

Preparation and Properties of Organosoluble, Colorless, and High-Pretilt-Angle Polyimides Based on an Alicyclic Dianhydride and Long-Main-Chain Alkyl-Group-Containing Diamines

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ABSTRACT: Alicyclic polyimides (PIs) were prepared from 3-carboxymethyl-cyclopentane-1,2,4-tricarboxylic acid dianhydride and α,ω -di(4-aminophenoxy)alkanes. These PIs possessed good solubility in aprotic, strongly polar solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethyl formamide, and *m*-cresol. They possessed high transparency in visible wavelengths and were almost colorless. The pretilt angle of a liquid-crystal display with these PIs as the alignment layer increased linearly as the length of the alkyloxy groups increased; it was close to 5° for the PI samples PI-10 and PI-12. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2814–2820, 2001

Key words: polyimide; alignment film; alicyclic; α,ω -di(4-aminophenoxy)alkanes; 3-carboxymethylcyclopentane-1,2,4-tricarboxylic acid dianhydride

INTRODUCTION

One of the major applications of polyimides (PIs) is as the alignment layer in liquid-crystal displays (LCDs).^{1–10} However, the application of conventional aromatic PIs as the alignment material in the modern LCD industry is somewhat limited by their intrinsic features. First, they are not organosoluble because of their strong intermolecular interactions and crystalline nature^{11–15} and are, therefore, processed at the precursor (polyamic acid) stage and then cured at a high temperature (250–300°C). This high temperature, however, may cause a slight distortion in the glass substrate of LCD devices. These kinds of PIs, therefore, cannot be applied to LCD devices with a large display area, in which a slight curving of the glass substrate would lead to

severe picture distortion. To lower the curing temperature, different types of organosoluble PIs have been studied. One of the most common methods for obtaining organosoluble PIs is replacing some of the aromatic groups with alicyclic groups^{16–19} (so-called alicyclic PIs.) Second, the conventional aromatic PIs usually have a deep brownish color due to the extended-conjugation structure and/or the existence of a charge-transfer complex (CTC).²⁰ The extended-conjugation structure and the CTC formation can be effectively reduced by the replacement of aromatic moieties with alicyclic moieties.^{16–19,21} Most of the alicyclic PIs are almost colorless.^{16–19} This colorlessness is essential for a color LCD. In addition to the low curing temperature and light color, the alignment materials applied to LCDs with a large display area, such as the supertwisted nematic-type (STN) LCD, must achieve a high pretilt angle, which is the angle between the direction of the liquid-crystal (LC) molecules and the substrate.⁴ The conventional PI alignment layer

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can only achieve a small pretilt angle, whereas the introduction of long alkyl groups into the PI structure (as the main chain or side group) has been observed to be effective at increasing the pretilt angle.^{11,14,15,22,23}

In a previous article, we reported a series of colorless, organosoluble, high-pretilt-angle PIs bearing side alkyl groups based on 3-carboxyl-methylcyclopentane-1,2,4-tricarboxylic acid dianhydride (TCAAH) and 4-*n*-alkoxy-benzene-1,3-diamine.²⁴ In this article, we report the syntheses and properties of a series of alicyclic PIs with long alkyl chains in the backbone based on TCAAH and α,ω -di(4-aminophenoxy)alkanes.

