] reported a series of SPI bearing basic groups from binaphthy-based tetracarboxylic dianhydride, a sulfonated diamine, and a TPA-based diamine for proton exchange membranes (Scheme 73). The electrolyte properties of the synthesized PIs were investigated and compared to those of PIs based on NTDA. The SPI exhibited much better water stability than those based on NTDA. Such improvement in stability could be attributed to the excellent hydrolytic stability of the binaphthalimide moieties. The basic TPA groups introduced in the main chains could effectively improve the proton conductivity and dimensional stability of PIs. Furthermore, the low methanol permeation rate was achieved by introducing the TPA into the SPI backbone.

Watanabe et al.[197–199] demonstrated that the introduction of aliphatic segments in both the main and side chains could effectively improve the hydrolytic stability of PI ionomers without sacrificing other preferable properties (proton conductivity, oxidative and mechanical stability). Both electronic and steric effects are crucial for the hydrolytic and oxidative stability. A significant decrease in the conductivity at low humidity observed for the linear ionomers was improved to the level nearly required for the practical fuel-cell applications by increasing the ion exchange capacity (IEC) and introducing a branching structure. Scanning transmission electron microscope (STEM) images have revealed that aggregation of ionic groups was suppressed by the branching and therefore small (<5 nm) and well-dispersed hydrophilic domains distributed throughout the
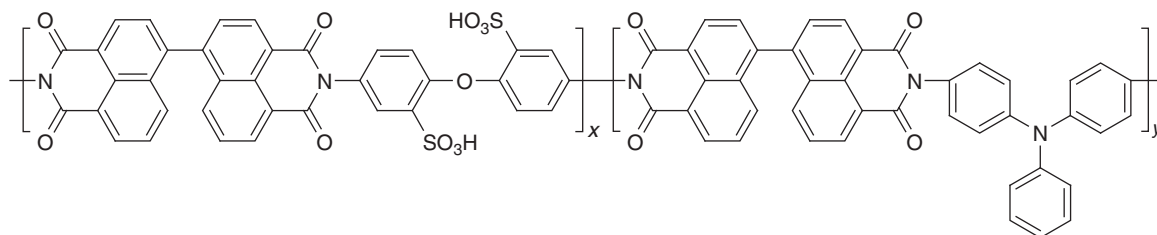
Scheme 73

membrane. The morphology is distinctive from that of the per-fluorinated ionomers (in which 5–10 nm-sized hydrophilic clusters are observed) and is likely to contribute better proton–conducting properties. Hydrogen and oxygen permeability of SPI membranes was more than 1 order of magnitude lower than that of Nafion under a wide range of conditions (40–120 °C and 0–90% RH). High-performance fuel cells have been achieved with the PI ionomer membrane. As evidenced in little changes in open circuit voltage (OCV) during the operation, the SPI membrane was durable for 5000 h, which is the longest fuel-cell operation reported for an alternative electrolyte membrane (Scheme 74).[199,200]

