

Temperature Dependence of Optical Retardation in Uniaxially Drawn Aromatic Polyimide Films

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Introduction

With the development of planar lightwave circuits and opto-electronic integrated circuits, polarization components such as waveplates, polarizers and beam splitters will be reduced in size and incorporated into such circuits.¹⁾ One of the examples is a waveplate using polyimide (PI), which is inserted into silica-based planar lightwave circuits to function as a transverse electric/transverse magnetic (TE/TM) polarization-mode converter.²⁾ In such a case, if there is a large temperature

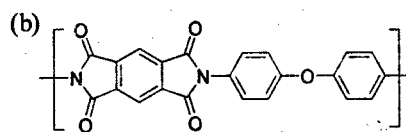
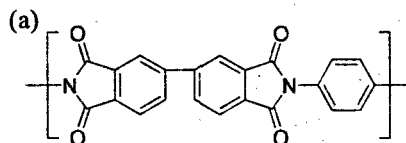


Fig.1 Molecular structure of (a) BPDA/PDA and (b) PMDA/ODA polyimides

dependence of retardation in PI films, the temperature change of surrounding environment should have large influence on the polarization dependence of circuit performance. Therefore, it is important to investigate the temperature dependence of retardation in uniaxially drawn PI films. In this study, we measured the temperature dependence of retardation for two kinds of uniaxially drawn PI films derived from 3,4,3',4'-biphenyltetracarboxylic dianhydride and *p*-phenylenediamine (BPDA/PDA) and from pyromellitic dianhydride and oxydianiline (PMDA/ODA) (Fig.1). Further, the intrinsic birefringence (Δn^0) for these PIs were estimated from the relationship between the molecular orientation and the in-plane birefringence (Δn_{YX}).

Theory

The coordinate system for expressing molecular orientation is defined as shown in Fig. 2. The X-, Y-, and Z-axes are defined as transverse, drawing, and out-of-plane directions of a film, respectively. In addition, the y-axis is defined as the direction of PI main chain. The average squared direction cosines ($\langle \cos^2(yW) \rangle$; W=X, Y, Z) provide a simple pictorial representation of the molecular orientation. The observed Δn_{YX} is related to the direction cosines and the intrinsic birefringence, Δn^0 as follows:³⁾

$$\Delta n_{YX} = \Delta n^0 \cdot (\langle \cos^2(yY) \rangle - \langle \cos^2(yX) \rangle)$$

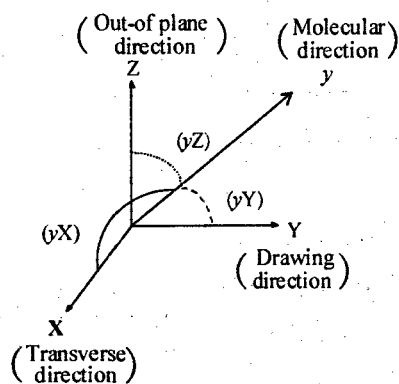


Fig.2 Definition of the coordinate system.

Experimental

Materials, Sample Preparation, Curing with Imidization, and Uniaxial Drawing

Two kinds of PIs were synthesized from 3,4,3',4'-biphenyltetracarboxylic dianhydride and *p*-phenylenediamine (BPDA/PDA) and from pyromellitic dianhydride and oxydianiline (PMDA/ODA). Uniaxially drawn PI films were prepared by the *in-situ* drawing method developed by the present authors.³⁻⁴ Firstly, poly(amic acid) (PAA) solutions, *i.e.* precursors of polyimides, were spin-coated onto Si substrates (4 inch-diameter) at room temperature. These films were dried at 70°C for 2h under nitrogen flow and then peeled from the substrates. PAA films (5 mm-wide and 15 mm-long) thus obtained were uniaxially drawn during thermal curing with constant loads (0 – 190 g for BPDA/PDA and 0 – 100 g for PMDA/ODA) using a thermal mechanical analyzer (TMA, Sinku-Riko TM-7000). The PAA films were heated to given final curing temperatures (420°C for BPDA/PDA and 480°C for PMDA/ODA) at a heating rate of 10°C/min, kept for 1 h, and then cooled to room temperature. The thicknesses (d) of the PI films thus obtained were 14.7 – 18.3 μm for BPDA/PDA and 20.2 – 28.0 μm for PMDA/ODA.

