

Optical anisotropy of flexible polyimide thin films

Baozhong Li, Tianbai He,^{a)} and Mengxian Ding

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Ping Zhang, Fubin Gao, and Feng Jing

Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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Optical anisotropy of thin films of an organo-soluble flexible polyimide based on 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 2,2-dimethyl-4,4'-methylene dianiline (DMMDA) was detected by a prism-coupler technique. A mechanism is proposed, based on the model of gel film collapse. The degrees of optical anisotropy of the thin films were evaluated via the level of negative birefringence. The residual solvent in the films lessens the levels of negative birefringence so that the residual solvent must be evacuated. The levels of negative birefringence are independent on the solid content of the initial solution, but dependent on the thickness of the films. For a film of 16 μm thick, zero birefringence was achieved, postulated from the dependence of negative birefringence on the thickness of thin films. The relationship between the optical anisotropy and solution properties shows that the degrees of optical anisotropy of thin films on the same scale of thickness depend on macromolecular sizes in their dilute solutions.

I. INTRODUCTION

Polyimides have been widely used in industry owing to their high mechanical, chemical, and optical performance.¹ Optical anisotropy of polyimide thin films has been reported.²⁻⁴ Chain stiffness contributes to negative birefringence of polyimide thin films mainly.^{5,6} Stress in polyimide thin films also induces negative birefringence.⁷ Recently, Coburn and Pottiger⁸ have given a review about the thermal curing of polyimide films and coatings. They concluded that negative birefringence of polyimide thin films was attributed to molecular alignment in the plane of the coating, resulting from gel film collapse. In the formation of gel film, anisotropic structure is fixed, because of the evaporation of the solvent and the frozen molecular aggregation. In this paper, thin films of an organo-soluble flexible polyimide were studied by the prism coupler technique, and a model is presented to explain the optical anisotropy of thin films of a flexible amorphous polyimide.

II. EXPERIMENTAL

A. Materials

The organo-soluble polyimide in this work was synthesized by stirring equivalents of dianhydride and diamine in the solvent of N,N-dimethyl acetamide (DMAc), at room temperature with nitrogen atmosphere, until a slight yellow color polyamic acid solution was

fulfilled. In this case, the dianhydride is not soluble in DMAc, and as long as there is no solid left in the solution, it is regarded that polyamic acid solution is obtained. It takes 24 h for triethylamine and acetic anhydride to undertake chemical imidization. The process to synthesize the polyimide is illustrated in Scheme 1. The final solution was poured into vigorously stirred 95% ethanol so that the polyimide can be precipitated. Washed three times, and dried, white powder of the polyimide was prepared. The powder is soluble in polar aprotic solvents such as DMAc, N,N-dimethyl formamide (DMF), chloroform, N-methyl pyrrolidone (NMP), epichlorohydrin, tetrahydrofuran (THF), and γ -butyrolactone, and so on.

