# Preparation and Properties of Organo-Soluble Polyimides Based on 4,4'-Diamino-3,3-dimethyldiphenylmethane and Conventional Dianhydrides

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ABSTRACT: 4,4'-Diamino-3,3'-dimethyldiphenylmethane was used to prepare polyimides in an attempt to achieve good organo-solubility and light color. Polyimides based on this diamine and three conventional aromatic dianhydrides were prepared by solution polycondensation followed by chemical imidization. They possess good solubility in aprotonic polar organic solvents such as *N*-methyl 2-pyrrolidone, *N*,*N*-dimethyl acetamide, and *m*-cresol. Polyimide from 4,4'-diamino-3,3'-dimethyldiphenylmethane and diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride is even soluble in common solvents such as tetrahydrofuran and chloroform. Polyimides exhibit high transmittance at wavelengths above 400 nm. The glass transition temperature of polyimide from 4,4'-diamino-3,3'-dimethyldiphenylmethane and pyromellitic dianhydride is 370°C, while that from 4,4'-diamino-3,3'-dimethyldiphenylmethane and diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride is about 260°C. The initial thermal decomposition temperatures of these polyimides are 520–540°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1299–1304, 1999

**Key words:** polyimide; organo-soluble; preparation; property; 4,4'-diamino-3,3'-dimethyldiphenylmethane

## INTRODUCTION

Although polyimides synthesized from conventional aromatic dianhydride and aromatic diamine monomers exhibit great thermal stability and excellent mechanical and electrical properties,<sup>1</sup> the applications of such polyimides are restricted because of their poor solubility in organic solvent and high glass transition temperatures that cause difficulty in fabrication. Conventional aromatic polyimides must be processed at their precursur stage, polyamic acids, which are, however, unstable at the room temperature and must be stored at a lower temperature; The imidization process should be carried out at a high temperature (250–300°C). This high temperature might cause damage on the substrate when polyimides are applied in the electronic industry; furthermore, a large amount of water is generated during the imidization process, which would reduce the chain packing and properties. To improve the processability of polyimides, many attempts have been tried to prepare polyimides that are either soluble or thermoplastic. Several approaches have been used such as the incorporation of flexible linkage in the main chain to reduce the packing force,<sup>2</sup> the introduction of bulky pendant groups to the main chain to enhance the free

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volume,  $^{3,4}$  replacing aromatic groups with alicyclic groups  $^{5-10}$  and the introduction of fluorinated groups.  $^{11-15}$ 

Optical transparency of a polyimide is of special importance when it is applied in optical devices.<sup>16,17</sup> Conventional aromatic polyimides, however, exhibit brownish color due to the existence of large conjugated structure and/or strong charge transfer complex. The color could be reduced either by the replacement of aromatic groups with alicyclic groups, which destroys the conjugated structure,<sup>5–10</sup> or by the application of fluorinated monomers that reduces the tendency of the formation of a charge transfer complex.<sup>18–20</sup>

The commonly used approaches to increase the solubility of a polyimide would also increase the chain flexibility and probably reduce the thermal stability. Similarly, to increase the optical transparency of a polyimide by using nonaromatic structure would also lead to lower thermal stability.<sup>5–10</sup> Although to use fluorinated structure to increase the solubility and the optical transparency may not reduce the chain flexibility and the thermal stability necessarily, fluorinated monomers are, however, usually of high cost.

Recently, Harris et al. found that the solubility and the optical transparency at visible light wavelength of 4,4',5,5'-biphenyltetracarboxylic dianhydride/benzidine-based polyimides were increased by introducing pendant groups in the 2and 2'-positions of dianhydrides or diamines.<sup>21</sup> They suggested that the improvements in the solubility and color of polyimides result from the twisting of the conformation caused by the existence of 2-, 2'-position substitutions, which inhibits chain packing and crystallization and breaks up the conjugation along the backbone.

