



Synthesis and characterization of an aromatic diamine and its polyimides containing asymmetric large side groups

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Received: 20 August 2019 / Revised: 14 November 2019 / Accepted: 19 December 2019 /

Published online: 1 January 2020

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Abstract

A novel aromatic diamine monomer with asymmetric large side group: 4-(2,4,6-trimethyl)phenoxy-1,3-diaminobenzene, was synthesized by a two-step organic reaction. The monomer was separately subjected to a one-step high-temperature polycondensation reaction with three commercial aromatic dianhydrides to obtain a series of polyimides. Their structures and properties were characterized and studied by FTIR, NMR, UV, TGA, DSC, etc. The obtained polyimides showed excellent solubility not only in high-boiling solvents such as NMP, DMAc, and DMF, but also in low-boiling solvents such as CHCl_3 and CH_2Cl_2 . Their tensile strength was in the range of 76.9–93.5 MPa, the elongation at break was between 4.8% and 7.3%, and the modulus of elasticity was in the range of 1.6–1.8 GPa. The obtained films exhibited good optical transparency, and the representative polyimide derived from 4,4'-oxydipthalic dianhydride exhibited a light transmittance of more than 83% at a wavelength of 450 nm. Moreover, these polyimides also possessed good thermal properties. Their glass transition temperatures are between 285 °C and 345 °C, and the 10% weight loss temperature in air and nitrogen is above 463 °C, showing excellent thermal properties.

Keywords Polyimides · Large side group · Solubility

Introduction

Aromatic polyimides were a class of important heterocyclic polymers with imide ring structure in the main chain. They possessed excellent thermal stability, mechanical properties, electrical properties, chemical resistance and low thermal expansion, and

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could be used as special engineering plastics, separation membrane materials, and high-temperature-resistant coatings in aerospace, petrochemical, microelectronics, gas separation and other fields [1–4]. However, for most aromatic polyimides, due to the rigid benzimidazole rings in the main chain and the structural regularity, they showed poor solubility and were difficult to directly form membrane. In addition, such polyimides also had deeper colors and poor optical transparency, which limited their application in the field of optoelectronics to a certain extent [5–10]. Therefore, the design and development of polyimides with good film formation and high optical transparency had important research significance and practical application value.

At present, it was found that the solubility and film formability for polyimides could be improved by reasonably designing based on their molecular structures, such as the introduction of flexible structural units [11], large substituted side groups [12–14], asymmetric structures [15–19], or twisted non-coplanar structures [20–23], and their original excellent properties also could be maintained. Among these modification methods, good modification effect could be achieved for polyimides by introducing asymmetric large substituted side groups, especially for their solubility and optical transparency [16, 18]. The introduction of asymmetric large substituted side groups could not only effectively increase the free volume of molecules and weaken the interaction between molecular chains, but also reduce the aromatic conjugation of molecular chains, which is very helpful for improving the solubility and optical transparency. In addition, it had been reported that the dielectric properties and gas separation properties of polyimides could also be improved by introducing asymmetric large substituted side groups [24, 25]. However, due to the difficulty of asymmetric chemistry, the design and synthesis of polyimides with asymmetrically substituted side groups were challenging. Currently, asymmetric monomers and their polyimides with large substituted side groups were very limited, and most of them usually needed to be prepared by complex multi-step organic reactions.

In this study, from the perspective of molecular structure design, a new type of asymmetric aromatic diamine monomer with large substituted side groups: 4-(2,4,6-trimethyl)phenoxy-1,3-diaminobenzene, was synthesized by a relatively convenient two-step organic reaction using 2,4-dinitrobromobenzene and 2,4,6-trimethylphenol as starting materials. Polyimides were further prepared by one-step solution polycondensation using this synthesized diamine monomer with three commercial aromatic dianhydrides. By asymmetrically introducing large side groups in the molecular structure of the polyimides, the spatial molecular structure of the macromolecular chain was further optimized, and the film-forming property and optical transparency of the obtained polymer would be improved. The structures of the monomer and polyimides were characterized in detail, and the relationship between the structure and properties for these polymers was also discussed in depth.

Experimental

Materials and measurements

2,4-Dinitrobromobenzene (98%) was purchased from Wuhan Changcheng Chemical Technology Development Co. and used as received. 2,4,6-Trimethylphenol (98%) was purchased from Tokyo Chemical Industry Co. and used as received. Hydrazine hydrate (99%) was purchased from Aladdin Reagent Co. *m*-Cresol (99%) was purchased from Aladdin Reagent Co. and used as received. Aromatic tetracarboxylic dianhydrides such as 4,4'-oxydiphthalic dianhydride (ODPA 98%), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA 98%), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA 98%) were purchased from TCI company and further purified by recrystallization from acetic anhydride. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), trichloromethane (CHCl₃), and other reagents were used as received.

