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Molecular weight and film thickness effects on linear optical anisotropy of 6FDA-PFMB polyimides

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Different molecular weight samples of a polyimide, 6FDA-PFMB, were synthesized from 2,2′-bis (3,4-dicarboxyphenyl) hexafluoropropane (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) in refluxing *m*-cresol at high temperatures through a one-step polymerization route. Films of 6FDA-PFMB ranging from 1 to 100 μm thickness were prepared via solution-casting and investigated using optical prism coupler wave-guide experiments. It has been found that these films exhibit a linear optical anisotropy in the refractive indices. Specifically, they have a large index along the in-plane direction and a smaller one in the out-of-plane direction. Films with this linear optical anisotropy have been recognized to possess uniaxial negative birefringence. For films with a fixed molecular weight, the refractive indices are constant in the film thickness below 15 μm, and the birefringence gradually decreases with further increasing the film thickness. On the other hand, the refractive index along the out-of-plane direction decreases while the in-plane refractive index increases when the polyimide molecular weight increases. Such films can be used as negative birefringent compensators in twisted and super-twisted nematic liquid crystal displays to improve display viewing angles. © 1997 Elsevier Science Ltd.

(Keywords: compensator; film thickness; liquid crystal display; molecular weight; polyimide; polyimide film)

INTRODUCTION

It has been recognized since the 1960s that aromatic polyimide films exhibit structural anisotropy in the directions parallel (in-plane) and perpendicular (out-of-plane) to the film surface. This phenomenon has been defined as 'in-plane orientation[1-5]. Recently, it has been recognized that this anisotropic structure leads to anisotropic thermal, mechanical, dielectric and optical properties along the in-plane and out-of-plane directions[5].

Our interests are particularly focused on the linear optical properties in solution-cast polyimide films and their applications. Since aromatic polyimide molecules generally tend to align parallel to the film surface during the film forming process[1-5], the in-plane refractive index is larger than the out-of-plane refractive index. The degree of in-plane orientation and the resultant extent of linear optical anisotropy in the films can be estimated readily using refractive index measurements. Therefore, the anisotropy can be expressed by the birefringence which is the difference in the refractive indices along the in-plane and out-of-plane directions. In the field of optics this phenomenon is defined as uniaxial negative birefringence. One of the applications for the linear optical anisotropy in polyimide films is that they may be utilized to design negative birefringement compensators for twisted and super-twisted nematic liquid crystal displays (TN- and STN-LCDs). Such films can be used in both active and passive forms to improve LCD viewing angles[6].

However, it is well known that aromatic polyimides are usually difficult to process since they do not melt flow before decomposition and are insoluble in conventional solvents. The traditional approach is to use a two-step polymerization route to make processing possible through the soluble poly(amic acid) precursors. For example, polyimide films are generally produced by solution-casting or spin-coating and then are either thermally or chemically imidized. The imidization history affects the ultimate structure, morphology and properties of the films[7,8]. Conventional aromatic polyimides synthesized via the two-step polymerization often possess strong optical absorption in the low wavelength region of the u.v.–vis spectra (< 450 nm). This is caused by the existence of electronic conjugation states formed by the phenylene and imide groups and results in the dark-yellow–brown colour of the films. Also, crystalline and ordered structures in the films introduce density fluctuations which generate light scattering and, consequently, increase the optical loss. Different degrees of imidization in films may also give rise to varying refractive indices along both the in-plane and out-of-plane directions. In the past, all these problems in aromatic polyimide films precluded them from applications in optical devices.

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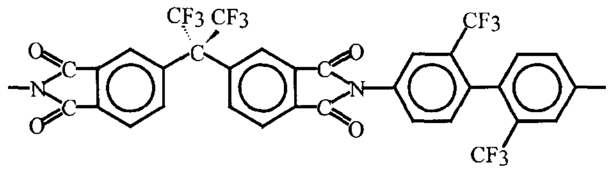
Over the past 6 years a family of organo-soluble, aromatic polyimides have been designed and synthesized in our laboratory. These polyimides were synthesized in refluxing *m*-cresol at high temperatures through the one-step route in which the intermediate poly(amic acid)s were not isolated[9]. Among the aromatic polyimides synthesized, the one prepared from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA) and 2,2′-bis (trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) (6FDA-PFMB) is considered to be one of the most promising for use in linear optical devices since it can be easily dissolved in common organic solvents including acetone, cyclopentanone, methyl ethyl ketone, tetrahydrofuran (THF), dimethylformamide, *N*-methylpyrrolidinone and dimethyl sulfoxide. 6FDA-PFMB can be directly processed to form films which can be used as negative birefringent retardation compensators in LCDs[6].

