Control of thermo-optic coefficients and their polarization dependence in polyimide films formed on Si substrates

Yoshiharu Terui and Shinji Ando*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology
Ookayama 2-12-1-S1-21, Meguro-ku, Tokyo 152-8552, JAPAN

ABSTRACT

Thermo-optic coefficients dn/dT for TE- and TM-polarized lights (dn_{TE}/dT and dn_{TM}/dT, respectively) were measured for aromatic polyimide (PI) films formed on Si Substrates. The values of dn/dT for the average refractive index (dn_{av}/dT) is in a range of −52 ~ −87 ppm/K, and amorphous PI films with large n_{av} have large $|dn_{av}/dT|$, which is well accounted by the temperature derivative of the Lorenz-Lorenz equation. On the other hand, the absolute values of dn_{TE}/dT were significantly larger than those for dn_{TM}/dT even for the PI films with very small polarization dependence in refractive index (Δn; in-plane/out-of-plane birefringence). This result can not be explained by the temperature derivative of the Vuks equation, which represents that the large polarization dependence in dn/dT is caused by the large Δn. Polarization dependence in dn/dT for the PI films with small Δn is caused by the temperature dependence in large stress birefringence. Based on these results, large thermal expansion and small stress birefringence (small residual stress or small polarization anisotropy) is essential for achieving large $|dn_{av}/dT|$ and small polarization dependence in dn/dT. To demonstrate this assumption, dn/dT measurements were carried out for PI films derived from a fluorine-containing dianhydride and aliphatic diamines, which exhibit loose chain packing and small polarizability anisotropy. As a result, these PI films exhibit small polarization dependence in dn/dT, and relatively large dn_{av}/dT compared to the aromatic PI films with almost the same n_{av}.

Keywords: Fluorinated polyimides, Thermo-optic coefficient, Polarization dependence, Waveguide, Residual stress

1. INTRODUCTION

Thermo-optic (TO) effect (i.e. thermally induced change in refractive index) attracts many attentions since the TO effect can be used to construct many types of active optical waveguide components However, TO coefficient (dn/dT; temperature gradient of refractive index) of silica[1] is small (ca. +10 ppm/K), therefore TO switches fabricated of silica-based waveguide materials require large driving power. On the other hand, dn/dT for polymeric materials[2,3] are one order of magnitude larger (~ -10^2 ppm/K) than those for inorganic glasses. Since large $|dn/dT|$ ensures small driving power and high speed response, polymeric waveguide materials are good candidate for the optical components utilizing TO effect. These active components must endure rapid and large temperature change in their use, therefore waveguide materials must have high thermal stability. In this point of view, fluorine-containing polyimides (FPIs) have the favorable properties[4-6] such as small optical loss in visible to near IR regions, high glass transition temperature, and small moisture sorption.

Optical waveguide components are generally fabricated on the Si substrates, hence, the values of dn/dT for polymer films on the Si substrates are essential properties in the designs and the fabrications of active waveguide components utilizing the TO effect. However, the reported values of dn/dT for polymer films s are limited for those having low thermal stabilities.[7,8] Although we have reported passive properties of FPIs and FPI-based optical components such as single-mode waveguides,[9] waveplates,[10-12] and polarizers,[13,14] we have not studied thermo-optic coefficients of FPI films. Recently, we reported dn/dT for thermally stable aromatic PI films formed on Si substrates.[15] As a result of the study, significant polarization dependences in dn/dT were observed for FPI films. Polarization dependence in dn/dT will cause polarization dependence in the properties of optical components (e.g. reply time, required temperature change for operations, and crosstalk noise), hence, precise control of polarization dependence in dn/dT is very important issue. In

---

*Corresponding author, e-mail: sando@polymer.titech.ac.jp this study, we investigated the origins of polarization dependence in dn/dT observed in thermally stable FPI films, and performed the control of TO coefficients and their polarization dependence.

