Chapter 22

Rodlike Fluorinated Polyimide as an In-Plane Birefringent Optical Material

Shinji Ando[1], Takashi Sawada[1], and Yasuyuki Inoue[2]

[1]NTT Interdisciplinary Research Laboratories, Midori-cho, Musashino-shi, Tokyo 180, Japan
[2]NTT Optoelectronics Laboratories, Tokai, Ibaragi 319–11, Japan

Fluorinated polyimide that has a rod-like structure is investigated as a novel in-plane birefringent optical material whose birefringence and/or retardation can be precisely controlled This material has good flexibility, high transparency, thickness controllability, and high thermal stability Three methods for generating in-plane birefringence in polyimide films are presented The in-plane birefringence can be controlled between 0 02 and 0 17, and the optical retardation is controlled to within 1% A thin, flexible optical half-waveplate at 1 55 μm, only 14 5 μm thick, which is 6 3 times as thin as a zeroth-order quartz waveplate, was prepared Its retardation was retained after annealing at 350°C for 1 hour

The most commonly used birefringent materials are calcite, the trigonal crystal of calcium carbonate, and quartz They are used for a variety of optical polarization components such as waveplates, polarizers, and beam splitters With the development of planar lightwave circuits (PLC), opto-electronic integrated circuits (OEIC), and multichip interconnections for optical communication, these polarization components will be reduced in size and incorporated into such circuits and modules For example, a small quartz waveplate is inserted into a silica-based waveguide as a TE/TM polarization mode converter (*1*) Such inorganic crystals have high optical transparency at the wavelengths of optical communication, 1 0-1 7 μm, and have good thermal and environmental stability However, their birefringence cannot be changed and they are difficult to make into thin plates or small components The thickness of a zeroth-order half-waveplate of calcite at 1 55 μm is about 5 μm which is almost impossible to grind and polish because of its fragility On the other hand, the low birefringence of quartz makes a half waveplate rather thick (92 μm) This results in considerable excess loss when the waveplate is inserted into a waveguide (*1*)

Polymeric materials such as polycarbonates and poly(vinyl alcohol) are also known as birefringent optical materials They are used as retardation plates for liquid

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crystal displays, with their birefringence and thickness being controlled by uniaxial drawing or rolling of the films However, it is difficult to generate large in-plane birefringence because of their small polarizability anisotropy and flexible molecular structure The in-plane birefringence of polymeric retardation plates is only as large as that of quartz waveplates In addition, the current manufacturing process for OEICs and multichip modules includes soldering at 260°C and short-term processes at temperatures of up to 400°C On the other hand, the PLCs for optical communication require very high reliability and durability The above-mentioned polymeric materials do not have such thermal and environmental stability Furthermore, their optical losses at the wavelengths of optical communication are much higher than in the visible region (0 4-0 8 μm) because their two or three types of C-H bonds which harmonically absorb infrared radiation give broad and strong absorption peaks at these wavelengths (*2-4*) There has been a strong demand for new optical materials having much larger birefringence than quartz while having good processability, good tractability, and high thermal and environmental stability

The transparency and optical anisotropy of polyimides have been investigated because their excellent thermal, chemical and mechanical stability could make them good waveguide materials (*4-6*) Optimally cured fluorinated polyimides can decrease optical losses to below 0 1 dB/cm in the visible region, and these losses are stable at temperatures up to 300°C (*6*) We have recently fabricated heat-resistant multi-mode (ridge-type) and single-mode (buried-type) optical waveguides using fluorinated polyimides with the propagation loss of about 0 3 dB/cm at 1 3 μm (*7,8*) Polyimides are known as optically anisotropic materials, in which the birefringence of polyimide films is, in general, defined as the difference of refractive indices of the two polarizations, parallel (n_{TE}) and perpendicular (n_{TM}) to the film plane A very large birefringence between n_{TE} and n_{TM} of 0 24 at 0 633 μm was observed for poly(*p*-phenylene biphenyltetracarboximide) (*9*) Polyimide films prepared on isotropic substrates, such as glass plates or silicon wafers, have no refractive index anisotropy in the film plane (*10*) However, uniaxial drawing of Kapton-type poly(amic acid) films can give highly oriented polyimide films with large in-plane birefringence (*11*) A maximum elongation of 83% was obtained for the poly(amic acid) film with 40wt% solvent Refractive index ellipsoids of polyimide prepared on isotropic substrates and uniaxially drawn polyimide are schematically shown in Figure 1 The in-plane birefringence of polyimide films (Δn) is defined as the difference between the largest (n_{TE1}) and the smallest in-plane refractive index (n_{TE2}). The optical axis of n_{TE1} coincides with the drawing direction The Δn of 0 18 at 0 633 μm obtained for the Kapton-type polyimide is larger than that of calcite (*11*) Several methods of drawing poly(amic acid) films uniaxially have been developed in order to improve the tensile mechanical properties of polyimides (*12,13*), but no methods of controlling the in-plane birefringence or the fabrication of polarization components from polyimide have been reported yet