In this publication we present our recent experimental results of the molecular weight dependence on refractive indices and negative birefringence in 6FDA-PFMB films. We also offer evidence showing that the negative birefringence is independent upon the film thickness in the films ranging from 1 to 15 μm. The chemical structure of 6FDA-PFMB is



EXPERIMENTAL

Materials and samples

Different molecular weight samples of 6FDA-PFMB were prepared by controlling the stoichiometry of these polyimides. The intrinsic viscosities were determined in THF at 30°C and the molecular weights and molecular weight distributions were measured in THF at 30°C using gel permeation chromatography (g.p.c.). The molecular were calculated using the Mark–Houwink–Sakurada constants of 6FDA-PFMB in THF at 30°C determined via light scattering experiments reported recently[10]. Twelve samples were used to prepare solution-cast films and their intrinsic viscosity ranges from 0.2 to 2.3 dl g^{-1}.

The film processing conditions were kept constant for all the samples. Namely, the polyimide was first dissolved in cyclopentanone to form 8% (w/v) solutions. The solutions were filtered by using Whatman 1 μm Teflon syringe filters and cast onto silicon wafers. The thickness of the films were controlled by using metering rods with different sizes. The films were cast on a hot plate where the temperature was controlled at 60°C to gently evaporate the solvent. After drying for 60 min at that temperature, the samples were dried at 150°C for 24 h in a vacuum oven to remove any residual solvent. The film formation procedure was extensively investigated and the processing procedure proposed here yielded reproducible results. The film thickness could be determined with an accuracy of ± 0.10 μm. The reproducibility of the refractive indices along the in-plane and out-of-plane directions in the films are ensured by measuring at least four different locations in each film. From this it was found that the refractive indices are constant within the experimental error (± 0.0005).

Instrument and experiments

The linear optical refractive indices of the polyimide thin films were measured using a prism coupling waveguide technique. An incident laser beam having a 632.8 nm wavelength and transverse electric (TE) polarization was used and changes in the reflected radiation intensities of the films were detected at different angles (θ) as shown in *Figure 1*. A similar diagram between the intensity and angle (θ) can also be obtained for the transverse magnetic (TM) polarization. The radiation angles of the resonance depend upon the thickness and refractive indices of the films. Each of the sharp resonant peaks, which corresponds to a wave guide mode, were used to calculate the refractive indices in both the TE and TM polarization modes. As long as two resonance peaks were found in each mode, the refractive indices of the films along the in-plane (TE) and the out-of-plane directions (TM), as well as the film thickness, can be deduced.

In order to examine linear optical isotropy within the film plane, the in-plane refractive indices along different light propagation directions are determined by rotating the film and prism with respect to the incident beam in the wave-guide coupling experiments. The in-plane refractive indices are found to always be constant regardless the molecular weight and film thickness. This indicates that the films are isotropic along the in-plane direction and they are thus optically uniaxial with the rotational symmetry axis perpendicular to the film surface[6].

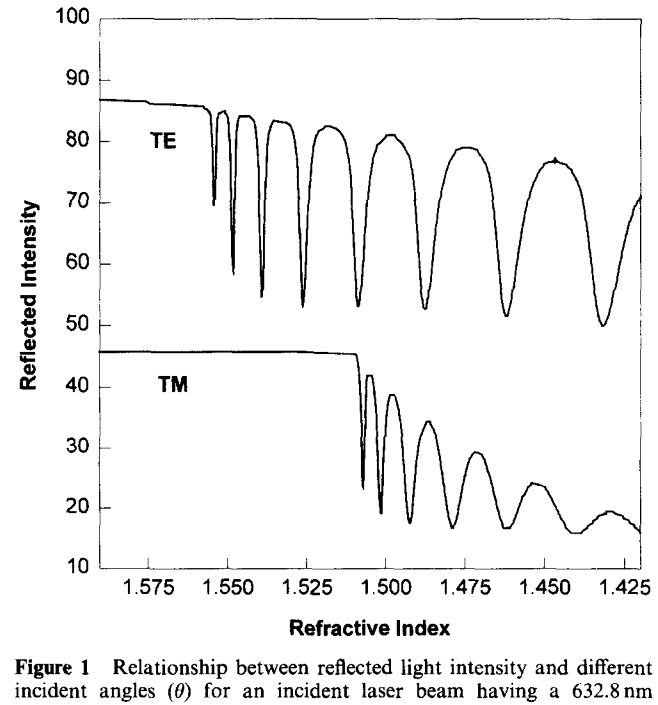


Figure 1 Relationship between reflected light intensity and different incident angles (θ) for an incident laser beam having a 632.8 nm wavelength at a transverse electric (TE) and transverse magnetic (TM) polarization

