

Synthesis and Properties of Novel Melt Processable Isomeric Polythioetherimides

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ABSTRACT: A series of 3,3',4,4'-diphenylthioether dianhydride (4,4'-TDPA), 2,3,3',4'-diphenylthioether dianhydride (3,4'-TDPA), and 2,2',3,3'-diphenylthioether dianhydride (3,3'-TDPA) isomer mixtures were synthesized from 3- and 4-chlorophthalic anhydride. Polythioetherimides derived from TDPAs with different ratios and 4,4'-oxydianiline (ODA) were prepared by a two-step polycondensation procedure via their soluble poly(amic acid) (PAA) precursors. Thermal properties, solubility properties, mechanical properties and melt processable properties of copolythioetherimides were investigated and compared with corresponding homopolyimides. The effects of chemical structures on these properties were discussed in this work to obtain an indication for the molecular design of high performance thermo-processable polyimides.

Introduction

Polyimides (PIs) are an important class of thermally stable materials because of their excellent combined properties and have been widely used in many industries such as aerospace, microelectronics etc.¹⁻³ However, the conventional proposed aromatic PIs have been limited in their application due to difficulty in melt molding because of their rigid chain structures.¹⁻³ The most well known melt-moldable (e.g. injection moldable and extrusion moldable) PIs is ULTEM developed by General Electric Co. and AURUM developed by Mitsui Chemicals Co.. As shown in **Figure 1**, the molecular structures of these PIs are always considering incorporation flexible spacer linkages or meta-substituted diamines into polymer main chain.

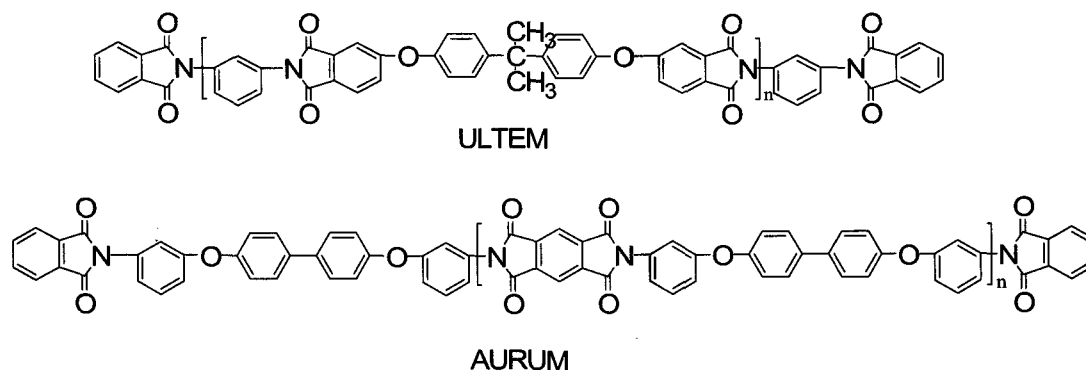


Figure 1. Molecular structures of commercial ULTEM and AURUM

Recently, researchers are more interested in the structure-property relationships of PIs based on isomeric dianhydrides to pursue the high performance polymer materials.⁴⁻⁶ It has been shown that the isomeric effects on polyimide properties: such as higher glass transition temperature, better solubility,

lower melt viscosity, wider processing window, and comparable thermal and mechanical properties may give us some indication of a series of new thermal-processable PIs by the strategy of molecular design. Furthermore, as far as we know, PIs prepared from mixtures of isomeric dianhydrides have little been researched before.⁷ Some novel properties might be expected by random arrangement and distribution of different isomeric dianhydride units compared to corresponding homopolymers. The properties of PI homopolymers based on 3,3,3',4'-diphenylthioether dianhydride (4,4'-TDPA), 2,3,3',4'-diphenylthioether dianhydride (3,4'-TDPA), and 2,2',3,3'-diphenylthioether dianhydride (3,3'-TDPA) isomers have been reported.⁸ In this paper, we will show the synthesis and properties of random copolymers derived from three TDPA isomeric mixtures in order to obtain novel high performance thermal-processable polyimides.

