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A comparative study of insoluble and soluble polyimide thin films

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Abstract

Physical properties of thin films of soluble and insoluble aromatic polyimides were compared by d.s.c., u.v.-visible and fluorescence spectroscopy, and prism coupler technique. D.s.c. results showed that the thermal properties of insoluble polyimides are superior to those of soluble ones, owing to the specific molecular interactions of insoluble polyimides, revealed by fluorescence spectroscopy. However, the specific molecular interactions sacrifice the transparency in their thin films, shown by u.v.-visible transmission spectra. Negative birefringence of thin films, not only for soluble polimides but also for polyamic acids of insoluble polyimides, was confirmed by prism coupler, while thin films of insoluble polyimides thermally imidized lack high levels of negative birefringence. It is regarded that thin films of insoluble polyimides thermally imidized are likely to be isotropic because of molecular relaxation above their glass transition temperatures (T_g) in the course of thermal imidization, according to Flory's principle. On the contrary, thin films of insoluble poyimide chemically imidized keep the same levels of negative birefringence as those of the relevant polyamic acid thin films. Judging from the opposite cases, it is recognized that molecular relaxation above T_g weakens the optical anisotropy of polyimide thin films. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimides; Polyamic acid; Negative birefringence

1. Introduction

The previous reviews [1,2] showed that polyimides (PI) with strawberry colour are insoluble, and their thin films must be prepared in the form of polyamic acids (PAA) by curing at 300°C. Attention has been paid [3] to improving solubility of polyimides, and successful progress has been achieved in preparing soluble polyimides. Soluble polyimides can be dissolved in organic solvents, in which their precursor can be dissolved; on the contrary, insoluble polyimides cannot. Consequently, soluble polyimides can be prepared by a one-step method, while insoluble polyimides must be prepared by two-step methods via either chemical or thermal imidization [4].

Negative birefringence of organic thin films has been studied over a wide range of polymers, from the typical flexible polystyrene [5,6] to the rigid cellulose acetate [7] and polyamic acids and polyimides of recent interest [8–16]. Negative birefringence of polyamic acid and polyimide thin films had been previously [8,9] thought to be due to in-plane orientation. In-plane orientation leading negative birefringence was confirmed by transmissive X-ray diffraction patterns [17,19]. Cheng et al. [18] had investigated comparatively thin films and oriented fibres of the same polyimide by X-ray diffraction. The results indicated that polyimide chains orient along the film plane randomly. Accordingly, from an optical point of view, polyimide thin films can be regarded as uniaxial crystal with the optical axis normal to the film plane. Prism coupler technique [20] had been used to measure in-plane and out-of-plane refractive indices of polyimide thin films [9].

2. Experimental

2.1. Synthesis and film formation

Soluble polyimides, PI(HQDPA-DMMDA) and PI(ODPA-DMMDA), whose chemical structures are listed in Scheme 1(A), were synthesized by polycondensation of equivalence of relevant dianhydrides and the diamine (2,2′-dimethyl-4,4′-methylene-dianiline) in N,N-dimethyl acetamide (DMAc) at room temperature for 24 h, and chemical imidization [4] proceeded for 24 h. The final mixed solutions were poured into vigorously stirred 95% ethanol so that the polyimides could be precipitated. After being washed three times and dried, white powders of the soluble polyimides were prepared. The powders were dissolved in DMAc to make 10% (wt/wt) polyimide solutions. Polyimide solutions thus formed were then clarified through a 20$\sim$40 mm glass filter. The clarified solutions were coated