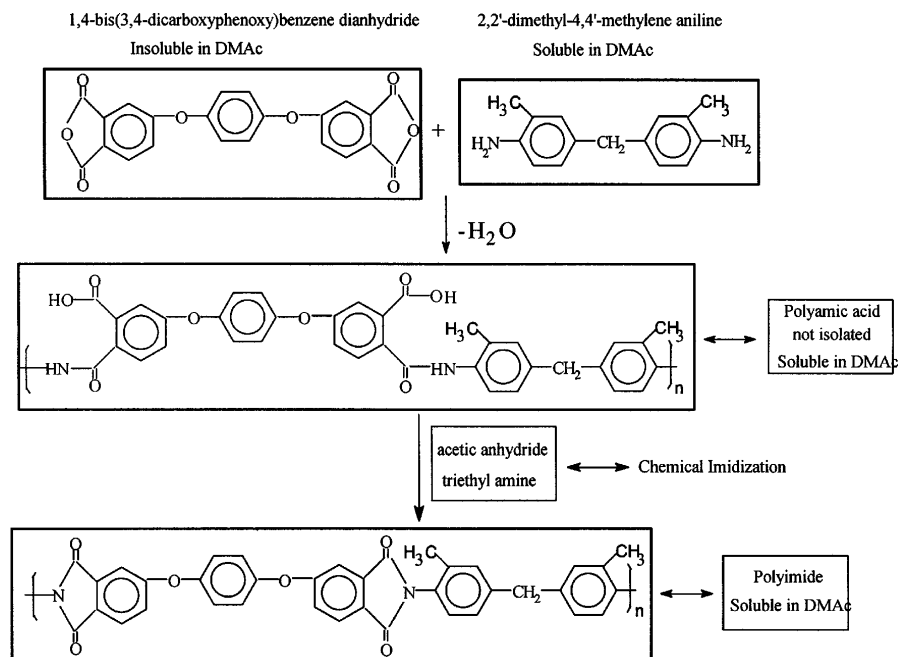
B. Film preparation

The organo-soluble polyimide solutions in different solvents with a solid content of 12 wt. % were coated on glass substrates by spray coating. The coatings were softly baked at 60 °C for 12 h so that gel films were obtained, and then residual solvent in gel films were evacuated at 160 °C in a vacuum oven for at least 8 h so that condensed films can be obtained. Condensed films of similar thickness from the solutions with different solid contents of polyimide were also prepared. All the solutions used in this study had been clarified through a 20–40 μm glass filter before being coated.

C. Prism coupler

In this experiment, a polarized He–Ne laser ($\lambda = 632.8 \text{ nm}$) and a high refractive index prism ($n =$

^{a)}Author to whom all correspondence should be addressed. e-mail: tbhe@ns.ciac.ac.cn. Fax: 011-86-431-5685653.



SCHEME 1. The process to prepare the organo-soluble polyimide.

1.7497) coupled with polyimide thin films coated on glass substrates ($n = 1.5163$) were utilized. The incidence angle pertaining to the reflected M-lines were measured for TE and TM modes, respectively. A programmed computer is used to calculate the refractive indices and the thickness of the films precisely.

D. Intrinsic viscosities

Viscosity measurements were performed in an Ubbelohde capillary viscometer, and carried out in a water bath regulated at 25.0 ± 0.01 °C. The intrinsic viscosities were obtained from the intercept of the plots of $(\eta_r - 1)/c$ vs c and $\ln \eta/c$ vs c in the limit $c \rightarrow 0$, where η_r is the relative viscosity.

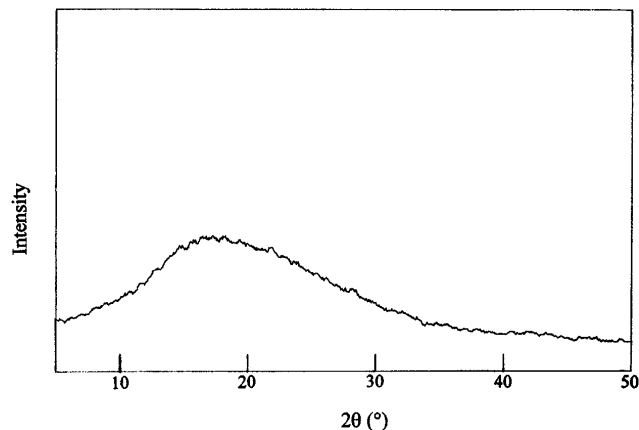


FIG. 1. X-ray diffraction pattern of thin film adhered to the glass substrate.

III. RESULTS AND DISCUSSION

The polyimide in this study is a flexible polymer,⁹ and an x-ray diffraction pattern of thin film adhered to a glass substrate shows that the thin film has an amorphous morphology, as represented in Fig. 1, and the amorphous properties are further confirmed by the DSC curve (Fig. 2), showing a glass transition temperature at 240 °C. According to Flory's prediction¹⁰ flexible glassy polymers tend to be isotropic in their condensed states; however, thin films of this polyimide show optical anisotropy. The model proposed by Coburn and Pottiger⁸ is quoted here to show the interpretation