In this study, we investigate fluorinated polyimide that has a rod-like structure as a novel in-plane birefringent optical material whose birefringence and retardation (birefringence x thickness) can be precisely controlled The fabrication of a thin, flexible half-waveplate is described and its thermal and optical properties are presented We have already reported fluorinated polyimides using 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) as a diamine (*14-17*) These polyimides exhibit high

transparency in the visible-near-infrared region, low water absorption, and low refractive indices These properties are desirable for materials for components used in optical circuits and modules, and are superior to those of conventional nonfluorinated polyimides, such as Kapton Nonfluorinated polyimides have high water absorption of about 2-3 wt%, which causes optical loss at the wavelengths of optical communication

EXPERIMENTAL

Materials. A fluorinated polyimide, PMDA/TFDB (Figure 2), synthesized from pyromellitic dianhydride and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl is used in this study The preparation of poly(amic acid), the precursor of the polyimide, has been described elsewhere (*14*) Films of poly(amic acid) were prepared by spin-coating N,N-dimethylacetamide solution (15 wt%, 450 poise) onto a 4-inch silicon wafer and drying then in nitrogen at 70°C for 1 h The solvent content of the films determined from the weight difference before and after curing was 23 8 wt% Small signals that can be assigned to the polyimide structure were observed in the ^{13}C NMR spectrum of the poly(amic acid) films dissolved in dimethylsulfoxide-d_6, even though the polyimide content was less than 5%

Measurements. The retardation of polyimide films was directly measured by the parallel-Nicole rotation method at 1 55 μm, the wavelength used for long-distance optical communications An Advantest TQ8143 laser diode was used as light source, and a Newport Model-835 as optical power-meter The polarizers were Glan-Thompson prisms from Sigma-Koki corporation Thickness (d) was measured from the interference fringe observed in the near-infrared absorption spectra The retardation and thickness were measured at the center of the films In-plane birefringence (Δn) was calculated by dividing retardation by thickness The largest and the smallest in-plane refractive index (n_{TE1} and n_{TE2}), and the out-of-plane refractive index (n_{TM}) at 1 523 μm were measured by sample rotation using a Metricon PC-2000 refractometer The Δn and the difference between n_{TE1} and n_{TE2} agree within the experimental error (±0 0005) Thermomechanical analysis (TMA) was conducted using a Sinku-Riko TM-7000 analyzer, in which specimen dimensions were 5 mm wide and 15 mm long Average thicknesses of poly(amic acid) and polyimide films were 23 μm and 16 μm, respectively

RESULTS AND DISCUSSION

Methods for Generating In-plane Birefringence. In order to control the in-plane birefringence (Δn) of fluorinated polyimide, we should examine the molecular structure, drawing methods, and curing conditions, because the Δn is determined by the polarizability anisotropy of the repeat unit and the degree of molecular orientation The PMDA/TFDB polyimide used in this study has a rod-like structure accompanied by a large polarizability anisotropy This seems advantageous for generating a large in-plane birefringence by uniaxial drawing This polyimide has a small thermal expansion coefficient of -5 x 10^{-6}°C^{-1}, which reveals the rigidity of the molecular structure