In this article, we use a 3,3'-di-substituted 4,4'diaminodiphenyl methane, 4,4'-diamino-3,3'dimethyldiphenylmethane, to replace the conventional 4,4'-diaminodiphenylmethane in an attempt to obtain polyimides with good organosolubility and light color.

## **EXPERIMENTAL**

## Materials

4,4'-Diamino-3,3'-dimethyldiphenylmethane (MMDA) was synthesized by the reaction between *o*-methyl aniline and formaldehyde. To a mixture of 47 mL 37% hydrochloric acid, 200 mL distilled water and 53.5 mL (0.5 mol) *o*-methyl aniline, 19 mL 40% (0.25 mol) formaldehyde (aqueous solution) was added dropwisely. The mixture was then maintained at 70–76°C for 4 h. The product was then cooled to 0°C. To it ammonia water was added slowly to basify the product. The resin-like solid generated in the basifying process was removed. Upon the complete basifying, the solid obtained was recrystallized with anhydrous ethanol. The product is a pale yellow crystal. The melting point of MMDA was 156°C.

Pyromellitic dianhydride (PMDA) (Chemical Reagent Grade) was purchased from Shanghai No. 1 Reagent Company and used as received. Diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride (ETDA) (Industrial Product) was purchased from the Shanghai Research Institute of Synthetic Resin and dried at 190°C for 2 h before use. Benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (BTDA) was prepared by a dehydration reaction of benzophenone-3,3',4,4'-tetracarboxylic acid (purchased from Beijing Tar Chemicals Company) with an excess amount of acetic anhydride at the refluxing temperature for 2 h. 4,4'-Diaminodiphenylmethane (MDA) (Chemical Reagent Grade) was purchased from the Shanghai No. 3 Reagent Company and recrystallized from ethanol under the protection of N<sub>2</sub> before use. N-Methyl-2-pyrrolidone (NMP) (Analytical Reagent Grade) was purchased from the Shanghai Reagent Company and dried over molecular sieves before use. Acetic anhydride (analytical reagent grade) and triethyl amine (analytical reagent grade) were purchased from the Shanghai No. 1 Reagent Company and Xin Da Chemical Factory, respectively, and used as received.

## Preparation of Polyimides

Polyimides based on MMDA were prepared from a solution polycondensation reaction between MMDA and a dianhydride monomer followed by chemical imidization. To a MMDA solution in NMP, equal mol of solid dianhydride (PMDA or ETDA or BTDA) was added. The mixture was stirred at room temperature for 4 h. As the dianhydride was dissolved, the viscosity of the system is obviously increased. The mixture of acetic anhydride and triethyl amine [diamine/acetic anhydride/triethyl amine = 4 : 36 : 9 (molar ratio)] were then added dropwise to the system to imidize the obtained polyamic acid. The imidization process was kept for 16 h at room temperature. The preparation process is described in Scheme 1.



The resultant polyimide was precipitated from distilled water and dried at 90°C under vacuum.

Polyimides based on MDA were prepared from solution polycondensation reaction between a dianhydride monomer at room temperature followed by thermal imidization. To a MDA/NMP solution, equal mol of solid dianhydride (PMDA or ETDA or BTDA) was added. The mixture was stirred for 4 h at room temperature. The obtained polyamic acid solution was then cast on a glass substrate and thermally imidized by heating at 200°C for 2 h.

#### **Characterization of Polyimides**

The IR spectra of polyimides were recorded on a PE 983 Infrared Spectrophotometer on their powder or film forms. The films were cast from their NMP solutions and dried at 90°C under vacuum.

The solubilities of these polyimides were determined by observing the solubility of the solid polyimides in various solvents at room temperature.

The intrinsic viscosities of polyimides were measured with an Ubbelodhe viscometer using NMP as the solvent at 30°C. The standard concentration was 1 g/dL.

Transmission UV-visible spectra of polyimides (cast from NMP solutions) were measured on a Shang Fen 7530 UV-Visible Spectrophotometer in the transmittance mode. The in-plane refractive indices and thickness of polyimides were measured using an optical waveguide method at 25°C with a wavelength of 632.8 nm.