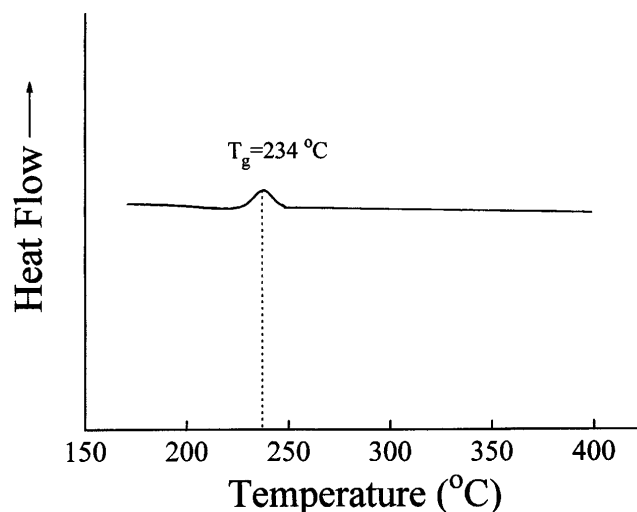


FIG. 2. DSC curve of the polyimide.

of this phenomenon. A gel film that begins to sustain a load can be processed from isotropic polyimide solution by evaporating the solvent. In the course of gel film formation, with the evaporation of the solvent, the concentration of the solvent changes gradually from dilute to semidilute and at last concentrated solutions. The structural anisotropy of thin films is induced, due to the difference between molecular dimensions along the film plane (x - y plane) and through the thickness direction (z -axis). The structural anisotropy is called in-plane-orientation^{12,13} confirmed by transmission x-ray diffractions. With the residual solvent further evaporated from the gel film at the boiling point of the solvent at reduced pressure, condensed films can be produced. Now that the drying temperature is lower than the glass transition temperature of the polyimide (DSC curves of the polyimide are illustrated in Fig. 2), the macromolecules are frozen and the anisotropic structure of gel films retains. Planar molecular sizes of condensed films may follow molecular sizes of the gel film, while

molecular size through the thickness direction becomes smaller, due to complete elimination of the solvent. The description of gel film and condensed film formations from a solution is schematically illustrated in Fig. 3.

There is some solvent left in gel films, because of polar interactions between the polyimide and the solvent. The residual solvents in thin films lower the value of negative birefringence, as the solvents are isotropic so that they contribute to n_{TE} and n_{TM} uniquely, as described below:

$$\begin{aligned}\Delta n &= (1-x)n_{TM}^0 + xn^s - [(1-x)n_{TE}^0 + xn^s] \\ &= (1-x)\Delta n^0,\end{aligned}\quad (1)$$

where x is the molar fraction of the solvent in the film, the superscript 0 refers to polymer film without the residual solvent, while s refers to the solvent. In gel films, x is not equal to zero, so that the level of negative birefringence of gel films is less than those of condensed films, as listed in Table I, in which the