Use of Anisotropic Substrates (Method 1). Figure 3 shows three methods of

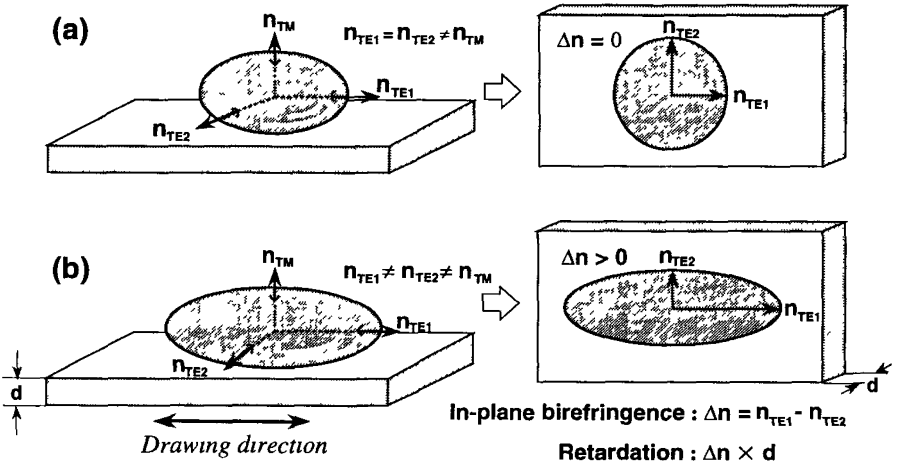
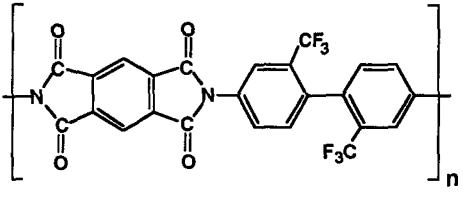


Figure 1 Schematic representation of refractive index ellipsoids of (a) polyimide prepared on isotropic substrates and (b) uniaxially drawn polyimide



