

A Study on the Preparation and Properties of Alicyclic Polyimides Based on 3-Carboxylmethylcyclopentane-1,2,4-Tricarboxylic Acid Dianhydride

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Received 16 May 1997; accepted 4 June 1997

ABSTRACT: Alicyclic polyimides were prepared from 3-carboxylmethyl-cyclopentane-1,2,4-tricarboxylic acid dianhydride and conventional aromatic diamines. These polyimides possess good solubility in strong polar solvents, such as *N*-methyl pyrrolidone, *N,N*-dimethyl acetamide, *N,N*-dimethyl formamide, and *m*-cresol. They are transparent and colorless. The glass transition temperatures are about 181°C, and the initial thermal decomposition temperatures in N₂ were observed to be 441–477°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2105–2109, 1998

Key words: polyimide; alicyclic; preparation; property; 3-carboxylmethylcyclopentane-1,2,4-tricarboxylic acid dianhydride

INTRODUCTION

Although polyimides synthesized from aromatic dianhydride and aromatic diamine monomers exhibit great thermal stability and excellent mechanical and electrical properties,¹ 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. In addition, these polyimides usually exhibit deep brown color because of their high aromaticity. Intense studies have been made to improve the solubility.^{2–4} Among various attempts tried, utilization of alicyclic monomers seems to have its own advantages. Polyimides based on alicyclic monomers exhibit good solubility in organic solvents and tend to be colorless.^{4–8}

In this article, the preparation of polyimides based on an alicyclic dianhydride, 3-carboxylmethylcyclopentane-1,2,4-tricarboxylic acid dianhydride, and three conventional aromatic diamines, and the characterization of their solubil-

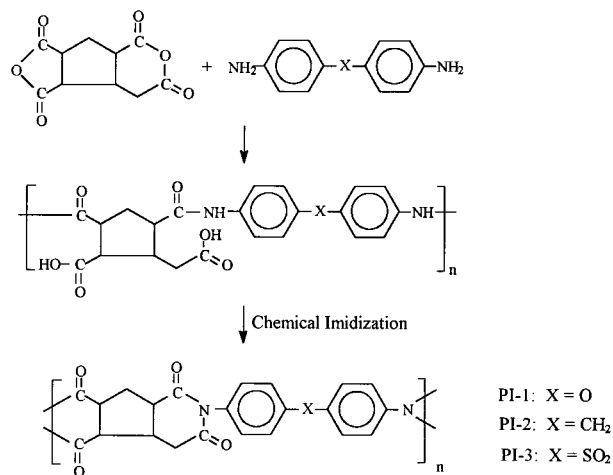
ity, optical properties, and thermal properties are presented.

EXPERIMENTAL

Materials and Instrumentation

3-carboxylmethylcyclopentane-1,2,4-tricarboxylic acid dianhydride was synthesized by our lab. 4,4'-Diaminodiphenylether (chemical reagent grade), 4,4'-diamino-diphenylmethane (chemical reagent grade), and 4,4'-diaminodiphenyl-sulfone (chemical reagent grade) were purchased from Shanghai No. 3 Reagent Factory and recrystallized from ethanol under the protection of N₂ before use. *N*-methyl pyrrolidone (NMP) (analytical reagent grade) and *N,N*-dimethyl acetamide (DMA) (analytical reagent grade) were purchased from the Shanghai Reagent Factory and dried over molecular sieves. Acetic anhydride (analytical reagent grade) and triethyl amine (analytical reagent grade) were purchased from the Shanghai No. 1 Reagent Factory and the Xin Da Chemical Factory, respectively, and used as received.

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Scheme 1

Preparation of Alicyclic Polyimides

Alicyclic Polyimides were prepared from a polycondensation reaction between 3-carboxymethylcyclopentane-1,2,4-tricarboxylic acid dianhydride and 4,4'-diaminodiphenylether or 4,4'-diaminodiphenyl methane in NMP (solid content = 10–15 wt %) with efficient agitation at room temperature for 4 h, followed by a chemical imidization with acetic anhydride and triethyl amine (diamine–acetic anhydride–triethyl amine = 4 : 36 : 9 molar ratio) at 25°C for 48 h (see Scheme 1). The polyimide with 4,4'-diaminodiphenylsulfone as monomer was polymerized at 50°C and imidized at room temperature. The resultant polyimides were precipitated from water and dried at 90°C under vacuum.