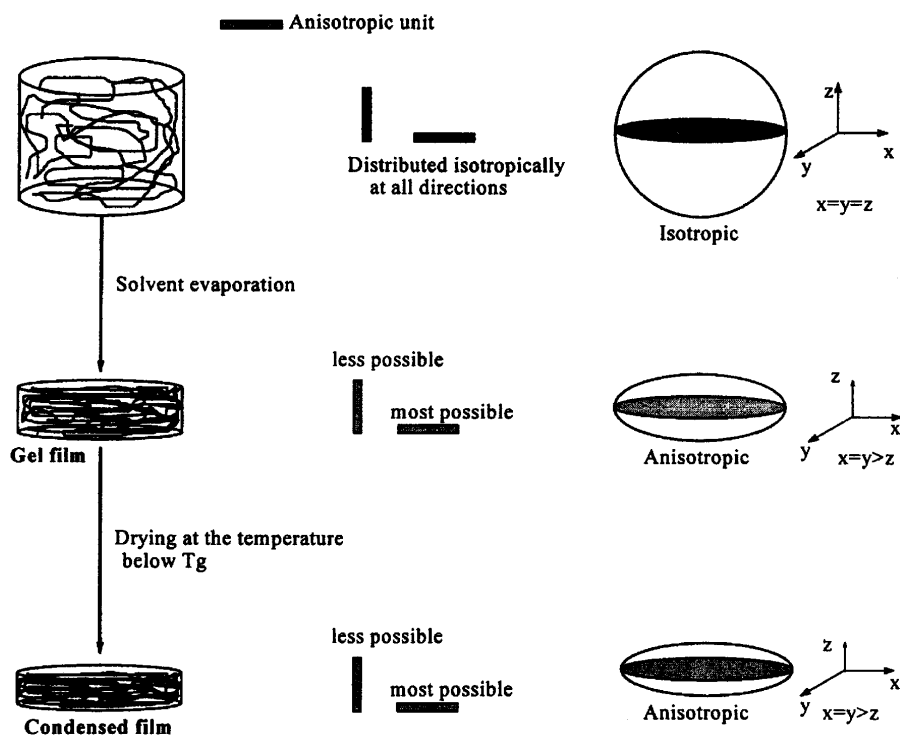


FIG. 3. Schematic description of polyimide gel film and condensed film formations from its solution. (Three-dimensional axes show macromolecular size comparatively. The slight dark bar depicts anisotropic unit, and the possibility of its position in space is outlined.)

TABLE I. Comparisons of negative birefringences between gel films and condensed films prepared from solutions in different solvents.

Solvents	DMAc		DMF		γ -butyrolactone	
	Gel	condensed	Gel	condensed	Gel	condensed
n_{TE}	1.6421	1.6564	1.6426	1.6567	1.6408	1.6546
n_{TM}	1.6130	1.6250	1.6158	1.6259	1.6163	1.6262
Δn	-0.0291	-0.0314	-0.0268	-0.0308	-0.0245	-0.0284

TABLE II. Negative birefringence of condensed thin films of $\sim 7 \mu\text{m}$ prepared from solutions with different solid contents.

Solid content (%)	2.0	3.8	5.6	7.4	10.7	13.4
Δn	-0.0232	-0.0232	-0.0223	-0.0232	-0.0232	-0.0210

TABLE III. The indices of thin films along the film plane (n_{TE}) and out-of-plane (n_{TM}).

Solvents	1	2	3	4	5	6
δ^a	22.1–22.8	24.9	18.9–19.0	22.9	21.9	26.2–31.7
n_{TE}	1.6223	1.6259	1.6171	1.6232	1.6163	1.6262
n_{TM}	1.6594	1.6567	1.6477	1.6542	1.6522	1.6546
d (μm)	4.8	4.8	4.8	4.8	4.8	4.6

^aSolubility parameter in (Mpa)^{0.5}; the data are quoted from Ref. 11. 1, 2, 3, 4, 5, and 6 refer to DMAc, DMF, chloroform, NMP, epichlorohydrin, and γ -butyrolactone, respectively.

negative birefringences of gel films and condensed films from solutions in different solvents are compared. The refractive indices and the level of negative birefringence of condensed films are higher than those of gel films, because of elimination of the remaining solvent. In order to increase the level of negative birefringence, it is necessary to eliminate the residual solvent in the film to fulfill condensed films. Because planar macromolecular sizes in condensed films follow those in solutions, solution properties will affect the optical anisotropy of the condensed thin films. However, the levels of negative birefringence of condensed thin films of similar thickness ($\sim 7 \mu\text{m}$) are independent of macromolecular sizes in the initial solutions with different solid contents, as listed in Table II. Moreover, solution properties of dilute polyimide solutions affect optical anisotropy of condensed thin films obviously. Table III lists the thickness and the indices along the film plane (n_{TE}) and out-of-plane (n_{TM}) of the condensed films prepared from different solutions.

Figure 4 shows the dependence of the level of negative birefringence of thin films and intrinsic viscosity on the solubility parameter of the solvents. It is easily seen that the level of negative birefringence of the film prepared from the solution of DMAc is the largest, and that the intrinsic viscosity of polyimide solution in DMAc is largest, indicating that the polyimide chain in DMAc is most expanded, according to Flory's anticipation.¹³ The homologous relationship between the optical anisotropy and solution properties implies that the more expanded the polyimide in solution, the higher the level of negative birefringence of thin film. It can be seen from the model shown in Fig. 3 that a higher degree of structural anisotropy may be formed for gel films from a solution at which the polyimide chain shows an expanded conformation; consequently, optical anisotropy shows obviously. Optical anisotropy is not applicable for all thin films; the limited thickness of thin film to show