PMDA / TFDB

Figure 2 Rod-like fluorinated polyimide for uniaxial drawing

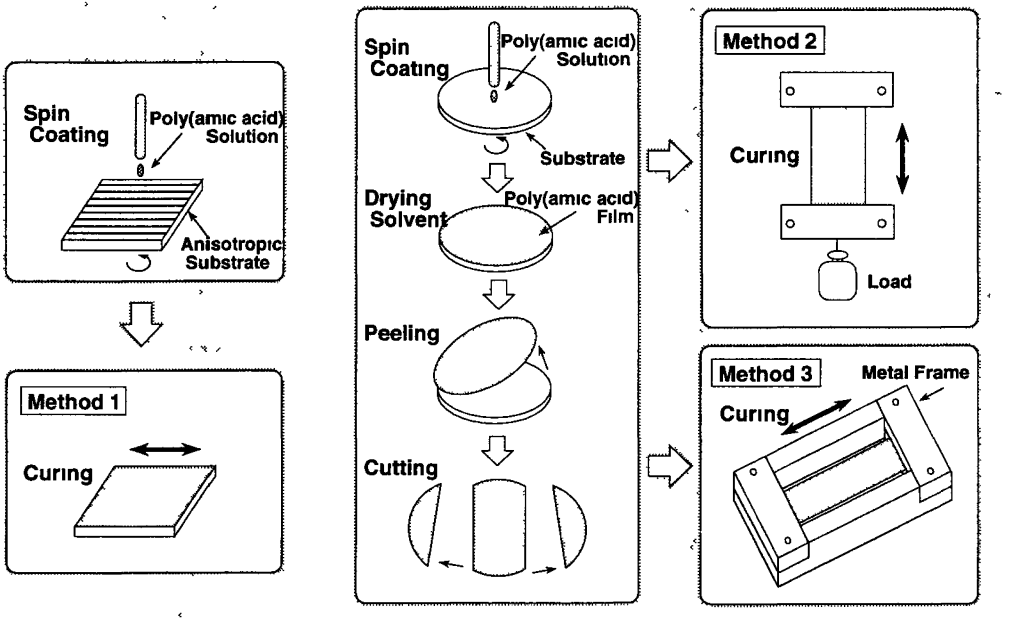


Figure 3 Methods of preparing in-plane birefringent polyimide films

preparing uniaxially drawn polyimide films Method 1 and Method 3 are newly devised for this study In Method 1, the thermal expansion anisotropy of the substrates is used as a drawing force Poly(amic acid) solution was spin-coated onto one isotropic (4-inch silicon wafer) and three anisotropic substrates (3-inch wafers of lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) and a quartz block (15x15x2 mm)) The *c*-axes of these crystal substrates were in the planes After the solvent was removed by drying, the poly(amic acid) films were heated to 350°C at 4°C/min in nitrogen, kept at 350°C for 1 h, and cooled to room temperature The anisotropy of thermal expansion coefficients ($\Delta\alpha$) of substrates and the Δn of the peeled polyimide films are listed in Table I The polyimide film cured on a silicon wafer has no birefringence in the film plane In contrast, anisotropic substrates give rise to in-plane birefringent polyimide films A larger $\Delta\alpha$ seems to generate a larger Δn from the comparison of $LiNbO_3$ and $LiTaO_3$ even though no simple relationship is observed between Δn and $\Delta\alpha$. From the refractive index measurements, the optical axis of the films with larger refractive indices (n_{TE1}) is along the crystal axis with higher thermal expansion coefficient This indicates that the polyimide molecules orient along the direction of the larger thermal expansion The Δn of the polyimides, however, are 6-10 times smaller than that for quartz, which are too small to fabricate polarization components It seems that the substrate $\Delta\alpha$ is insufficient to effectively draw the polyimide chains during curing

Drawing with a Load during Curing (Method 2). Poly(amic acid) films were uniaxially drawn during curing with constant loads in Method 2 This experiment was conducted using a thermal mechanical analyzer (TMA) The effects of final curing temperature (Tf), heating rate, and load on the in-plane birefringence (Δn) were examined As shown in Figures 4-6, the Δn are linearly proportional to Tf, heating rate, and load These relationships are useful for controlling the Δn In addition, this method gives a larger Δn, which can be controlled between 0 02 and 0 17 by changing the curing and loading conditions

Varying the final curing temperature is, in particular, effective in generating a large Δn, however, the Δn observed at Tf = 350°C and 440°C are slightly deviated from linearity The largest Δn of 0 17 is slightly smaller than that observed by Nakagawa (*11*), however the Δn does not saturate even after curing at Tf = 440°C In contrast, the variation of the heating rate does not cause a considerable change in Δn The variation of the load showed the best controllability of Δn among the three parameters Figure 7 shows the temperature profile and TMA curve measured for the films prepared under the standard condition of Method 2 (Tf 350°C, heating rate.4°C/min, load 20g) The poly(amic acid) film begins to shrink at 120°C and then to elongate at 180°C ^{13}C NMR study on the imidization process of 6FDA/TFDB polyimide synthesized from 2,2-bis(3,4,-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl which has a more flexible dianhydride structure and better solubility in polar solvents shows that imidization reaction becomes significant at 120°C and is almost complete at 180°C (*18*) After that, the film elongates at the constant rate as the temperature increased, but at a slightly higher rate above 300°C This film elongation causes the polyimide molecules to orient along the loading direction and, hence, to generate in-plane birefringence The magnitude of Δn in Method 2 can be explained in terms of the elongation after the completion of imidization As shown in Figure 8, Δn shows a linear relationship with the normalized

Table I Anisotropy of Thermal Expansion Coefficients of Substrates and In-plane Birefringence of Polyimides Prepared by Method 1

Substrate	α_c	α_a	$\Delta\alpha$	Δn
		($\times 10^{-5}$)		
Silicon	0 42	0 42	0	0 0000
$LiNbO_3$	0 75	1 54	0 79	0 0009
$LiTaO_3$	0 41	1 61	1 20	0 0011
Quartz	0 80	0 01	0 79	0 0015