RESULTS AND DISCUSSION

6FDA-PFMB films of varying thicknesses were prepared from a polyimide having an intrinsic viscosity of 1.50 to study the thickness effect on the refractive indices. *Figure 2* shows that the refractive indices are fairly independent of the film thickness in the range of 1 to 15 μm. Above thickness 15 μm, the difference between the in-plane and out-of-plane refractive indices (TE, TM) gradually decreases with increasing the film thickness. This indicates that the thin film linear optical properties gradually approach the bulk properties, which should be three-dimensionally isotropic. A similar observation in another polyimide film synthesized via two-step polymerization route was also reported[11].

For high molecular weight 6FDA-PFMB films, the linear optical anisotropy expressed as the uniaxial negative birefringence (Δn), is -0.045 when the film thickness is between 1 and 15 μm. The uniaxial negative birefringence values of those aromatic polyimides will change drastically and systematically with modifications to the polyimide backbone chemical structures. This indicates that molecular rigidity, linearity and intrinsic linear optical polarizability may play important roles in the formation of the negative birefringence in polymer films[6]. From a microscopic standpoint, the molecules in films are restricted in three-dimensional space between two walls having different characters: one is the silicon wafer surface (hard wall) and the other is the air–polymer surface (soft wall). Aromatic polyimides have relatively high degrees of rigidity and persistence lengths in solution and possess intrinsically large differences in the refractive indices along and perpendicular to the molecular chain directions. As a result, the polyimides may form in-plane orientation and generate highly anisotropic negative birefringences during the solvent evaporation process. On the other hand, the film thickness in this study is at least one to several orders of magnitude greater than the molecular size. The in-plane orientation may thus not be directly caused via film thickness constraint but is a result of the solvent evaporation and the internal force field built up during the film processing.

The high negative birefringence value in 6FDA-PFMB films is extremely useful to design retardation compensators in LCDs[6,12]. It has been known that some of the major drawbacks of the TN- and STN-CDs include the asymmetric viewing angle characteristics along the horizontal and vertical directions as well as the narrow range of viewing angles. This is a critical issue for applications such as avionic information displays where cross-cockpit viewing is required. Loss of the contrast ratio at high viewing angles for the LCDs is the result of light leakage in the black (field-on) state of normally white LCDs. From a molecular point of view, the liquid crystal molecules in the field-on state are in a homeotropic arrangement having a uniaxial positive birefringence in the LCDs. Therefore, an off-axis light beam with an incident angle θ from the normal direction of the LCD surface undergoes a retardation due to the contribution from both the ordinary (n_0) and extraordinary (n_e) refractive indices of the liquid crystal molecules. Consequently, light leakage occurs which causes a low contrast ratio in the oblique direction and it shows angular dependency. In order to eliminate the light transmission in the oblique viewing direction, a negative birefringent optical compensator (R_{OC}) can be designed and inserted between the cross polarizers of the LCDs. This compensates the positive retardation of the liquid crystal molecules (R_{LC}). Theoretically, the total retardation becomes that $R = R_{LC} + R_{OC} = 0$. As a result, the off-axis of the light transmission with respect to the normal direction under the field-on state ideally approaches zero[6,12].

The retardation term of the liquid crystals is equal to the product of the liquid crystalline positive birefringence (Δn) and the cell thickness (d). After excluding the retardation introduced by two polarizers, this positive retardation is in a range of 50–300 nm. Roughly speaking, this value can be compensated by the polyimide film

