Synthesis and properties of polyimides from isomeric bis(dicarboxylphenylthio)diphenyl sulfone dianhydrides

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Abstract

4,4′-Bis(3,4-dicarboxyphenylthio)diphenyl sulfone dianhydride(4,4′-PTPSDA) and 4,4′-bis(2,3-dicarboxyphenylthio)diphenyl sulfone dianhydride(3,3′-PTPSDA) were synthesized from chlorophthalic anhydrides and bis(4-mercaptophenyl)sulfone. Their structures were determined via IR spectra, ^{1}H NMR and elemental analysis. A series of polyimides were prepared from isomeric PTPSDAs and aromatic diamines in 1-methyl-2-pyrrolidinone (NMP) via the conventional two-step method. Polyimides based on 4,4′-PTPSDA and 3,3′-PTPSDA have good solubility in polar aprotic solvents and phenols. The 5% weight-loss temperatures of isomeric polyimides were near 500 °C in N_2. DMTA and DSC analyses indicated that the glass-transition temperatures of polyimides from 3,3′-PTPSDA are higher than those of polyimides from 4,4′-PTPSDA. The wide-angle X-ray diffraction showed that all polyimides are amorphous. The polyimides from 3,3′-PTPSDA showed higher permeability but lower permselectivity compared with those from 4,4′-PTPSDA.
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Keywords: PTPSDA; Isomeric polyimides; Structure—property relations

1. Introduction

Aromatic polyimides are considered to be one of the most important classes of high-performance polymers because they have excellent thermal, mechanical and electrical properties as well as outstanding chemical resistance [1–3]. However, their applications are often limited because of their poor solubility and high processing temperature partly due to the strong interchain interaction. To overcome these limitations, many efforts have been made to improve the processability of polyimides while maintaining their excellent properties [4–9]. Different structural modifications of the polymer backbone have been studied to reduce the chain interaction, such as the introduction of flexible links (O, S, CO, SO, CH₂, etc.) to the main chains which disrupt the conjugation and increase the chain flexibility, the addition of bulky substituents which hinder the chain packing but do not affect the glass

transition temperature [10], and the introduction of geometrically asymmetric units by altering catenation patterns of dianhydride which have attracted much attention recently [11–21]. Recently, the researchers in our lab have studied the preparation and properties of a series of polyimides based on isomeric dianhydrides, such as mellanophanic dianhydride (MPDA), biphenyltetracarboxylic acid dianhydride (BPDA), benzophenonetetracarboxylic acid dianhydride (BTDA), oxy(diphthalic anhydride) (ODPA), diphenylthioether dianhydride (TDPA) and 1,4-bis(dicarboxyphenoxy) benzene dianhydride (HQPDA), and found many interesting rules about them [16–21].

Polyetherimides or their thio analogues have been receiving great attention as they may provide good processability owing to the presence of flexible ether or thioether links. Polythioetherimides derived from bis(thioetheranhydride)s have been reported since the work of Williams in 1970s [22–25]. As a part of the work about isomeric polyimides in our lab, we present the comparative study on the synthesis and properties of polyimides based on isomeric bis(dicarboxylphenylthio)diphenyl sulfone dianhydrides(PTPSDAs) in this paper.

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2. Experimental

2.1. Materials

3-Chlorophthalic anhydride (97%), 4-chlorophthalic anhydride (99%) and 1,4-bis(4-aminophenoxy) benzene (APB) were synthesized in our laboratory. 4-Chlorophenyl sulfone and sodium hydrosulfide hydrate were purchased from Aldrich Chemical Co. All other reagents were purchased from Shanghai Chemical Reagent Plant. 4,4′-Diamino-diphenyl ether (ODA) was purified by sublimation in vacuo. *N*, *N*-Dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) were dried over phosphorus pentoxide and then distilled under reduced pressure and stored over 4 Å molecular sieves. Other reagents were of analytical grade and used as received.