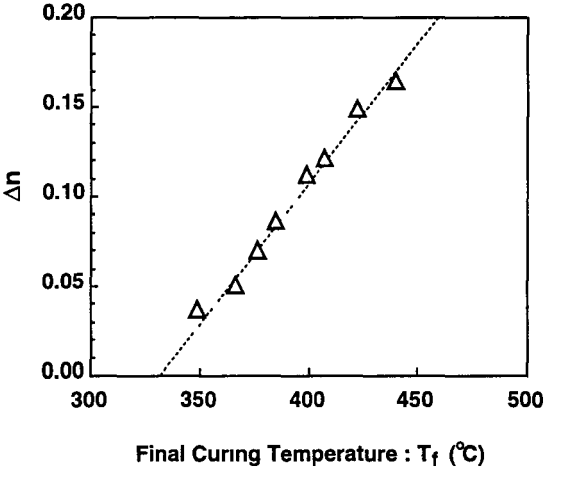


Figure 4 Final curing temperature versus in-plane birefringence of polyimide films prepared by Method 2 (heating rate 4°C/min,load 20g)

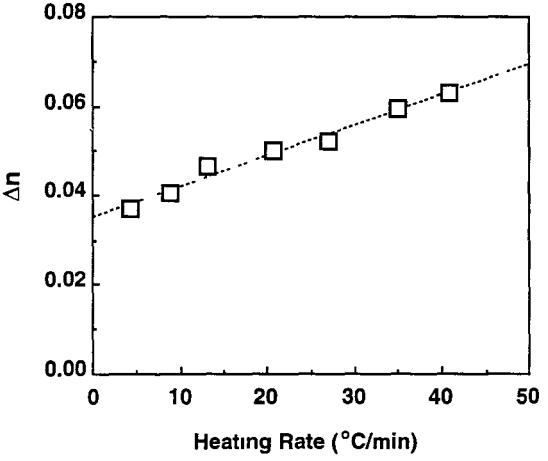


Figure 5 Heating rate versus in-plane birefringence of polyimide films prepared by Method 2 (Tf 350°C, load 20g)

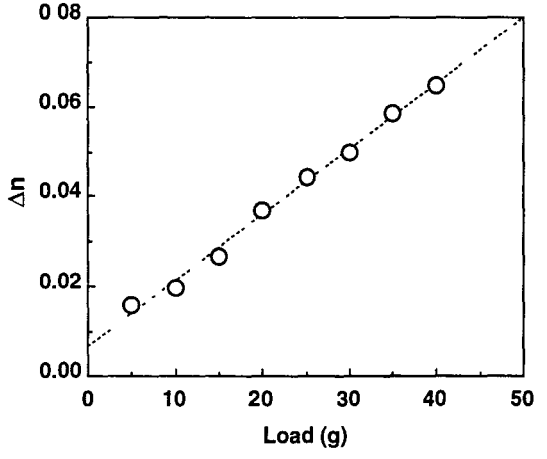


Figure 6 Load versus in-plane birefringence of polyimide films prepared by Method 2 (Tf 350°C, heating rate 4°C/min)

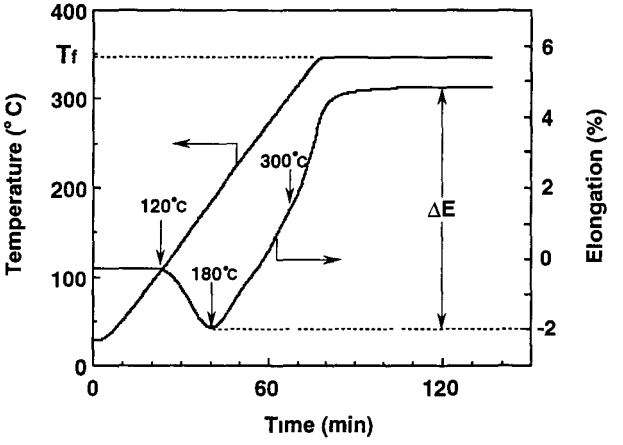


Figure 7 Temperature profile and elongation of poly(amic acid) film prepared under the standard condition of Method 2