Experimental

3- and 4-chlorophthalic anhydride were obtained from Harbin Shidai Science and Technology Ltd., Co. and used as received. Anhydrous sodium sulfide was purchased from Inner Mongolia Lichuan chemistry Ltd, Co. and used as received. All of the other reagents were from the Shanghai Chemical Reagent Co. and were of analytical grade.

Measurements

The inherent viscosities were determined at 30 °C with an Ubbelohde viscometer and the concentration was 0.5g/dL in 1-Methyl-2-pyrrolidone (NMP) or m-cresol. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Nicolet 6700 FTIR spectrophotometer. The differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer Diamond DSC system at a heating rate of 20 °C/min under a nitrogen atmosphere. The thermal stability of polyimides was estimated using a Perkin-Elmer Diamond TG/DTA thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen or an air atmosphere. The thermal durability of the polyimide powders was evaluated from the isothermal weight loss at 390°C over 300 min in an air atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (Mettler-Toledo, Inc., Switzerland) in a tensile mode at a heating rate of 3 °C/min from 30 °C to 300 °C and at a frequency of 1 Hz in air. The tensile measurements were carried out on an Instron model 5567 tensile tester at a crosshead speed of 5 mm/min at room temperature. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Bruker D8 Advance with Cu K radiation (40kV, 40mA) at a scanning rate of 3°/min from 2° to 50°. The rheological properties of polyimides were investigated via a rotational Physica MCR 301 rheometer in an Oscillation model. Sample discs of 25 mm diameter and 1mm thickness were prepared by press-molding of the polyimide powder at 80 °C under high pressure, which were then loaded in the rheometer fixture equipped with 25 mm diameter parallel plates. The complex viscosity as a function of the scanning temperature were measured by scanning the temperature from 200 to 420 °C at a ramp rate of 4 °C/min with a frequency of 1Hz and a strain of 1%.

Monomer synthesis

3,3'-TDPA and 4,4'-TDPA and three isomeric mixtures were synthesized as reported previously using chlorophthalic anhydride isomers as starting materials.⁹ 3,4'-TDPA was synthesized by a method revealed by a Chinese Patent.¹⁰

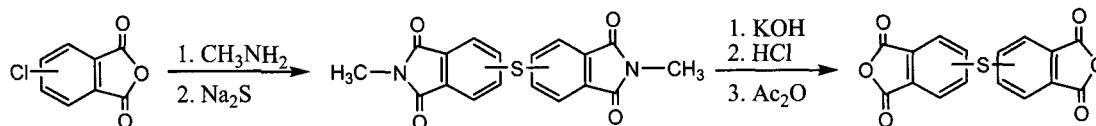
Polyimide synthesis

Polyimides based on isomeric TDPAs and ODA were prepared in the conventional two-step process via poly(amic acid) (PAA) polymerization and successive thermal imidization. A typical procedure is as follows: 9.8 mmol dianhydride powder was charged into the 40 mL NMP solution of 10 mmol diamine with continuous stirring at room temperature for 20h, and then 0.4 mmol phthalic anhydride (PA) (represented as '2%PA') was added into the solution with stirring for another 4h; a PAA solution is formed. Then, a 4 mL 1,2-dichlorobenzene was added into the solution and the PAA solution was refluxed at 180 °C for 5h. The solution was poured slowly into ethanol with vigorous stirring. The precipitate was collected by filtration, extracted with ethanol in a Soxhlet extractor, and dried in vacuum at 200 °C to afford polyimide powder. The PI powder so obtained was dissolved in NMP at room temperature to afford about 10 wt% solution which was cast at 70 °C for 12 h, then gradually cured at higher temperatures and finally 280 °C for 1h to form 20-80 μm thick PI films.

