

## SYNTHESIS AND CHARACTERIZATION OF HIGHLY SOLUBLE AROMATIC POLYIMIDES\*

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**Abstract** Two highly soluble aromatic polyimides were synthesized successfully from a diamine with two *tert*-butyl groups (MBTBA) and dianhydrides with a thioether or sulfone moiety (DTDA and DSDA). Both of them showed excellent solubility in common solvents such as chloroform, tetrahydrofuran and dioxane at the room temperature. The number-average molecular weight was  $6.0 \times 10^4$  and  $8.3 \times 10^4$  according to gel permeation chromatography relative to a polystyrene standard, and the polydispersity index was 1.80 and 1.82 respectively. The glass-transition temperatures of them were 286°C and 314°C (or 315°C and 358°C) respectively, as measured by differential scanning calorimetry (or dynamic mechanical analysis). The 5% weight loss temperature of both was near 490°C in N<sub>2</sub> by thermogravimetric analysis. These results indicated that the *tert*-butyl pendent groups reduced the interactions among polymer chains and the thioether or sulfone moiety was flexible which may improve their solubility in conventional organic solvents without the loss of thermal stability. Transparent and flexible films of the two polyimides were obtained *via* solution casting. The MBTBA-DTDA membrane had higher storage moduli than those of the MBTBA-DSDA membrane.

**Keywords:** Aromatic polyimide; Solubility; Sulfone-bridged; *tert*-butyl groups; Thioether-bridged.

### INTRODUCTION

Aromatic polyimides are a kind of high-performance polymer materials widely used in aerospace, automobile, electronics and semiconductor fields *etc.* They often possess some outstanding properties such as high thermal stability, good mechanical properties as well as superior chemical and radiation resistance. However, their rigid polymer backbones and the strong chain interactions result in poor solubility and high softening or melting temperature for most of aromatic polyimides, which limit the use of commercial purposes<sup>[1–3]</sup>. In order to overcome these limitations, considerable efforts have been devoted to improving the solubility and fusibility by the introduction of flexible hinges (O, CO, SO<sub>2</sub>, CH<sub>2</sub>, *etc.*) or bulky lateral substitutions into the polymers, by the design of geometrically asymmetric structures, or by the copolymerization with other monomers<sup>[4–9]</sup>. In our previous papers, we synthesized an aromatic diamine containing *tert*-butyl groups to polymerize with some aromatic tetracarboxylic dianhydrides and the resulting polyimides showed excellent solubility in organic solvents without sacrificing their thermal stability<sup>[10, 11]</sup>.

In recent years, polythioetherimides have been attracted great attention as they may provide good processability owing to the presence of flexible thioether links. The work of Williams have reported the polythioetherimides derived from bis(thioetheranhydride)s since 1970s<sup>[12, 13]</sup>. Ding and coworkers synthesized a

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series of isomeric diphenylthioether dianhydrides and studied the properties of the corresponding polythioetherimides<sup>[14–16]</sup>. Otherwise, El and co-workers investigated the blends comprising a polyether sulfone and an imide-containing copolymer of thioether bis(phthalic anhydride) and various diamine comonomers. The blends showed a unique combination of excellent mechanical behavior, admirable thermal properties and good solubility; furthermore, the resin components showed unexpectedly compatible<sup>[17]</sup>.

In this article, we also used the aromatic diamine containing *tert*-butyl groups to polymerize with other two dianhydrides containing a thioether or sulfone moiety *via* a one-pot method. The various properties of the resulting polyimides were investigated in detail.

## EXPERIMENTAL

### Materials

2-*tert*-Butylaniline (*t*-BA; Aldrich), formaldehyde hydrate (Pacific Ocean Chemical Group Co.) and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA) (Tokyo Chemical Industry Co. Ltd.) were used without further purification. 4-Chlorophthalic anhydride (Zibo Xingpeng Chemical Co.), *N,N'*-dimethyl formamide (DMF) and *m*-cresol were purchased and purified by vacuum distillation before use. Quinoline, methanol, glacial acetic acid and other solvents were purchased from domestic chemical market and used without further purification.

