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Optical Properties of Polyimide Thin Films.   Effect of Chemical Structure and Morphology

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ABSTRACT: The optical properties of polyimide (PI) thin films with various backbone structures were investigated with prism coupler. PI films were prepared from two types of dianhydrides: pyromellitic dianhydride (PMDA) and 4,4′-hexafluoroisopropylidene bis(phthalic anhydride) (6FDA), and two type of diamines: 4,4′-oxydiphenylene diamine (ODA) and *p*-phenylene diamine (PDA). To relate the free volume change with refractive indices in PI thin films, the fractional free volume and the average refractive index were estimated for PI thin films. The fractional free volume of PI thin films varied from 0.2168 to 0.3865, and was in the following increasing order: PMDA-PDA < PMDA-ODA < 6FDA-ODA < 6FDA-PDA. The average refractive indices varied from 1.5778 to 1.7427, and were in the following increasing order: 6FDA-PDA < 6FDA-ODA < PMDA-ODA < PMDA-PDA. Morphological structure of the films was characterized with wide-angle X-ray diffraction (WAXD) analysis. The birefringence for different PIs was measured from in-plane and out-of-plane refractive indices using the prism coupler technique. The birefringence of PI film was in the following order: PMDA-PDA > PMDA-ODA > 6FDA-PDA ≈ 6FDA-ODA. Finally the effect of film thickness on birefringence was determined by preparing PI films having various backbone structures with different thickness. Thus effect of morphological structure, including their in-plane orientation and molecular packing on optical properties of PI thin films were studied.

KEY WORDS   Polyimide / Refractive Index / Fractional Free Volume / Morphological Structure / Birefringence / Orientation /

Optical properties of polymer films are of great importance in linear and nonlinear optical components, sensor applications, in a host of opto-electronic systems and magneto-optical recording.[1,2] These properties are generally dictated by the intrinsic optical anisotropy of the polymer chain and by the orientation induced during the casting operation.[3–6] By studying these properties, one can model the operating characteristics property and compare them with actual performance. Different techniques have been used to study the optical properties of polymer films, specially the measurements of refractive index and birefringence.[7–11] Thin PI films are widely used in microelectronics as passivation layers on top of devices or as dielectric interlayer between two levels of metallization.[12–16] Recently, much attention has been devoted to PIs as light waveguide materials, because of their thermal and environmental stability.[17,18] These thin layers are known to develop an in-plane orientation, resulting in measurable optical anisotropy. This optical anisotropy is responsible for the variations in the moisture absorption, electrical, thermal and mechanical properties that ultimately affect the functionality and the reliability of microelectronic devices.[19–21] By measuring a visible dichroic spectrum, the effects of PI chain structure, film thickness, heating rate, and residual solvent on a spontaneous in-plane orientation phenomenon was studied by Hasegawa *et al.*[22–24] Matsuura *et al.*[25] have investigated optical loss and refractive indices of fluorinated PIs and copolyimides for application to optoelectronic components.

This paper focuses on measuring refractive index and birefringence of PI thin films prepared from two type of dianhydride: PMDA and 6FDA and two type of diamines: ODA and PDA using a prism coupler. The effects of chemical structure and morphology of polymer structure on optical properties were investigated by group contribution method and WAXD patterns.

EXPERIMENTAL

Materials and Sample Preparation

Pyromellitic dianhydride (PMDA), 4,4′-hexafluoroisopropylidene bis(phthalic anhydride) (6FDA), *p*-phenylene diamine (PDA), 4,4′-oxydiphenylene diamine (ODA), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich Chemical Co. and Chriskev Chemical Co. PMDA, 6FDA, and PDA were purified by sublimation under reduced pressure and ODA was purified by recrystallization in ethanol. NMP was dried with phosphorus pentoxide (P_2O_5) and subsequently distilled under reduced pressure.   All the poly(amic acid) (PAA) precursors, poly(4,4′-oxydiphenylene pyromellitamic