The glass transition temperatures  $(T_g)$  of polyimides were obtained from differential scanning calorimetric analysis (DSC). The DSC spectra were recorded on a PE DSC7 under the protection of N<sub>2</sub>. The scan rate was 20°C/min. All samples experienced two heating processes from 25 to 300°C and the second one was recorded.

The thermal stabilities of these polyimides were characterized by their thermogravimetric analysis (TGA). The TGA spectra were recorded on a PE TGA7 under the protection of  $N_2$ . The scan rate was 20°C/min.

### **RESULTS AND DISCUSSIONS**

The polyimide prepared from MMDA and PMDA was named PI-MMDA/PMDA. That from MMDA and ETDA was PI-MMDA/ETDA. That from MMDA and BTDA was PI-MMDA/BTDA. Similarly, three polyimides based on MDA were named PI-MDA/PMDA, PI-MDA/ETDA and PI-MDA/BTDA, respectively.

## **IR Spectra of Polyimides**

Figure 1 is the IR spectrum of PI-MMDA/BTDA powder. Absorption bands at 1715 cm<sup>-1</sup> and 1775 cm<sup>-1</sup> characteristic of C=O stretching in imide groups and those at 1375 cm<sup>-1</sup> and 725 cm<sup>-1</sup> characteristic of C-N stretching and C-N bend-



Figure 1 IR spectrum of PI-MMDA/BTDA.

Sample	Ethanol	Acetone	Toluene	$\mathrm{CHCl}_3$	THF	DMA	NMP	m-Cresol
PI-MMDA/PMDA	_	_	_	_	_	+	+	+
PI-MMDA/ETDA	—	_	_	+	+	+	+	+
PI-MMDA/BTDA	_	_	_	+	_	+	+	+
PI-MDA/PMDA	—	_	_	_	_	_	_	_
PI-MDA/ETDA	_	_	_	_	_	_	_	_
PI-MDA/BTDA	_	_	_	_	_	_	_	_

Table I Solubility of Polyimides in Various Organic Solvents (25°C)

+: Soluble; -: Insoluble.

ing, respectively, in imide groups are observed. The observation of these bands clearly indicates the existence of imide groups and confirms the successful synthesis of polyimide.

#### **Solubility of Polyimides**

The solubility of these polyimides in various organic solvents is listed in Table I.

It was observed that all the polyimides prepared from MMDA, even with a "rigid" dianhydride, PMDA, are soluble in aprotonic polar solvents such as NMP, DMA, and m-cresol. Apart from these aprotonic polar solvents, polyimide from MMDA and ETDA can also be dissolved in the common low boiling point solvents tetrahydrofuran (THF) and chloroform. Those from MDA, however, precipitated from NMP upon chemical imidization and are insoluble in organic solvents. The increase in solubility of MMDAbased polyimides clearly comes from the introduction of the two methyl side groups, which increase the free volume and reduce the chain packing of the polyimides. Furthermore, the existence of the methyl side groups also reduce the conjugation between the aromatic ring in a dianhydride unit and that in a diamine unit. This decrease in the conjugation would lead to the decrease of the intermolecular interaction and thus the crystallinity tendency. This result clearly indicates that the increase in the polyimide chain flexibility is not necessary for the increase of solubility. Other approaches to reduce the intermolecular interaction could also increase the solubility efficiently.

#### **Intrinsic Viscosity**

These polyimides have quite high molecular weights. The intrinsic viscosities of PI-MMDA/ PMDA, PI-MMDA/ETDA, and PI-MMDA/BTDA using NMP as the solvent at 30°C were found to be 0.65, 0.95, and 1.02 dL/g, respectively (see Table II).