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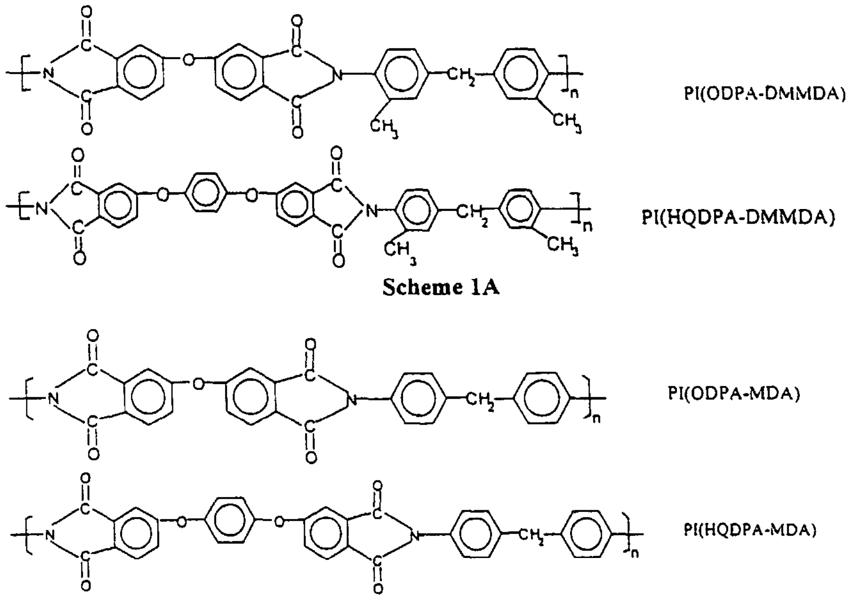

Scheme 1A

Scheme 1B

Scheme 1.

on substrates. The coatings were first gently baked at 50°C for 6 h, and then at 160°C for 12 h in a vacuum oven to evaporate the solvents completely.

Polyamic acids are precursors of their corresponding polyimides. In the case of insoluble polyimides, PI(HQDPA-MDA) and PI(ODPA-MDA), whose chemical structures are listed in Scheme 1(B). PAA(HQDPA-MDA) and PAA(ODPA-MDA) were first synthesized by mixing an equivalence of relevant dianhydride and the diamine (4,4′-methylene dianiline) at room temperature in DMAc solutions, reacting for 24 h. The solutions were also clarified and coated on substrates. When the coatings were gently baked at 50°C for 3–4 h, with most of solvent withdrawn, gel films were formed. If gel films were isothermally treated at 160°C in reduced pressure for 12 h to evacuate the solvents remaining in the films, polyamic acid thin films were obtained. Finally, polyamic acid thin films were cured at 300°C in vacuum for 16 h to accomplish imidization so that thin films of the insoluble polyimides were obtained. The descriptions of prepared thin films are listed in Table 1. For comparison, thin films of insoluble polyimides chemically imidized were also prepared by immersing polyamic acid thin films in the mixed solution of triethylamine and acetic anhydride at room temperature for 120 h.

Table 1
Nomination of thin films formed at different stages of processing

Processing conditions	Gel films	PAA films	PI films
50°C/6 h	●	●	●
160°C/12 h		●	●
300°C/61 h			●

●indicates that the condition is involved to prepare the films

2.2. *Fluorescence spectroscopy*

Fluorescence spectroscopic studies of the polyimide thin films adhered to quartz glass substrates were carried out in a SPEX FL-2T2 spectrofluorometer at room temperature. Excitation spectra of thin films, characterizing the transition that promotes a chromophore from the ground state to an excited single state and which is followed by fluorescence emission when the chromophore relaxes back down, were measured by monitoring the emission intensity at the wavelengths (λ_{em}) corresponding to the maximum peaks in fluorescence emission spectra. While the emission spectra of them were recorded by exciting the films at the wavelengths (λ_{ex}) at which the maximum peaks in excitation spectra appear. Table 2 lists λ_{em} and λ_{ex} of the films.