2. EXPERIMENTAL

2.1 Preparations of polymer films

All PI films (thickness: 8 – 11 μm) were prepared by thermal imidization of their precursor, poly(amic acid) (PAA) for aromatic PIs and poly(amic acid trimethylsilyl ester) (PASE) for semi-aliphatic PIs in this study. PAA solutions were prepared by polycondensation of equimolar dianhydrides and diamines in *N*,*N*-dimethylacetamide (DMAc). PASE solutions were prepared from equimolar dianhydrides and diamines using *in situ* silylation method[16] in DMAc. Precursor solutions were spin-coated onto 3-inch silicon wafers (coated with adhesion promoter), followed by drying at 70°C for 30 min and thus thermal imidization at 350°C for 1 h under nitrogen flow. The heating rate was 5°C/min. Poly(methyl methacrylate) (PMMA) film was prepared by spin-coating of the toluene solution of PMMA. Spin-coated PMMA solution was dried at 40°C/20 min, 65°C/20 min, and 80°C/20min in a convection oven, followed by annealing at 120°C under reduced pressure.

2.2 Variable temperature measurement of refractive index

A prism coupler (Metricon, model PC-2000) equipped with a home-built temperature controlling apparatus was used for the refractive index measurements at elevated temperatures. The temperature controlling apparatus is shown in Fig. 1. Measurement system is heated by the ceramic heaters (100V / 1A, 10 × 20 mm) glued on the prism cramp and a supporting 4-inch silicon substrate. The temperature was controlled by adjustable voltage. Conductive silver paste was used as an adhesive between the supporting substrate and the sample substrate to achieve good thermal contact. Sample temperature was monitored by a K-type thermocouple glued on the prism with a small amount of silver paste. A laser beam ($\lambda = 1.32$ μm) with TE and TM polarization was used for the measurements. The refractive index of the prism (gallium gadolinium garnet) at each temperature was calculated using the values[17] of $n_{\mathrm{prism}} = 1.939$ at 25°C and $dn_{\mathrm{prism}}/dT = +17.2$ ppm/K at a wavelength of 1.32 μm. In order to avoid the effect of moisture sorption, all measurements were proceeded on the cooling cycle from 85°C to 35°C on a dried atmosphere (~20 % relative humidity).

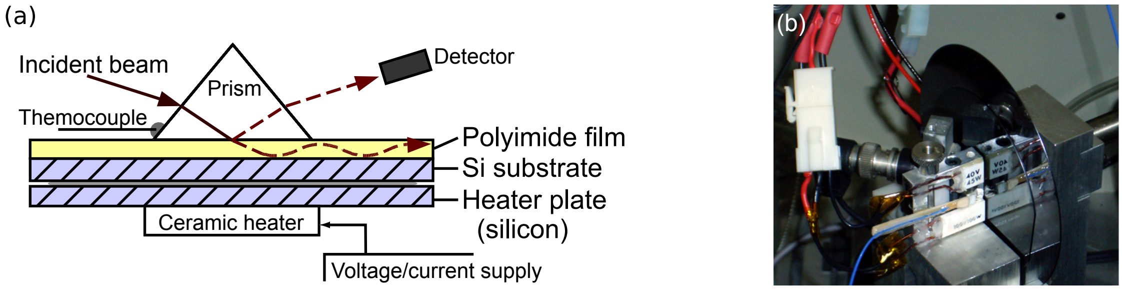


Fig. 1. (a) Schematic and (b) photograph of measurement system of refractive index with temperature controlling apparatus.

2.3 Measurement of residual stress

Residual stress σ on the films formed on Si substrates were calculated from the curvature of the samples R using the relationship[18] expressed as follows:

$$\sigma = \frac{E_s}{6(1-\nu_s)}\frac{t_s^{\,2}}{t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right) \qquad (1)$$

where E_s, ν_s, t_s, t_f, and R_0 represent the Young' moduli, the Poison's ratio, thickness of the substrates (380 μm), thickness of the polymer films, and initial curvature of the substrates without films, respectively. The value of $E_s/(1-\nu_s)$ is 30087 MPa for the Si substrates. Curvature R of the samples were measured using a depth profiler (Veeco Instruments, Dektak 3), and $1/R_0$ was considered as zero since the surfaces of the Si substrates were flat and $1/R_0$ is negligibly small compared to $1/R$.

2.4 Measurement of stress-optical coefficients

The values of stress-optical coefficients were evaluated from the relationship between the applied stress and retardation with a series of incident beam angles. Length, width, and thickness of the samples (without clipping area) were 50 mm, 8 mm, and 10 μm, respectively. Applied stress is limited in a range of 0.1 to 5 MPa to prevent the irreversible deformations of the samples.

Glass transition temperatures of polyimides were evaluated using the differential scanning calorimeter (Seiko Instruments, Inc., SSC/5200 DSC 220) with a heating rate of 20°C/min. Thermal stabilities of polyimides were evaluated using thermogravimetric analyzer (Shimadzu Corporation, TGA-50) with a heating rate of 10°C/min under nitrogen.