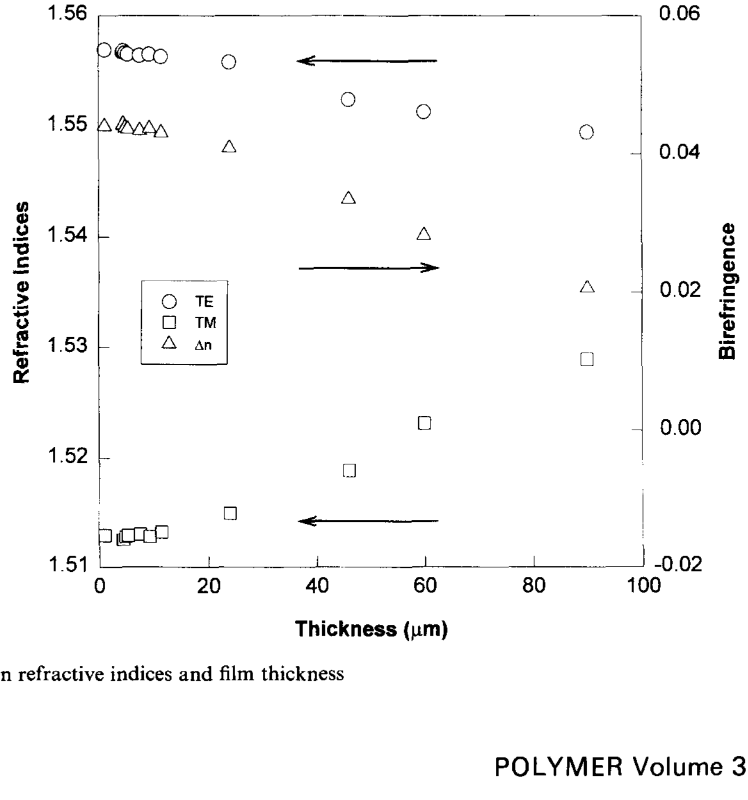


Figure 2 Relationship between refractive indices and film thickness

with a negative birefringence. The 6FDA-PFMB films in the thickness range of 1 to 8 μm may thus be used to meet these requirements. The birefringence independence of the thickness in this range is important for the design of retardation compensators.

It is interesting that the refractive indices along the in-plane and out-of-plane as well as negative birefringence value of the 6FDA-PFMB films exhibit an intrinsic viscosity (molecular weight) dependence as shown in *Figure 3*. The thickness of the films is controlled to be about 4 μm. The refractive index along the in-plane direction initially increases while the refractive index of the out-of-plane direction decreases and therefore, a resulting negative birefringence of the film increases as increasing the intrinsic viscosity. After a critical intrinsic viscosity of around 1.1 is reached, these changes level off. It is known that the linear optical property of the films is dependent not only on molecular parameters such as rigidity, linearity and intrinsic polarizability, but also on the packing of the chain molecules in the film condensed state. Molecular weight differences in 6FDA-PFMB films may affect molecular packing due to changes in the chain end group density. It is evident that chain end groups may possess a higher free volume fraction and therefore disrupt the molecular packing. When the molecular weight reaches a critical value, the effects of end groups on the packing becomes secondary compared with other factors.

It is also recognized that the refractive index of the film can be correlated with other parameters, such as coefficients of thermal expansion and dielectric behaviour, which reflect structural changes in the thin films. Let us consider the free energy (or internal energy) term. The first derivative of the energy term with respect to pressure is volume and that with respect to the applied electric field is the electric polarization or dipole moment. The second derivatives of these quantities are thus associated with the coefficient of thermal expansion, dielectric constant and refractive index. Note that these three parameters all belong to the second order type. As a result, it is expected that they may share the common microscopic origin of the structural changes.

Molecular weights of the 6FDA-PFMB samples can be converted to different degrees of polymerization (DP) for the 6FDA-PFMB samples. In *Figure 4*, the refractive indices along the in-plane and out-of-plane directions and the negative birefringence of the films are plotted as a function of $(\mathrm{DP})^{-1}$. The parameter $(\mathrm{DP})^{-1}$ is roughly proportional to the end-group density, which approaches zero when the molecular weight increases to infinity. From *Figure 4*, it is evident that in the molecular weight range studied here the refractive indices of the films along the in-plane direction (TE) decrease, while the refractive indices along the out-of-plane direction (TM) increase with increasing $(\mathrm{DP})^{-1}$ and both show the linear relationships. This significantly enhances the uniaxial negative birefringence value of the films with increasing molecular weight (*Figures 3* and *4*). Since the refractive index is proportional to the polarizability per unit volume in an electromagnetic field, it seems that the different end group densities in chain molecules and therefore, the uncoupled chain ends may significantly affect the polarizability along both the in-plane and the out-of-plane direction.

A molecular orbital calculation for polyethylene (PE) polarizabilities, both parallel and perpendicular to the PE molecular axes, was recently reported. It was found that the birefringence of PE molecules increases with the number of repeating units[13]. These calculated results show a reasonable agreement with experimental data of the refractive indices and resulting birefringence in alkanes with different molecular lengths[14]. The correlation between these linear optical properties and molecular length in the case of PE is qualitatively similar to the relationships shown in *Figures 3* and *4*. However, aromatic polyimide molecules possess higher intrinsic polarizabilities and therefore, a greater birefringence compared to the flexible chain molecules.