2.3. *Differential scanning calorimetry*

Glass transition temperatures (T_g) of the polyimides were measured by a differentiatial scanning calorimeter (Perkin–Elmer DSC-7) with a heating rate of 20°C min^{-1} in a N_2 atmosphere. Thermogravimetry analysis (Perkin–Elmer TGA-7) was conducted with a heating rate of

Table 2
Maximum excitation and absorption wavelengths for the polyimide films

	Insoluble PI films		Soluble PI films	
	PI(ODPA-MDA)	PI(HQDPA-MDA)	PI(ODPA-DMMDA)	PI(HQDPA-DMMDA)
λ_{em} (nm)	478	470	511	556
λ_{ex} (nm)	363	372	442	468

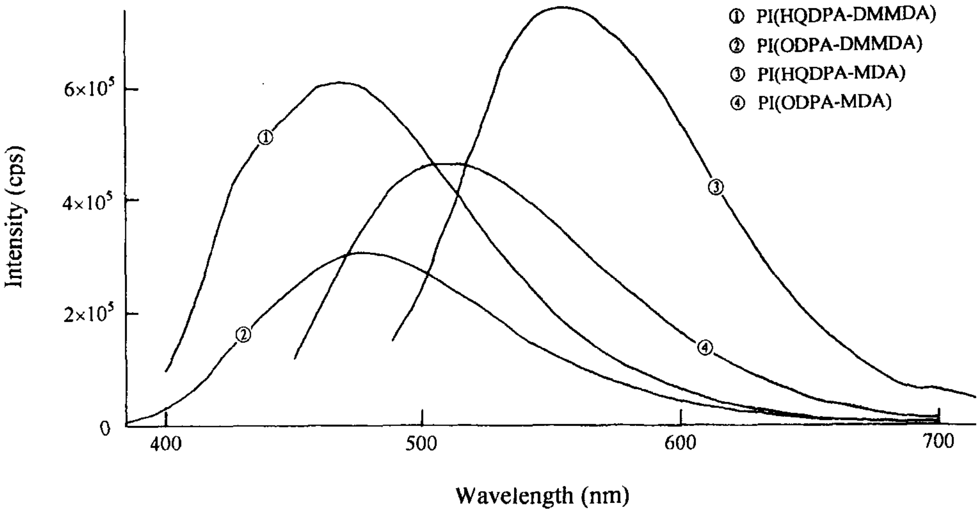

Fig. 1. The fluorescence emission spectra of the polyimide thin films adhered to quarts glass substrates.

10°C min^{-1}, in air. In the case of the insoluble polyimides, they were first preheated from room temperature to 350°C at a rate of 20°C min^{-1} in order to not only evacuate all the solvents reminded in the films, but also to turn the specimens into complete polyimides, then cooled to room temperature at the same rate. The precured specimens were subjected to d.s.c. and t.g.a. measurements.

2.4. U.v.-visible spectroscopy

U.v.-visible spectroscopy of polyimide thin films was carried out on a CARY 1E UV-Visible spectrophotometer (Varian Co.). Transmission of the films was scanned from 200 to 800 nm in ambient conditions. The spectra were collected automatically with elimination of reference substrates.

2.5. Prism coupler

By a prism coupler, n_{TE} and n_{TM} of the polyimide thin films were determined. The details of the principle and the procedure can be found elsewhere [20]. The preocedure of the determination for the refractive indice of thin films had been described in detail previously [21].

3. Results and discussion

From the structural point of view, the delocalized π bonds and charge transfer interactions in polyimides may take effect according to Lee's model [22]. As far as the insoluble polyimides are concerned, there are bridging groups (–CH_2–) to restrain delocalized π electrons from sharing among two adjoining phenyl rings. On the other hand, the