Characterization of Polyimides

The infrared (IR) spectra of polyimides were recorded on a PE 983 IR spectrophotometer on their film form. The films were cast from their NMP solutions and dried at 90°C under vacuum.

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

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

The glass transition temperatures (T_g) of polyimides were obtained from their differential scanning calorimetry (DSC) spectra. The DSC spectra were recorded on a PE DSC7 under the protection of N₂. 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 stability of polyimides was characterized by their thermogravimetric analysis (TGA)-spectra. The TGA spectra were recorded on a PE TGA7 under the protection of N₂. The scan rate was 20°C/min.

The transparencies of polyimide films ($\sim 4 \mu\text{m}$, cast from NMP solutions) were characterized by UV–visible (uv–vis) spectra on a Perkin-Elmer Lambda 1 UV–vis spectrophotometer.

RESULTS AND DISCUSSIONS

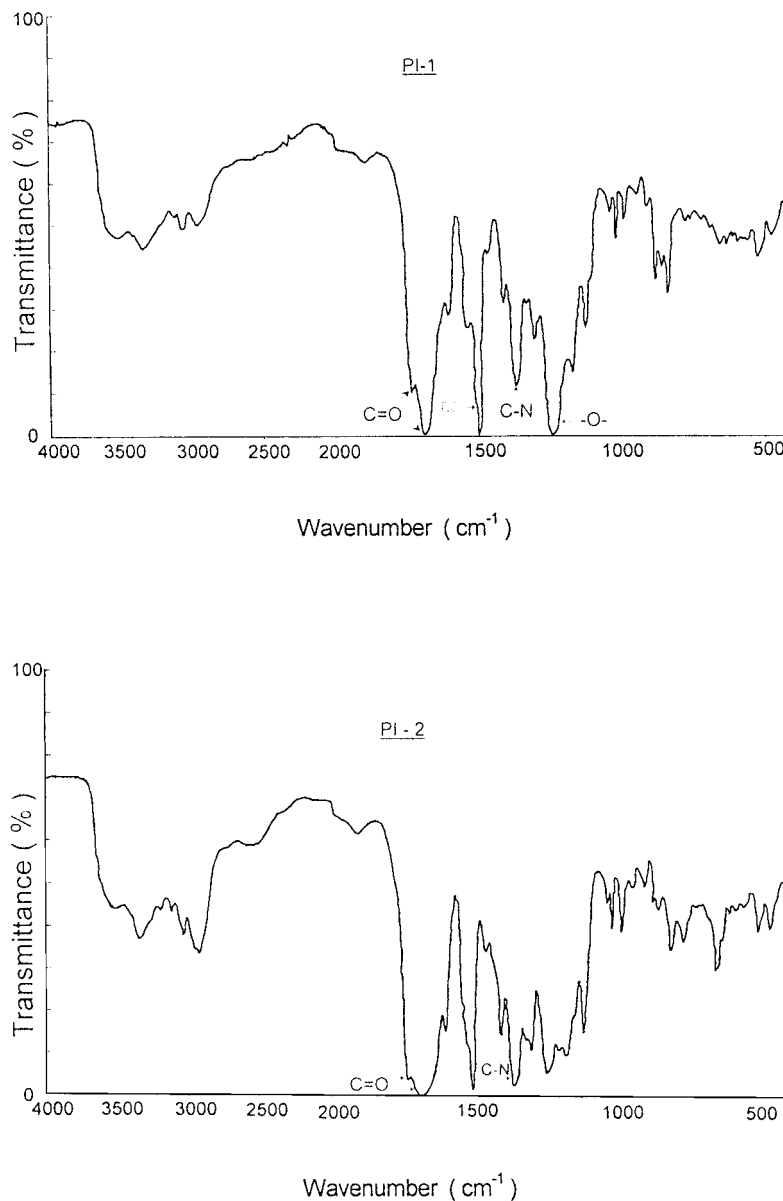
IR Spectra of Polyimides

The IR spectra of PI-1 and PI-2 are shown in Figure 1. The clear appearance of ~ 1735 and $\sim 1685 \text{ cm}^{-1}$ bands characteristic of the stretching of C=O in imide rings and the $\sim 1365 \text{ cm}^{-1}$ band characteristic of the stretching of C–N in imide rings indicate the success of the synthesis. (1735 and 1365 cm^{-1} bands do not exist in corresponding polyamic acids). These bands appear at lower wave numbers compared to Kapton-type polyimide.^{1,9} This slight shift in the wavelength was also observed in other polyimides prepared from alicyclic dianhydride and aromatic diamines.⁸ The band at $\sim 1500 \text{ cm}^{-1}$ is characteristic of the vibration of the benzene rings in the polyimide backbone.⁹ The presence of the absorption band at $3600\text{--}3200 \text{ cm}^{-1}$, which is characteristic of O–H and N–H stretching, may indicate the incompleteness of the imidization.