#### **Optical Transparency**

UV-Vis spectra of polyimides ( $\sim 1 \ \mu m$ ) are shown in Figure 2. It was observed that polyimides based on MMDA are almost transparent at the wavelength above 400 nm. PI-MDA/BTDA, however, exhibits clear absorption at the wavelength of 400–460 nm. This result supports the claim that the optical absorption in the visible and near UV range could be effectively reduced by approaches other than the introduction of highly electronegative fluorine atoms or the replacement of aromatic groups with nonaromatic groups. The incorporation of substitution to the aromatic rings of the polyimide backbones could bring in steric hindrance, which would lead to the distortion of the conjugation and, consequently, result in the "blue-shift" of the absorption wavelength.

#### **Refractive Indices**

The in-plane refractive indices of PI-MMDA/ ETDA and PI-MMDA/BTDA measured at 632.8

#### Table II Properties of Polyimides

Sample	$\begin{matrix} [\eta] \\ (dL/g)^a \end{matrix}$	$\underset{(°C)^{\mathrm{b}}}{T_g}$	$\underset{(°C)^{c}}{T_{d}}$	$n^{\mathrm{d}}$
PI-MMDA/PMDA PI-MMDA/ETDA PI-MMDA/BTDA PI-MDA/PMDA PI-MDA/ETDA	$0.65 \\ 0.95 \\ 1.02$	370.0 259.9 ND ND ND	537 519 530	$1.648 \\ 1.657$
PI-MDA/BTDA		ND		

<sup>a</sup> Solvent: NMP, 30°C.

<sup>b</sup> Measured by DSC, scan rate: 20°C/min.

 $^{\rm c}$  Scan rate: 20°C/min,  $\rm N_2$  protection.

<sup>d</sup> Measured with an optical waveguide method at 25°C with a wavelength of 632.8 nm; ND: not detected.

nm at 25°C and shown in Table II were observed to be 1.648 and 1.657, respectively. The refractive index of PI-MMDA/BTDA is slightly greater than that of PI-MMDA/ETDA. Both polyimides, however, possess smaller refractive indices than the conventional Kapton type polyimide.<sup>22</sup>

#### **Glass Transition Temperature**

The glass transition temperatures  $(T_g)$  of polyimides obtained from DSC are listed in Table II.  $T_g$ s of PI-MMDA/PMDA and PI-MMDA/ETDA are 370.0 and 259.9°C, respectively. Polyimide based on PMDA exhibits a much higher  $T_g$  than that based on ETDA. This is clearly caused by the higher rigidity of the PMDA structure and the increase in the chain flexibility of ETDA introduced by the "flexible" —O— structure. No obvious glass transition was observed for polyimides based on MDA in the temperature range of 50– 400°C.

#### **Thermal Stability**

The TGA spectrum of PI-MMDA/BTDA is shown in Figure 3. An initial thermal decomposition temperature ( $T_d$ , on-set-temperature) of 530°C was obtained. PI-MMDA/PMDA and PI-MMDA/ETDA exhibit  $T_d$ s at 537 and 519°C, respectively. It is understandable that PI-MMDA/PMDA possesses slightly higher thermal stability than PI-MMDA/ETDA and PI-MMDA/BTDA, which is caused by the higher rigidity and thermal stability of the PMDA structure.



**Figure 2** UV-Vis spectra of PI-MMDA/ETDA (1), PI-MMDA/BTDA (2), and PI-MDA/BTDA (3) films.



**Figure 3** TGA spectrum of PI-MMDA/BTDA scan rate: 20°C/min, N<sub>2</sub> protection.

#### CONCLUSIONS

Aromatic polyimides based on 4,4'-diamino-3,3'dimethyldiphenylmethane are soluble in aprotonic polar solvents such as NMP, DMA, and *m*cresol. These polyimides exhibit high transmittance at wavelengths above 400 nm. The glass transition temperature of polyimide from 4,4'diamino-3,3'-dimethyldiphenylmethane and pyromellitic dianhydride is 370°C, while that from 4,4'-diamino-3,3'-dimethyldiphenylmethane and diphenylether-3,3',4,4'-tetracarboxylic acid dianhydride is about 260°C. The initial thermal decomposition temperatures of these polyimides are 520–540°C.

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