2.2. Characterizations

Fourier transform infrared (FTIR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ^{1}HNMR spectra were recorded on a Varian Unity spectrometer at 400 Hz with tetramethylsilane as an internal standard. Elemental analyses were performed on an elemental analyzer MOD-1106 (Italyd). Melting points were determined on an XT-4 melting point apparatus (Beijing Taike Apparatus, Inc.) and were uncorrected. Inherent viscosities were determined at 30 °C with an Ubbelodhe viscometer, and the concentration was 0.5 g/dL in *p*-chlorophenol. Thermogravimetric analyses were obtained at a heating rate of 10 °C/min in nitrogen atmosphere with a Perkin–Elmer TGA-2 thermogravimetric analyzer. The differential scanning calorimetry (DSC) experiments were carried out on a Perkin–Elmer DSC-7 system at a heating rate of 20 °C/min in N_2. Dynamic mechanical thermal analysis (DMTA) was performed on dynamic mechanical thermal analyzer V (Rheometric Scientific, Inc.) in a tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku max 2500V PC X-ray diffractometer (Japan) with Cu Kα radiation (40 kV, 200 mA) at a scanning rate of 2 °C/min from 2 to 50 °C. The tensile measurements were carried out on an Instron model 1122 at room temperature. The gas permeabilities were carried out at an equipment (yhs-1) made in our lab at 30 °C.

2.3. Monomer synthesis

2.3.1. Bis(4-mercaptophenyl) sulfone (**1**)

It was prepared according to the procedure in the literature [26], mp 138–140 °C (literature [26], mp 137–139 °C).

2.3.2. 4,4′-Bis(3,4-dicarboxyphenylthio) diphenyl sulfone dianhydride (**2**)

4-Chlorophthalic anhydride (20.09 g, 0.11 mol), bis(4-mercaptophenyl)sulfone (**1**) (14.12 g, 0.05 mol), and triethylamine (11.31 g, 0.11 mol) were placed in a 250 ml, three-necked, round-bottom flask containing 150 ml DMAc. The mixture was heated to 60 °C and stirred for 3 h in nitrogen atmosphere. After cooling to room temperature, the yellow mixture was poured into 1000 ml dilute hydrochloric acid solution. The yellow precipitation was filtered and washed with water. After recrystallization from acetic anhydride, a white crystalline solid (20.11 g, 70%) was obtained; mp 230–232 °C (literature [24], mp 227–231 °C).

IR (KBr): 1851 (asym C=O str), 1774 (sym C=O str), 1324 (asym S=O str), 1158 (asym S=O str). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.06–8.04 (d, d, 4H), 8.04–8.02 (d, d, 2H), 7.96 (s, 2H), 7.90–7.86 (d, d, 2H), 7.68–7.66 (d, d, 4H). Elem. anal. calcd For $C_{28}H_{14}O_8S_3$: C, 58.29%; H, 2.42%; S, 16.71%. Found: C, 58.29; H, 2.40; S, 16.81%.

2.3.3. 4,4′-Bis(2,3-dicarboxyphenylthio) diphenyl sulfone dianhydride (**3**)

It was prepared according to the synthesis of 4,4′-PTPSDA. The obtained dianhydride was recrystallized from the mixture solvents of acetic anhydride and DMSO (*v:v* = 1:1); yield 68%; mp 289–291 °C.

IR (KBr): 1846 (asym C=O str), 1767 (sym C=O str), 1320 (asym S=O str), 1158 (asym S=O str). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.08–8.06 (d, 4H), 7.96–7.94 (d, 2H), 7.88–7.84 (t, 2H), 7.78–7.74 (d, 2H), 7.50–7.48 (d, 4H). Elem. anal. calcd For $C_{28}H_{14}O_8S_3$: C, 58.29%; H, 2.42%; S, 16.71%. Found: C, 58.32%; H, 2.40; S, 16.85%.