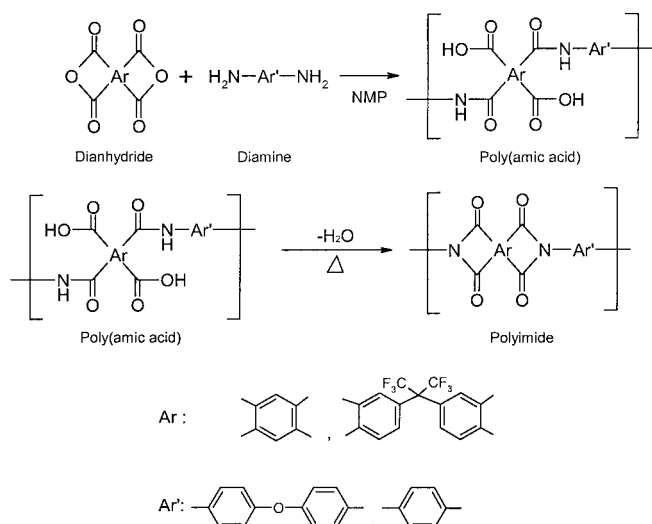[†]To whom correspondence should be addressed (Tel: +82-2-2123-2764, Fax: +82-2-312-6401, E-mail: hshan@yonsei.ac.kr).

Figure 1. Synthetic scheme of the PAA precursor and its PI.

Figure 2. Chemical backbone structures of PIs.

acid), PAA(PMDA-ODA), poly(4,4′-oxydiphenylene 4,4′-hexafluoroisopropylidene diphthalamic acid) PAA(6FDA-ODA), poly(p-phenylene pyromellitamic acid) PAA(PMDA-PDA), and poly(p-phenylene 4,4′-hexafluoroisopropylidene diphthalamic acid) PAA(6FDA-PDA), were prepared under nitrogen atmosphere by the addition of dianhydride to diamine in anhydrous NMP as in previous studies.[25–27] The synthetic route for the PAAs and their respective PI are given in Figure 1. These solutions had a solid content of 13 wt%.

All the precursor solutions, PAA(PMDA-ODA), PAA(PMDA-PDA), PAA(6FDA-ODA), and PAA(6FDA-PDA), were spin-coated onto silicon (100) substrates, and this was followed by soft baking at $80\,°C$ for $60\,min$. The soft-baked precursor films were thermally imidized in an oven by an imidization protocol: $150\,°C$ for $30\,min$, $230\,°C$ for $30\,min$, $300\,°C$ for $30\,min$, and $400\,°C$ for $60\,min$ with a ramping rate of $2.0\,°C\,min^{-1}$. After the thermal imidization, the samples were cooled at a rate of $2.0\,°C\,min^{-1}$. The series of PIs utilized in this work are shown in Figure 2. Thickness of PI thin films was controlled with in the range of 2.369–$12.430\,μm$ by a spin coater.[28, 29] The thickness of the imidized films were measured with a surface profiler (KLA-Tencor Alpha Step 500). Cured films were taken off from the substrates with deionized water and washed with distilled water several times and dried.

Measurements

The out-of-plane and in-plane refractive indices of the PI thin films were measured with a prism coupler (Metricon Model 2010) equipped with a He–Ne laser light source (wavelength = $632.8\,nm$) which is controlled by a personal computer. Measurements of the
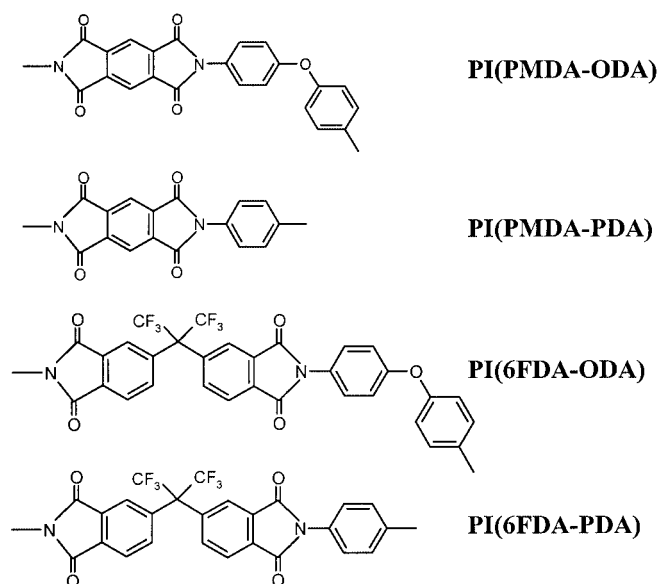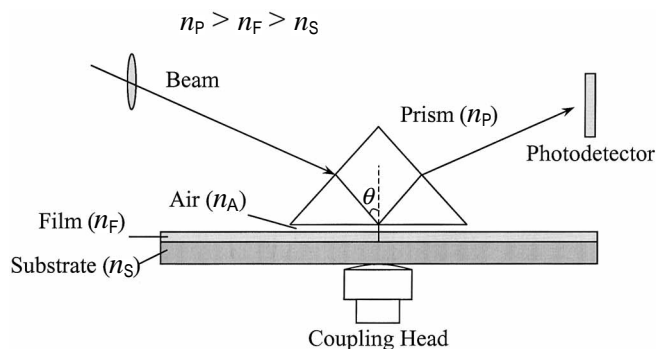