3. RESULTS

3.1 Thermo-optic coefficients and their polarization dependence for polyimide films

Experimental values of refractive indices (n_{av}), in-plane/out-of-plane birefringence (Δn), residual stress (σ), and thermo-optic properties for seven kinds of aromatic PI (Fig. 2) films are shown in Table 1. The values of n_{av} and Δn are consistent with those previously reported for these PI films.[19] Seven kinds of PI films distinctively differ in their optical properties, especially in Δn. The films of PI **1**–**3** exhibit large Δn, whereas PI **4**–**7** exhibit very small Δn, which reflects the difference in the degrees of chain orientations. It is noted that the value of dn_{av}/dT for PMMA film in this study is smaller than that reported previously.[8] The large value of dn/dT in previous study may be caused by the sorption of moisture during temperature changes.[15,20,21]

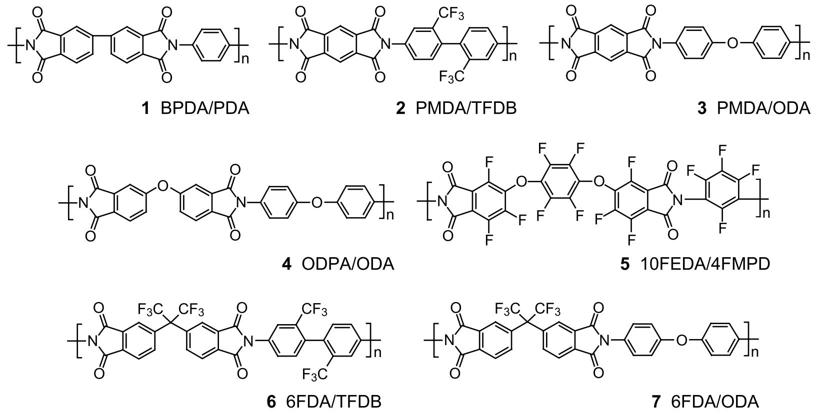


Fig. 2. Molecular structures of aromatic polyimides used in this study.

At first, we investigate the relationship between the molecular structures and dn/dT for average refractive indices (dn_{av}/dT). Theoretically, dn_{av}/dT is related to the n_{av} and volume expansion coefficient β as follows:

$$\frac{dn_{av}}{dT} = -\frac{\left(n_{av}{}^2 - 1\right)\left(n_{av}{}^2 + 2\right)}{6n_{av}}\beta . \tag{2}$$

According to Eq. 2, large $|dn_{av}/dT|$ is achieved by high n_{av} or large β. As shown in Fig 3, dn_{av}/dT for amorphous PI films were closely related to n_{av} although film of PI **1** (BPDA/PDA), which PI readily forms crystalline or ordered phase, did not exhibit large $|dn_{av}/dT|$ despite the large n_{av}. The small dn_{av}/dT for PI **1** originated from the small volume expansion coefficient β.[22] Compared to the other optical polymers, dn_{av}/dT for PI films were not large (e.g. $dn_{av}/dT = -88$ ppm/K for PMMA) despite the large n_{av} of aromatic PIs. According to Eq. 2, this result represents that the thermal

Table 1. Average refractive index (n_{av}), in-plane/out-of-plane birefringence (Δn), in-plane, out-of-plane, average thermo-optic coefficients (dn_{TE}/dT, dn_{TM}/dT, and dn_{av}/dT, respectively), polarization dependence in thermo-optic coefficients ($d(\Delta n)/dT$), and residual stress (σ) of polymer films formed on Si substrates. Optical properties were measured at 36.6°C under dried (~20% relative humidity) atmosphere.

polymer	n_{av} [a]	Δn [b]	dn_{TE}/dT [ppm/K]	dn_{TM}/dT [ppm/K]	dn_{av}/dT [ppm/K]	$d(\Delta n)/dT$ [c] [ppm/K]	σ [d] [MPa]
1 BPDA/PDA	1.7191	0.1874	−99	−60	−87	−39	−13.4
2 PMDA/TFDB	1.5691	0.1151	−87	−78	−84	−9	−21.5
3 PMDA/ODA	1.6469	0.0693	−99	−59	−86	−40	23.4
4 ODPA/ODA	1.6425	0.0099	−88	−53	−76	−34	42.8
5 10FEDA/4FMPD	1.5221	0.0074	−72	−48	−64	−24	60.0
6 6FDA/TFDB	1.5180	0.0076	−57	−41	−52	−16	53.2
7 6FDA/ODA	1.5604	0.0074	−76	−57	−70	−20	47.8
PMMA	1.4782	−0.0003	−87	−89	−88	2	~ 0