Nuclear magnetic resonance spectroscopy (NMR) spectra were obtained using a Bruker AV400 instrument with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) or CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using a Nicolet NEXUS 670 spectrometer. Polymer molecular weight test: gel permeation chromatography (GPC) on soluble polymers, was performed using a Waters 1515 system equipped with a triple detector array and a packing column (Styragel HT4 WAT044210, 7.8×300 mm) using tetrahydrofuran (THF) as an eluent at 25 °C and the flow rate of 1 mL/min. The glass transition temperatures (*T*_g) of the membranes were characterized using differential scanning calorimetry (DSC, PE diamond DSC instrument). The samples were tested for two consecutive scans at the heating rate of 20 °C/min. The first cycle of ramping and cooling was carried out to eliminate any thermal history of the samples. The *T*_g of each sample was obtained based on the mid-point transition temperature of the second heating curve. Thermogravimetric analysis (TGA) of the polymer samples was performed using a Netzsch TG 209F1 instrument at the heating rate of 20 °C/min under nitrogen and oxygen atmosphere, respectively. The tensile properties were obtained using an Instron 5565 Tensile Apparatus with a 5-kg load cell at the crosshead speed of 5 mm/min on the strips approximately 60 mm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least three individual determinations was used. Ultraviolet–visible (UV–Vis) spectra of the polymer films were obtained using a PerkinElmer Lambda 35 UV–Vis spectrophotometer at room temperature.

Synthesis of diamine monomer

- (1) Synthesis of the intermediate 4-(2,4,6-trimethyl)phenoxy-1,3-dinitrobenzene

14.8200 g (0.06 mol) of 2,4-dinitrobromobenzene, 8.1714 g (0.06 mol) of 2,4,6-trimethylphenol, 9.9511 g (0.072 mol) of anhydrous K_2CO_3 , and 100 mL of DMAc were sequentially added to a 250-mL three-necked flask. Under nitrogen protection, the mixture was stirred at room temperature for 10 min and further heated to 140 °C for 8 h. Then, the reaction was terminated and the mixture was transferred to an ethanol/water (1/4) solution. The crude product was recrystallized from DMAc and dried in vacuo to give a pale yellow product: 4-(2,4,6-trimethyl)phenoxy-1,3-dinitrobenzene, yield: 90%. 1H -NMR (DMSO, 400 MHz, δ): 8.91 (d, $J=2.8$ Hz, 1H), 8.39 (dd, $J=9.3, 2.8$ Hz, 1H), 7.07 (s, 2H), 6.79 (d, $J=9.3$ Hz, 1H), 2.29 (s, 3H), 2.04 (s, 6H). IR (KBr, ν): 3080, 2922, 2853, 1539, 1350, 1189 cm^{-1} .

(2) Synthesis of diamine 4-(2,4,6-trimethyl)phenoxy-1,3-diaminobenzene

9.3707 g (0.031 mol) of the intermediate dinitro compound, 0.468 g of palladium carbon catalyst, and 100 mL of ethanol were sequentially added to a 250-mL three-necked flask equipped with a reflux condenser and a mechanical stirrer, and the mixture was heated to 95 °C with stirring. Then, 9 mL of hydrazine hydrate was slowly added dropwise in a constant pressure dropping funnel, and added in three portions. After refluxing for 7 h, the reaction was terminated. The solution was subjected to hot filtration, cooling, crystallization, and then the product was filtered out and dried under vacuum. The product was named as 4-(2,4,6-Trimethyl)phenoxy-1,3-diaminobenzene, yield: 85%, mp: 118 °C by DSC at the scan rate of 10 °C/min. 1H -NMR (DMSO, 400 MHz, δ): 6.88 (s, 2H), 6.02 (d, $J=2.5$ Hz, 1H), 5.77 (d, $J=8.4$ Hz, 1H), 5.59 (s, 1H), 4.73 (s, 2H), 4.37 (s, 2H), 2.22 (s, 3H), 2.02 (s, 6H). ^{13}C -NMR ($CDCl_3$, 126 MHz, δ): 149.63, 140.90, 138.96, 136.29, 133.93, 131.08, 129.50, 113.16, 104.98, 103.56, 20.82, 16.13. IR (KBr, ν): 3408, 3347, 3109, 2920, 2853, 1212 cm^{-1} .