Figure 3. Single prism coupler for refractive index.

refractive indices were carried out in transverse electric (TE) and transverse magnetic (TM) mode. The TE measurement in which the electric field is in the film plane provides the in-plane refractive index (n_{xy}) whereas the TM measurement in which the electric field is out-of-plane gives the out-of-plane refractive index (n_z). All measurements were performed using a cubic zirconia prism of $n_{xy} = n_z = 2.1677$ at $632.8\,nm$ as shown in Figure 3.

Both in-plane, n_{xy}, and out-of-plane, n_z, refractive indices were used to compute the three-dimensional average refractive index as given in eq 1. The dielectric constant was calculated with Maxwell's identity, shown in eq 2.

$$n_{av} = (2n_{xy} + n_z)/3 \qquad (1)$$
$$\varepsilon' = n^2 \qquad (2)$$

Positron annihilation measurements have been extensively used for the fractional free volume (V_{FF}) in polymers, and computer simulation has been explored by others.[30, 31] The method used here was the group additivity technique popularized by Bondi and widely ap-

Table I. Optical properties of the various PIs

Polymer	Thickness (μm)	Refractive Indices at 632.8 nm				
		In-plane	Out-of-plane	Birefringence	Average	
		n_{TE}	n_{TM}	Δn	n_{av}	ε'
PI(PMDA-PDA)	5.326	1.8216	1.5849	0.2367	1.7427	3.0370
PI(PMDA-ODA)	5.963	1.7267	1.6363	0.0904	1.6966	2.8783
PI(6FDA-ODA)	6.665	1.5921	1.5833	0.0088	1.5892	2.5255
PI(6FDA-PDA)	6.776	1.5805	1.5725	0.0080	1.5778	2.4896

plied for a number of different purposes.[32−35] This was carried out by estimating the van der Waals or "occupied" volume, using group additivity tables and subtracting it from the molar volume (M/ρ), which is the total volume taken up by 1 mol of repeat units, including free and occupied volume. The fractional free volume is then given by

$$V_{FF} = \frac{(M/\rho) - VDW}{M/\rho} \qquad (3)$$

where M is the formula weight of a polymer repeat unit, ρ is the density, and VDW is the estimated van der Waals volume.[39]

WAXD patterns were obtained for the PI thin film specimens with a Rigaku horizontal X-ray diffractometer (Model D/Max-200B) with a nickel-filtered radiation. One diffractometer was set up for the transmission mode (*i.e.*, reflections from lattice planes normal to the film surface) with a thin asymmetric cut (101) quartz plate monochromator bent to a section of a logarithmic spiral and located in the diffracted beam. The other was used for the reflection mode (*i.e.*, reflections from lattice planes parallel to the film surface) with a curved graphite monochromator in the diffracted beam. The CuKα radiation source ($\lambda = 1.54$ Å) was operated at 35 kV and 40 mA. All the WAXD measurements were carried out $\theta/2\theta$ mode. The 2θ scan data were collected from 5 to 60° at 0.02° intervals with a scan speed of 0.3–0.5° min^{-1}, depending upon whether a reflection or transmission scan was being made. The measured X-ray diffraction intensities were corrected for the background run and then normalized for the film samples by the matching of the integrated intensity over the range of 58–60° (2θ). The 3D structures of the polyimides, depicted in Figure 4 are generated using the Chem office software, CS Chem office 3D pro (version 5.0).