Measurements

Optical retardation was measured using the parallel-Nicole rotation method at wavelengths of 1.31 and 1.55 μm ,⁴ and thickness was measured from interference fringe observed in near-infrared absorption spectra. Δn_{yx} was calculated by dividing a observed retardation by a film thickness. Moreover, samples were heated on a hot-stage (FP82HT, Mettler Toledo) to measure their temperature dependence of retardation, $d(\Delta n \times d)/dT$. For eliminating the effect of absorbed moisture,⁵ $d(\Delta n \times d)/dT$ was estimated from the data taken in cooling process (from 180 to 40°C at 20°C intervals). Attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectra were measured with a Nicolet Avatar 320 FT-IR with a robust single-reflection accessory (Thunderdome, Spectra-Tech Co. Ltd.) having a germanium IRE (45° incident-angle). The method for estimating orientation coefficients of uniaxially oriented PI films has been reported elsewhere.³

Results and Discussion

Intrinsic Birefringence (Δn^0) for BPDA/PDA and PMDA/ODA

Fig. 3 shows the relationship between the draw ratio (R) and the average squared direction cosines for BPDA/PDA and PMDA/ODA PIs. Undrawn PI films with $R=0.97$ (BPDA/PDA) and 1.00 (PMDA/ODA) exhibit little in-plane anisotropy but significant in-plane/out-of-plane anisotropy as evidenced by a large difference between $\langle \cos^2(yY) \rangle$ and $\langle \cos^2(yZ) \rangle$. This remarkable planar orientation was generated during spin-coating and drying of PAA films and enhanced during curing as clarified by Hasegawa et. al.⁶ On the other hand, at higher draw ratios, $\langle \cos^2(yZ) \rangle$ are almost same as $\langle \cos^2(yX) \rangle$, which means the uniaxial orientation along drawing direction. The relationship between the observed Δn_{yx} and the estimated values of $(\langle \cos^2(yY) \rangle - \langle \cos^2(yX) \rangle)$ is shown in Fig. 4. From the slopes of liner fitted lines passing

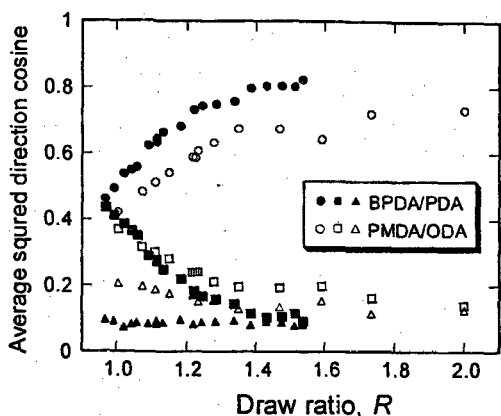


Fig.3 Plots of the average squared direction cosines as a function of draw ratio. Direction cosines: (●, ○) $\langle \cos^2(\gamma Y) \rangle$, (■, □) $\langle \cos^2(\gamma X) \rangle$, and (▲, △), $\langle \cos^2(\gamma Z) \rangle$.

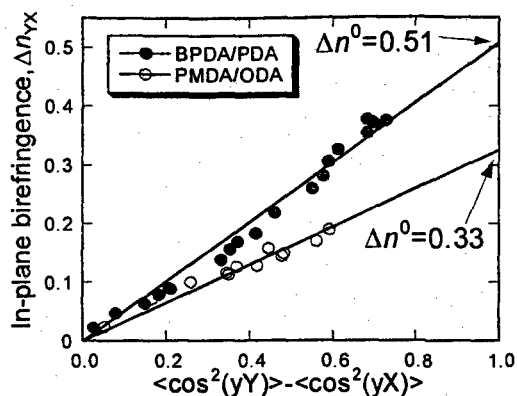


Fig.4 The relationship between Δn and the difference between the direction cosines along the y-direction to the Y and X axes.

through the origin, the value of Δn^0 are estimated as 0.51 for BPDA/PDA and 0.33 for PMDA/ODA PIs. Such a large Δn^0 for BPDA/PDA should be caused by its structural linearity, rigidity, and the large anisotropy in polarizability of the biphenyltetracarboxylic diimide moiety. The Δn^0 for BPDA/PDA has been experimentally estimated as 0.66 ($\lambda=589$ nm) by Hasegawa et. al.⁶⁾ The discrepancy should be caused by the wavelength dependence of the refractive index.⁷⁾ Moreover, a calculated value of Δn^0 has been reported as 0.470 for BPDA/PDA,⁸⁾ which almost agrees with our experimental value. On the other hand, experimental and calculated values of Δn^0 have been reported for PMDA/ODA as 0.33⁹⁾ and 0.38,⁸⁾ respectively, which also agree with our results.