Synthesis of polyimides

Polyimides synthesis was exemplified by PI-BPDA. Under nitrogen protection, 1.2116 g (0.005 mol) of diamine monomer, 1.4711 g (0.005 mol) of biphenyltetracarboxylic dianhydride, 12 mL of *m*-cresol, and 5–6 drops of isoquinoline were added to a 100-mL three-necked flask. The temperature was raised to 100 °C and stirred. After the reaction system was dissolved, the temperature was further adjusted to 190 °C. When the reaction was carried out for 8–10 h, a viscous polymer solution was obtained. The reaction is then terminated, diluted with 5 mL solvent, and precipitated in ethanol. The white filamentous polymer was obtained. The resulting fiber-like precipitate was obtained by washing with hot water several times, and drying overnight at 120 °C under vacuum.

PI-BPDA. 1H -NMR ($CDCl_3$, 400 MHz, δ): 8.26 (d, $J=13.9$ Hz, 2H), 8.11 (d, $J=9.8$ Hz, 4H), 7.63 (s, 1H), 6.90 (s, 2H), 6.64 (d, $J=8.8$ Hz, 1H), 2.30 (s, 3H), 2.11 (s, 6H). IR (film, ν): 3109, 2920, 2853, 1782, 1727, 1360, 1246 cm^{-1} .

Preparation of polyimide films

The films were produced by means of glass plate casting. Approximately 0.05 g of the polymer was weighed and dissolved in 15 mL of DMAc. A sample film with a thickness of 0.02 mm was obtained in the same manner and was used for FTIR and UV tests. Another sample film with a thickness of 0.06 mm was obtained in the same manner and was used for DSC and mechanics tests. All membranes were immersed in ethanol solution for 6 h and then dried in an oven.

Results and discussion

Synthesis and characterization of diamine monomer

4-(2,4,6-Trimethyl)phenoxy-1,3-diaminobenzene was obtained through two-step organic reactions, and the synthetic route is shown in Fig. 1. Firstly, the 2,4-dinitro-bromobenzene and 2,4,6-trimethylphenol were subjected to an aromatic substitution reaction to prepare a dinitro compound, 4-(2,4,6-trimethyl) phenoxy-1,3-dinitrobenzene, using anhydrous K_2CO_3 as a catalyst. Then, the dinitro compound was reduced to the diamine monomer of 4-(2,4,6-trimethyl)phenoxy-1,3-diaminobenzene with a palladium carbon and hydrazine hydrate as catalyst and reductant, respectively. Both of these two-step reactions had a high yield.

The FTIR spectra of the dinitro compound and the diamine monomer are shown in Fig. 2. It could be seen from the figure that the dinitro compound exhibits the stretching of the nitro group ($-NO_2$) at 1350 and 1539 cm^{-1} , respectively. After the reduction to diamine monomer, the absorption peak disappeared, and a typical amino multiple splitting stretching vibration peak appeared at 3347 cm^{-1} and 3408 cm^{-1} , indicating that the dinitro group was successfully reduced to diamine monomer. Further, both the dinitro compound and the diamine had distinct methyl ($-CH_3$) groups in the chemical structural formula, and in the FTIR spectrum, a characteristic peak appeared in the range of $2853\text{--}3109\text{ cm}^{-1}$. 1H NMR spectrum of the dinitro compound 4-(2,4,6-trimethyl)phenoxy-1,3-dinitrobenzene is shown in Fig. 3. As shown in Fig. 3, proton peaks on the methyl groups were found at $\delta=2.03$ and $\delta=2.26$ (number 6 and 5 in Fig. 3). Other proton peaks appeared in the range of $\delta=6.77\text{--}8.90$, respectively. The proton peaks at position 1 in Fig. 3 appeared at