RESULTS AND DISCUSSION

Refractive Index : Effect of Fractional Volume and Chemical Structure

The effect of chemical structure on the optical properties of the PIs was investigated. The optical properties for various PIs, PMDA-ODA, PMDA-PDA, 6FDA-ODA, and 6FDA-PDA, were measured by using prism

Table II. Fractional free volume (VFF) of the PIs

Polymer	Density[a] (g cm^{-3})	VDW_{bondi}[b]	V_{FF}
PI(PMDA-PDA)	1.6500	137.8	0.2168
PI(PMDA-ODA)	1.4000	186.6	0.3167
PI(6FDA-ODA)	1.4494	270.0	0.3568
PI(6FDA-PDA)	1.4320	221.2	0.3865

[a]Obtained from ref 12, 32, and 33. [b]Obtained from ref 34.

coupler at an optical frequency of 474.08 THz (that is, 632.8 nm). The results are shown in Table I.

For the PI with various backbone structures, the average refractive index (n_{av}) varied from 1.5778 to 1.7427, and was in the following increasing order: 6FDA-PDA < 6FDA-ODA < PMDA-ODA < PMDA-PDA. The average refractive indices of 6FDA-ODA and 6FDA-PDA PI thin films were relatively lower than that off PMDA-ODA and PMDA-PDA. PI(6FDA-PDA) film showed lowest refractive index and PI(PMDA-PDA) film showed highest refractive index. In general the refractive index of the polymer depends on the molecular refraction and molecular volume,[24] *i.e.*, polarizability of the atoms present in the unit volume of the polymer backbone.[36] Increase in the free volume, decrease the number of polarizable groups in a unit volume[37] and hence the refractive index decreases. Accordingly, it suggests that the refractive index of the polymer could be affected by the change of free volume. As the fractional free volume increased refractive index decreased.

To correlate the free volume change to refractive indices in PI thin films, the fractional free volumes (V_{FF}) were estimated for PI thin films. The results are given in Table II.

The fractional free volumes which was calculated from the density and van der Waals volume varied from 0.2168 to 0.3865, and were in the following increasing order: PMDA-PDA < PMDA-ODA < 6FDA-ODA < 6FDA-PDA. For all the PIs, with increasing fractional free volumes, average refractive index decreased, as shown in Table III.

Fractional free volume was maximum for PI films prepared using 6FDA. The incorporation of fluorine in polymer backbone increases free volume. Increase in free volume can be attributed to the greater steric volume of fluorine relative to hydrogen, which may inter-

fere with efficient chain packing. In addition, the significant mutual repulsion of fluorine atoms on different chains and the often-lower degree of polymerization, may influence the free volume. Furthermore, the electronic polarization is always lowered with fluorine substitution because of the smaller electronic polarizability of the C–F bond relative to C–H. In addition, hexafluoroisopropylidene group [–C(CF$_3$)$_2$] in the PI main chain, due to their bulkiness, imparts steric hindrance, and hence prevent the close packing of polymer chains, results in polymer with higher fractional free volume and low refractive index.[37] Therefore, the fractional free volumes of 6FDA-ODA and 6FDA-PDA PI thin films were relatively higher than that of PI(PMDA-ODA) and PI(PMDA-PDA) films. This shows that the bulky hexafluoroisopropylidene group in the 6FDA moiety lead to the increase in the fractional free volume, causing low refractive indices in PI thin films. High fractional free volume of the PMDA-ODA among the PMDA based PI thin films may be due to the hinged ODA moieties on the PI chain, which act as larger free volume contributor.

For various PIs, with increasing fractional free vol-

umes, average refractive index decreased. Trend of the fractional free volumes is consistent with that of average refractive index. This shows that average refractive index of polymide with various backbone structures was closely related to the free volume.

PMDA-ODA has relatively higher fractional free volume than PMDA-PDA whereas 6FDA-PDA has higher fractional free volume than 6FDA-ODA. Fractional free volumes of the 6FDA based PIs were not in the same trend as that based on PMDA based PI thin film. This suggest that the fractional free volumes of the 6FDA based PIs may not be affected by hinged ODA moieties, but significantly by 6FDA moiety having bulky hexafluoroisopropylidene group.

