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Correlation between chain conformations and optical anisotropy of thin films of an organo-soluble polyimide

Baozhong Li[a], Tianbai He[a],* and Mengxian Ding[a]
[a]*Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*
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An organo-soluble polyimide was successfully synthesized by two step polycondensation accompanied with chemical imidization. Optical anisotropy of thin films was detected by a prism-coupler technique. The results showed that the optical anisotropic properties of thin films prepared from solutions in different solvents depend on the solution properties. It is concluded that the more expanded the chain conformation in solution, the larger the negative birefringence of thin films. © 1997 Elsevier Science Ltd.

(Keywords: organo-soluble polyimide; dilute solution; thin films)

Introduction

Polyimides have been widely used in industry owing to their high mechanical, chemical and optical performance[1]. Negative birefringence of polyimide thin films had been reported[2–5]. Recently, Coburn and Pottiger[6] have reviewed the thermal curing in 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.

Previously, the insolubility of polyimides restrains their application as thin films, because polyimide films of those kinds are always prepared from their precursors, polyamic acid, by curing at above 250°C, with water released, thus micropores in the films may be formed so that optical and dielectric properties become poor. Up to now, we have successfully synthesized an organo-soluble polyimide[7] based on 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 2,2'-dimethyl-4,4'-methylene dianiline (DMMDA).

Experimental

Materials. The organo-soluble polyimide in this work (chemical structure is listed in *Scheme 1*) was synthesized by stirring equivalents of dianhydride and diamine in the media of *N,N*-dimethyl acetamide (DMAc), at room temperature for 48 h, until a polyamic acid solution was obtained. It takes 24 h for chemical imidization carried out by triethylamine and acetic anhydride to be fulfilled. Vigorously stirred 95% ethanol was poured into the final solution so that the polyimide can be precipitated. By washing three times, and being dried, a white powder of the polyimide was prepared. The typical characterizations of the polyimide have been reported elsewhere[7]. The powder is soluble in DMAc, *N,N*-dimethyl formamide (DMF), chloroform (CHF), *N*-methyl pyrrolidone (NMP), epichlorohydrin (EPC), tetrahydrofuran (THF), dioxane (DIO) and γ-butyrolactone (BUT), etc.

Film preparation. The thin films of the organo-soluble

polyimide were prepared by spray coating from their solutions in the above solvents with a solid content of 12% (wt/wt). They were softly baked at 60°C for 12 h and then at 160°C in a vacuum oven for at least 8 h.

Intrinsic viscosities. Viscosity measurements were performed in Ubbelohde capillary viscometers, and carried out in a water bath regulated at 30.0°C. The intrinsic viscosities were obtained from the intercept of the plots of $(\eta_r - 1)/c$ versus c and $\ln\eta_r/c$ versus c in the limit $c \rightarrow 0$, where η_r is the relative viscosity.

Fluorescence spectroscopy. The polyimide was dissolved in different solvents at a concentration of 3–11 g/l. Fluorescence spectroscopy of the solutions above were conducted in a SPEX FL-2T2 spectrofluorometer at room temperature, and the fluorescence spectroscopy of the solvents were measured. The polyimide solution and the relevant solvent contained in standard quartz cells were excited in a front-face arrangement to minimize self-absorption at the same maximum excitation wavelength, where maximum absorption of the dilute solution occurs. *Table 1* lists the maximum excitation wavelengths for the solutions in different solvents. By subtracting the fluorescence spectroscopy of the solvents from that of the solutions respectively, the fluorescence spectroscopic spectra of the solute were obtained. The emission spectra of the solute, of interest in this work, has been normalized, as the concentration of the polyimide is 1 g/l.

Results and discussion

The indices of polyimide thin films were measured by a prism-coupler technique. *Table 2* lists the thickness (*d*) and the indices along the film plane (n_{TE}) and out-of-plane (n_{TM}) of the films prepared from different solutions. The birefringence (Δn) is defined as $n_{TM} - n_{TE}$. It suggests that these polyimide thin films possess negative birefringence.