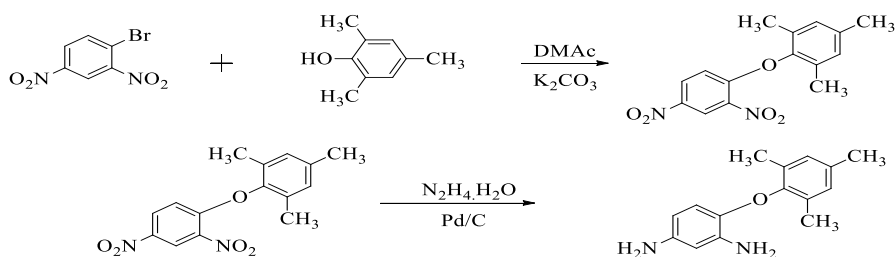


Fig. 1 Synthesis of the diamine monomer

Fig. 2 FTIR spectrum of the dinitro compound, diamine monomer, and PI-BPDA

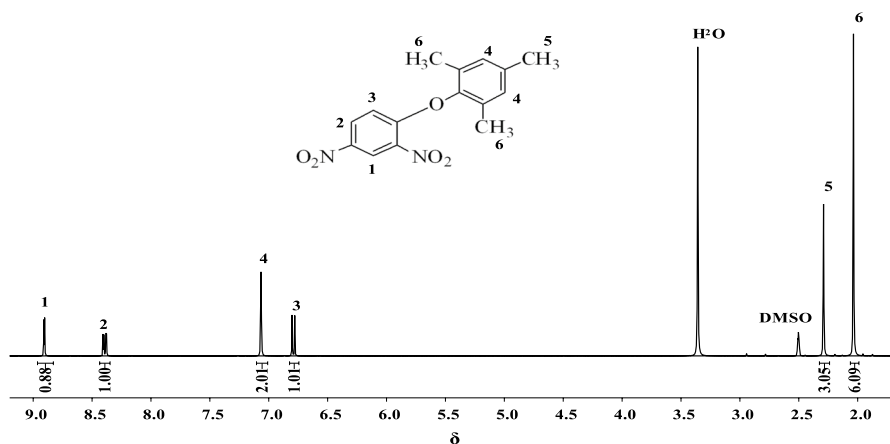
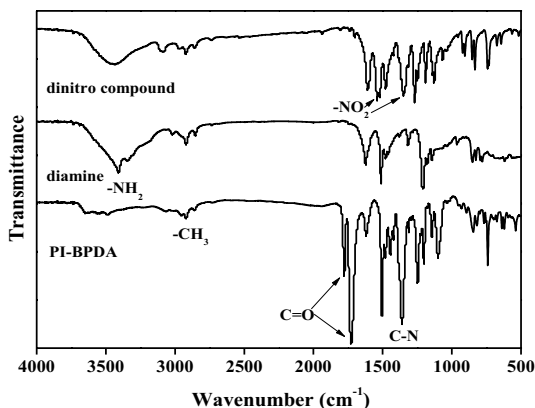


Fig. 3 ^1H NMR spectrum of the dinitro compound in DMSO

the lowest field due to the strong electron-withdrawing action of the nitro group. ^1H NMR spectrum of the diamine monomer is shown in Fig. 4. As could be seen from the figure, significant amine matrix peaks (number 7, 8) were found at $\delta=4.36$ and $\delta=4.78$. Among them, due to the electron-donating ability of the amine groups, the electron density around the protons (number 1, 2, 3) on the benzene ring was enhanced, the shielding effect was increased, and the chemical shift value was decreased, which occurred in the range of $\delta=5.58\sim\delta=6.01$. At the same time, the ^{13}C NMR spectrum of the diamine monomer is shown in Fig. 5. The C atoms on the diamine monomer could find a reasonable attribution on the spectrum, and the chemical shift of the C atom on the methyl group (number 6 and 5) appeared at $\delta=16.10$ and $\delta=20.59$ in the figure. The chemical shift of C atoms on the benzene ring was in the range of $\delta=103.40\sim\delta=149.56$. Corresponding test results further confirmed that the structure of the prepared monomer is completely consistent with the designed chemical structure.