When compared to ether group, hexafluoroisopropylidene group in the PI main chain influence the morphological structure, especially, molecular packing in the PI thin films to a greater extent. These three-dimensional (3-D) structures are depicted in Figure 4. From point of distance between hexafluoroisopropylidene groups in the repeating units of the PIs, distance d1 and d2 in 6FDA-ODA is longer than distance d3 and d4 of 6FDA-PDA, as shown in Figure 4. It shows that in 6FDA-PDA, the distance between the bulky hexafluoroisopropylidene groups in the repeating units is short and hence 6FDA-PDA experience a greater steric hindrance compared to 6FDA-ODA. The steric hindrance of the bulky [–C(CF$_3$)$_2$] plays a major role in controlling the morphology than the hinged nature of the ODA chains.

Thus bulky hexafluoroisopropylidene group affect

Table III. Fractional free volume and average refractive indices of the PIs

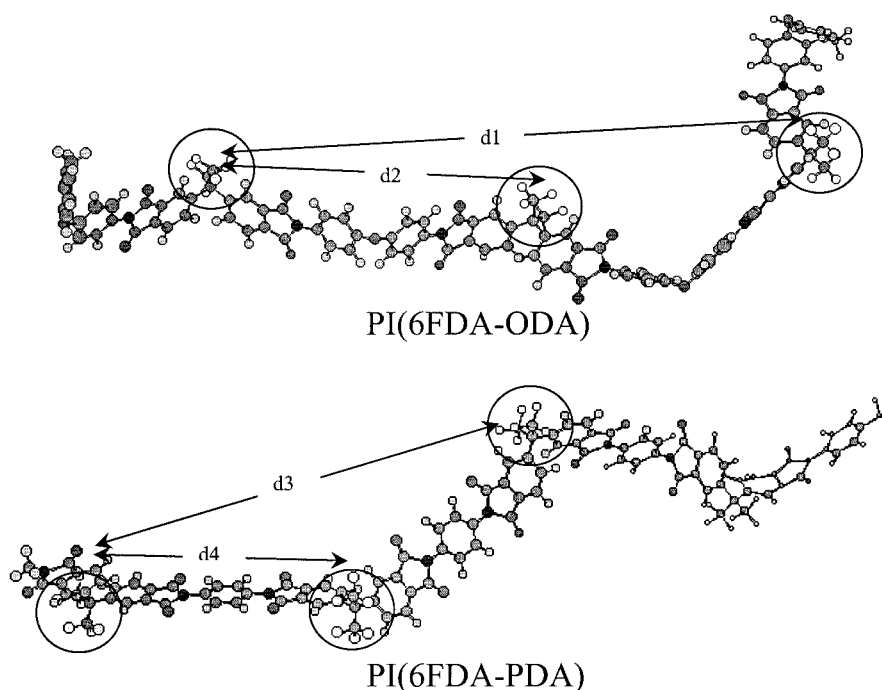| Polymer	V_{FF}	Average n_{av}
PI(PMDA-PDA)	0.2168	1.7427
PI(PMDA-ODA)	0.3167	1.6966
PI(6FDA-ODA)	0.3568	1.5892
PI(6FDA-PDA)	0.3865	1.5778

PI(6FDA-ODA)

PI(6FDA-PDA)