Temperature Dependence of Retardation and In-plane Birefringence for Uniaxially Drawn PI Films

Fig. 5 shows the temperature dependence of retardation observed for uniaxially drawn PI films. The retardation demonstrates significant decrease with the increase in temperature. It has been reported that film thickness increases with increase in temperature, and that the estimated CTEs along the thickness direction are 101–118 ppm/K and 141–154 ppm/K for BPDA/PDA and PMDA/ODA PIs, respectively.¹⁰⁾ Since retardation is the product of film thickness and in-plane birefringence, the increase in thickness should make retardation increase, however, retardation is decreasing as the temperature increases. Therefore, Δn_{yx} should be decreasing greatly with the increase in temperature. The temperature dependence of birefringence considering the effect of CTE along the thickness direction is shown in Fig. 6. The temperature dependence of Δn is 26.8 ppm/K for BPDA/PDA and 49.0 ppm/K for PMDA/ODA. Fig. 7 shows the relationship between

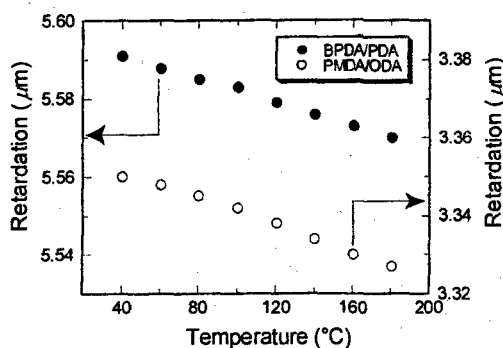


Fig. 5 Temperature dependence of retardation for uniaxially drawn PI films.

$d(\Delta n_{YX})/dT$ and Δn_{YX} for BPDA/PDA and PMDA/ODA PIs. As clearly seen in the figure, proportional relationships are observed between Δn_{YX} and $d(\Delta n_{YX})/dT$. This relationship can be explained in terms of the temperature derivative of the Vuks equation¹¹⁾:

$$\frac{d(\Delta n_{YX})}{dT} = \frac{n_{av}}{n_{av}^2 - 1} \left(1 + \frac{1}{n_Y n_X} \right) \frac{dn_{av}}{dT} \Delta n_{YX}$$

where T is the temperature, n_{av} the average refractive index. According to this equation,

$d(\Delta n_{YX})/dT$ should increase with an increase in Δn_{YX} . On the other hand, we have recently reported the temperature dependence of in-plane/out-of-plane birefringence, $d(\Delta n_{YZ})/dT$, for spin-coated PI films formed on Si substrates as -39 ppm/K for BPDA/PDA (at $\Delta n=0.1877$) and -32 ppm/K for PMDA/ODA (at $\Delta n_{YZ}=0.0686$)⁵⁾ The values of $d(\Delta n_{YX})/dT$ for the uniaxially drawn PI films is significantly smaller than those of the PI on Si substrates for a same value of birefringence. The large $d(\Delta n_{YZ})/dT$ values of the spin-coated films should be originated from the residual stress on substrates, which has been generated due to the mismatch of thermal expansion between the substrates and PIs.¹²⁾

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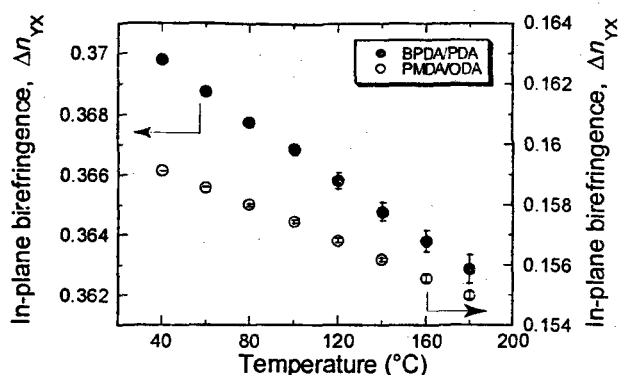


Fig.6 Temperature dependence of estimated in-plane birefringence for PI films. Error ranges represent the distribution of estimated Δn_{YX} caused by the variations of reported CTE.

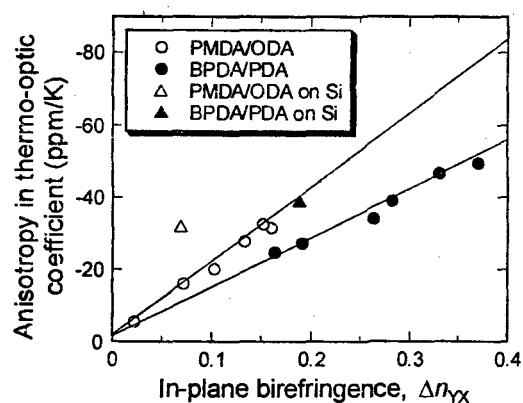


Fig.7 The relationships between $d\Delta n/dT$ and Δn for uniaxially drawn PI films.