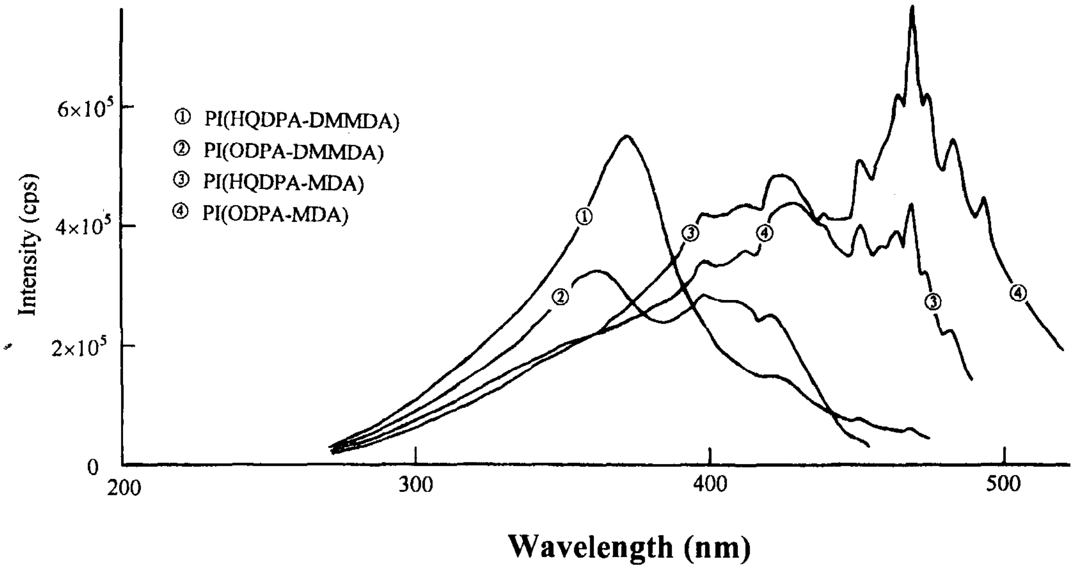

Fig. 2. The fluorescence excitation spectra of the polyimide thin films adhered to quarts glass substrates.

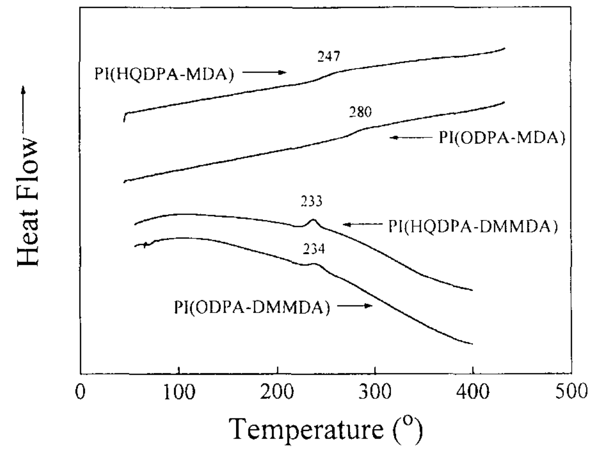

Fig. 3. D.s.c. thermograms of the polyimides.

imide rings and the phenyl rings attached to the diamine moiety are likely to be coplanar so that π electrons among them may be delocalized. While for the soluble polyimides, delocalized π bonds are not likely to be formed, because of not only the effect of the bridging groups, but also the steric effect of methyl groups, whose ortho-positions to C atom connecting to N can hinder the neighbouring imide ring and phenyl ring from coplanarity. Based on the above consideration, it is assumed that the electronic natures differ between soluble and insoluble polyimides. The assumption can be confirmed by the fluorescence emission spectra of the four polyimide thin films, shown in Fig. 1, showing different emission peaks for the four polyimide thin films.

The absorptions of the four polyimide thin films can be revealed by their fluorescence excitation spectra, shown in Fig. 2. Thin films of soluble polyimides confer maximum peaks at approximately 360 nm in their fluorescence excitation spectra. However, they do not show obvious absorptions at long wavelengths. On the other hand, thin films of insoluble polyimide show predominantly the excitation bands at longer wavelengths centred at 470 nm, besides excitation bands centred at 360 nm. The comparison indicates that the basic molecular interactions of the four polyimides are almost the same, owing to the excitation bands at shorter wavelengths, and that specific molecular interactions for insoluble polyimides come into being, because of the additional absorptions at longer wavelengths.