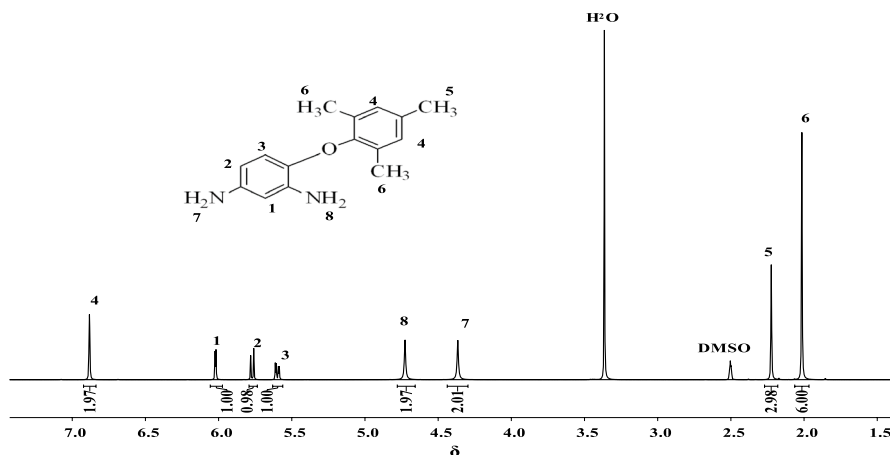


Fig. 4 ^1H NMR spectrum of the diamine in DMSO

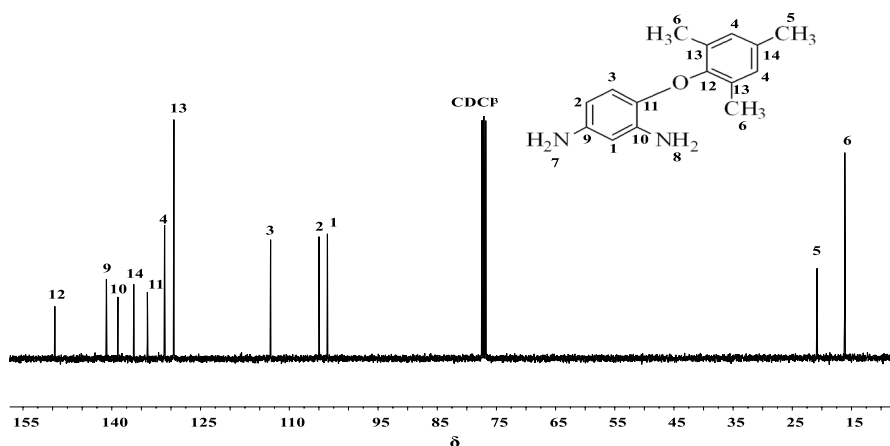


Fig. 5 ^{13}C NMR spectrum of diamine monomer in CDCl_3

Synthesis and characterization of polyimides containing large pendant groups

The aromatic diamine monomer containing the asymmetric large side group structure was subjected to polycondensation reaction with three aromatic dianhydride monomers (3,3',4,4'-oxydiphthalic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride) in one-step high-temperature solution to obtain a series of novel polyimides (PI-ODPA, PI-BPDA, and PI-BTDA), respectively. The synthetic route is shown in Fig. 6. The entire polymerization process was carried out in a homogeneous solution, indicating that the designed polyimides had good solubility in the *m*-cresol. Table 1 shows the results of the molecular weights and intrinsic viscosities of these PIs. It could be seen that the number-average molecular weights

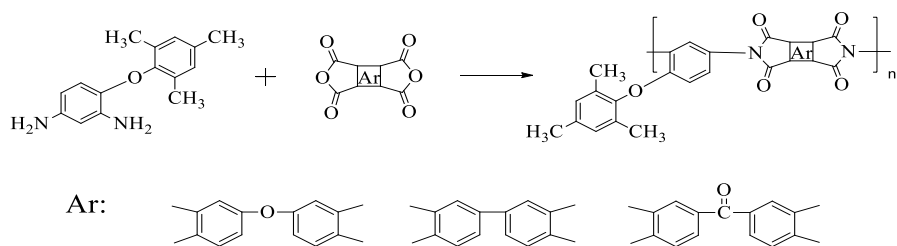


Fig. 6 Synthesis of polyimides

Table 1 Inherent viscosities^a and GPC molecular weights of the PIs

PI	η_{inh} dL(g)	GPC		
		$M_n \times 10^4$	$M_w \times 10^4$	PDI
PI-ODPA	0.82	4.72	7.75	1.65
PI-BPDA	0.76	4.56	7.48	1.64
PI-BTDA	0.73	4.00	6.38	1.59

^aMeasured at the concentration of 0.5 g/dL in NMP at 25 °C

of the obtained polymers were in the range of 4.00×10^4 – 4.72×10^4 , the weight-average molecular weights were in the range of 6.38×10^4 – 7.75×10^4 , and the polydispersity index (PDI) was between 1.59 and 1.65. Their intrinsic viscosity was 0.73–0.82 dL/g. The results indicated that these polymers had high molecular weight and moderate molecular weight distribution.

