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Abstract

Pyridazine-containing aromatic diamine monomer, 3,6-bis(4-aminophenoxy)pyridazine (APPD), was successfully synthesized by a nucleophilic substitution reaction of 3,6-dichloropyridazine with *para*-aminophenol. The aromatic heterocyclic diamine was employed to synthesize a series of polyimides (PIs) by polycondensation with various commercially available aromatic dianhydrides in *N,N*-dimethylacetamide via the conventional two-step method and further thermal imidization forming polyimides. The inherent viscosities of the resulting poly (amic acid)s were in the range of 0.47–1.51 dL g⁻¹. Meanwhile, strong and flexible PI films were obtained, which had good thermal resistance, with the glass transition temperatures of 214–305°C and the temperature at 5% weight loss of 421–463°C under nitrogen atmosphere, as well as outstanding mechanical properties with tensile strengths of 61–102 MPa and elongations at break of 2.8–64.7%. The cutoff wavelength of the PI films were ranged in 357–413 nm.

Keywords

Polyimide synthesis, pyridazine, heterocyclic diamine

Introduction

Over many years, polyimides (PIs) have been shown to be very useful and a class of high-performance polymers exhibiting a series of outstanding characters, such as high mechanical strength and excellent electrical properties, high thermal stability as well as good chemical resistance.^{1–5} Therefore, PIs have been widely employed in the fields of the aerospace, microelectronics, functional membranes, composites, and so on.^{6–8} However, with the fast development of these high-tech fields, the performances of the polymer materials are simultaneously put forward to higher requirements.

It is an effective way to improve thermal and mechanical properties of PIs by incorporating heterocyclic units into PI main chain since this class of groups tend to increase the rigidity of the polymer backbones and provide relatively high molar refraction.^{9–11} In recent years, many studies have been carried out to incorporate aromatic nitrogen (N₂)-containing heterocyclic moieties into polymer backbones, such as pyridazine,¹¹ pyridine,^{12–14} pyrimidine,^{15–17} benzimidazole,^{18–20} and phthalazinone.^{21,22} The design and synthesis of new monomers and their incorporation into PIs

backbones while maintaining the desirable properties are of particular interest. In this article, a novel pyridazine-containing diamine, 3,6-bis(4-aminophenoxy)pyridazine (APPD) was synthesized and the corresponding PIs were prepared based on APPD and commercial dianhydrides. The synthesis and characterization of APPD was conducted, and the thermal, mechanical, and optical properties and solubilities of the resulting PIs were investigated.

Experimentation

Starting materials

Pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 2,3',3,4' -oxydiphthalic

Alan G. MacDiarmid Institute, Jilin University, Changchun, People's Republic of China

Corresponding author:

Xiaogang Zhao, Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, People's Republic of China.

Email: xiaogang@jlu.edu.cn

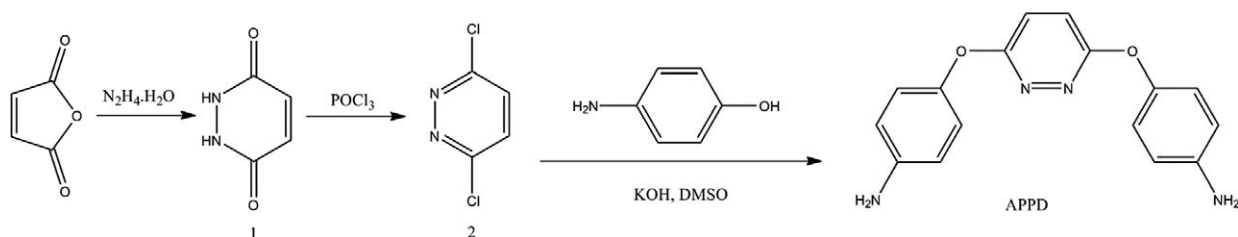


Figure 1. Preparation of the APPD monomer. APPD: 3,6-bis(4-aminophenoxy)pyridazine.

anhydride (3,4-ODPA), 3,3',4,4'-oxydiphthalic anhydride (4,4-ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd (Beijing, China), and these aromatic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuum at 150°C for 10 h prior to use. *para*-Aminophenol (Acros, Beijing InnoChem Science & Technology Co., Ltd, Beijing, China) was used as received. Dimethyl sulfoxide (DMSO), toluene, and *N,N*-dimethylacetamide (DMAc) were purified by vacuum distillation over calcium hydride and stored over 4 Å molecular sieves prior to use. The other commercially available reagents and solvents were used without further purification.