Figure 4. 3-D structures of PI(6FDA-ODA) and PI(6FDA-PDA) repeating unit; Inside of circles shows (CF$_3$)$_2$ groups of PIs.
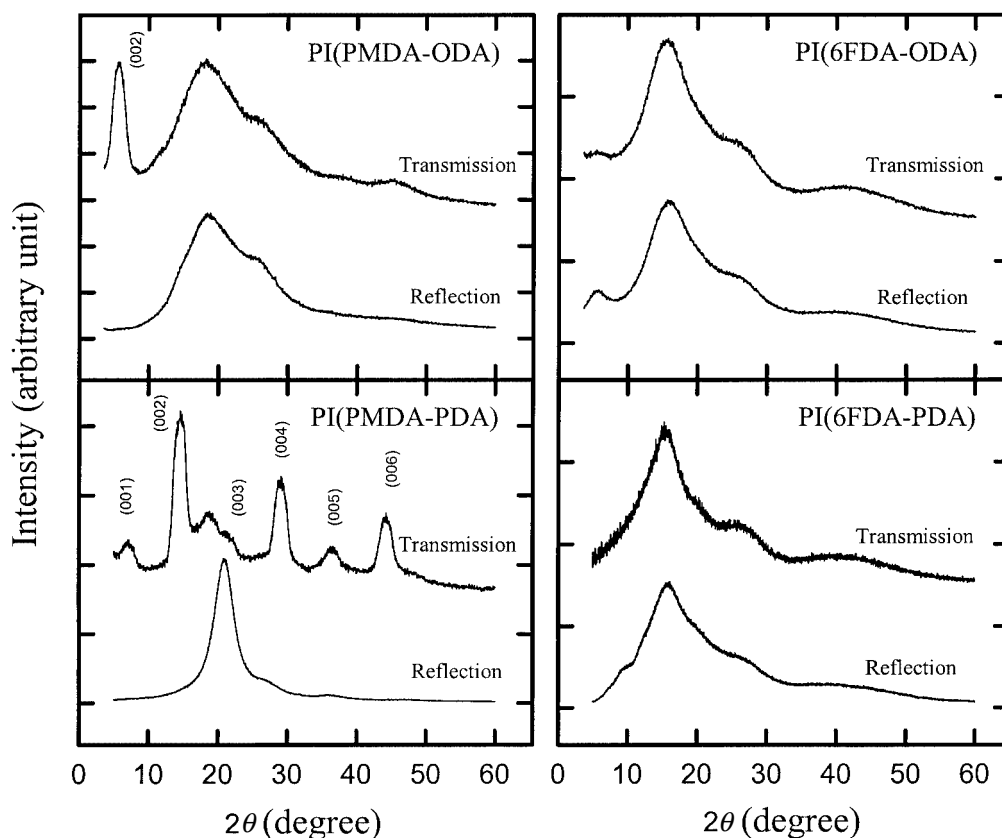
Figure 5. WAXD transmission and reflection patterns of PIs prepared from PAA by thermal imidization at 400 °C.

the morphology of the 6FDA-PDA to a greater extent than in 6FDA-ODA.

The morphological structure of the PI thin films, which were thermally imidized at 400 °C, was further investigated using WAXD, in both transmission and reflection geometries, as represented in Figure 5.

To correlate the morphological structure with average refractive index and fractional free volumes, the mean intermolecular distance in the PI films, which may be a critical factor for the average refractive index, was calculated from the characteristic transmission and reflection peaks, as shown in Table IV.

The mean intermolecular distance, which is a parameter of molecular packing, varied from 4.74 to 5.80 Å for the reflection pattern, and from 4.24 to 5.60 Å for the transmission pattern. They were in the following increasing order: PMDA-PDA < PMDA-ODA < 6FDA-ODA < 6FDA-PDA. As the mean intermolecular distance increases, the close packing arrangement between the chains decreases, resulting in high fractional volume and low refractive index. From WAXD analysis it was found that 6FDA based PI film showed higher mean intermolecular distance than PMDA based one. These results were in agreements with those obtained from refractive index measurements using prism coupler. Therefore, the average refractive index of the PI thin film was affected by chemical structure of the poly-

Table IV. Mean intermolecular distances in PIs

Polymer	Mean Intermolecular Distance (Å)	
	In-Plane[a]	Out-of-Plane[b]
PI(PMDA-PDA)	4.74 (18.68°)	4.24 (20.92°)
PI(PMDA-ODA)	4.84 (18.30°)	4.77 (18.58°)
PI(6FDA-ODA)	5.72 (15.48°)	5.57 (15.88°)
PI(6FDA-PDA)	5.80 (15.26°)	5.60 (15.80°)

[a]Calculated from the peak maximum of amorphous halo in the transmission WAXD patterns. [b]Calculated from the peak maximum of amorphous halo in the reflection WAXD patterns.

mer.