EXPERIMENTAL

Materials

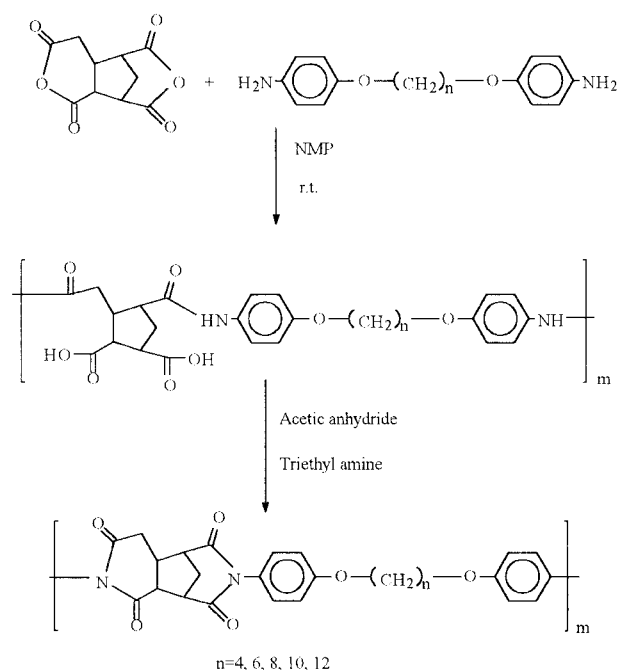
TCAAH was synthesized by our lab. α,ω -Di(4-aminophenoxy)alkanes were synthesized from the condensation between α,ω -dibromoalkane and *p*-nitrophenol followed by a reduction reaction. Their syntheses and characterization are described elsewhere.²⁵ *N*-Methyl-2-pyrrolidone (NMP) (analytical-reagent-grade; Shanghai Reagent Factory, Shanghai, China) was dried over molecular sieves. Common reagents, such as acetic anhydride and triethyl amine, and solvents for solubility measurements, such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), NMP, *m*-cresol, ethanol, acetone, toluene, tetrahydrofuran (THF), chloroform, and concentrated sulfuric acid, were used as received.

Syntheses of Alicyclic PIs

Alicyclic PIs were synthesized from a polycondensation reaction between TCAAH and α,ω -di(4-aminophenoxy)alkane 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 triethylamine (diamine/acetic anhydride/triethylamine = 4/36/9 molar ratio) at 25°C for 16 h (see Scheme 1). The resultant PIs were precipitated from water and dried at 90°C *in vacuo*.

Characterization and Property Measurements

The IR spectra of PIs were recorded on a PE 983 IR spectrophotometer in their film form. The films were cast from an NMP solution and dried *in*



Scheme 1 Synthesis of PIs.

vacuo at 90°C. The ¹H-NMR spectra of PIs (in DMSO-*d*₆) were recorded on a Bruker AM-400 NMR spectrometer (Switzerland). A Perkin Elmer Lambda 20 ultraviolet–visible (UV–vis) spectrophotometer (Norwalk, CT) was used to record the UV–vis spectra of PI films. The solubility of PIs was determined by the observation of the solubility of solid PIs in various solvents at room temperature. The intrinsic viscosities of PIs were measured with NMP as the solvent at 30°C. The standard concentration was 1 g/dL. The glass-transition temperatures (*T_g*'s) of PIs were obtained from differential scanning calorimetry (DSC) curves. The DSC curves were recorded on a Perkin Elmer DSC7 under the protection of N₂ at a scan rate of 20°C/min. All samples experienced two heating processes from 25 to 300°C, and the second scan was recorded. The thermal stability of PIs was characterized by thermogravimetric analysis (TGA). TGA was conducted on a Perkin Elmer TGA7 under the protection of N₂ at a scan rate of 20°C/min.

Pretilt-Angle Measurement

The glass substrates were cleaned with distilled water and acetone in an ultrasonic bath and dried at 70°C for 30 min. The PI films were cast onto the glass from NMP solutions (3 wt %) by spin-coating at 500 rpm for 5 s and at 2000 rpm for 10 s.

Table I Solubility of Alicyclic PIs in Various Solvents at 25°C

	Ethanol	Toluene	CHCl ₃	Acetone	THF	NMP	DMF	DMAc	<i>m</i> -Cresol	H ₂ SO ₄
PI-4	—	—	—	—	—	+	+	+	+	+
PI-6	—	—	—	—	—	+	+	+	+	+
PI-8	—	—	—	—	—	+	+	+	+	+
PI-10	—	—	—	—	—	+	+	+	+	+
PI-12	—	—	—	—	—	+	+	+	+	+

+ = soluble (> 10 wt %); — = insoluble.