There are different points of view about the effects of thickness on negative birefringence of polyimide thin films. Boese et al.[5,9] thought thickness does not affect the value of negative birefringence of thin films. On the other hand, Coburn et al.[10] observed that the value of negative

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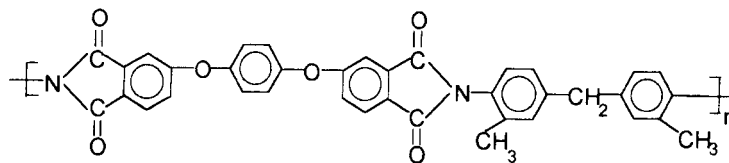
Scheme 1 Chemical structure of the organo-soluble polyimide

Table 1 The maximum excitation wavelengths of the polyimide solutions in different solvents

Solvents	DMAc	DMF	CHF	DIO	THF	EPC	BUT
λ_{ex} (nm) [a]	378	387	391	368	367	392	394

[a] Maximum excitation wavelength

Table 2 The indices of thin films along the film plane (n_{TE}) and out-of-plane (n_{TM})

Solvents	CHF	EPC	DMAc	NMP	DMF	BUT
δ [a]	18.9~19.0	21.9	22.1~22.8	22.9	24.9	26.2~31.7
n_{TE}	1.6171	1.6163	1.6223	1.6232	1.6259	1.6262
n_{TM}	1.6477	1.6522	1.6594	1.6542	1.6567	1.6546
d (μm)	4.8	4.8	4.8	4.8	4.8	4.6

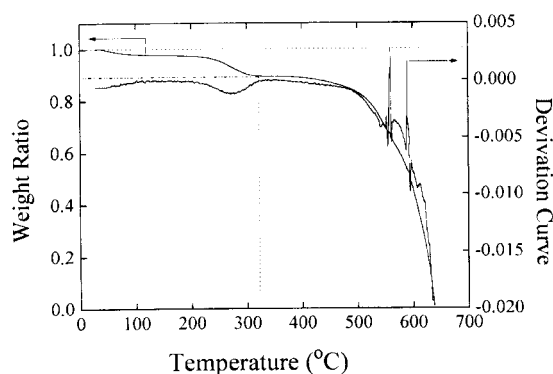[a] Solubility parameter in (MPa)$^{0.5}$, the data are quoted from Ref. [8].

Figure 1 Thermogravity diagram of a *ca.* 50 μm film prepared from the polyimide solution in NMP
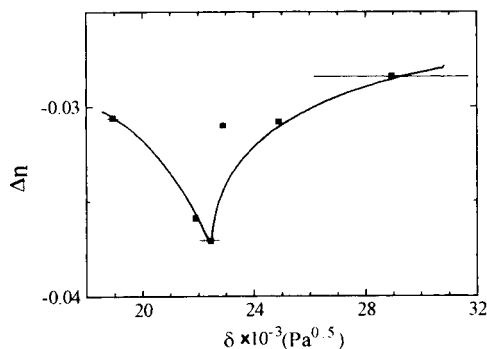

Figure 2 Dependence of the birefringence of thin films on the solubility parameter of the solvents

birefringence of polyimide thin films decreases with increasing thickness. No matter how film thickness affects the value of negative birefringence of polyimide thin films, the effect of film thickness was intended to be neglected by choosing the films with almost the same thickness for this study, as listed in *Table 2*.

Table 3 The weight of the final thin films prepared from its NMP solution with time

Weight (mg)	2.862	2.860	2.859
Time length (h)	0	10	20

Since the solvents are isotropic so that they contribute to n_{TE} and n_{TM} of the films uniquely, accordingly the residual solvents in thin films may lower the value of negative birefringence, as described below:

$$\Delta n = x n_{TM}^{0} + (1-x)n^{s} - x n_{TE}^{0} - (1-x)n^{s} = x(n_{TN}^{0} - n_{TE}^{0})$$

$$= x\Delta n^{0} \tag{1}$$

where x is the molar fraction of the polyimide in the film, the superscript 0 refers to a polymer film without residual solvent, and s refers to the solvent. Δn^{0} is the birefringence of a thin film without any solvent left.