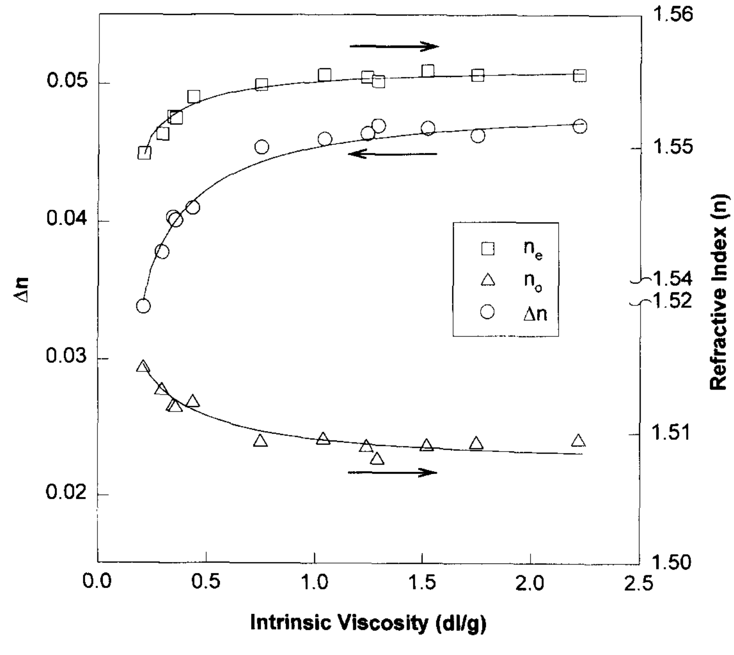


Figure 3 Relationship between refractive indices and negative birefringence with intrinsic viscosity for 6FDA-PFMB thin films

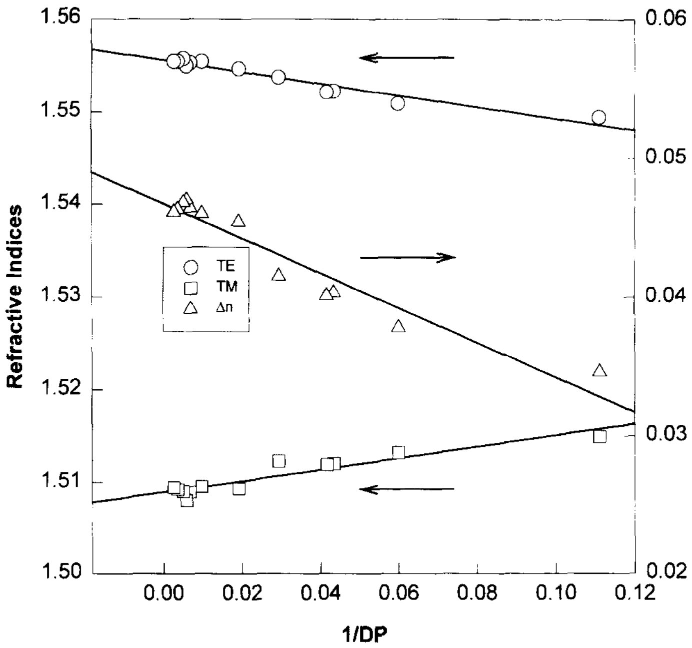


Figure 4 Relationships between refractive indices and negative birefringence of the thin films and $(DP)^{-1}$

CONCLUSION

In summary, the uniaxial negative birefringence of thin films is fairly independent on the film thickness up to at least 15μm. Further increasing the film thickness, however, leads to a decrease of the birefringence which is caused by the reduction of the refractive indices along the in-plane and the increase of the refractive indices along the out-of-plane directions. On the other hand, with increasing molecular weight the refractive indices along the in-plane direction of the films increase and the refractive indices in the out-of-plane direction decrease. This leads to a significant increase of the negative birefringence value. The linear relationships between the refractive indices and $(DP)^{-1}$ can be found. It is academically important to understand the effect of the structural and intrinsic parameters of chain molecules in the film condensed state on the linear optical and other second order material parameters which are anisotropic. In addition, this linear optical anisotropy is technologically useful in applications such as increasing viewing angles in LCDs.

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