2.4. Polymerization

All polymerization reactions were carried out in air atmosphere with a mechanical stirrer. An equimolar amount of dianhydride and diamine monomers were used in all cases. A representative polymerization procedure is as follows: ODA (0.4005 g, 2 mmol) and NMP (15 ml) were charged in a 50 ml three-necked flask equipped with a mechanical stirrer. After the dissolving of ODA, 4,4′-PTPSDA (1.1492 g, 2 mmol) was added in one portion. The mixture was stirred at room temperature for 12 h to afford a viscous solution polyamic acid (PAA). An aliquot of PAA solution was taken out and cast on a glass plate and dried at 80 °C for 12 h, followed by heating at 150 °C (1 h), 200 °C (1 h), 250 °C (1 h), 300 °C (1 h) to afford film of polyimide 4a. The acetic anhydride (2 ml) and triethylamine (1 ml) were added to the remainder PAA solution, and then the mixture was stirred for 24 h to afford a yellow viscous solution. The solution was poured slowly into 100 ml ethanol with stirring. The precipitate was collected by filtration and extracted with ethanol in a Soxhlot extractor for 24 h and dried at 200 °C in vacuo for 4 h to afford powder of polyimide 4a with the yield of 95%.

IR (KBr): 1775 (asym C=O str), 1713 (sym C=O str), 1372(C–N str), 1322 (asym S=O str), 1156 (asym S=O str), 737 (C=O ben). Elem. anal. calcd for $C_{40}H_{22}O_7N_2S_3$: C, 65.03%; H, 3.00%; N, 3.79%; S, 13.02%. Found: C, 64.53%; H, 2.95%; N, 3.70%; S, 13.52%.

2.4.1. Polyimide 4b
Yield, 96%. IR (KBr): 1775 (asym C=O str), 1715 (sym C=O str), 1373 (C–N str), 1323 (asym S=O str), 1156 (asym S=O str), 737 (C=O ben). Elem. anal. calcd for $C_{46}H_{26}O_8N_2S_3$: C, 66.49%; H, 3.15%; N, 3.37%; S, 11.58%. Found: C, 65.83%; H, 3.07%; N, 3.40%; S, 11.52%.

2.4.2. Polyimide 5a
Yield, 97%. IR (KBr): 1772 (asym C=O str), 1713 (sym C=O str), 1378 (C–N str), 1322 (asym S=O str), 1158 (asym S=O str), 737 (C=O ben). Elem. anal. calcd for $C_{40}H_{22}O_7N_2S_3$: C, 65.03%; H, 3.00%; N, 3.79%; S, 13.02%. Found: C, 64.73%; H, 2.90%; N, 3.67%; S, 13.40%.

2.4.3. Polyimide 5b
Yield, 94%. IR (KBr): 1772 (asym C=O str), 1714 (sym C=O str), 1378 (C–N str), 1323 (asym S=O str), 1158 (asym S=O str), 737 (C=O ben). Elem. anal. calcd For $C_{46}H_{26}O_8N_2S_3$: C, 66.49%; H, 3.15%; N, 3.37%; S, 11.58%. Found: C, 65.62%; H, 3.00%; N, 3.30%; S, 11.32%.

3. Results and discussions

3.1. Synthesis of monomer

Bis(4-mercaptophenyl) sulfone was prepared by the method reported in the literature [22]. To avoid oxidation, it was dried at room temperature in vacuo. 4,4′-PTPSDA and 3,3′-PTPSDA were successfully synthesized via the way reported in the literature (shown in Scheme 1) [22,27, 28]. Triethylamine was used instead of inorganic bases to minimize the hydrolysis reaction of the chlorophthalic anhydride. Although this would probably increase the side reaction, which produces disulfide, the side product can be

easily removed by recrystallization. The structures of 4,4′-PTPSDA and 3,3′-PTPSDA were confirmed by IR spectra, ^{1}H NMR and elemental analysis.
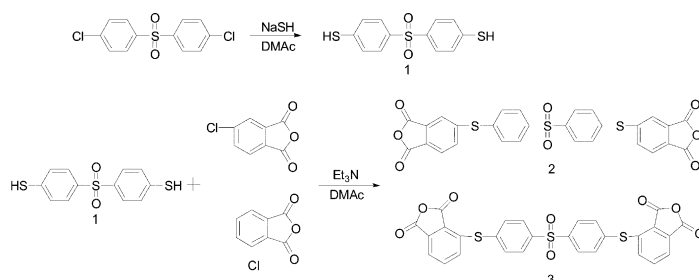
3.2. Synthesis of polymers