In order to see whether there are solvents left in the thin films, thermogravity analysis of a thick film (about 50 μm) prepared from the polyimide solution in NMP, taken as an example, was conducted (as illustrated in *Figure 1*). The reason why the film prepared from its NMP solution was chosen is that NMP has the highest boiling point among the solvents used. As it is difficult to remove all the solvents from the thick film, as for this case, the amount of residual solvent in the thick film is about 10% (wt/wt); while the weights of the NMP solution cast final thin film treated at 200°C in vacuum for different lengths of time remain nearly constant, as listed in *Table 3*. Therefore it is the case that the residual solvents in the thin films are very limited, as the solvents are much easier to evaporate in thin films than in thick ones. Consequently, it is confirmed that the effect of residual solvents in the thin films can be omitted, that is, x is all but equal to 1.0.

The dependence of the birefringence on the solubility parameter of the solvents is illustrated in *Figure 2*. It is easily seen that the value of negative birefringence of the
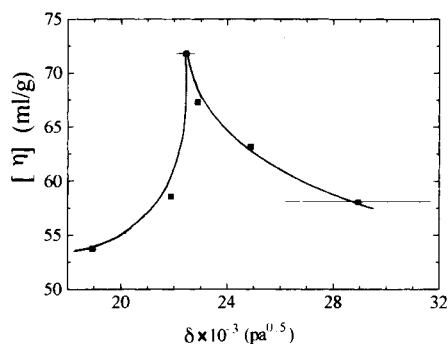
Figure 3 Dependence of the intrinsic viscosities on the solubility parameter of solvents
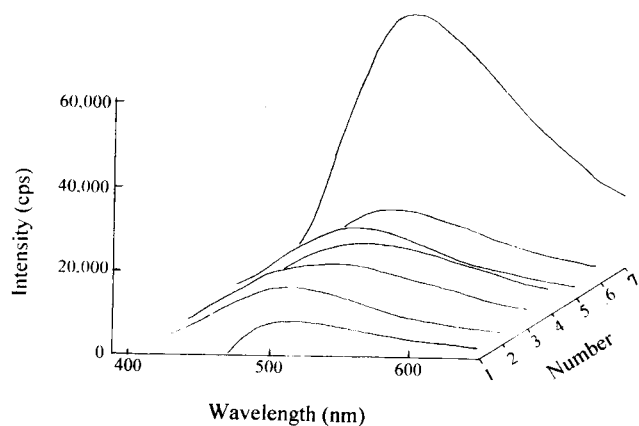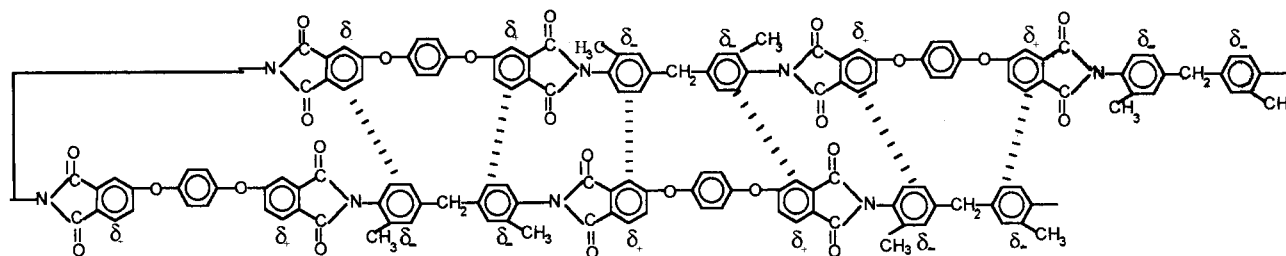

Wavelength (nm)

Figure 4 The normalized emission spectra of the polyimide in different solvents. 1, 2, 3, 4, 5, 6 and 7 denote for the solvents DMAc, EPC, DIO, THF, DMF, CHF and BUT, in which the polyimide is dissolved respectively
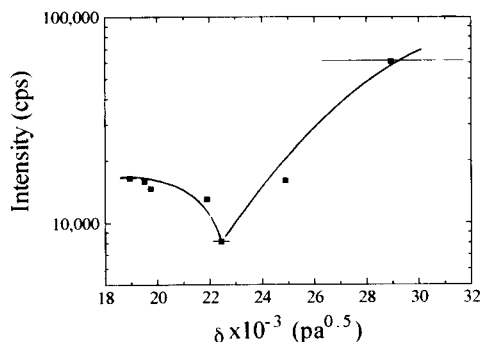
film prepared from the solution of DMAc is the largest. This may suggest that the negative birefringence of thin films depends on the chain conformation in solutions, from which the films are prepared, for the polyimide chain in the solution from which the thin film with the largest value of birefringence was prepared shows the most expanded conformation, as characterized by means of the intrinsic viscosity measurement and fluorescence spectroscopy.