Measurements

Inherent viscosities (η_{inh}) of poly (amic acid) PAA were measured with an Ubbelohde viscometer with 0.5 g dL⁻¹ of DMAc solution at 20°C. Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-300 spectrometer (Swiss Bruker Co., Ltd) at 300 MHz for proton (¹H) NMR in deuterated DMSO. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer at a resolution of 4 cm⁻¹ in the range of 400–4000 cm⁻¹. All spectra were measured at room temperature and represented the average of 128 scans. Dynamic mechanical analysis (DMA) was carried out with a TA instrument DMA Q800 (New Castel, Delaware, USA) at a heating rate of 5°C min⁻¹ and a load frequency of 1 Hz in film tension geometry, glass transition temperature (T_g) was regarded as the peak temperature of loss modulus (E''). Differential scanning calorimetric (DSC) analysis was performed on a TA instrument DSC Q100 at a scanning rate of 10°C min⁻¹ in a N₂ flow of 50 mL min⁻¹. Thermogravimetric analysis (TGA) was conducted with the TA 2050 at a heating rate of 10°C min⁻¹ under N₂ atmosphere. Ultraviolet–visible (UV-Vis) spectra of PI films were recorded with a Shimadzu UV-Vis 2501 spectrometer (Tokyo, Japan) in transmittance mode at room temperature. The cutoff wavelength (λ_{cutoff}) was used as the parameter to evaluate the transparency of the films. Mechanical properties of the films were measured at room temperature on a Shimadzu AG-I

universal testing apparatus with a crosshead speed of 5 mm min⁻¹, tensile modulus (T_M), tensile strength (T_S), and elongation at break (E_B) were calculated as the average of five strips. Water uptake (WU) of the films was measured by the weight differences before and after immersion in deionized water at room temperature for 24 h, using the following equation (1):

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where W_{wet} is the weight of the film samples after immersion in deionized water and W_{dry} is the initial weight of the film samples.

Synthesis of the monomers

3,6-Dichloropyridazine (compound 2) and APPD were prepared by a known procedure,^{23,24} as shown in Figure 1. 3,6-Dichloropyridazine was synthesized by the following procedure: first, maleic anhydride and hydrazine monohydrate were mixed in ethanol and refluxed for several hours to obtain 1,2-dihydropyridazine-3,4-dione (compound 1). Then, compound (1) was refluxed with phosphorus oxychloride to give 3,6-dichloropyridazine (compound 2). Furthermore, APPD was prepared by aromatic nucleophilic chloro-displacement reaction of 3,6-dichloropyridazine with *p*-aminophenol and potassium phenoxide in DMSO, and dry toluene was added to remove water from a Dean–Stark trap.

Synthesis of 3,6-dichloropyridazine (compound 2)

3,6-Dichloropyridazine was prepared, as previously reported.²³ Melting point (MP): 68°C (DSC at a heating rate 10°C min⁻¹ under N₂ atmosphere). ¹H NMR (300 MHz, deuterated DMSO (DMSO-*d*₆), ppm): δ = 8.02 (d, 2H).