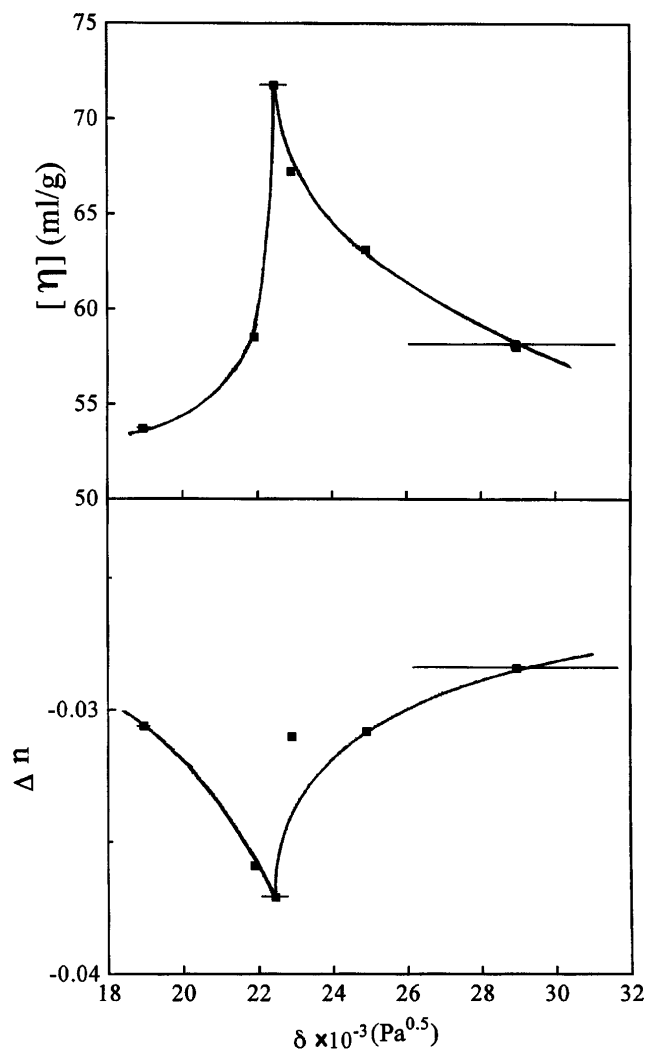


FIG. 4. Dependence of negative birefringence of thin films and intrinsic viscosities on solubility parameters of solvents.

negative birefringence is $16 \mu\text{m}$ approximately, postulated from Fig. 5, depicting the dependence of the level of negative birefringence on the thickness of thin films.

IV. CONCLUSION

Effects of residual solvents of polyimide thin films were discussed via an additional contribution technique. With solvents remaining in thin films, the degree of optical anisotropy of thin films is lessened. A model of gel film collapse is proposed to explain structural anisotropy, leading to optical anisotropy (negative birefringence to be exact). The levels of negative birefringence are independent of the solid content of the initial solution, but dependent on the thickness of the films. For a film of $16 \mu\text{m}$ thick, zero birefringence was achieved, postulated from the dependence of negative birefringence

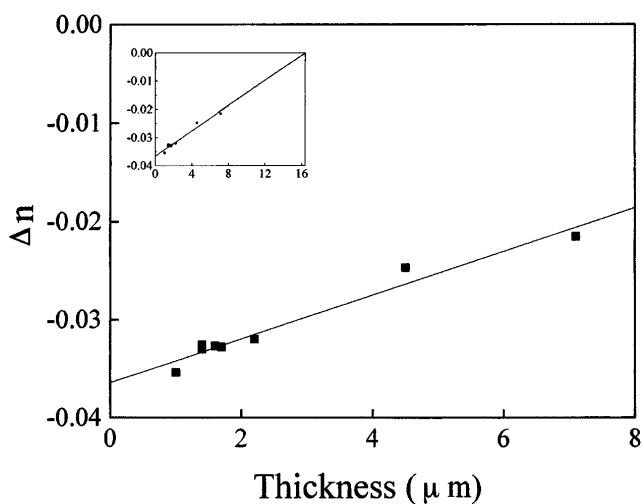


FIG. 5. The negative birefringence of thin films with different thicknesses.

on the thickness of thin films. The relation between the optical anisotropy and solution properties shows that the degrees of optical anisotropy of thin films on the same scale of thickness depend on macromolecular sizes in their dilute solutions.

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