In addition, Watanabe et al. also developed an effective approach to improve the proton conductivity of polymer electrolyte membranes by simply incorporating acid-functionalized polysilsesquioxane (Scheme 75).[201] Nanocomposite membranes prepared by in situ sol–gel processing showed much higher proton conductivity (up to 30 times) than that of the original membranes and less dependence of the conductivity on the humidity. The nanocomposite membranes are expected to
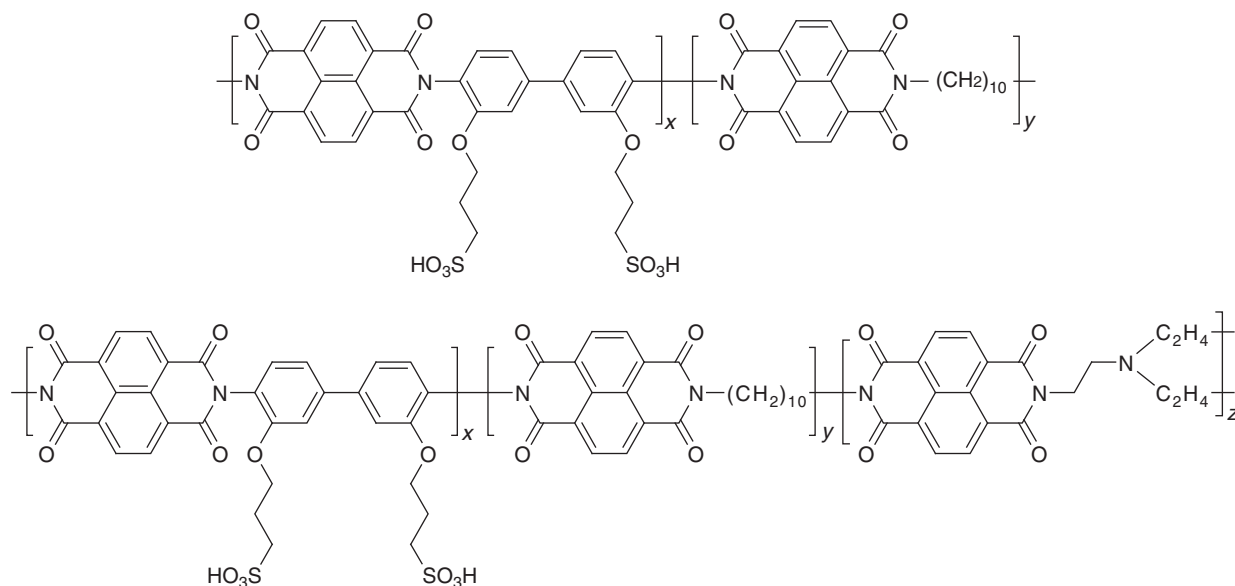
Scheme 74
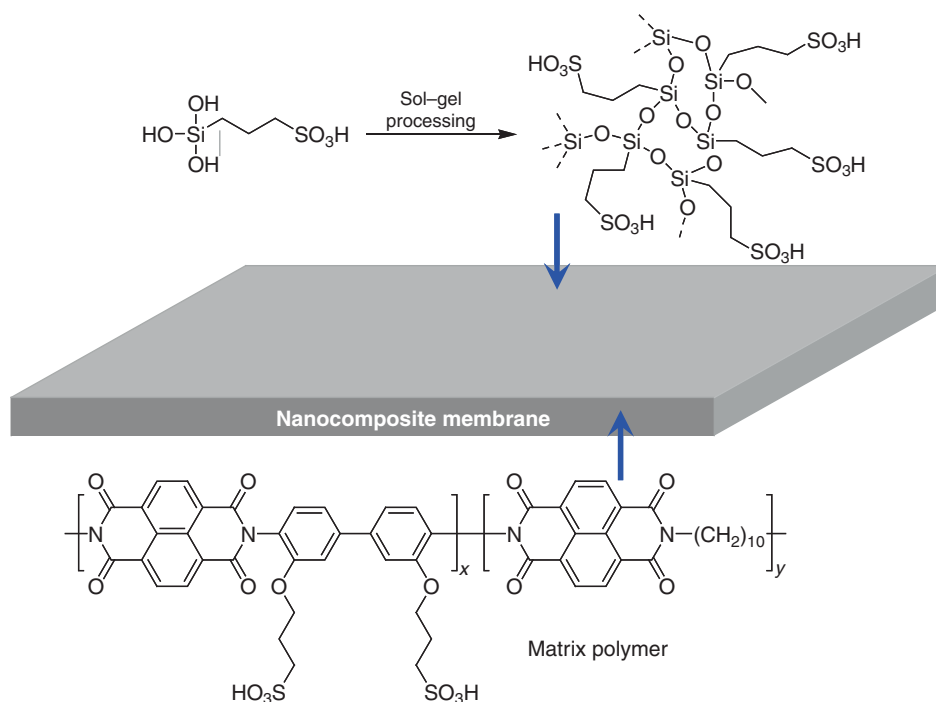
Scheme 75
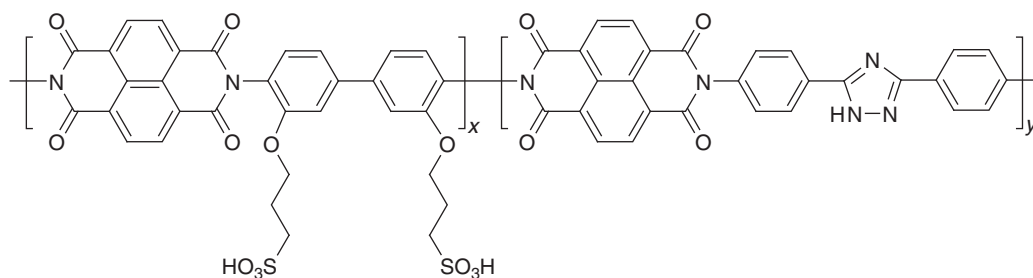
Scheme 76

have an impact on the field of solid electrolyte science, especially conductive membrane materials.

Recently, novel SPI ionomer containing triazole groups has also been proposed. The SPI membranes exhibit high proton conductivity, and thermal, oxidative, chemical, and good mechanical stability (Scheme 76).[202,203] The aim of this work was to evaluate the durability of the SPI membrane in polymer electrolyte fuel-cell (PEFC) operation. Watanabe *et al.* have confirmed that the triazole-based membrane could also be durable for 5000 h at 80 °C in single fuel-cell operation. Changes in the terminal voltage at constant current density, OCV, mass activity, and ohmic cell resistance were monitored during cell operation. Posttest analyses of the membrane characteristics were carried out, including thickness, IEC, and molecular weight.

5.20.4   Conclusions

PI synthesis has been explored to a significant extent as solution–processable high-performance polymers with superior properties such as high thermal stability, exceptional mechanical properties, and outstanding optical characteristics along with electrical and chemical resistance. An excellent combination of these properties makes them suitable for a wide range of applications from engineering plastics in aerospace industries to membranes for fuel-cell applications and gas or solvent separation. The functional PIs having potential applications such as electrochromic, luminescent, memory devices, high refractive, and fuel-cell materials were introduced and discussed.

This chapter also covered a majority of the works in the recent decade involving the synthesis and property evaluation of functional PIs as well as their structural design by using the respective monomers. This summarized information may be helpful for scientists to extend further research related to high-performance polymers and develop novel polymeric materials with an even wider range of useful properties.

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