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

Polyimide	Ethanol	Toluene	CHCl ₃	Acetone	THF	NMP	DMF	DMA	<i>m</i> -Cresol
PI-1	–	–	–	–	–	+	+	+	+
PI-2	–	–	–	–	–	+	+	+	+
PI-3	–	–	–	–	–	+	+	+	+
Kapton	–	–	–	–	–	–	–	–	–

Note: + represents soluble; – represents insoluble.


Figure 1

Solubility of Alicyclic Polyimides

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

It can be seen that the alicyclic polyimides prepared are soluble in strong polar organic solvents such as NMP, DMA, DMF, or *m*-cresol and cannot be dissolved in weak polar or nonpolar solvents, such as tetrahydrofuran (THF), chloroform, toluene, ethanol, and acetone, while the Kapton-type polyimide cannot be dissolved in any organic solvents studied. The improvement in the solubility of alicyclic polyimides results from the disappearance of the extended π bond structure existing in conventional aromatic polyimides, such as Kap-

ton. This disappearance in the extended π bond would lead to the decrease in the crystallization tendency and intermolecular interaction.

Table II Glass Transition Temperatures (T_g) and Initial Thermal Decomposition Temperatures (T_d) of Alicyclic Polyimides

Samples	PI-1	PI-2	PI-3	Kapton
T_g ($^{\circ}\text{C}$) ^a	182.2	180.8	180.8	> 450 ¹⁰
T_d ($^{\circ}\text{C}$) ^b	447.6	441.8	477.4	> 600 ¹⁰

^a Scan rate: 20 $^{\circ}\text{C}/\text{min}$

^b Scan rate: 20 $^{\circ}\text{C}/\text{min}$; N_2 protection.