Synthesis of APPD

3,6-Bis(4-aminophenoxy)pyridazine was prepared, as previously reported.²⁴ MP: 208°C (DSC at a heating rate 10°C min⁻¹ under N₂ atmosphere). FTIR (casting film, cm⁻¹): 3210, 3301 (N–H), 3067 (C–H aromatic ring), 1539, 1499 (C=C aromatic ring), 1427 (C–N, pyridazine ring), 835

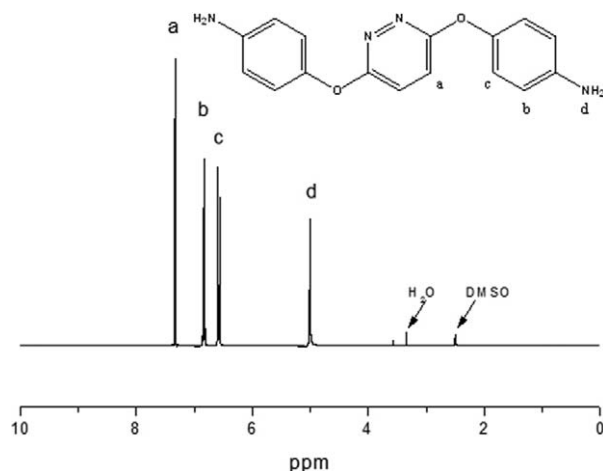


Figure 2. ^1H NMR spectra of APPD. ^1H NMR: proton nuclear magnetic resonance; APPD: 3,6-bis(4-aminophenoxy)pyridazine.

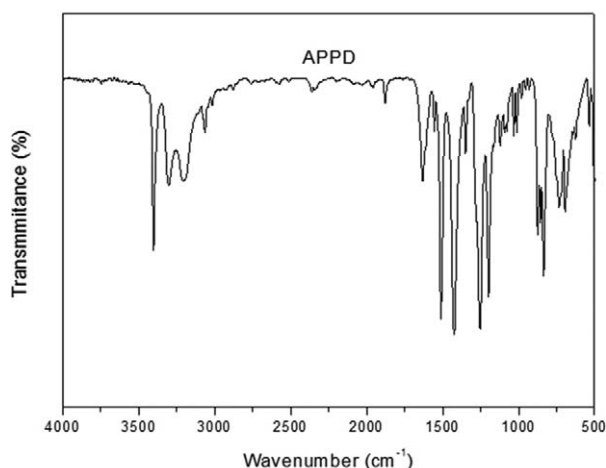


Figure 3. FTIR spectra of APPD. FTIR: Fourier transform infrared; APPD: 3,6-bis(4-aminophenoxy)pyridazine.

(*p*-substituent of aromatic ring). ^1H NMR (300 MHz, $\text{DMSO}-d_6$, ppm): δ = 7.16–7.44 (m, 2H), 6.75–6.96 (m, 4H), 6.48–6.65 (m, 4H), 4.99 (d, 4H). MS (ESI): m/e 295.1 ($\text{M} + \text{H}$) $^+$. (Figures 2 and 3)

Synthesis of the PIs

PIs were prepared by employing a two-step polycondensation of aromatic dianhydrides with APPD in DMAc as solvent to form soluble PAA precursors, followed by thermal imidization at elevated temperatures (as shown in Figure 4). PIs based on PMDA, BPDA, 3,4-ODPA, 6FDA, BTDA, 4,4'-ODPA, and BPADA were abbreviated as PI-a, PI-b, PI-c, PI-d, PI-e, PI-f, and PI-g, respectively. The synthesis of PI PMDA/APPD is used as an example to illustrate the general synthetic route to produce the PIs. 0.8725 g PMDA (4 mmol) was added to a solution of 1.1772 g APPD (4 mmol) in 5 g DMAc in two portions. Extra 6.61 g DMAc was

added to adjust the solid content of the reaction system to 15% by weight. The reaction mixture was stirred at room temperature for 24 h to give a viscous PAA solution. The values of η_{inh} of the PAA solutions were in the range of 0.47–1.51 dL g^{-1} , as shown in Table 1.