### Instruments

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were measured on a 400 MHz Bruker NMR spectrometer with DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub> as solvents. FTIR spectra were recorded on a PE FTIR spectrometer. Elemental analyses were run with a Perkin-Elmer Model 2400 C, H, N instrument. UV/Vis spectra were recorded on a PE Lambda 20 UV/Vis spectrometer. Thermogravimetric analysis (TGA) was performed on a PE Pyris-7 thermal analyzer under the nitrogen atmosphere. The sample was heated from 50°C to 800°C at a scan rate 20 K/min. Differential scanning calorimetry (DSC) was conducted on a PE Pyris-1 thermal analyzer under the nitrogen atmosphere. The sample was heated from 50°C to 380°C by the heating rate 20 K/min. Dynamic mechanical analysis (DMA) was conducted on a DMA242 Instrument (TA) at a frequency of 1 Hz under the nitrogen atmosphere at a heating rate 10 K/min. The specimen dimensions for DMA measurements were about 20 mm × 5 mm × 0.045 mm.

### Monomer Synthesis

#### 3,3',4,4'-Diphenylthioethertetracarboxylic dianhydride (DTDA)

DTDA was prepared from 3-chlorophthalic anhydride according to the literatures<sup>[15,18]</sup>.

Yield: 68%; m.p. 202.5°C (by DSC); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.95–7.97 (d, 2H), 8.01 (s, 2H) and 8.08–8.10 (d, 2H); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 124.65, 127.11, 127.32, 130.90, 133.07, 135.79 and 138.38; IR (KBr, cm<sup>-1</sup>): 1768, 1851 (—COOC—, anhydride) and 1114 (Ar—S—Ar); Elem. Anal. Calcd. for C<sub>16</sub>H<sub>6</sub>O<sub>6</sub>S: C, 58.90%; H, 1.85%; O, 29.42%; S, 9.83%. Found: C, 58.95%; H, 1.87%; O, 29.38%; S, 9.82%.

#### 4,4'-Methylenebis(2-*tert*-butylaniline) (MBTBA)

MBTBA was prepared according to our previous papers<sup>[10,11]</sup>.

Yield: 68.5%; m.p.: 82.6°C (by DSC); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 1.28 (s, 18H), 3.33 (H<sub>2</sub>O), 3.56 (s, 2H), 4.54 (s, 4H), 6.50–6.52 (d, 2H), 6.66–6.68 (d, 2H) and 6.90 (s, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>,  $\delta$ ): 29.93, 34.55, 40.06, 118.28, 127.40, 131.11, 133.99 and 142.62; IR (KBr): 3384–3352 (N—H), 2779–3032 (Ar—CH<sub>2</sub>—Ar); Elem. Anal. Calcd. for C<sub>21</sub>H<sub>30</sub>N<sub>2</sub>: C, 81.24%; H, 9.74%; N, 9.02%. Found: C, 81.32%; H, 9.68%; N, 9.00%.

### Polymer Synthesis

A typical polymerization process is as follows: 2.102 g (6.44 mmol) DTDA, 2.000 g (6.44 mmol) MBTBA, 36 mL *m*-cresol and three drops of quinoline were added into a 100 mL three-necked flask with a mechanical stirrer, a condenser and a nitrogen inlet/outlet. The mixture was stirred and heated slowly to 50°C until all solids dissolved completely. Then the mixture was heated to 100°C for 10 h, 180°C for 10 h and 200°C for 12 h. After

cooling to the room temperature, the mixture was diluted by a proper amount of chloroform and then carefully poured into 400 mL vigorously stirred methanol to give fiber-like precipitates. The polymer was washed with methanol several times to remove the residual *m*-cresol. Finally, the product was vacuum-dried at 120°C for 24 h. The polymer was purified by reprecipitating twice.

#### MBTBA-DTDA

Yield: 95%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.30, 4.09, 6.93, 6.94, 7.12, 7.14, 7.46, 7.80, 7.82, 7.88, 7.90, 7.93 and 7.95; IR (KBr, cm<sup>-1</sup>): 1371, 746 (N–C=O), 2961 (–CH<sub>3</sub>) and 1098 (Ar–S–Ar); Elem. Anal. Calcd. for (C<sub>37</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>S)<sub>n</sub>: C, 73.98%; H, 5.37%; N, 4.66%; O, 10.65%; S, 5.34%. Found: C, 74.33%; H, 5.35%; N, 4.70%; O, 10.18%; S, 5.44%.