Results and discussion

Monomer Synthesis

As shown in **Scheme 1**, pure 3,3'-TDPA, 4,4'-TDPA and three mixtures of TDPAs were obtained using 3- and 4-chlorophthalic anhydride as starting materials.⁹



Scheme 1. Synthesis of isomeric and mixed TDPAs from chlorophthalic anhydride

Their structures were confirmed by FTIR, NMR and elemental analysis. The isomer ratios of 3,3'-TDPA, 4,4'-TDPA, and 3,4'-TDPA were determined by integration of aromatic representative hydrogen signals of each pure TDPA in ¹H NMR spectra. As shown in **Table 1**, the percentage distribution of three isomers is dependent on the original ratios of 3- and 4-chlorophthalic anhydrides. It is noted that each TDPA mixtures has a more than 40% content of 3,4'-TDPA, independent of the ratio change of 3- to 4-chlorophthalic anhydrides range from 1:3 to 3:1.

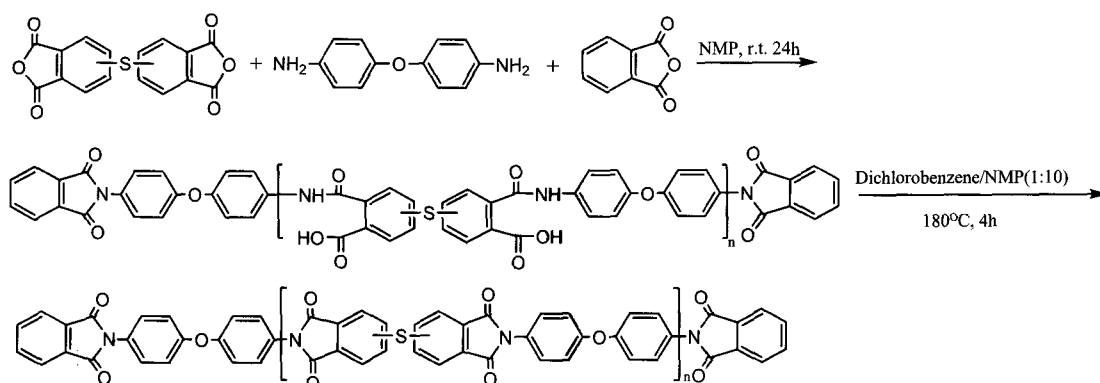
Table 1. Ratio of chlorophthalic anhydride isomers and corresponding TDPA isomers

NO.	Ratio of chlorophthalic anhydride isomers (3:4)	Ratio of TDPA isomers (3,3':4,4':3,4'), Represented as R
1	1:3	7.4:50.4:42.6 (R1)
2	1:1	22.2:20.7:57.1 (R2)
3	3:1	53.5:4.6:41.9 (R3)

Polyimide Synthesis

As shown in **Scheme 2**, all the polyimides were synthesized in two steps through the polycondensation reactions of isomeric and mixed TDPAs with ODA, firstly forming PAA solutions, followed by thermal imidization. The solid concentration of PAA solutions was at about 15% and 1,2-dichlorobenzene was employed as the azeotropic reagent to carry out the water and to complete the polymerization. All the polyimides are able to form flexible films which are used for measurement

of DMA and mechanical properties. All the polyimides exhibit characteristic imide group absorptions around 1780 and 1720 (imide carbonyl asymmetrical and symmetrical stretching), 1380 (C-N stretching), and 730 cm^{-1} (imide ring deformation), indicating the successful thermal conversion from PAAs to PIs.



Scheme 2. Synthesis of polyimides from isomeric and mixed TDPA

Properties of Polyimides

Table 2 gives the inherent viscosities and solubility of all the TDPA-based polyimide powders. The inherent viscosities were controlled ranging from 0.37 to 0.60 dL/g using PA as an end-capped reagent, indicating medium molecular weight polymers were obtained. It was found that PIs from mixture TDPA (PI-1, PI-2, PI-3) are easily soluble in polar aprotic solvents such as dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and NMP, demonstrating the similar behavior as PI-3 and PI-4. PI-5 based on 4,4'-TDPA/ODA has poor solubility, which is just fully soluble in *m*-cresol. It is well known that the difference in solubility may be attributed to the more bent chain structure for PIs from 3,3'-TDPA and 3,4'-TDPA, creating a steric hindrance effect and enhancing solubility.⁶ It is clear that all the mixed dianhydrides have a major content of 3,4'-TDPA. Moreover, the random polymerization may give more 3,4'- and 3,3'-monomer chain structure, increasing the irregularity of the chain structure and solubility.