The obtained polyimides were subjected to FTIR spectrum and ^1H NMR test analysis. The FTIR spectrum of a representative PI-BPDA is shown in Fig. 2. It could be seen from the figure that PI-BPDA had a typical characteristic vibration absorption peak of the imide ring at about 1782, 1727, and 1360 cm^{-1} compared with the FTIR spectrum of the diamine monomer. And the amine-based multiple-cleavage absorption peaks in the range of 3347–3408 cm^{-1} completely disappeared in the figure; it can be interpreted as polycondensation led to consuming of NH_2 groups, and a one-step reaction led to full imidization. ^1H -NMR spectrum of a representative PI-BPDA is shown in Fig. 7. It could be seen from the figure that the characteristic peaks of amino protons (at $\delta = 4.36$ and $\delta = 4.78$, Fig. 4) completely disappeared in the spectrum of PI-BPDA. At the same time, the proton peaks on the benzene ring in the structural units of the biphenyl dianhydride (protons numbered 1, 2, 3) appeared in Fig. 7. They were directly affected by the strong electron absorption of the carbonyl group on the imide group, and the resonance absorption peaks appeared at the lowest field high chemical shift position. The corresponding chemical shifts were $\delta = 8.08$, $\delta = 8.13$ and $\delta = 8.26$, respectively. The results of FTIR and NMR testing confirmed that the prepared diamine monomer and the aromatic dianhydride were polycondensed to obtain a corresponding polyimide.

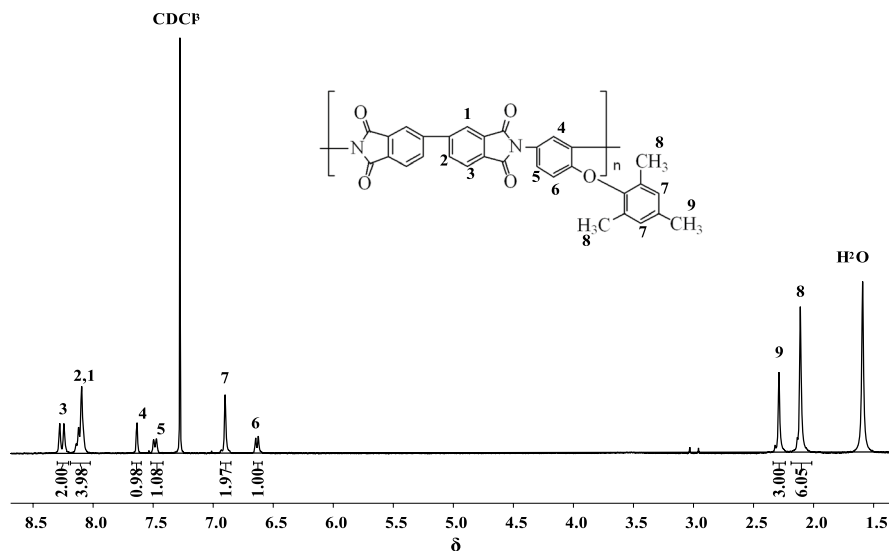


Fig. 7 ^1H NMR spectrum of PI-BPDA in CDCl_3

Solubility of polyimides

Aromatic polyimides generally exhibited poor solubility because they had highly rigid macromolecular chains. The solubility of these prepared polyimides with asymmetric large side structure was tested (Table 2), and the results indicated that they had excellent solubility. They not only can be dissolved in high-boiling solvents such as NMP, DMAc, and DMF at room temperature, but also can be dissolved in low-boiling solvents such as CHCl_3 and CH_2Cl_2 . These polyimides also showed comparable solubility properties to some of the polyimides containing other large substituted pendants reported in the previous issues [3–5, 13]. The excellent solubility was mainly due to the introduction of 2,4,6-trimethylphenoxy pendant groups on the polyimides macromolecular backbone. The introduction of asymmetric large side groups could increase the distance between the polymer chains, reduce the regularity of polymer chains, and weaken the interaction force between polymer chains. The solvent molecules were more easily infiltrated, thereby effectively improving the solubility of the polymer. Excellent solubility could effectively improve the film formation of polymer, which was convenient for the application of polyimides. It

Table 2 Solubility behavior of the polymers

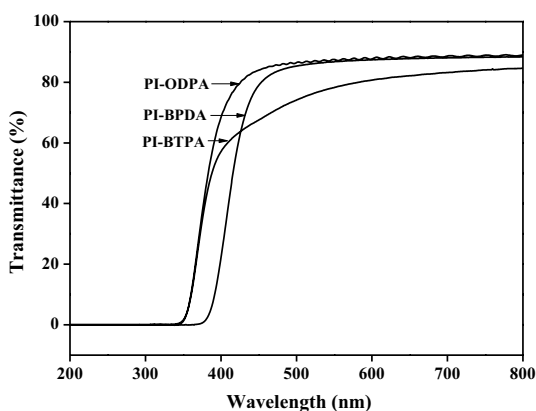
PI	NMP	DMAc	DMF	DMSO	CHCl_3	CH_2Cl_2
PI-ODPA	+++	+++	+++	+	+++	+++
PI-BPDA	+++	++	+	–	++	++
PI-BTDA	+++	++	++	S	++	++

+++; 0.1 g sample dissolved in 1 mL solvent (10 wt %); ++, soluble at 5 wt %; +, soluble at 1 wt %; S, swelling; –, insoluble



Fig. 8 The membranes of PI-ODPA, PI-BPDA, and PI-BTDA

Fig. 9 The UV spectra of PIs



could be further found from the solubility test that PI-ODPA had the highest solubility, while PI-BPDA had the lowest solubility, which is mainly due to the different rigidity of the dianhydride structure.