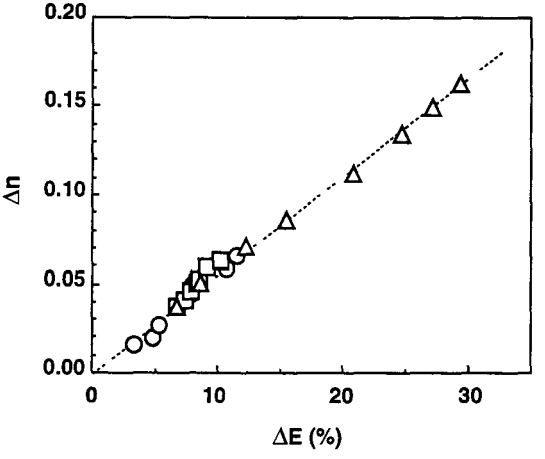


Figure 8 Normalized elongation in TMA curves, ΔE, versus in-plane birefringence of polyimide films prepared by Method 2 Symbols correspond to those in Figures 4-6

elongation (ΔE) between the most shrunken state at 180°C and the most elongated state at Tf The larger ΔE, the larger Δn This relationship is also useful for controlling the Δn

Figures 9-11 show TMA curves of polyimides prepared under the thermal and loading conditions described above Figure 9 show that curing above 350°C is much more effective in drawing films than curing below that temperature This polyimide does not exhibit any apparent glass transition in TMA measurement but molecular re-orientation is appreciably promoted above 350°C The linear relationship between Δn and Tf shown in Figure 4 is attributed to the linearity of this TMA curve between 370°C and 420°C Films cured above 420°C (Tf 422°C,440°C) showed very large Δn, however, optical defects with diameter of less than 20 μm were observed under a polarizing microscope throughout the films This may be ascribed to localized crystallization As seen in Figure 10, a high heating rate gives a larger elongation at Tf and a small shrinkage at about 180°C To obtain highly elongated polyimide film, the magnitude of shrinkage occurring between 120°C and 180°C should be small This suggests that a reaction which inhibits the orientation of polyimide molecules occurs during the imidization process The ^{13}C NMR study described above showed that depolymerization at amide-groups of poly(amic acid) occurs at around 120°C, and the molecular weight decreases considerably This low-molecular-weight polymer is converted into a high-molecular weight polyimide by subsequent curing, but this depolymerization process should inhibit the uniaxial orientation of the polymer chain This is why the fast imidization reaction under high heating rates produce large in-plane birefringence Figure 11 indicates that a heavy load gives a large elongation at Tf and a small shrinkage at about 180°C This relationship agrees well with that of Figure 10

All the films prepared by the above methods were pale yellow, tough, and flexible However, the polyimide film prepared at a heating rate of 2°C/min was cut during the heating at 190°C At 190°C, the film was at the most shrunken state with no ΔE This film cooled to room temperature was brittle and had no in-plane birefringence This result coincides with the linear relationship between ΔE and Δn (Figure 8) The onset of depolymerization at about 120°C should considerably decrease the tensile strength of the film

Fix in a Metal Frame during Curing (Method 3). In Method 3, the poly(amic acid) film was peeled from the substrate, two of its sides were cut off, and it was fixed in a brass frame by the other sides The film was then heated to 350°C at 4°C/min As the temperature increased, polymer chains seemed to orient along the fixed direction as the result of the tensile stress arising from the shrinkage of the polymer film and evaporation of the solvent It is worthwhile to note that the polyimide film elongated about 6 % after the curing compared to the poly(amic acid) film along the fixed direction This indicates that polyimide film spontaneously elongates even after the drawing force has disappeared The values of Δn, n_{TE1}, n_{TE2}, and n_{TM} for the film 55 mm long and 60 mm wide were 0 053, 1 638, 1 585, and 1 484 respectively The n_{TE1} and n_{TE2} were observed to be parallel and perpendicular to the fixed direction, respectively Comparing with the n_{TE} (1 612) and n_{TM} (1 484) of the film prepared on a silicon wafer, the n_{TM} does not show any difference between in-plane birefringent and non-birefringent films Uniaxial drawing of polyimide films only causes optical anisotropy in the film plane Considering the thermal expansion of the brass frame, the