#### MBTBA-DSDA

Yield: 96.5%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.27, 4.08, 6.87, 6.89, 7.10, 7.12, 7.47, 8.14, 8.16, 8.47, 8.48 and 8.52; IR (KBr, cm<sup>-1</sup>): 1372, 748 (N–C=O), 2963 (–CH<sub>3</sub>) and 1144 (Ar–SO<sub>2</sub>–Ar); Elem. Anal. Calcd. for (C<sub>37</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>S)<sub>n</sub>: C, 70.24%; H, 5.10%; N, 4.43%; O, 15.17%; S, 5.07%. Found: C, 70.41%; H, 5.00%; N, 4.30%; O, 15.27%; S, 5.02%.

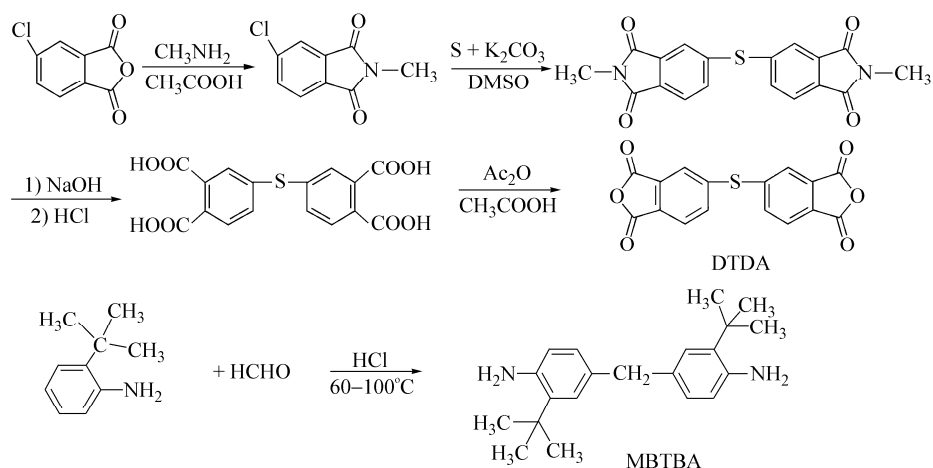
#### Membrane Preparation

Membranes of the resulting polyimides were prepared by casting their DMF solutions (*ca.* 5 wt%) onto the dust-free glass plates and then dried at 70°C for two days. After cooling to ambient temperature, the membranes were soaked in water and peeled off from the substrates. The membranes were thoroughly rinsed with deionized water and then dried in a vacuum oven at 150°C for 24 h. The thickness of the membranes was in the range from 30 μm to 45 μm.

## RESULTS AND DISCUSSION

#### Monomer Synthesis

The synthetic routine of the monomers (DTDA and MBTBA) was outlined in Scheme 1. The chemical structure of them was confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR, DSC and Elem. Anal.

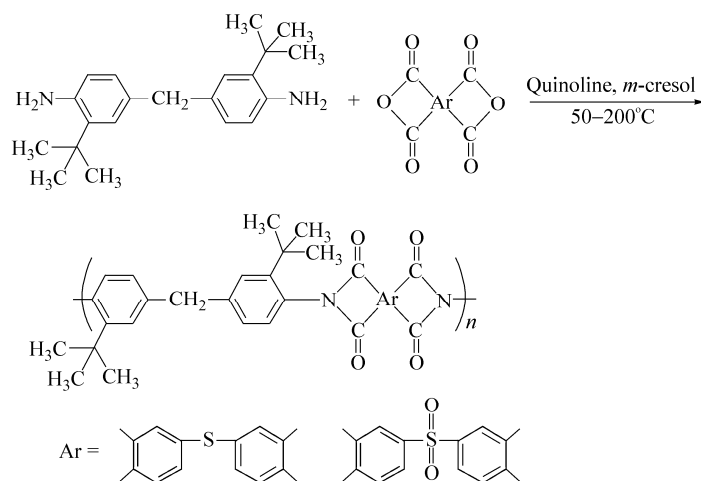


**Scheme 1** Synthetic routes of the monomers

#### Polyimide Synthesis

In general, polyimides can be prepared from the polycondensation of a diamine and a dianhydride through either a two-step approach or a one-pot method<sup>[19]</sup>. Although the monomer MBTBA and the two dianhydrides were pure and dry, an increase in viscosity was not observed when the polycondensation was carried out at room temperature for many hours. In other words, no polyimide with a high molecular weight was formed under this

condition because of the steric hindrance of the *tert*-butyl groups of MBTBA. As shown in Scheme 2, both polyimides with high molecular weights were obtained only when one-pot polycondensation in solution at a high temperature was adopted. On the other hand, the polymerization temperature must be controlled carefully to avoid gelation. So the reactive mixture was heated slowly to 50°C to form a transparent solution, then the temperature was raised to 100°C for 10 h, 180°C for 10 h and 200°C for 12 h to finish the imidization. The viscosity of the yellow transparent solution increased smoothly during the polycondensation process, and the polymerization solution remained homogeneous when the solid content was kept at or below 20 wt%.