They were baked *in vacuo* at 80°C for 12 h and 160°C for 2 h to remove the solvent and then were rubbed with a velvet cloth according to the method adopted in LCD series production. A multicomponent nematic LC ($n_o = 1.5040$, $n_e = 1.6609$; Qinghua Liquid Crystal Materials Co., Shijiazhuang, China) was assembled in cells with antiparallel-rubbed surfaces for the measurement of the pretilt angle. The desired cell gap ($\sim 10 \mu\text{m}$) was achieved by polymer spacers being placed on the rubbed PI surface. The pretilt angle was measured with the crystal rotation method.²⁶

RESULTS AND DISCUSSION

The alicyclic PIs prepared were named after the length of the alkyl chain. For example, the PI

prepared from α,ω -di(4-aminophenoxy)butane was named PI-4. Other PIs were named PI-6, PI-8, PI-10, and PI-12. All the alicyclic PIs prepared had reasonable intrinsic viscosities of 0.37–0.42 (see Table I). Although the intrinsic viscosities of the PIs were not very high, freestanding and tough films were obtained.

Fourier Transform Infrared (FTIR) Spectra

The FTIR spectrum of PI-8 is shown in Figure 1. The clear appearance of bands at about 1735 and 1685 cm^{-1} , characteristic of the C=O stretching (symmetrical and unsymmetrical, respectively) of imide groups, and a band at about 1365 cm^{-1} , characteristic of the C—N stretching of imide groups, indicates the success of the synthesis. These bands appear at lower wave numbers with

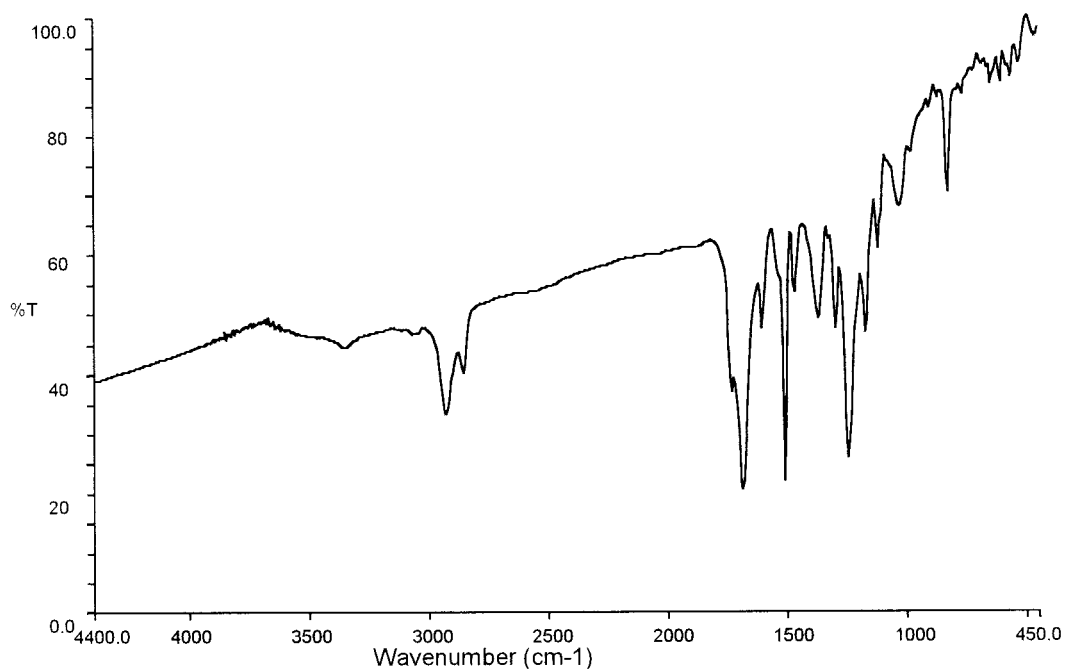


Figure 1 FTIR spectrum of PI-8.