[a] $n_{av}^2 = 2\, n_{TE}^2 + n_{TM}^2$, [b] $\Delta n = n_{TE} - n_{TM}$, [c] $d(\Delta n)/dT = dn_{TE}/dT - dn_{TM}/dT$, [d] positve σ represents expansion stress.

expansion β is small for aromatic PIs, which caused by rigid structures of aromatic PIs and strong intermolecular interactions derived from the imide structures.

On the other hand, polarization dependence in dn/dT of a medium without CTE anisotropy can be expressed from the temperature derivative of the Vuks equation[23] as follows:

$$\frac{dn_{TE}}{dT} - \frac{dn_{TM}}{dT} = \frac{d(\Delta n)}{dT} = \frac{n_{av}}{n_{av}^2 - 1}\left(1 + \frac{1}{n_{TE}\, n_{TM}}\right)\frac{dn_{av}}{dT}. \qquad (3)$$

According to Eq. 3, polarization dependence in dn/dT does not exist for PI films without Δn (e.g. PMMA film). However, all PI films virtually exhibit significant polarization dependence in dn/dT as shown in Fig. 4. It is noted that the PI films with very small Δn (PI **4**–**7**) exhibit polarization dependence in dn/dT in the same degree as highly oriented PI films (PI **1**–**3**). Regarding the PI **4**–**7**, the degrees of chain orientation are very small, hence the anisotropy in CTE should be very small. However, PMMA film, which also exhibits very small degree of chain orientation, does not shows polarization dependence in dn/dT. Most important difference between the films of PMMA and PI **4**–**7** is the magnitude of residual stress. Since the PI films have large moduli and large CTE mismatch to Si substrates, large expansion stress (and its temperature dependence) remains in the films of PI **4**–**7** (see Table 1). Moreover, the residual stress decreases with increasing temperature,[24] hence, stress birefringence exhibits large temperature dependence. This

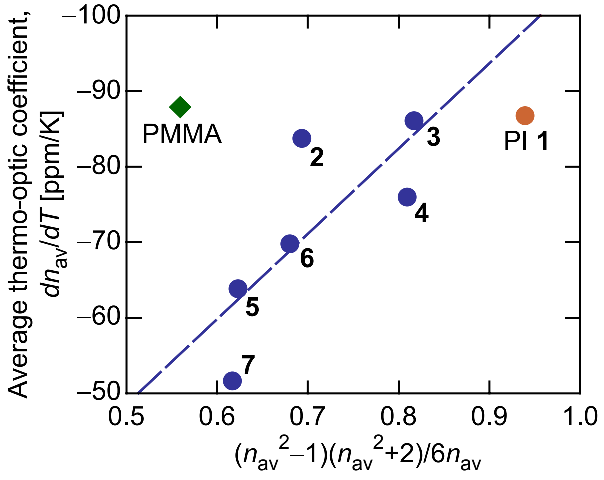


Fig. 3. Relationship between the average refractive index n_{av} and average thermo-optic coefficient dn_{av}/dT. The numbers in the figure correspond to those in Fig. 2.

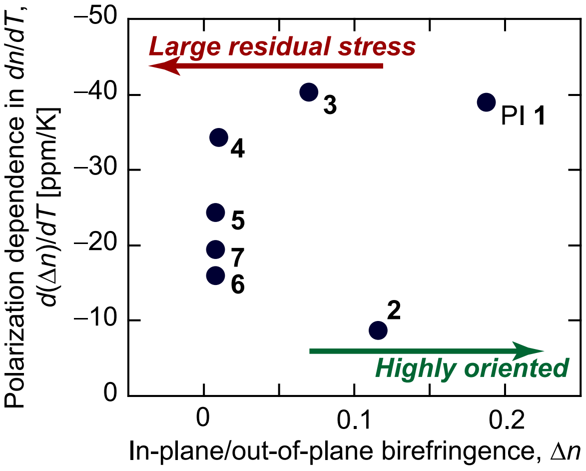


Fig. 4. Relationship between the in-palne/out-of-plane birefringence Δn and polarization dependence in thermo-optic coefficient $d(\Delta n)/dT$.