Table 2. Polymerization and solubility of PIs from mixed and isomeric TDPA

PIs	Compositi on	η_{inh}^a (dl/g)	THF	CHCl_3	DM F	DM Ac	DMSO	NMP	<i>m</i> -cresol
PI-1	R1/ODA	0.38	-	±	+	+	+	+	+
PI-2	R2/ODA	0.47	-	±	+	+	+	+	+
PI-3	R3/ODA	0.37	-	±	+	+	+	+	+
PI-4	3,3'-TDPA /ODA	0.46	-	⊕	+	+	⊕	+	+
PI-5	4,4'-TDPA /ODA	0.47 ^b	-	⊖	±	±	⊖	±	+
PI-6	3,4-TDPA/ ODA	0.60	-	±	+	+	±	+	+

Key: +, fully soluble at room temperature; ±, partially soluble on heating; -, insoluble on heating.

^a Inherent viscosity measured with 0.5 g/dL in NMP at 30°C.

^b Inherent viscosity measured with 0.5 g/dL in *m*-cresol at 30°C.

The thermal and mechanical properties of PIs derived from isomeric and mixed TDPAs are summarized in **Table 3**. And the data of DMA and mechanical properties were obtained from flexible and tough films casted from the solution of polyimides. The glass transition temperature (T_g) values of the polyimides, measured by DSC and DMA, display a decreasing trend in order of the catenation pattern of the dianhydrides (3,3'->3,4'->4,4'-) due to the restricted rotation around the bond between the bridge thioether and the carbon in phthalimide.⁵ As shown in **Figure 2**, regarding the peak temperature in the $\tan \delta$ curves as the glass transition temperature, the T_g of copolymers increased with the increasing of 3,3'-TDPA content (PI-3 > PI-2 > PI-1). This trend is in good agreement with the results obtained from the DSC measurements.

Table 3. Thermal and mechanical properties of polyimides from mixed and isomeric TDPAs

PIs	T_g (°C)		T_{d5} (°C)		Rw^a	Tensile Strength (MPa)	Modulus (MPa)	Elongation (%)
	DSC	DMA	N ₂	Air				
PI-1	260	253	545	540	65%	94	2701	7.1
PI-2	265	256	520	538	60%	117	2982	6.2
PI-3	267	261	513	530	61%	118	3207	5.8
3,3' PI-4	281	267	525	545	58%	130	3355	5.2
4,4' PI-5	251	243	543	529	60%	91	2619	7.6
PI-6	270	260	511	529	60%	87	3098	5.9

^a Residual weight at 700 °C in N₂.