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[11]. The polyimide chain in different solutions shows a varied degree of chain expansion, as shown in *Figure 3*, illustrating the dependence of the intrinsic viscosities on the solubility parameter of solvents.

The degree of chain expansion in different solvents can be also evidenced by the fluorescence spectroscopy. *Figure 4* depicts the normalized emission spectra of the polyimide dissolved in different solvents. Polyimides in dilute solutions show an intramolecular charge transfer effect, and broad and structureless emission spectra come into view[12]. Based on the report of Lee[13], intramolecular charge transfer interaction is induced by aromatic rings with sufficient and deficient electrons as depicted in *Scheme 2* for the polyimide of this work.

The intensities of the normalized emission spectra of the polyimide dissolved in different solvents are shown in *Figure 5*. In dilute polyimide solutions, it is not likely that the aromatic rings with sufficient and deficient electrons are adjacent enough to take charge transfer interaction efficiently in the same chain. The result that the intensity of the emission spectrum of the polyimide dissolved in DMAc is the lowest indicates that the intramolecular charge transfer interaction takes effect inefficiently, resulting from the most expanded chain conformation in DMAc.

Scheme 2 Intramolecular charge transfer interaction

Figure 5 The intensities of normalized emission spectra of the polyimide dissolved in different solvents

Conclusion

A correlation was primarily established between polyimide chain expansion in dilute solutions and the value of negative birefringence of thin films. It shows that the value of birefringence of thin films depends on polyimide conformations in the initial dilute solutions. The more expanded the polyimide chain, the higher the value of negative birefringence of the thin film.

References

1. Li, F., Kim, K., Kulig, J.J., Savitski, E.P., Birtttain, W.J., Harris, F.W., Cheng, S.Z.D., Hubbard, S.F. and Singer, K.D., *J. Mater. Chem.*, 1995, **5**, 253.
2. Russell, T.P., Gugger, H. and Swalen, J.D., *J. Polym. Sci.: Polym. Phys. Ed.*, 1981, **21**, 1745.
3. Lin, L. and Bidstrup, S.A., *J. Appl. Polym. Sci.*, 1993, **49**, 1277.
4. Hubbard, S.F., Singer, K.D., Li, F., Harris, F.W. and Cheng, S.Z.D., *Appl. Phys. Lett.*, 1994, **65**, 265.
5. Herminghaus, S., Boese, D., Yoon, D.Y. and Smith, B.A., *Appl. Phys. Lett.*, 1991, **59**, 1043.
6. Coburn, J.C. and Pottiger, M.T., in *Polyimides: Fundamentals and Applications*, eds. M. K. Ghosh and K. L. Mittal, Marcel Dekker, Inc., New York, 1996.
7. Li, B.H.T., Li, Y. and Ding, M., *Polym. Adv. Tech.*, 1997, **15(8)**.
8. Van Krevelen, D.W., *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, Elsevier Scientific Publishing Company, Amsterdam, 1970.
9. Boese, D., Herminghaus, S., Yoon, D.Y., Swalen, J.D. and Rabolt, J.F., *Mat. Res. Soc. Symp. Proc.*, 1991, **227**, 379.
10. Coburn, J.C., Pottiger, M.T., Noe, S.C. and Senturia, S.D., *J. Polym. Sci.: Polym. Phys. Ed.*, 1994, **32**, 1271.
11. Flory, P.J., *Principle of Polymer Chemistry*, Conell University Press, Ithaca, NY, 1953.
12. Viallat, A., Bom, R.P. and Cohen-Addad, J.P., *Polymer*, 1994, **35**, 2730.
13. Lee, C.J., *J. Macromol. Sci.: Rev. Macromol. Chem. Phys.*, 1989, **C29**, 431.