Birefringence : Effect of Morphological Structure and Film Thickness

Birefringence expresses the level of optical anisotropy in the film, and it is defined as the difference in refractive index between two orthogonal planes of polarization. The effects of chemical structure and thickness on the birefringence of the various PI films were investigated. The birefringence in a polymer film is a measure of the molecular in-plane orientation, where the orientation angle is defined by the angle between the polymer chain axis and the film plane. There are two types of contributions to birefringence. One is intrinsic and the other is form. Intrinsic contributions arise due to the orientation at

Table V. Film thickness effect on optical properties of the various PI thin films

Polymer	Thickness (μm)	Refractive Indices at 632.8 nm			
		In-plane n_{TE}	Out-of-plane n_{TM}	Birefringence Δn	Average n_{av}
PI(PMDA-PDA)	2.972	1.8234	1.5840	0.2394	1.7436
	3.546	1.8234	1.5845	0.2389	1.7438
	4.725	1.8219	1.5833	0.2386	1.7424
	5.326	1.8216	1.5849	0.2367	1.7427
	6.680	1.8216	1.5849	0.2367	1.7427
	9.240	1.8214	1.5854	0.2360	1.7427
PI(PMDA-ODA)	3.247	1.7267	1.6357	0.0910	1.6964
	4.125	1.7260	1.6356	0.0904	1.6959
	5.963	1.7267	1.6363	0.0904	1.6966
	7.205	1.7226	1.6377	0.0849	1.6943
	9.710	1.7197	1.6356	0.0841	1.6917
	11.160	1.7188	1.6363	0.0825	1.6913
PI(6FDA-PDA)	2.369	1.5834	1.5732	0.0102	1.5800
	2.945	1.5845	1.5744	0.0101	1.5811
	4.700	1.5828	1.5729	0.0099	1.5795
	6.776	1.5805	1.5725	0.0080	1.5778
	7.480	1.5802	1.5720	0.0082	1.5775
	9.724	1.5800	1.5720	0.0080	1.5773
PI(6FDA-ODA)	3.015	1.5927	1.5832	0.0095	1.5895
	4.320	1.5925	1.5835	0.0090	1.5895
	6.665	1.5921	1.5833	0.0088	1.5892
	8.155	1.5922	1.5836	0.0086	1.5893
	10.560	1.5922	1.5848	0.0074	1.5897
	12.430	1.5911	1.5839	0.0072	1.5887

the molecular segmental level of the polymer chains. It is this effect that gives rise to the stress-optical rule. A homopolymer melt and as well as most polymer solutions will have only this contribution. Multicomponent and multiphase systems, however, can give rise to form effects due to the contrast between the refractive indices of different phases.[40]

In general, structural polymers including crystalline polymers are in biphasic (ordered and disordered) state. For the two phase systems, usually the intrinsic birefringence is considered, neglecting the form birefringence.[8] The molecular in-plane orientation in the films was investigated by measuring the birefringence.

The birefringence of the films was estimated from the in-plane and out-of-plane refractive indices measured using the prism coupling technique. The PI thin films with various backbone structures and different thickness in the range of 2.369–12.430 μm. were prepared. The results of birefringence ($\Delta n = n_{xy} - n_z$) are given in Table V and Figure 6.

For various PI thin films, the birefringence varied from 0.2360 to 0.2394 for PMDA-PDA, from 0.0825 to 0.0910 for PMDA-ODA, from 0.0080 to 0.0102 for 6FDA-PDA and from 0.0072 to 0.0095 for 6FDA-ODA. Depending on the chemical structure, different PI film showed different birefringence which was in
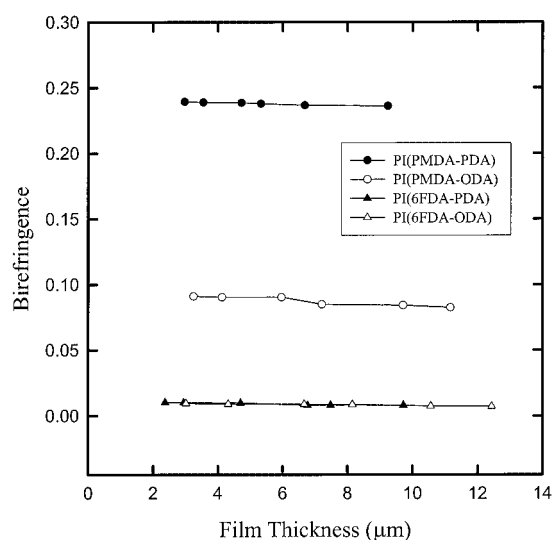
Figure 6. Birefringence of PIs depending upon the thickness.