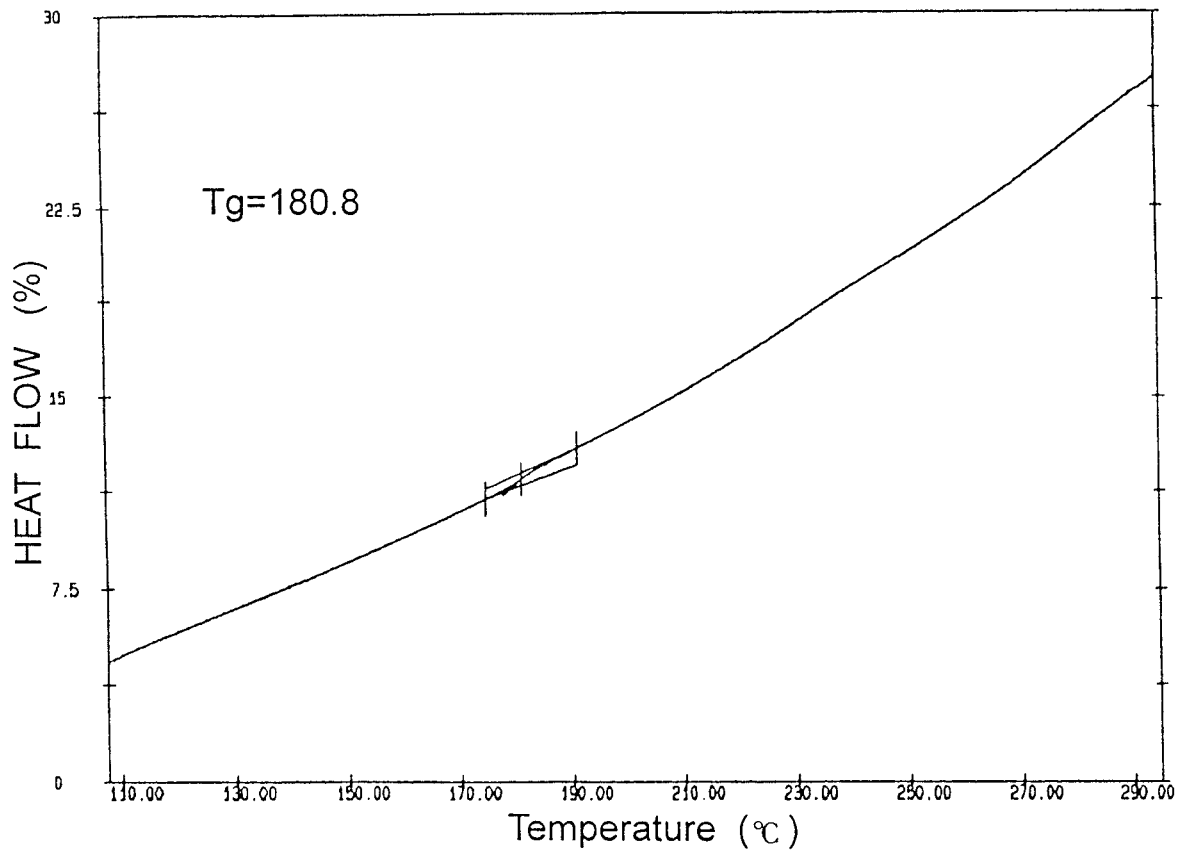


Figure 2

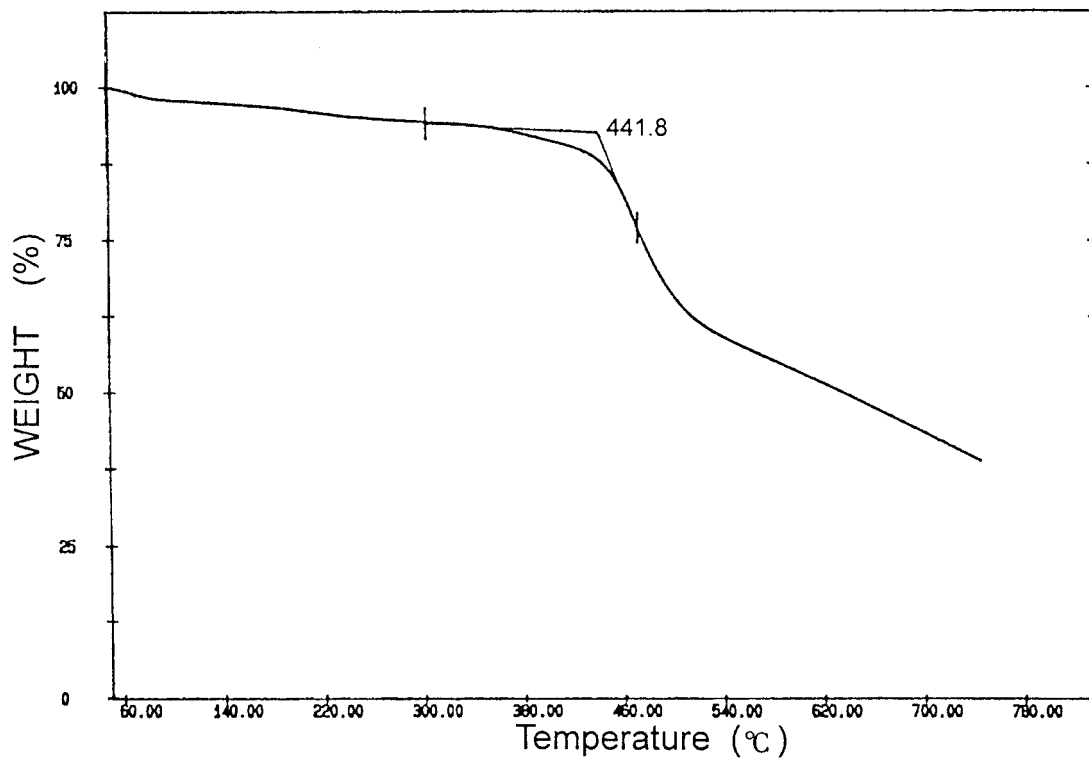


Figure 3

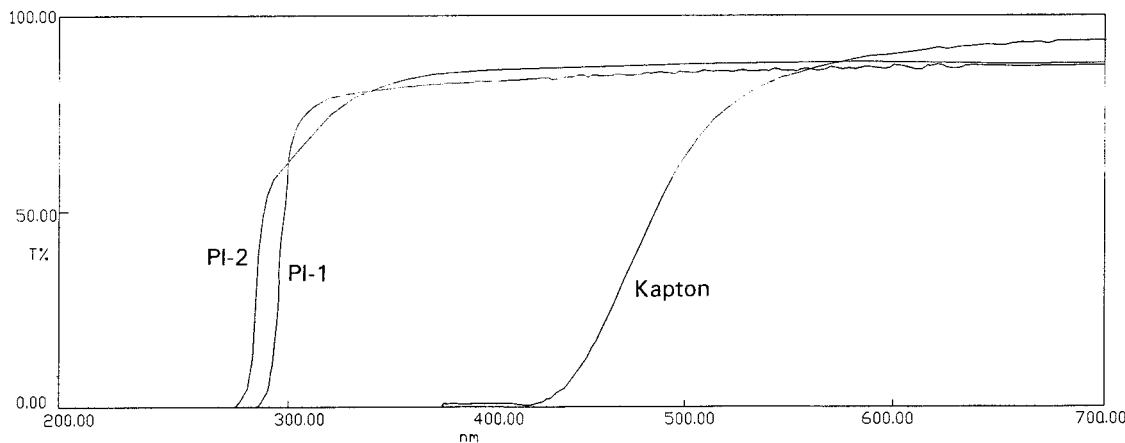


Figure 4

Intrinsic Viscosity of Alicyclic Polyimides

Intrinsic viscosities of PI-1, PI-2, and PI-3 measured at 30°C using NMP as a solvent were 0.54, 0.60, and 0.35, respectively. The intrinsic viscosity of PI-3 is somewhat smaller. This may be caused by the lower reactivity of 4,4'-diaminodiphenylsulfone.

Thermal Properties of Alicyclic Polyimides

The differential scanning calorimetry (DSC) curve of PI-3 is shown in Figure 2, and T_g s of PI-1, PI-2, and PI-3 are listed in Table II. It can be seen that all three alicyclic polyimides exhibit much lower T_g than Kapton-type aromatic polyimide. This clearly indicates that the alicyclic group possesses much higher flexibility than the aromatic group. Furthermore, the three alicyclic polyimides have almost identical T_g s (182.2, 180.8, and 180.8°C, respectively). This identity in T_g of polyimides based on diamines with different rigidity may also indicate that the alicyclic group in polyimides exhibits much greater flexibility and plays a deciding role in the possibility of segment motion.

The TGA spectrum of PI-2 is shown in Figure 3, and the initial thermal decomposition temperatures (T_d) of PI-1, PI-2, and PI-3 are listed in Table II. It can be observed that all three PIs exhibit lower T_d than the conventional aromatic polyimides, such as Kapton.^{1,10} This is due to the fact that the alicyclic group has a lower thermal stability than aromatic one and is the weakest point in PI molecules in the thermal decomposition process.