As shown in Scheme 2, all the polyimides were synthesized in conventional two-step method by the polycondensation reactions of 4,4′-PTPSDA or 3,3′-PTPSDA with ODA or APB to form PAAs, followed by thermal or chemical imidization. The complete imidization of polymers was confirmed by IR spectra. All the polymers showed the characteristic absorption bands of the imide ring near 1780 (asym C=O str), 1720 (sym C=O str), 1380 (C–N str), and 730 (imide ring deformation) cm^{-1}. There was no existence of the characteristic absorption bands of the amide groups near 3363 (N–H str) and 1674 (C=O str) cm^{-1}, indicating polymers had been fully imidized. In addition to the IR spectra, the elemental analysis results of polymers also generally agreed well with the calculate values for the proposed structures. The reaction of 3,3′-PTPSDA with diamines were carried out at an elevated temperature from 25 to 40 °C to avoid the gelation which appeared at lower temperature, while the heating should be controlled carefully to prevent the depolymerization of PAAs. We also tried the one-step polymerization in *m*-cresol, but failed because of the poor solubility of the resulted polyimides.

3.3. Properties of polymers

3.3.1. Solubility
The solubility of the polyimide powders derived from 4,4′-PTPSDA and 3,3′-PTPSDA was summarized in Table 1. Inherent viscosity of the polymers is in the range of 0.93–1.50 dl/g in *p*-chlorophenol at 30 °C. The inherent viscosity of the polyimides derived from 3,3′-PTPSDA is higher than that of the polyimides derived from 4,4′-PTPSDA. In general, the solubility of polyimide from 3,3′-PTPSDA, even the PAAs, is poorer than those from 4,4′-PTPSDA. We also synthesized a series of polyimides from isomeric PTPSDAs with similar viscosity (from 0.43 to 0.48 dl/g), and found that polyimides from 3,3′-PTPSDA here also have poor solubility. This result is contrary to that previously reported on the solubility of the isomeric

Scheme 1. Synthesis of isomeric PTPSDAs.
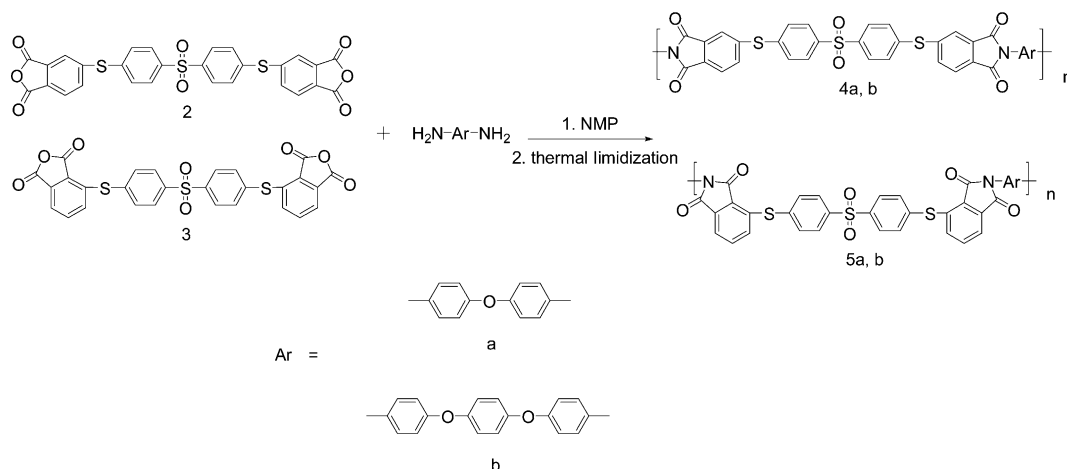
Scheme 2. Synthesis of polyimides from isomeric PTPSDAs.

polyimides [19,29,30], which is often thought that the polyimides from 3,3′-dianhydrides have better solubility than those from 4,4′-dianhydrides. But we cannot explain this phenomenon clearly.