the following decreasing order: PMDA-PDA > PMDA-ODA > 6FDA-PDA ≈ 6FDA-ODA. Rigid, chain segmented PI(PMDA-PDA) film having highest order, showed maximum birefringence. Bulky hexa fluoroisopropylidene group makes the polymers prepared using 6FDA less ordered and hence resulted in low birefringence. Specially, the birefringence of the PMDA-PDA was relatively more than that of the PMDA-ODA. The birefringences of the 6FDA based PIs were relatively

lower than the PMDA based PIs. It is well known that the birefringence of the PI thin films is related to the molecular order and orientation, which changes with the difference in chemical structure of the polymer. To relate the birefringence with morphological structure, a careful consideration was given to WAXD patterns of the PI thin films. As shown in Figure 5, all PMDA based PI thin films showed (00*l*) diffraction peaks in the transmission pattern corresponding to the molecular order along the chain axis. In the case of PI(PMDA-ODA), it showed one sharp (002) peak at $2\theta = 5.74°$ and one amorphous peak at $18.58°$. The rigid PI(PMDA-PDA) showed multiple (00*l*) diffraction peaks at whole angle range. This indicated that the PI(PMDA-PDA) film has higher degree of order and good in-plane orientation than the PMDA-ODA. In contrast, the reflection patterns corresponding to the molecular order along the chain plane are quite different from the transmission patterns as shown Figure 5. The reflection WAXD patens of the both films exhibited only one amorphous halo peak. In the reflection pattern, the absence of the (00*l*) peak is an evidence for the polymer chains were aligned in the film plane. Specifically, PI(6FDA-ODA) and PI(6FDA-PDA) showed only one amorphous halo in the transmission and reflection. It indicated that 6FDA-ODA and 6FDA-PDA have very poor packing order in the directions of the film thickness and plane. Therefore, the WAXD results showed good agreements with the birefringence results. The higher birefringence in the films might have resulted mainly from the enhancements of in-plane orientation.

The birefringence data for the change in the film thickness are presented in Figure 6 and Table V.

With increasing film thickness n_{xy} decreased, leading to the decrease in the film birefringence. In this study, all PI samples were prepared from the same synthetic method and curing process, and their film thickness was controlled by only varying the spin speed. These changes indicate that the molecular in-plane orientation degrades as film thickness increases. This means that the birefringence of PI thin films is affected by the change in morphological structure due to the change in film thickness.

CONCLUSION

The optical properties of PI thin films with various backbone structures were investigated with prism coupler. To relate the free volume change with refractive indices in PI thin films, the fractional free volume and the average refractive index were estimated. The fractional free volumes of PI thin films varied from 0.2168 to 0.3865, and were in the following increasing order:

PMDA-PDA < PMDA-ODA < 6FDA-ODA < 6FDA-PDA. The average refractive indices varied from 1.5778 to 1.7427, and were in the following increasing order: 6FDA-PDA < 6FDA-ODA < PMDA-ODA < PMDA-PDA. With increasing fractional free volumes, average refractive index decreased. It is consistent with the results of the mean intermolecular distance from WAXD patterns. It shows that the average refractive index of the PIs, having different backbone structure are closely related to the morphological structure, especially molecular packing, induced by chemical structures. Depending on the chemical structure and molecular order, PI films showed different birefringence, in the following decreasing order: PMDA-PDA > PMDA-ODA > 6FDA-PDA $\approx$ 6FDA-ODA. It means that the birefringences of the PI thin films depend on the morphological structure of the polymer, especially in-plane orientation, which changes with the difference in chemical structure. In addition, the anisotropy of PI thin films decreased with increasing film thickness. Therefore, the optical properties of PI film with various backbone structures were closely related to the morphological structure, including their chain orientation molecular packing.

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