PI films were prepared by thermal imidization of PAA solutions cast onto glass plates, followed by a preheating program (40°C/2 h, 60°C/2 h) and an imidization procedure under vacuum (200°C/1 h, 300°C/1 h). The freestanding films were obtained by soaking in water to release from the glass substrates. As shown in FTIR spectra of the obtained PI films (Figure 5), the absorptions in the vicinity of 1780 and 1720 cm^{-1} were assigned to the asymmetric and symmetric C=O stretching vibrations in imide groups, the absorption at 1380 cm^{-1} was attributed to the C–N stretching vibration, indicating the accomplishment of imidization procedure.

Results and discussion

Thermal properties of the PIs were determined using TGA, DSC, and DMA, and the results are listed in Table 1. DSC curves are shown in Figure 6, T_g s of the PIs were in the range of 214–305°C and 217–331°C, as obtained by DSC and DMA, respectively. The slight differences of T_g values obtained by DSC and DMA were mainly attributed to the different responses of the samples to the two characterization methods. Generally, T_g values of polymers are determined by molecular packing and chain rigidity of the polymer backbones. As a result, PMDA-based PI-a with the most rigid polymer backbone exhibited the highest T_g , whereas PI-f derived from BPADA possessed the lowest T_g owing to its flexible polymer chain structure. Other PIs' T_g values were basically consistent with the rigidity order of the dianhydrides component except that PI-d showing (derived from 6FDA) a higher T_g value than that of PI-e (derived from BTDA). This exception might be attributed to inhibition of free rotation of the polymer segments due to the existence of CF_3 group in the backbone.²⁵ From Table 1, it can be seen that the T_g of PI-d (282°C, derived from 6FDA and APPD) was very similar to that (281°C) of PI derived from 6FDA and 1,4-bis(4-aminophenoxy)benzene (BAPB, with the same skeletal structure without N_2 as compared to APPD) and that the T_g of PI-b (295°C, derived from BPDA and APPD) was higher than those of PIs derived from BPDA and BAPB,^{26,27,28} the result indicated the rigidity of pyridazine was slightly higher than the benzene ring.

Thermal stabilities of the PIs were evaluated using TGA under N_2 atmosphere (as shown in Figure 7), and the results are summarized in Table 1. As can be seen from Figure 7, the PIs did not show obvious weight loss before 400°C, implying that no thermal decomposition occurred, and the onset decomposition temperatures were as high as 408°C. 5% and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) under N_2 atmosphere were located in the range of 421–463°C and 449–