With the specific interactions in insoluble polyimides confirmed, their thermal properties are superior to those of soluble polyimides. Fig. 3 shows d.s.c. thermograms of the polyimides, from which, it is recognized that T_g of insoluble polyimides are higher than those of soluble polyimides based on a same dianhydride. In addition to higher T_g of insoluble polyimides, thermal stability for insoluble polyimides is superior to that of soluble ones as referred to in Table 3 listing $T_{5\%}$ (the temperature at which 5% weight loss occurs) for the four polyimides.

Table 3
$T_{5\%}$ in air of the polyimide thin films

PI	HQDPA-DMMDA	ODPA-DMMDA	HQDPA-MDA	ODPA-MDA
$T_{5\%}$ (°C)	332	338	479	530

Table 4
Transmission properties of the polyimide films

PI films[a]	HQDPA-DMMDA	ODPA-DMMDA	HQDPA-MDA	ODPA-MDA
$\lambda_{\text{on-set}}$ (nm)[b]	419.0	455.8	510.4	581.2
$\lambda_{\text{cut-off}}$ (nm)[c]	358.8	370.0	337.1	332.7
$T_{\max}$ (%)[d]	100	100	66	98

[a] The thickness of thin films is approximately 5 μm
[b] Transparency on-set wavelength in nm
[c] Transparency cut-off wavelength in nm
[d] Maximum transparency in %

Although the thermal properties of insoluble polyimides are outstanding compared with those of soluble polyimides, the optical transparency for insoluble polyimide thin films is sacrificed, as shown in Fig. 4. $\lambda_{\text{cut-off}}$ and $T_{\max}$ of thin films of insoluble polyimides decrease sharply, as listed in Table 4.

Refractive indices and negative birefringece ($\Delta n = n_e - n_o$) of soluble polyimide thin films are listed in Table 5. Thin films of soluble polyimides do possess negative birefringence. On the contrary, the processing conditions, based on which thin films of insoluble polyimides were formed, show great impact on their optical anisotropy as discussed below.

Because of polar interactions between the solvent and polyamic acids, gel films of polyamic acids contain some amount of solvents. Based on the additive contribution to refractive index [23,24] (shown in Eqn 1) , the refractive indices of gel films of polyamic acids, are much lower than those of polyamic acid thin films without solvent residual as listed in Table 6.

$$n^{gf}_{TM} = (1 - x)n^{0}_{TM} - xn^{s} \quad (1)$$

$$n^{gf}_{TE} = (1 - x)n^{0}_{TE} - xn^{s}$$

In Eqn. 1, χ is the molar fraction of residual solvent, n^0_{TM} and n^0_{TE} refer to the refractive indices of pure polyamic acid thin films, n^s is the refractive index of the solvent, and gf is a short form of gel films. As mentioned in a previous paper [25], $n_{\mathrm{TM}} = n_e$ and $n_{\mathrm{TE}} = n_o$. According to the definition of optical birefringence, the effect of residual solvent on the

Table 5
The refractive indices and negative birefringence of thin films of soluble polyimides

PI(HQDPA-DMMDA)		PI(ODPA-DMMDA)	
$n_o = 1.6457$	$n_o = 1.6482$	$n_o = 1.6492$	$n_o = 1.6498$
$n_e = 1.6144$	$n_e = 1.6182$	$n_e = 1.6202$	$n_e = 1.6202$
$\Delta n = -0.0313$	$\Delta n = -0.0300$	$\Delta n = -0.0290$	$\Delta n = -0.0296$
$d = 2.2$ μm	$d = 1.3$ μm	$d = 2.8$ μm	$d = 3.1$ μm