Optical properties of polyimides

Due to high aromatic conjugation and strong charge complex transfer in polymer chains, PI films usually have dark colors (yellow or reddish yellow) and poor optical transparency in the UV–visible region. A comparative picture of PI-ODPA, PI-BPDA, and PI-BTDA is shown in Fig. 8. The optical transparency of the obtained films was tested by an ultraviolet–visible spectrophotometer. Figure 9 shows the transmittance curves of the films at 200 nm to 800 nm. As can be seen from the figure, the polyimide films had good optical transparency in the visible light wavelength range. Their cutoff wavelength was in the range of 338–361 nm, and the transmittance under 500-nm wavelength light was above 74.2% (as shown in Table 3). These prepared polyimides with asymmetric large side structure also had comparable optical transparency to the reported polyimides with fluorine-containing

Table 3 Optical transparency of the PI films

PI	<i>d</i> (μm)	T (%)			λ_{cutoff} (nm) ^a
		450 nm	500 nm	550 nm	
PI-ODPA	19	83.9	86.5	87.6	338
PI-BPDA	17	78.9	85.3	86.7	361
PI-BTDA	18	67.5	74.2	78.3	341

^aCutoff wavelength

large side structure [3, 4]. Good optical transparency was mainly due to the introduction of large substituted side groups in the main chain of the polyimide structures, which effectively reduced the aromatic conjugation and charge complex transfer in polymer chains. In comparison, the PI-ODPA had a lower cutoff wavelength and higher optical transparency, and its transparency at light of 450 nm reached 83.9%. The excellent optical transparency was mainly attributed to the further affection of the ether linkage in the dianhydride structural units. The prepared PI-BTDA had a slightly poor optical transparency, and the carbonyl group in the dianhydrides was a chromogenic group, so that the film exhibited a light yellow color and lower optical transparency.

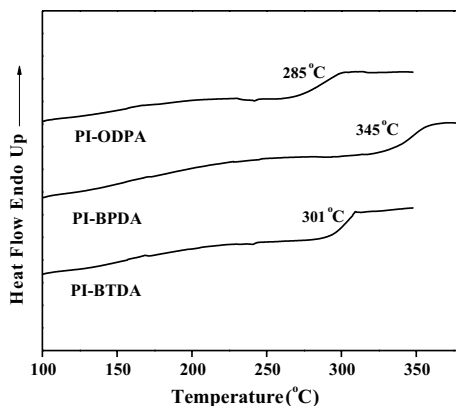
Thermal properties of polyimides

The glass transition temperatures and thermal stability of the polyimides were tested by DSC and TGA, respectively, and the test results are shown in Table 4. Figure 10 shows the DSC curves of the obtained polymers. It could be seen from the figure that this type of polyimides exhibited high glass transition temperatures with the values of 285–345 °C. The polymers produced in this study had higher glass transition temperatures than some other polyimides with large substituted pendant structures [3–5, 13, 21]. Generally, the introduction of large side groups may decrease the glass transition temperature due to the increase in the free volume of molecular chains. But the designed diamine was a very rigid monomer, and the two amino groups were located on the same benzene ring, which made the prepared polyimides have highly rigid molecular backbone structure. In addition, the large substituted

Table 4 Thermal properties of polyimides

PI	T_g (°C)	T_{10}^b (°C)		R_w^c (%)
		in Air	in N ₂	
PI-ODPA	285	479	501	50.7
PI-BPDA	345	489	506	47.8
PI-BTDA	301	463	496	52.3

^aMeasured by DSC at the heating rate of 20 °C/min^b5% Weight loss temperature in TGA at 20 °C/min heating rate^cResidual weight retention at 800 °C

Fig. 10 DSC curves of polyimides

side groups may also hinder the free rotation of polymer molecular chains. Based on these, the glass transition temperature of the prepared polyimides was maintained at a high level. Compared to PI-ODPA and PI-BTDA, PI-BPDA exhibited a higher glass transition temperature, mainly due to the more rigid biphenyl structural unit in its molecular structure. Figures 11 and 12 show the thermal weight loss curves of PI under N₂ and air, respectively. The data were summarized in Table 4. As shown in Table 4, the obtained polyimides exhibited good thermal stability: The 10% weight loss temperature ($T_{10\%}$ °C) exceeded 463 °C and 496 °C under air and nitrogen atmospheres, respectively, and the mass retention rates at 800 °C exceeded 47.8%.