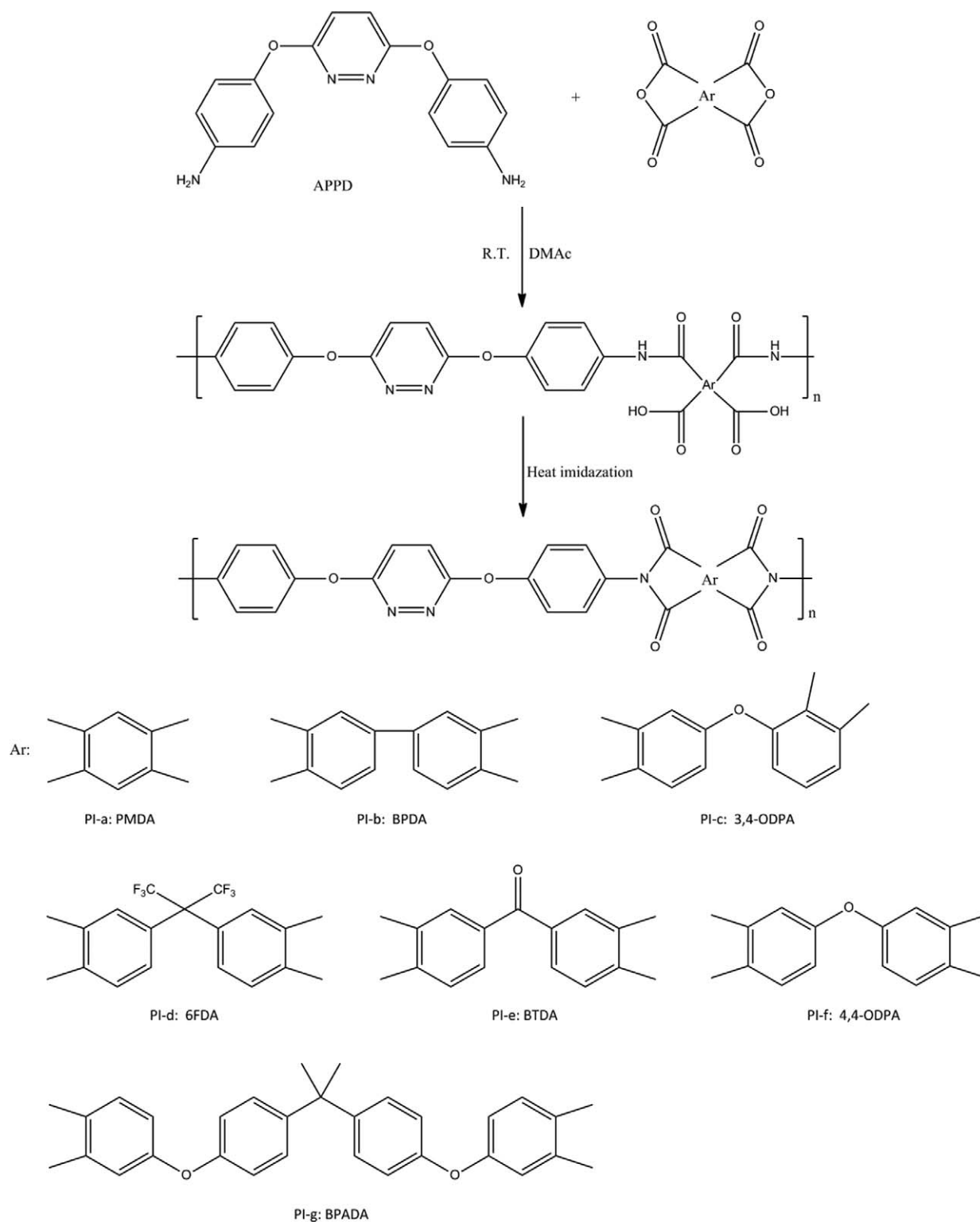


Figure 4. Preparation of the polyimides.

486°C, respectively. All the polymers showed a two-stage decomposition profile as observed from the corresponding derivative thermogravimetric curves (the inset of Figure 7). The first decomposition before 500°C is probably due to the

thermal degradation of pyridazine moiety.¹¹ The residual weight retentions at 800°C were in the range of 41–58%. TGA results indicated that the obtained PIs possessed fairly good thermal stability. For comparison, $T_{10\%}$ of PI-b and

Table 1. Thermal properties of the PI films and inherent viscosities of PAA.

PIs	η_{inh} of PAA (dL g ⁻¹) ^a	T_g (°C)		T_d (°C) ^d	$T_{5\%}$ (°C) ^e	$T_{10\%}$ (°C) ^e	R_w (%) ^f
		DSC ^b	DMA ^c				
PI-a	0.50	305	331	439	445	465	49.7
PI-b	1.03	295	290	443	454	479	58.1
PI-c	0.47	253	—	408	421	449	51.7
PI-d	1.38	282	286	448	463	486	51.8
PI-e	0.48	286	282	427	439	477	41.4
PI-f	0.47	254	257	437	450	473	54.9
PI-g	1.51	214	217	441	447	464	49.3
ref-PI ^g	1.27	281	—	—	—	570	58
ref-PI ^h	1.94	275	—	—	—	589	63

PI: polyimide; PAA: poly (amic acid); T_g : glass transition temperature; T_d : onset decomposition temperature; $T_{5\%}$: 5% weight loss temperature; $T_{10\%}$: 10% weight loss temperature; η_{inh} : inherent viscosity; N₂: nitrogen; DMA: dynamic mechanical analysis; TGA: thermogravimetric analysis; R_w : residual weight; 6FDA: 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; BAPB: 1,4-bis(4-aminophenoxy)benzene; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride.

^a η_{inh} of PAA was measured at 20°C with a concentration of 0.5 g dL⁻¹.