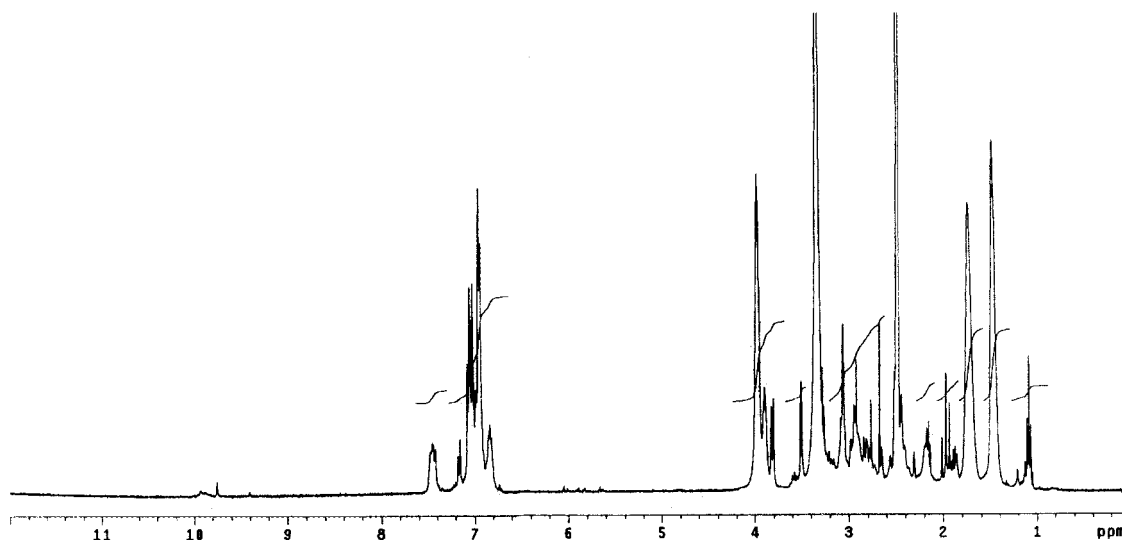


Figure 2 $^1\text{H-NMR}$ spectrum of PI-6 in $\text{DMSO-}d_6$.

respect to Kapton-type PI.¹¹ This slight shift in the wavelength was also observed in other PIs from alicyclic dianhydride and aromatic diamines.^{16–19} The band at about 1500 cm^{-1} is characteristic of the vibration of the benzene ring in the PI backbone. All other PIs gave very similar FTIR spectra.

$^1\text{H-NMR}$ Spectra

The $^1\text{H-NMR}$ spectrum of PI-8 is shown in Figure 2. The multiplets at δ (ppm) = 1.05–1.80 (8H) and δ = 3.80–4.10 (4H) are signals from the methylene protons in the middle of the alkyl chains and next to the oxygen atoms, respectively. The multiplets at δ = 1.90–3.80 (8H) are from the protons

of the alicyclic moiety.^{24,27} The multiplets at δ = 6.70–7.55 are from the protons of benzene rings. The peak at δ = 9.9 is from the proton of the N—H group. That signal from the N—H proton is very small indicates that the imidization degree of the PI is very high. Similar results indicating that a high imidization degree can be achieved by chemical imidization for alicyclic PIs based on TCAAH have been reported.²⁷ The sharp peak at δ = 2.50 is from $\text{DMSO-}d_6$.

Solubility

The solubilities of alicyclic PIs in various solvents are listed in Table I. All the alicyclic PIs exhibited great organosolubility: They were soluble in aprotic, strongly polar solvents such as NMP,

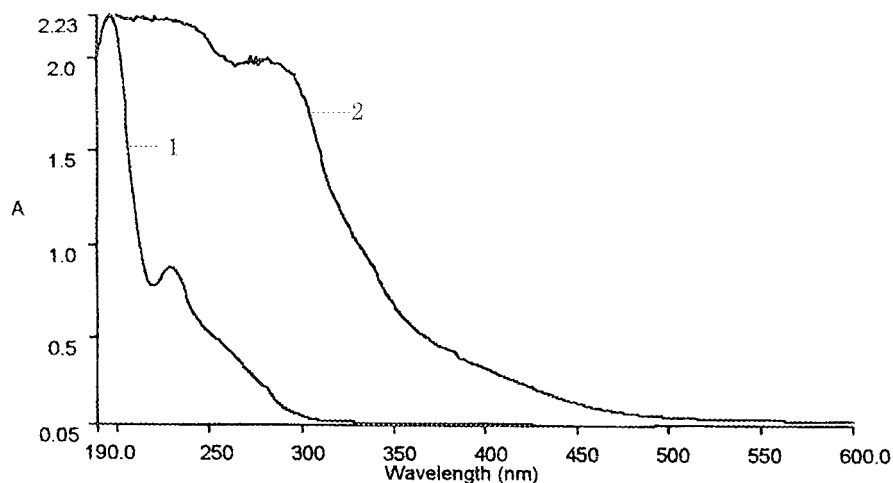


Figure 3 UV-vis spectra of (1) PI-6 and (2) PI(PMDA-ODA) films.