3.3.2. Thermal and mechanical properties

The thermal and mechanical properties of isomeric polyimides were summarized in Table 2. All data are obtained from the transparent, flexible and tough films which are cast from corresponding PAA solutions and cured at 150 °C/1 h + 200 °C/1 h + 250 °C/1 h + 300 °C/1 h. The temperatures of 5% weight loss ($T_{5\%}$) of polyimides are around at 500 °C, so it is clear that the isomeric polyimides have similar thermal stability. The tensile strengths of isomeric polyimides at break, the modulus, and the elongations at break are 97–103 MPa, 1.28–1.56 GPa, and 14–19%, respectively. The values of the tensile strengths, modulus of polyimides from isomeric PTPSDAs are similar, but the elongations of polyimides from 4,4′-PTPSDA are slightly higher than those from 3,3′-PTPSDA. This is consistent with the result of other isomeric polyimides [11–21].

The DMTA results of isomeric polyimides were shown in Fig. 1. The original storage modulus of the isomeric polyimides ranged from 1.20 to 1.74 GPa. Regarding the peak temperature in the tan δ curves as the glass transition temperature (T_g), the polymer 4,4′-PTPSDA/ODA exhibits a T_g at 261 °C, 3,3′-PTPSDA/ODA at 288 °C, 4,4′-PTPSDA/APB at 240 °C, and 3,3′-PTPSDA/APB at 269 °C. Combined with the data from DSC, the T_gs of polyimides based on 3,3′-PTPSDA are higher than those of polyimides based on 4,4′-PTPSDA. It could be explained that the polyimides from 3,3′-PTPSDA have more rigid chain structure and more restricted rotation around the bond between phthalimide and S than those from 4,4′-PTPSDA. This result is also in agreement with those for the other isomeric polyimides [11–21].

3.3.3. X-ray diffraction

As shown in Fig. 2, the crystallinity of isomeric polyimides is examined by wide angle X-ray diffraction. All of the polymers show amorphous patterns.

3.3.4. Gas permeabilities and permselectivities

The gas permeabilities and permselectivities of isomeric polyimides were summarized in Table 3. In general, the polyimides from 3,3′-PTPSDA have higher permeability and lower permselectivity than those from 4,4′-PTPSDA. This is because that the polyimides based on 3,3′-dianhydrides may have higher fractional free volume and lower chain segment mobility than the polyimides based on 4,4′-dianhydrides. This result is consistent with the result previously on the gas permeabilities and permselectivities of polyimdes based on other isomeric dianhydrides [20,31,32].

Table 1
Solubility of isomeric polyimides

Polymer	η_{inh} (dl/g)[a]	CHCl$_3$	TCE[b]	THF	DMAc	DMSO	NMP	m-cresol	p-chlorophenol
4,4′-PTPSDA/ODA	0.93	−	+	−	+	+	+	+	+
4,4′-PTPSDA/APB	0.95	−	±	−	±	+	+	+	+
3,3′-PTPSDA/ODA	1.50	−	+	−	−	±	±	±	+
3,3′-PTPSDA/APB	1.36	−	+	−	±	±	+	±	+

Key: +, fully soluble at room temperature; ±, partially soluble on heating; −, insoluble on heating.
[a] Inherent viscosity measured with 0.5 g/dl at 30 °C in p-chlorophenol.
[b] TCE, 1,1,2,2-terachloroethane.

Table 2
Thermal and mechanical properties of isomeric polyimides

Polymer	T_g (°C)		$T_{5\%}$ (°C)[c]	Tensile strength (MPa)	Modulus (MPa)	Elongation (%)
	DMTA[a]	DSC[b]				
4,4′-PTPSDA/ODA	261	237	504	103	1560	19
4,4′-PTPSDA/APB	240	224	497	98	1540	16
3,3′-PTPSDA/ODA	288	262	496	99	1470	14
3,3′-PTPSDA/APB	269	245	500	97	1280	14

[a] Obtained from DMTA at heating rate of 3 °C/min at 1 Hz.
[b] Obtained from DSC at a heating rate of 20 °C/min in N_2.
[c] Five percent weight loss obtained from TGA at a heating rate of 10 °C/min in N_2.