^bObtained at the baseline shift in the second heating DSC traces, with a heating rate of 10°C min⁻¹ under N₂ atmosphere.

^cMeasured by DMA at a heating rate of 5°C min⁻¹ and a load frequency of 1 Hz in film tension geometry.

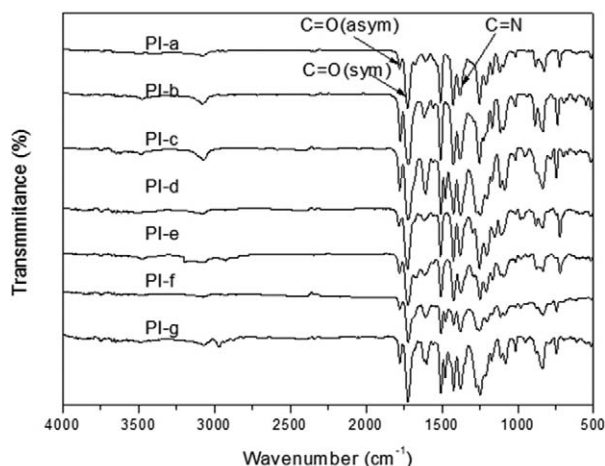
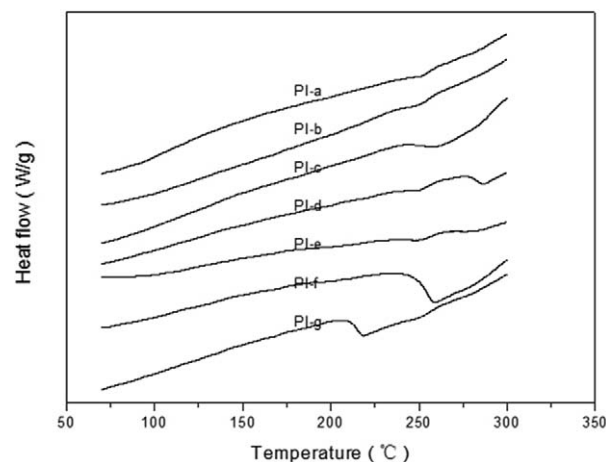
^d T_d by TGA at a heating rate of 10°C min⁻¹ under N₂ atmosphere.

^e $T_{5\%}$ and $T_{10\%}$ measured by TGA at a heating rate of 10°C min⁻¹ under N₂ atmosphere.

^f R_w retention at 800°C by TGA at a heating rate of 10°C min⁻¹ under N₂ atmosphere.

^g6FDA/BAPB.²⁶

^hBPDA/BAPB.²⁶

**Figure 5.** FTIR spectra of the PIs. FTIR: Fourier transform infrared; PIs: polyimides.**Figure 6.** DSC curves of PI films. DSC: differential scanning calorimetry; PI: polyimide.

PI-d were remarkably smaller than those of PI derived from BAPB, as well as the residual weight percentage at 800°C under N₂ atmosphere, indicating that the thermal stability of pyridazine-based PIs is inferior to the wholly aromatic PI structure.

The PI films were tested for mechanical properties at room temperature, as summarized in Table 2. The T_g of the films was as high as 102 MPa, with the T_M in range of 2.2–3.1 GPa, indicating that the obtained PI films were tough and strong. From Table 2, it can be seen that the mechanical properties of PI-d (6FDA/APPD) were comparable with that of ref-PI derived from 6FDA and BAPB.