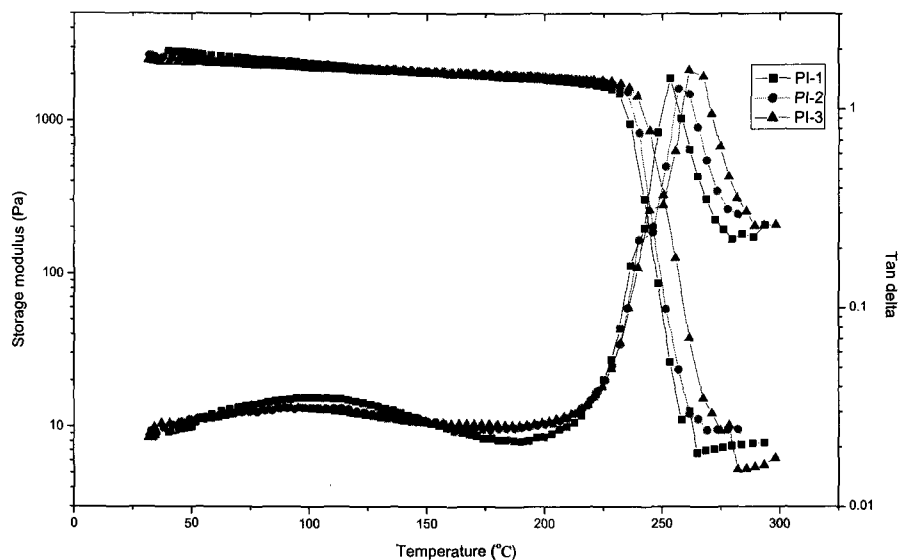


Figure 2. DMA analysis plots of PI-1, PI-2 and PI-3

From the TGA measurements (**Table 3**), all the PIs maintained nearly 100% of their original weights up to 450 °C and 5% weight loss greater than 510 °C in either air or N₂ and more than 60% of their weights at 700 °C in nitrogen, demonstrating that these polyimides possess nice thermal and thermoxidative stability. A typical TGA curve of PI-2 in both air and N₂ is shown in **Figure 3**.

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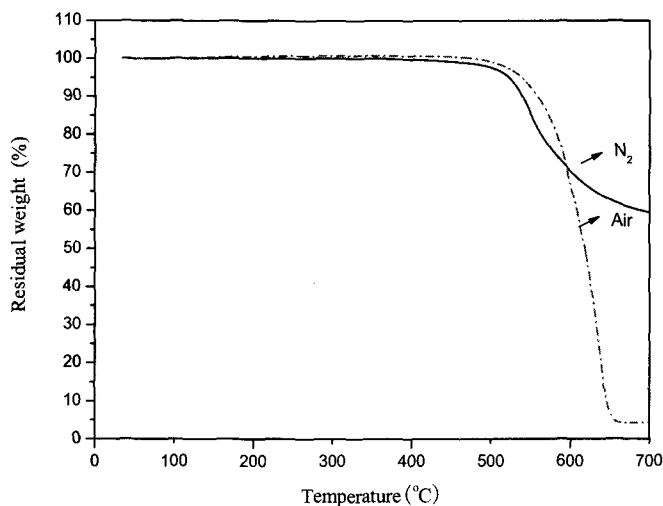


Figure 3. TGA curves of PI-2 under N₂ and air.

The long term thermal stability of PI-5 was compared with that of ULTEM 1000. **Figure 4** displays the isothermal weight loss at 390 °C in air for 300 minutes as an accelerated test. The weight loss occurred very slowly for PI-2 powder whereas the weight of ULTEM 1000 powder decreased much faster. This result revealed how the present isomeric copolyimides have much higher thermooxidative stability than ULTEM including the thermally unstable isopropylidene units.

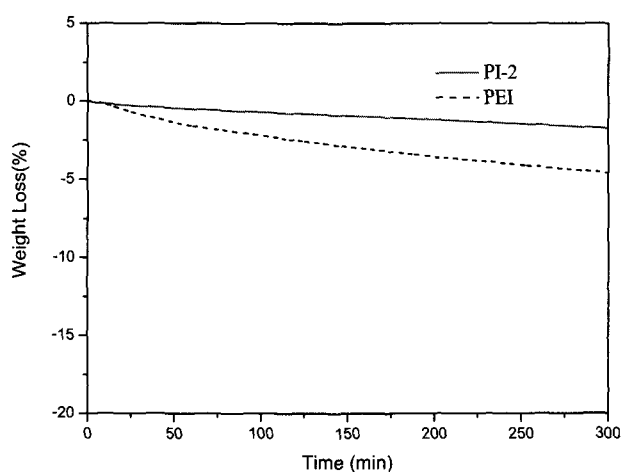


Figure 4. Isothermal weight loss curves of PI-2 and PEI (ULTEM 1000) at 390 °C in air for 300 min

Furthermore, as shown in **Table 3**, all the polyimide films from isomeric and mixed TDPAs have comparable tensile strengths (around 100 MPa), modulus (around 3 GPa) and elongation(around 6%).