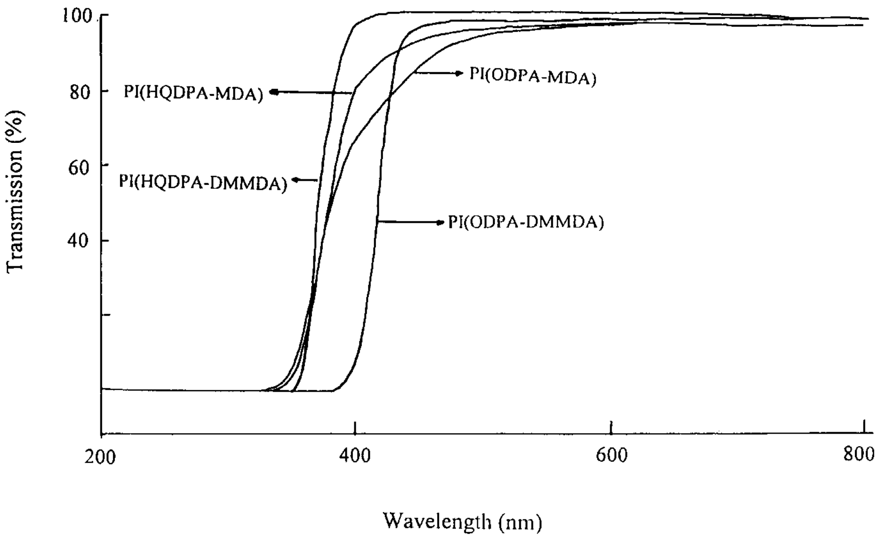

Fig. 4. U.v.-visible transmission spectra of polyimide thin films adhered to glass substrates.

Table 6
Optical anisotropy of thin films of polyamic acids and their respective polyimides

Gel films		PAA films		PI films	
HQDPA-MDA	ODPA-MDA	HQDPA-MDA	ODPA-MDA	HQDPA-MDA	ODPA-MDA
$n_o = 1.6251$	$n_o = 1.6317$	$n_o = 1.6417$	$n_o = 1.6428$	$n_o = 1.6494$	$n_o = 1.6436$
$n_e = 1.6113$	$n_e = 1.6191$	$n_e 1.6275$	$n_e = 1.61254$	$n_e = 1.6409$	$n_e = 1.6411$
$\Delta n = -0.0138$	$\Delta n = -0.0126$	$\Delta n = -0.0142$	$\Delta n = -0.0174$	$\Delta n = -0.0085$	$\Delta n = -0.0025$
$d = 7.5$ μm	$d = 6.7$ μm	$d = 3.3$ μm	$d = 3.2$ μm	$d = 3.3$ μm	$d = 3.2$ μm

birefringence of gel films can be outline, as illustrated in Eqn.2.

$$\Delta n^{gf} = n^{gf}_{TM} - n^{gf}_{TE} = (1-x)\Delta n^{0} \qquad (2)$$

It is easy to make out the reason why the level of birefringence of gel film is lower than that of polyamic acid thin films with the solvent completely evacuated. In order to increase the levels of negative birefringence of polyamic acid thin films, complete elimination of the solvent is of necessity.

The optical anisotropic properties of insoluble polyimide thin films depend on the method of imidization. Table 6 lists the comparison of the optical anisotropy of thin films between polyamic acids and their respective polyimides thermally imidized. The levels of optical anisotropy of thermally imidized polyimide thin films are much lower than those of polyamic acid thin films, in that thermal imidization is usually carried out at 250–300°C above their T_g so that polyimide molecules relax to induce isotropic properties, according to the conformation of glassy polymers [26]. As far as chemically imidized polyimide thin films are concerned, optical anisotropy of them keeps the same level as that of polyamic acid thin films, as listed in Table 7, comparing the negative birefringence of polyamic acid thin film and chemically imidized polyimide thin films of HQDPA-MDA.

Table 7
Optical anisotropy of thin films of PAA(HQDPA-MDA) and PI(HQDPA-MDA) chemically imidized

Polyamic acid thin film	Chemically imidized polyimide thin film
$n_o = 1.6513$	$n_o = 1.6526$
$n_e = 1.6302$	$n_e = 1.6321$
$\Delta n = -0.0211$	$\Delta n = -0.0204$
$d = 1.2$ μm	$d = 1.1$ μm

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