The optical transparency of PI films were measured by UV-Vis spectroscopy, the value of λ_{cutoff} was used as the parameter to evaluate transparency. As listed in Table 2, λ_{cutoff} values were in the range of 371–412 nm. According to the theory of charge transfer complex (CTC),²⁹ strong electron donors and electron acceptors stabilize both the ground and the excited state of electrons and reduce the electronic transition energy between occupied and the unoccupied molecular orbitals. Clair and Clair³⁰ revealed that bulky electron-withdrawing groups such as $-\text{SO}_2-$ and $-\text{C}(\text{CF}_3)_2-$, flexibilizing groups such as $-\text{O}-$ lighten the color and increase the solubility. These phenomena

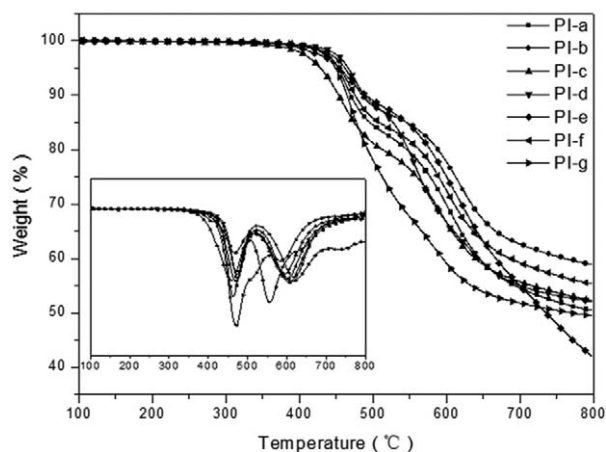


Figure 7. TGA curves of PI films. The inset shows the corresponding DTG curves. TGA: thermogravimetric analysis; PI: polyimide; DTG: derivative thermogravimetric.

were attributed to the reduction of the intermolecular CTC formation. Figure 8 shows UV-Vis absorption spectra of the PIs derived from APPD and seven dianhydrides. BPADA, 6FDA, and 4,4-ODPA produce fairly transparent PI films in contrast to other dianhydrides. On the other hand, PIs based on 3,4-ODPA, PMDA/APPD, BPDA, and BTDA have low transparency in the UV-Vis region.³¹ When the diamine structures are fixed, the value of λ_{cutoff} of PI films are directly related to the color intensity of PI films and the electron-withdrawing properties of the dianhydrides. Ando et al.³¹ reported the arrangements of dianhydrides in the order of color intensity of PIs from deep to pale when the diamine structures were fixed: BTDA > PMDA > BPDA > 4,4-ODPA > 6FDA. PIs derived from 6FDA and 4,4-ODPA have similar λ_{cutoff} , but the former one exhibits higher transparency at shorter wavelengths (380–400 nm) than the latter one and lowest λ_{cutoff} value among all the PI films. The light colors of 6FDA/APPD having $-\text{C}(\text{CF}_3)_2-$ groups in their dianhydride moieties can be explained from the decreased intermolecular

interactions. The deep color of the PI prepared from BTDA can be explained by cross-linking reactions occurring at benzophenone $\text{C}=\text{O}$ groups and the cross-linked portion usually shows a deep yellow color.

The PI films exhibited the WU of 0.64–1.53% as shown in Table 2. Since water absorption rate of Upilex[®]-75 S (Ube Industries Ltd, Japan) was measured to be 1.49% under the same conditions,³² these results implied that introduction of pyridazine moiety did not deteriorate the water absorption behavior of the PIs.

Solubility of the PIs was determined at room temperature for 24 h, and the results were summarized in Table 3. The obtained PIs exhibited good chemical resistance, and most of them were insoluble in common solvent such as NMP, DMF, DMAc, and DMSO at room temperature. PI-c, PI-d, and PI-g showed better solubility than other polymers, due to their distinguishing backbone structures: 3,4-ODPA-based PI-c possessed bent and distorted polymer chain conformation arising from the dianhydride component, the intermolecular interaction of PI-c was weak, enduing PI-c with better solubility,^{33,34} bulky pendant CF_3 group of 6FDA derived PI-d inhibited close packing of the polymer chain,³⁵ making PI-d easier to be dissolved; pendant CH_3 unit and flexible ether linkage of BPADA component also imparted PI-g better solubility. PI-d (derived from 6FDA/APPD) has better solubility than the comparable PI (derived from 6FDA/BAPB) in aprotic polar solvents. This improvement in the organosolubility of the PI-d can be attributed to the incorporation of N_2 -containing pyridazine ring into PI main chains, which disrupt the close packing of the polymer chains and decrease the interchain interactions.