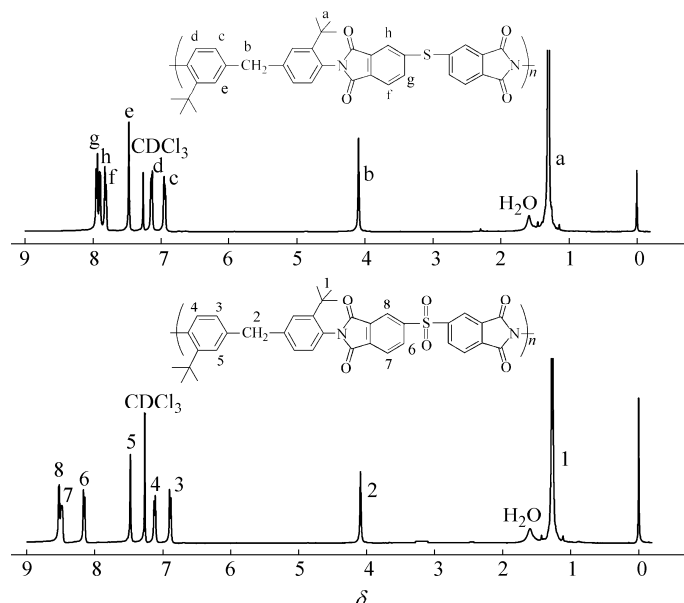
**Scheme 2** Preparation of MBTBA-DTDA and MBTBA-DSDA

### Polyimide Characterization

FTIR spectra of the two polyimides showed imide carbonyl peaks around 1780 and 1720  $\text{cm}^{-1}$  and did not show an amide carbonyl peak at 1650  $\text{cm}^{-1}$ , indicating the complete imidization during polycondensation. In other words, the byproduct  $\text{H}_2\text{O}$  in the reaction system was removed rapidly with a nitrogen flow to destroy the equilibrium between water and the imide groups. The chemical structures of the two polyimides were confirmed by  $^1\text{H-NMR}$  spectra in Fig. 1. The water peak was found at about  $\delta = 1.6$  in  $^1\text{H-NMR}$  spectra for both of polyimides. It is likely that the solvent ( $\text{CDCl}_3$ ) contained a little water or the polyimide films absorbed a little water. All the other signals were labeled by letters or numbers and ascribed to the corresponding protons in the resulting polyimides.

Although the reactivity of the hindered diamine MBTBA was low, high-molecular weight polyimides were still obtained by the one-pot approach. The molecular weights ( $M_n$ ,  $M_w$  and the polydispersity index) of both polyimides are shown in Table 1. From Table 1, it is found the molecular weights of both polyimides are related to the structure of the dianhydrides used. The number-average molecular weight of MBTBA-DTDA was about  $6.0 \times 10^4$  and slightly lower than that of MBTBA-DSDA ( $8.3 \times 10^4$ ), and the PDIs of both aromatic polyimides were about 1.8.

The UV spectra of both polyimide films are shown in Fig. 2. Both polyimide films were obtained by polymer solution casting onto quartz pieces at a concentration of 0.5 wt% and displayed high transmission around 90% in the wavelength range 400–800 nm. It seems the *tert*-butyl groups increased the intermolecular distance and decreased the interaction between the polyimide chains, resulting in good optical transparency. Furthermore, the thioether or sulfone groups can also improve the transmission of the polyimide films. Between them, the transmission of MBTBA-DSDA polyimide film is a little better than that of MBTBA-DTDA polyimide film. This may be attributed to the sulfone group in MBTBA-DSDA, which is more beneficial to reduce the probability of forming intermolecular charge-transfer complex (CTC) among the polyimide chains.