We have studied the rheological properties of polyimides from isomeric and mixed TDPAs. According to literature,⁸ the 3,4'-dianhydride based polyimide showed the lowest melt viscosity compared with the 3,3'- and 4,4'-dianhydride based polyimides when they have the similar molecular weight. This can be attributed to the irregular chain structure derived from asymmetrical

3,4'-monomer chain structure which reduces intermolecular interaction so the minimum melt viscosity is obtained. As shown in **Figure 5**, it is noted that all three copolyimides show the similar lower melt viscosity (about 1000 Pa·S at 380 °C) as the corresponding 3,4'-TDPA based homopolymer⁸ when they have similar molecular weight ($\eta_{inh} = 0.40$ dL/g). This could be attributed to the more irregular and random chain structures derived from three isomeric monomers in addition to a major content of 3,4'-TDPA monomers. It is interesting to note that there is no marked difference of the melt viscosity for copolymers even though they have different 3,3'-TDPA monomer content (PI-3 > PI-2 > PI-1). The results suggested that copolymerization is an effective way to decrease chain sequence regularity and consequently weaken intermolecular weight.

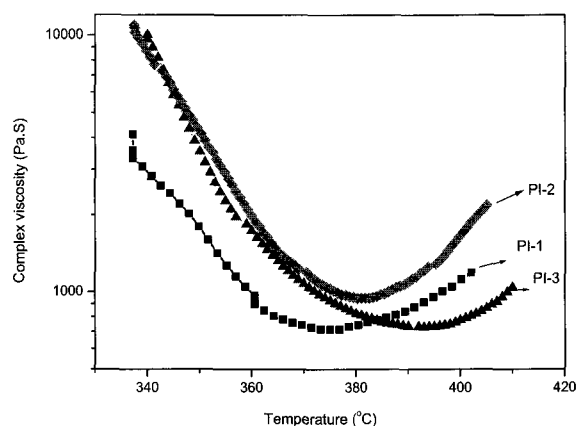


Figure 5. Complex viscosity of polyimides as a function of temperature

Figure 6 displays WAXD of polyimides powder based on isomeric and mixed TDPAs. All of the polyimide powders have a broad peak which suggests that all PIs we prepared are amorphous.

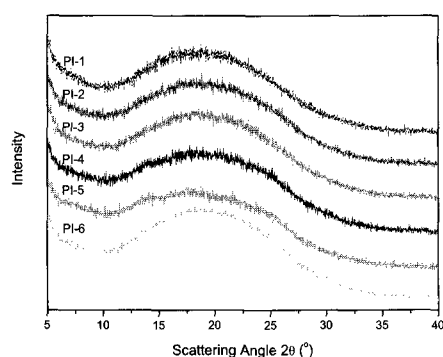


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Figure 6. WAXD curves of polyimides from isomeric TDPAs

Conclusions

A series of isomer mixtures of 3,3'-TDPA, 3,4'-TDPA and 4,4'-TDPA were synthesized using 3- and 4-chlorophthalic anhydride as starting materials. We found that PIs based on mixtures of 3,3'-TDPA, 3,4'-TDPA and 4,4'-TDPA showed excellent solubility in DMAc, DMSO, NMP and

DMF than homopolymer based on 4,4'-TDPA. Furthermore, copolymers based on three isomeric dianhydrides showed good thermal and thermoxidative stability and *T*_gs of copolymers increased with the increasing of 3,3'-TDPA content. Of particular interest was that copolyimide resins and 3,4'-TDPA based homopolymers displayed similar better processability (lower melt viscosity) as compared with corresponding 3,3'-TDPA and 4,4'-TDPA based homopolymers. The good combined properties of the copolyimides make them potential candidates for novel melt processable materials.

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