Conclusions

PIs were prepared based on a novel diamine-containing pyridazine moiety APPD and various aromatic dianhydrides via a two-step polymerization process. These PIs with inherent viscosities of 0.47–1.51 dL g⁻¹ exhibited

Table 2. Mechanical and optical properties and water uptake of PI films.

PIs	T_S (MPa)	T_M (GPa)	E_B (%)	λ_{cutoff} (nm)	WU(%)
PI-a	— ^a	—	—	412	0.77
PI-b	72	3.1	2.8	396	1.39
PI-c	61	2.2	3.5	388	1.53
PI-d	90	2.3	10.5	371	0.64
PI-e	91	2.7	6.9	413	1.45
PI-f	91	2.4	59.9	375	1.22
PI-g	102	2.6	64.7	372	0.67
ref-PI ^b	103	2.1	16	—	—

PI: polyimide; T_S : tensile strength; T_M : tensile modulus; E_B : elongation at break; λ_{cutoff} : cutoff wavelength; WU: water uptake; PMDA: pyromellitic dianhydride; 6FDA: 2,2'-(bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; BAPB: 1,4-bis(4-aminophenoxy)benzene.

^a PI-a based on PMDA was too brittle to conduct tensile tests.

^b 6FDA/BAPB.²⁶

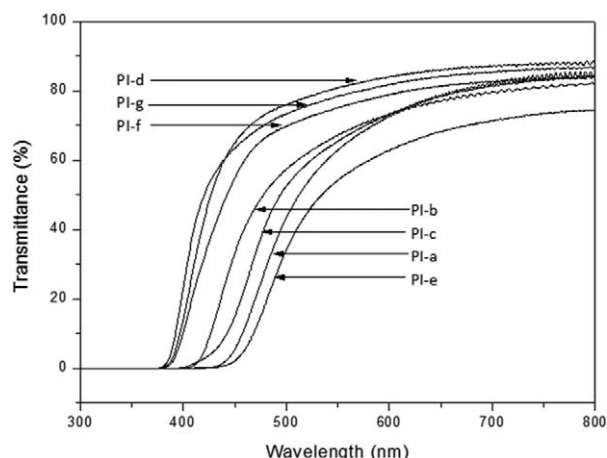


Figure 8. UV-Vis spectra of PIs. UV-Vis: ultraviolet–visible; PIs: polyimides.

high enough molecular weight to give tough and flexible thin films by solution casting. The PI films had good combination of properties. T_g values and thermal stabilities denoted by $T_{5\%}$ temperature of PI films varied from 214 to 305°C and from 421 to 463°C, respectively, depending on the rigidity of the polymer backbones. The PIs also have good mechanical properties, T_S of 61–102 MPa, T_M of 2.2–3.1 GPa, and E_B of 2.8–64.7%. The values of λ_{cutoff} of PI films were ranged in 357–413 nm.

Funding

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Table 3. Solubility of the polyimides PIs in organic solvents.^a

Solvent	NMP	DMAc	DMF	DMSO	CHCl ₃	THF
PI-a	--	--	--	--	--	--
PI-b	--	--	--	--	--	--
PI-c	+-	++	++	+-	--	--
PI-d	+-	++	++	+-	++	+-
PI-e	--	--	--	--	--	--
PI-f	--	--	--	--	--	--
PI-g	+-	++	++	+-	++	+-
ref-PI ^b	+-	+-	++	--	--	++

PI: polyimide; NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMF: dimethylformamide; DMSO: dimethyl sulfoxide; CHCl₃: chloroform; THF: tetrahydrofuran; ++: soluble at room temperature; +-: partially soluble; --: insoluble; 6FDA: 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; BAPB: 1,4-bis(4-aminophenoxy)benzene.

^a Solubility was determined with 10 mg of PIs in 1 mL of solvent at room temperature.

^b 6FDA/BAPB.²⁶

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