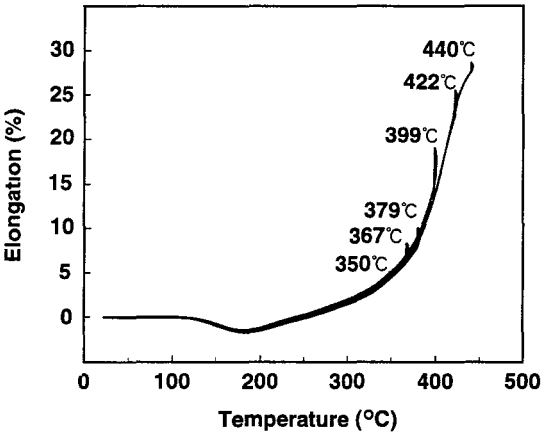


Figure 9 TMA curves with different final curing temperatures in Method 2 (heating rate 4°C/min, load 20g)

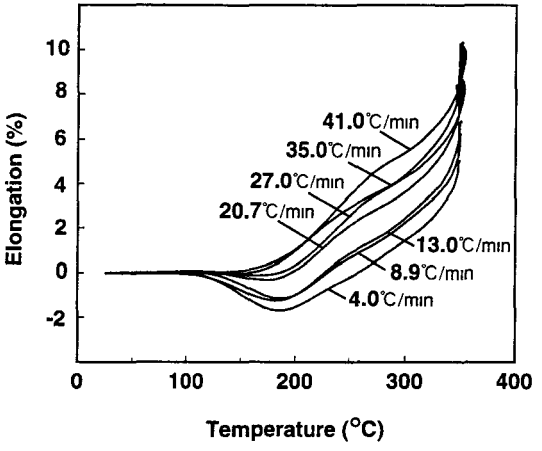


Figure 10 TMA curves with different heating rates in Method 2 (Tf 350°C, load 20g)

poly(amic acid) film is prevented from shrinking and is forced to elongate about 0 1% between 120°C and 180°C This condition is similar to the TMA behavior that was measured for the film cured at 27 0°C/min in Method 2 As seen in Figure 10, the length of this film is constant below 180°C, and it starts to elongate above that temperature The Δn and ΔE were 0 052 and 7%, respectively which coincide with the Δn (0 053) and ΔE (6%) obtained for Method 3

Fabrication of a Half-Waveplate at 1.55 μm. The Δn of 0 053 obtained in Method 3 is large enough to fabricate a thin half-waveplate at the wavelengths of optical communication Since retardation is the product of the thickness and in-plane birefringence, precise control of retardation requires control of film thickness It is well-known that the thickness of polyimide film can be controlled by changing the spinning speed of the poly(amic acid) solutions As shown in Figure 12, the retardation of the polyimide films is linearly proportional to the spinning speed and the thickness This indicates that Δn of polyimides prepared by Method 3 show a constant Δn of 0 053 for different thicknesses From this figure, the spinning speed for producing a half wavelength retardation at 1 55 μm should be 570 rpm 1 55 μm is the wavelength used in current long-distance optical communication systems The retardation of a film thus obtained was 0 772, which indicates that the retardation of polyimide films can be controlled with an error of less than 1% In addition, this half-waveplate was only 14 5 μm thick, which is 6 3 times as thin as a quartz waveplate This will considerably decrease excess loss caused by inserting a waveplate into a waveguide An attempt to use this polyimide waveplate as a TE/TM polarization mode converter in silica-based planer lightwave circuits is under way (*19*) Polyimide waveplates are tough and flexible and have superior processability and tractability to inorganic crystals Polyimides are easily cut by scissors and do not wrinkle even after being folded double