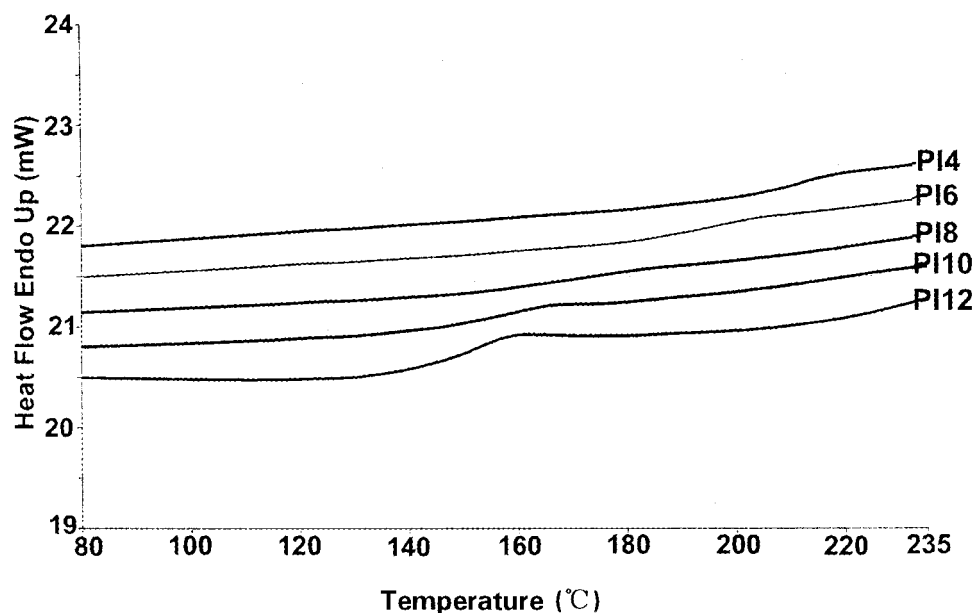


Figure 4 DSC curves of PIs.

DMAC, DMF, *m*-cresol, and concentrated sulfuric acid and could not be dissolved in weakly polar or nonpolar solvents such as THF, chloroform, toluene, ethanol, and acetone. The good solubility resulted from the restriction of the extended-conjugation structure existing in the aromatic PIs when the alicyclic moieties were introduced and led to a decrease in the crystallization tendency and intermolecular interactions. This good organosolubility ensures the low curing temperature required in the manufacturing of LCDs with large display areas.

Optical Transparency of Alicyclic PIs

Figure 3 shows the UV-vis spectra of PI-6 and PI films based on pyromellitic dianhydride

(PMDA) and 4,4'-diaminodiphenylether (ODA) [PI(PMDA-ODA) for comparison]. The PI-6 film possessed very low absorption at wavelengths above 300 nm and was almost colorless. All other PIs gave similar UV-vis spectra. PIs based on conventional aromatic diamines and aromatic dianhydrides usually are brown because of the existence of the extended-conjugation structure and/or the formation of CTC, which leads to strong absorption at a wavelength of about 400 nm [see the UV-vis spectrum of PI(PMDA-ODA)]. The replacement of the aromatic moiety with an alicyclic group limits the extended-conjugation structure, and the resulting PI shifts its absorption to a shorter wavelength and is transparent in a visible wavelength. This high transparency in a visible

Table II Properties of PIs

Samples	PI-4	PI-6	PI-8	PI-10	PI-12
$[\eta]^a$	0.38	0.42	0.37	0.37	0.39
T_g^b	204.8	183.3	155.5	145.7	140.1
T_5^c	394.4	414.7	397.6	415.7	422.6
T_{10}	430.6	438.7	437.6	439.2	447.7
WR ₆₅₀	26.0	21.7	19.3	17.5	15.5
T_d (°C)	437.2	441.0	445.8	443.2	455.6
θ_P (°) ^d	1.97	3.13	3.35	4.61	5.44

^aIntrinsic viscosity measured at 30°C in NMP with a standard concentration of 1.0 g/dL.