means that temperature change in n_{TE} is larger than that of n_{TM}.[25] To investigate how much the temperature dependence in stress birefringence affects on $d(\Delta n)/dT$ in the films of PI **4**–**7**, we calculate the value of $d(\Delta n)/dT$ derived from residual stress. The relationship between the residual stress σ and $d(\Delta n)/dT$ is expressed as follows:

$$\left.\frac{d(\Delta n)}{dT}\right|_{residual\,stress} = C_{\mathrm{G}}'\cdot\frac{d\sigma}{dT} \approx C_{\mathrm{G}}'\cdot\frac{\sigma}{\Delta T} \qquad (4)$$

where C_{G}' is the biaxial in-plane/out-of-plane stress-optical coefficient and ΔT is the difference between the room temperature and the glass transition temperature T_{g} (or imidization temperature T_{i} in case that $T_{\mathrm{g}} > T_{\mathrm{i}}$). Using the experimental value of C_{G}' for PI **7** (ca. 120 ppm/MPa), $d(\Delta n)/dT$ derived from residual stress is calculated as −20 ppm/K for PI **7**, which is very close to the experimental value of $d(\Delta n)/dT$. Therefore, we conclude that the temperature dependence in residual stress is the main origin of $d(\Delta n)/dT$ in the films of polyimides for light waveguide applications.

3.2 Control of polarization dependence in TO coefficients

As mentioned in the section 1, there exist many applications of thermo-optic effect on active waveguide components. Large $|dn_{\mathrm{av}}/dT|$ and negligibly small $d(\Delta n)/dT$ are desired for the waveguide materials to high speed responses, low power consumptions, and low crosstalk in those applications. Based on the investigations in section 3.1, we can introduce some strategies to achieve large $|dn_{\mathrm{av}}/dT|$ and small $d(\Delta n)/dT$. At first, we consider the strategy for achieving large $|dn_{\mathrm{av}}/dT|$. According to Eq. 2, large $|dn_{\mathrm{av}}/dT|$ is achieved in PIs with high n_{av} and large β. In fact, amorphous PIs having high n_{av} exhibited large $|dn_{\mathrm{av}}/dT|$ as shown in Fig. 3. However, it is difficult to obtain PIs having higher n_{av} than those shown in Table 1 since aromatic moiety is one of the most polarizable molecular structures available in organic polymers. Moreover, fluorine atoms are frequently introduced in the molecular structures of polymeric waveguide materials to reduce optical loss, which causes decrease in n_{av}. Therefore, to enlarge β is more available way to increase $|dn_{\mathrm{av}}/dT|$. In the case of aromatic PIs, β will become large by the hindrance of intermolecular interaction and the reduction of rigidity of main chains of PIs.

Next, we consider the strategy for achieving small $d(\Delta n)/dT$. As mentioned in the previous section, temperature dependence of stress birefringence is the origin of $d(\Delta n)/dT$ in waveguide PI films. Since the temperature dependence of σ is caused by the mismatch in CTE between the films and substrates, $d\sigma/dT$ can be expressed as follows:

$$\frac{d\sigma}{dT} = \left(\alpha_{\mathrm{f}} - \alpha_{\mathrm{s}}\right)\frac{E_{\mathrm{f}}}{1-\nu_{\mathrm{f}}} \qquad (5)$$

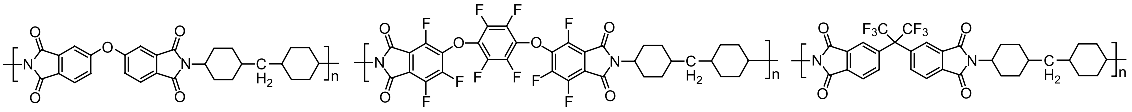
where α_{f} and α_{s} represent in-plane CTE of polymer films and substrates, respectively. According to Eqs. 4 and 5, there are three approaches to reduce $d(\Delta n)/dT$; (a) reduce the CTE mismatch between the substrate and the PI, (b) reduce the stress-optical coefficient C_{G}', and (c) reduce the modulus of PI film. However, it is difficult to reduce CTE mismatch on waveguide PI films. Although large degree of chain orientation is needed for matching of CTE between the Si substrates and PI films,[18] chain orientation generally causes polarization dependence in optical properties of PI films. On the other hand, small anisotropy in polarizability will bring small stress-optical coefficients,[26] hence, introduction of flexible and little-planer molecular structure is effective to reduce C_{G}' of PIs. Moreover, flexible structure will hinder the intermolecular interactions, thus modulus of PI will also be reduced by the introduction of flexible structures.