Thermal Stability of Retardation. Retardation of waveplates must have sufficient thermal stability, in order to be compatible with high performance optical circuits and modules We examined the effect of thermal treatment by annealing the polyimide waveplates at 250°C, 300°C, 350°C, 380°C, and 400°C for 1 hour As shown in Figure 13, the retardation does not change below 350°C, the final curing temperature of the polyimide waveplates Above 350°C, the retardation increases with annealing, suggesting that self-orientation of polyimide molecules takes place This agrees well with the spontaneous elongation observed for Method 3 A similar phenomenon has been observed by Cheng et al (*20*)

CONCLUSIONS

Fluorinated polyimide that has a rod-like structure (PMDA/TFDB) can be used as an in-plane birefringent optical material with good flexibility, thickness controllability, and large birefringence In order to generate and control the in-plane birefringence (Δn) and/or retardation of the polyimide films, three methods of uniaxial drawing were investigated Polyimide films cured on anisotropic substrates show very small Δn The Δn of the polyimides cured with constant loads were linearly proportional to the final curing temperature, the heating rate, and the load The polyimides fixed in a metal

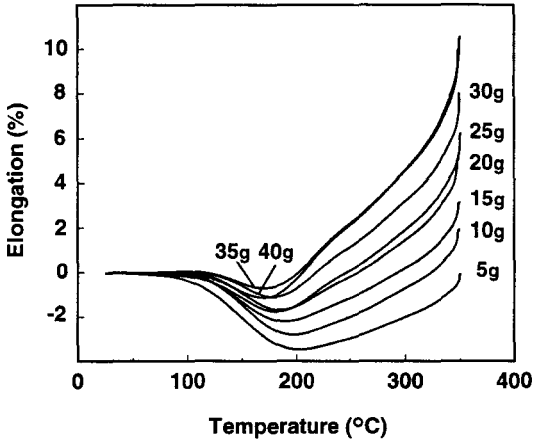


Figure 11 TMA curves with different loads in Method 2 (Tf 350°C, heating rate 4°C/min)

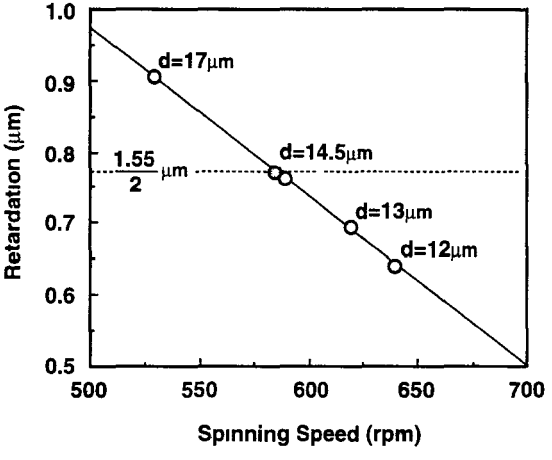


Figure 12 Retardation and thickness of polyimide films versus speed of spin-coating in Method 3

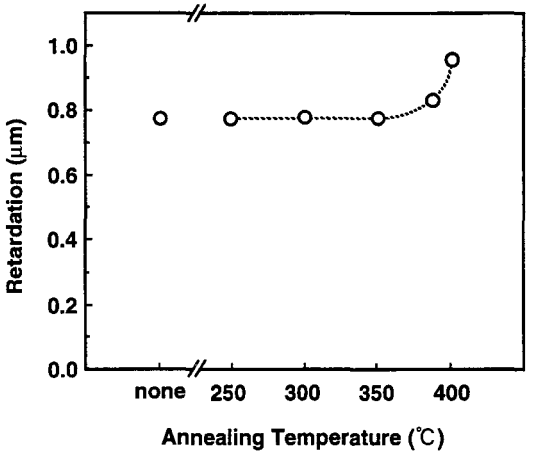


Figure 13 Retardation of a polyimide half-waveplate after annealing for 1h at various temperatures

frame had the same Δn for different thicknesses As a result, the Δn of this fluorinated polyimide can be controlled between 0 02 and 0 17, and the retardation can be controlled to within 1% The retardation of these polyimide films is retained after annealing at 350°C for 1 hour

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