**Fig. 1**  $^1\text{H-NMR}$  spectra of the polyimides based on MBTBA-DTDA (top) and MBTBA-DSDA (bottom)

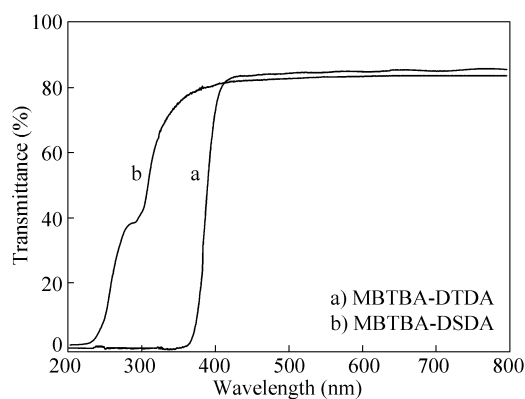
**Table 1.** Characterization of the polyimides

Polyimides	$M_n$	$M_w$	PDI	$T_g$ ( $^{\circ}\text{C}$ )		$T_d$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	
				DSC <sup>a</sup>	DMA <sup>b</sup>	$T_{5\%}$	$T_{10\%}$
MBTBA-DTDA	$6.0 \times 10^4$	$1.1 \times 10^5$	1.80	286	315	491	502
MBTBA-DSDA	$8.3 \times 10^4$	$1.5 \times 10^5$	1.82	314	358	470	479

<sup>a</sup> Obtained from DSC at a heating rate of 20 K/min in  $\text{N}_2$ ;

<sup>b</sup> Obtained from DMA at heating rate of 10 K/min at 1 Hz in  $\text{N}_2$ ;

<sup>c</sup>  $T_d$  decomposition temperature obtained from TGA at a heating rate of 20 K/min in  $\text{N}_2$ ;  $T_{5\%}$ : 5% weight loss temperature;  $T_{10\%}$ : 10% weight loss temperature



**Fig. 2** UV spectra of the polyimide films based on MBTBA-DTDA and MBTBA-DSDA

The solubility of MBTBA-DTDA and MBTBA-DSDA in various organic solvents at the room temperature is shown in Table 2 and the concentration of polymer solutions is 2 mg/mL. Both polyimides can easily dissolve in polar aprotic solvents such as NMP, DMF, DMAc, DMSO and pyridine, or even in non-polar solvents such as THF, DCM and  $\text{CHCl}_3$ . They partially dissolve in acetone and are insoluble in hexane. The enhanced solubility of them may be attributed to the introduction of *tert*-butyl groups and thioether/sulfone groups in the repeating units. Both aromatic polyimides were processed easily in solution to prepare transparent, flexible and tough

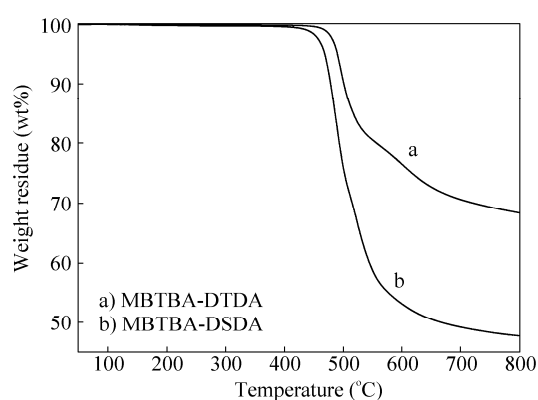
films. The good solubility also makes them as the potential candidates for practical applications by spin- or dip-coating processes.

**Table 2.** Solubility of MBTBA-DTDA and MBTBA-DSDA polyimides

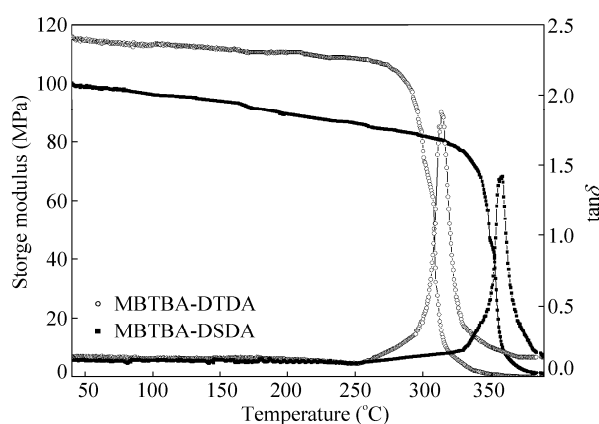
Polyimide	NMP	DMF	DMAc	DMSO	Py	THF	DCM	CHCl <sub>3</sub>	Acetone	Hexane
MBTBA-DTDA	+	+	+	+	+	+	+	+	±	–
MBTBA-DSDA	+	+	+	+	+	+	+	+	±	–