Optical Property of Alicyclic Polyimides

The UV-vis spectra of PI-1, PI-2, and Kapton films ($\sim 4 \mu\text{m}$) are shown in Figure 4. The absorptions of the alicyclic polyimides are quite low, not only in the visible light range (400–700 nm), but also in the near-UV range (300–400 nm). The Kapton film, however, not only absorbs the light in the near UV range (300–400 nm) almost completely but also possesses high absorption at 400–550 nm. The Kapton film is brownish in appearance, while PI-1 and PI-2 films are almost transparent and colorless. The lower absorption of the alicyclic polyimides at the near-UV and visible light ranges results from the disappearance of the extended π bond structure existing in Kapton.

REFERENCES

1. C. E. Sroog, in *Polyimides*, D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., Blackie, Glasgow, 1990, Chap. 9.
2. M. Arai, P. E. Cassidy, and J. M. Farley, *Macromolecules*, **22**, 989 (1989).
3. T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, *Macromolecules*, **24**, 5001 (1991).
4. B.-W. Chun, *Polymer*, **35**, 4203 (1994).
5. M. Yamada, M. Kusama, T. Matsumoto, and T. Kurosaki, *Macromolecules*, **26**, 4961 (1993).
6. T. Matsumoto and T. Kurosaki, *React. Funct. Polym.*, **30**, 55 (1996).
7. W. Volsen, H. J. Cha, M. I. Sanchez, and D. Y. Yoon, *React. Funct. Polym.*, **30**, 61 (1996).
8. H.-Y. Wang, J. Yin, X.-R. Wang, L.-M. Sun, J.-H. Fang, H.-J. Xu, and Z.-K. Zhu, *Polym. Mater. Sci. Eng.* (in Chinese), **13**, 83 (1997).
9. J.-Y. Jeon and T.-M. Tak, *J. Appl. Polym. Sci.*, **61**, 524 (1996).
10. C. E. Sroog, *J. Polym. Sci., Macromol. Rev.*, **11**, 161 (1976).