Table 3
Gas permeabilities and permselectivities of isomeric polyimides

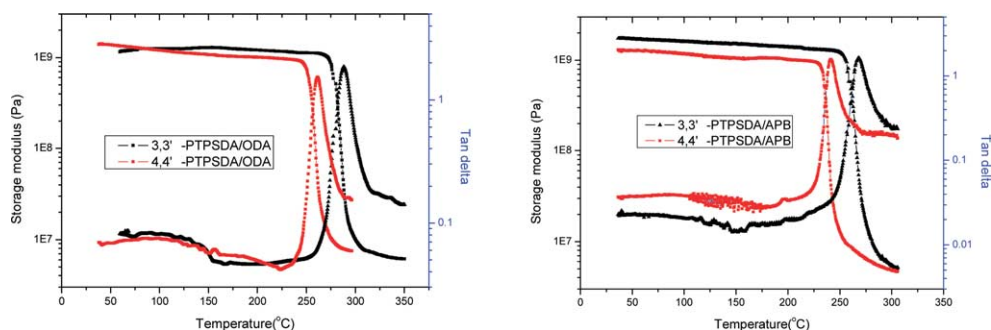| Polymer	P^* (H_2) (Barrar)	P^* (O_2) (Barrar)	P^* (N_2) (Barrar)	α_{H_2/N_2}	α_{O_2/N_2}
4,4′-PTPSDA/ODA	2.9157	0.1388	0.08536	34.1577	1.6261
4,4′-PTPSDA/APB	2.6352	0.1969	0.04591	57.4118	4.2898
3,3′-PTPSDA/ODA	3.8738	0.3247	0.2627	14.5250	1.2361
3,3′-PTPSDA/APB	4.2433	0.6241	0.3549	33.2122	1.7586

Key: all data was obtained at 30 °C.

Fig. 1. DMTA curves of isomeric polyimides from 4,4′-PTPSDA and ODA, 3,3′-PTPSDA and ODA, 4,4′-PTPSDA and APB and 3,3′-PTPSDA and APB.

4. Conclusions

4,4′-PTPSDA or 3,3′-PTPSDA were synthesized from 4-chlorophthalic anhydride or 3-chlorophthalic anhydride and bis(4-mercaptophenyl) sulfone. A series of polyimides derived from isomeric PTPSDAs and aromatic diamines were prepared via conventional two-step method. The polyamic acids and polyimides from 3,3′-PTPSDA show poorer solubility in organic solvents than those from 4,4′-PTPSDA. The polyimides based on isomeric PTPSDAs have similarly thermal stability. Polyimides from 4,4′-PTPSDA have similar mechanical properties but slightly higher elongations compared with polyimides from 3,3′-PTPSDA. Polyimides from 3,3′-PTPSDA have higher T_gs than that from 4,4′-PTPSDA. All of the isomeric polyimides are amorphous. The polyimides from 3,3′-PTPSDA show higher permeability but lower permselectivity than those from on 4,4′-PTPSDA.
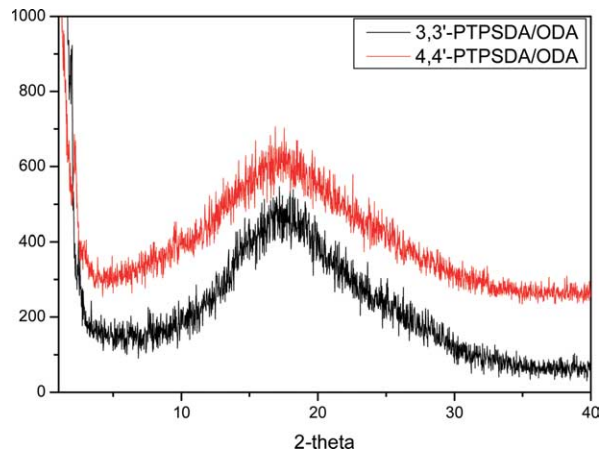

Fig. 2. WAXD diagram of polyimides from 4,4′-PTPSDA and ODA, and 3,3′-PTPSDA and ODA.

Acknowledgements

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