Measured at a polymer concentration of 2 mg/mL in solvent; Solubility: +, soluble; ±, partially soluble; –, insoluble at room temperature; NMP (*N*-methyl-2-pyrrolidinone), DMF (dimethyl formamide), DMAc (*N,N*-dimethylacetamide), DMSO (dimethyl sulfoxide), Py (pyridine), THF (tetrahydrofuran), DCM (dichloromethane)

The thermal properties of both polyimides were evaluated by TGA and DSC under nitrogen atmosphere, and the results are also summarized in Table 1. The typical TGA curves were shown in Fig. 3. Both aromatic polyimides were stable up to 450°C and the residual weight at 800°C was above 45%. The temperature of 5% weight loss was greater than 490°C for the MBTBA-DTDA polyimide and 470°C for the polyimide MBTBA-DSDA, which demonstrated that the thermooxidative stability of the polyimide MBTBA-DTDA was better than that of the polyimide MBTBA-DSDA. This may be attributed to the thioether link, which is more flexible and resistant to thermal oxidation. The glass transition temperatures ( $T_g$ ) of the polyimides measured by DSC are also shown in Table 1. The  $T_g$  of the polyimide MBTBA-DSDA was 314°C and relatively higher than that of the polyimide MBTBA-DTDA because of its rigid backbone and the higher molecular weight. This indicates that the thermal stability of polyimide is not only related to the monomer structure but also connected to the molecular weight of the polyimide. As a result, the pendent *tert*-butyl groups attached to the polyimide backbone can improve their solubility greatly without sacrificing their thermal stability at the same time.



**Fig. 3** TGA curves of the polyimides MBTBA-DTDA and MBTBA-DSDA



**Fig. 4** DMA curves of the polyimides MBTBA-DTDA and MBTBA-DSDA

The dynamic mechanical properties of the polyimide membranes were measured by dynamical mechanical analysis (DMA), and the results are illustrated in Fig. 4. The storage moduli of the membranes are quite high, which are attributed to the rigid backbones of the polyimides. The MBTBA-DTDA membrane presented higher storage modulus than that of MBTBA-DSDA membrane, which results from the different bridged groups ( $-S-$  and  $-SO_2-$ ) in the main chain of polyimides. The storage moduli of the polyimide membranes decreased with the increase of the temperature in the testing range. For MBTBA-DTDA membrane, the storage modulus went down slowly in the range from 30°C to 280°C, but went down rapidly after 280°C. But for MBTBA-DSDA membrane, the storage modulus went down rapidly until after 330°C.

The curves of the loss tangent ( $\tan\delta$ ) versus temperature for these polyimide membranes are also shown in

Fig. 4 and the corresponding data are given in Table 1. For all the membranes, the  $T_g$ s were obtained from the corresponding peak in the  $\tan\delta$  curve and all membranes exhibited the relatively broad glass transition regions. The results indicated that the  $\tan\delta$  peaks ( $\tan\delta_{\max}$ ) of the MBTBA-DTDA and the MBTBA-DSDA were at 315°C and 358°C, respectively. Generally, the measurement of the  $T_g$  by DMA is much more sensitive than that by DSC. The  $T_g$  values from the DMA analyses of the polyimide membranes were higher than those from the DSC analyses.

## CONCLUSIONS

In summary, two aromatic polyimides with high molecular weights were synthesized successfully from MBTBA and DTDA or DSDA. Both of them showed excellent solubility in common solvents at the room temperature. The glass-transition temperatures of them were 286°C and 314°C (or 315°C and 358°C) respectively, as measured by DSC (or DMA). The 5% weight loss temperature of both was about 470°C in  $N_2$  by thermogravimetric analysis. These results indicated that the *tert*-butyl pendent groups reduced the interactions among polymer chains and the thioether or sulfone moiety was flexible which may improve their solubility in organic solvents without the loss of thermal stability. Transparent and flexible films of the two polyimides were obtained *via* solution casting. The good solubility also makes them as the potential candidates for practical applications by spin- or dip-coating processes.

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