^bObtained from DSC measurements; scan rate = 20°C/min. N₂ protection.

^cScan rate = 20°C/min. N₂ protection.

^dPretilt angles measured at room temperature with the crystal rotation method.

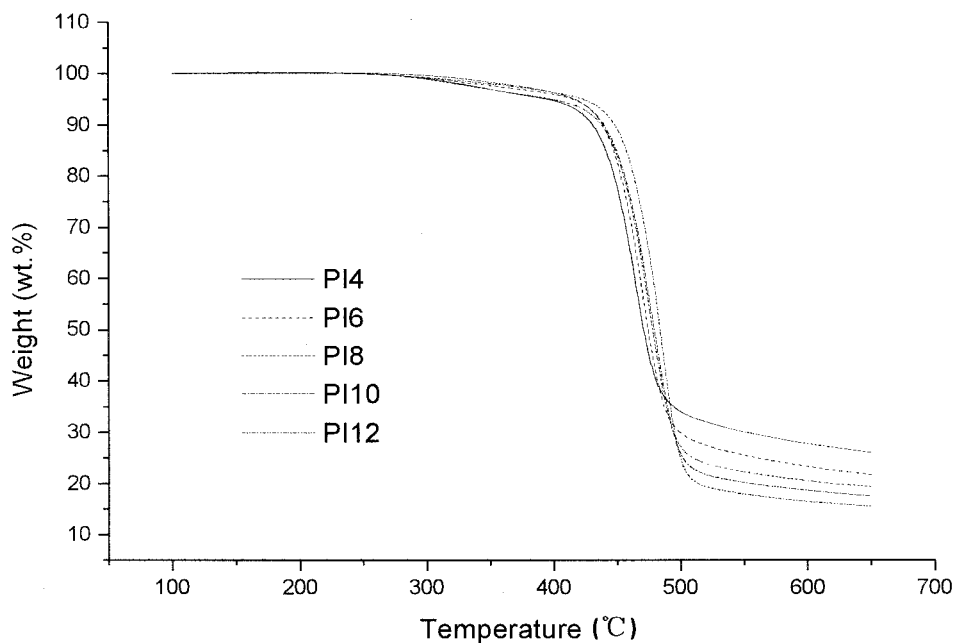


Figure 5 TGA curves of PIs.

wavelength is extremely desirable when PIs are applied to optical devices such as color LCDs.

Thermal Property

DSC curves of PIs are shown in Figure 4. The T_g 's obtained from DSC are listed in Table II. T_g decreased with the increasing length of the alkyl chain. This was clearly caused by increasing flexibility as the length of the alkyl chain increased. Furthermore, this relationship seems to be non-linear. This is quite different from most aromatic PIs containing main-chain long alkyl groups, the T_g 's of which decrease linearly with the increasing length of the alkyl group.^{25,28}

The TGA curves of PIs are shown in Figure 5. The initial thermal-decomposition temperature (onset; T_d), the temperature at a 5% weight loss (T_5), the temperature at a 10% weight loss (T_{10}), and the weight residual at 650°C (WR_{650}), as obtained from TGA measurements, are listed in Table II. T_d , T_5 , and T_{10} of the alicyclic PIs ranged from 430 to 470, 394 to 422, and 430 to 447°C, respectively, and were basically independent of the length of the alkyl chain. This may indicate that the alicyclic group is the most thermally unstable part of PI molecules in the thermal-decomposition process or at least decomposes in almost the same temperature range as the alkyl

chain. As the length (and the weight percentage) of the alkyl groups increased, WR_{650} decreased.

Pretilt Angle

The pretilt angles of the PIs measured with the crystal rotation method are listed in Table II. The pretilt angle increased almost linearly as the length of the alkyl chain increased. Those of PI-10 and PI-12 were close to 5°, which is generally regarded to be adequate for STN LCDs. However, the pretilt angle of a PI with main-chain alkyl groups was much smaller than that of a PI with a side alkyl group of the same length.²⁴

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