Mechanical properties of polyimides

The mechanical tensile properties of the prepared polyimide films were tested. It can be seen from Fig. 13 that the tensile strength of the polymers was in the range of 76.9–93.5 MPa, the elongation at break was in the range of 4.8–7.3%, and the modulus of elasticity was in the range of 1.6–1.8 GPa. The results showed that the

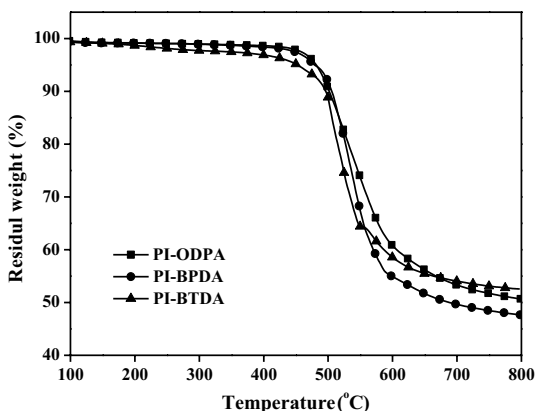
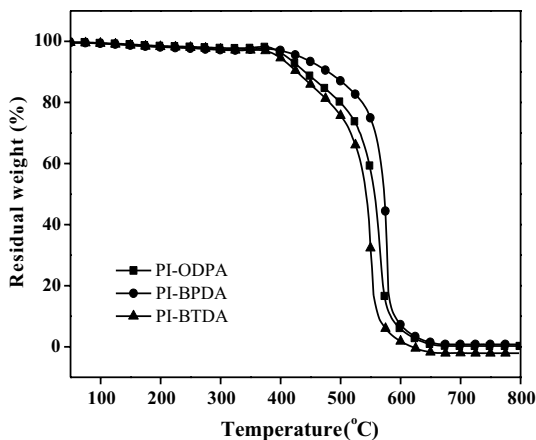
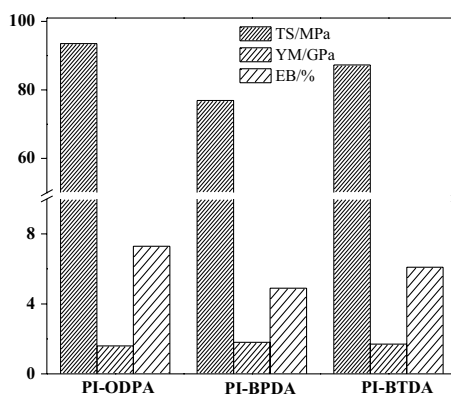
Fig. 11 TGA curves of polyimides in N₂

Fig. 12 TGA curves of polyimides in air**Fig. 13** Mechanical properties of polyimides

molecularly modified polyimides still had good tensile strength and modulus. PI-ODPA film had a large elongation at break of 7.3%, which may be attributed to the introduction of relatively flexible ether linkages in its dianhydride structural unit. The PI-BPDA film exhibited a maximum modulus of elasticity of 1.8 GPa, which was mainly attributed to the highly rigid biphenylimide structure in the dianhydride building block.

Conclusion

A novel aromatic diamine containing asymmetric large side group was synthesized by two organic reactions using conventional 2,4-dinitrobromobenzene and 2,4,6-trimethylphenol as the starting materials. This diamine monomer was reacted with three commercial dianhydride monomers to obtain a series of modified polyimides having a relatively high molecular weight. The obtained polyimides had excellent solubility and film-forming properties. Their films exhibited good optical

transparency, thermal properties, and mechanical properties. This type of polyimides had potential application value in the field of high-performance engineering plastics and functional separation membrane materials. This work provides a reference method for the design and synthesis of asymmetrically functionalized polyimides.

Acknowledgements Foundation items: National Natural Science Foundation of China (21404016); Key Research Project of Jiangsu Province (BE2017645); Scientific Research and Innovation Project for Graduate Students in Jiangsu Province (SJCX18-0954), and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions of China.

Funding information No funding supports this study.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical standard This work complies with ethical standard.

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