In order to achieve large $|dn_{\mathrm{av}}/dT|$ and small $d(\mathrm{D}n)/dT$, we examined the use of alicyclic diamines, 4,4'-methylenebis(cyclohexylamine) (DCHM). Since the molecular structure of DCHM has flexible methylene (–CH2–) linkage and much kinked cyclohexane moieties, the use of DCHM will reduce intermolecular interactions by the hindrance of dense molecular packing. Further, replacement of benzene rings by cyclohexane structures will reduce C_{G}' since benzene ring exhibits large anisotropy in polarizability. Although aliphatic diamines are generally difficult to prepare high molecular-weight PAA solutions, we can obtain good semi-aliphatic PI films from thermal imidization of PASE solution using *in situ* silylation method. Molecular structures of semi-aliphatic PIs used in this study are shown in Fig. 4. All semi-aliphatic PI films are transparent without any cracks.

Table 2. The values of n_{av}, Δn, dn_{TE}/dT, dn_{TM}/dT, dn_{av}/dT, $d(\Delta n)/dT$, and residual stress σ of semi-aliphatic polyimide films formed on Si substrates. Optical properties were measured at 36.6°C under dried atmosphere (~20% relative humidity).

polymer	n_{av} [a]	Δn [b]	dn_{TE}/dT [ppm/K]	dn_{TM}/dT [ppm/K]	dn_{av}/dT [ppm/K]	$d(\Delta n)/dT$ [c] [ppm/K]	σ [d] [MPa]
8 ODPA/DCHM	1.5709	0.0042	−92	−74	−86	−18	19.4
9 10FEDA/DCHM	1.5182	0.0056	−83	−64	−77	−19	31.7
10 6FDA/DCHM	1.5079	0.0028	−73	−64	−70	−9	37.8

[a] $n_{av}^2 = 2\, n_{TE}^2 + n_{TM}^2$, [b] $\Delta n = n_{TE} - n_{TM}$, [c] $d(\Delta n)/dT = dn_{TE}/dT - dn_{TM}/dT$, [d] positve σ represents expansion stress.



8 ODPA/DCHM **9** 10FEDA/DCHM **10** 6FDA/DCHM

Fig. 5. Molecular structures of semi-aliphatic polyimides used in this study.

As shown in Table 2, all semi-aliphatic PI films exhibited very low n_{av}, which shopuld bring small Rayleigh scattering loss. Moreover, these PI films exhibited smaller Δn than the aromatic FPI films because of low linearity of molecular structures and small residual stress. Thermo-optic properties of the semi-aliphatic PIs also differed significantly from the aromatic PIs using the same dianhydrides. The semi-aliphatic PIs exhibited relatively large $|dn_{av}/dT|$ despite the small n_{av}, which represents that the thermal volume expansion β for the semi-aliphatic PIs are significantly large compared to those for the aromatic PIs. In addition, $d(\Delta n)/dT$ for the semi-aliphatic PIs were smaller than those for aromatic PIs. It is noted that the residual stress on the semi-aliphatic PIs were much smaller than those on the amorphous aromatic PIs even though the large β should cause large CTE mismatch. This result shows that the moduli of the semi-aliphatic PIs are much smaller than those of the aromatic PIs.

To evaluate the effect of the introductions of the alicyclic diamine on the properties of optical components, calculated values of required temperature change (t_r) for 0.3% decrease in n_{TE} or n_{TM} (i.e. required temperature change to turn off the TO switch with a relative refractive index difference of 0.3%) are shown in Fig. 6. Since $|dn/dT|$ for the semi-aliphatic PIs are larger than those for the aromatic PIs despite the small refractive indices, t_r^{TE} and t_r^{TM} for the semi-aliphatic PIs are significantly smaller than those for the aromatic PIs. Furthermore, polarization dependence in t_r are reduced by the use of DCHM, which is obtained by large $|dn_{av}/dT|$ and small $d(\Delta n)/dT$. In paticular, PI **10** (6FDA/DCHM) exhibits very small polarization dependence in t_r.

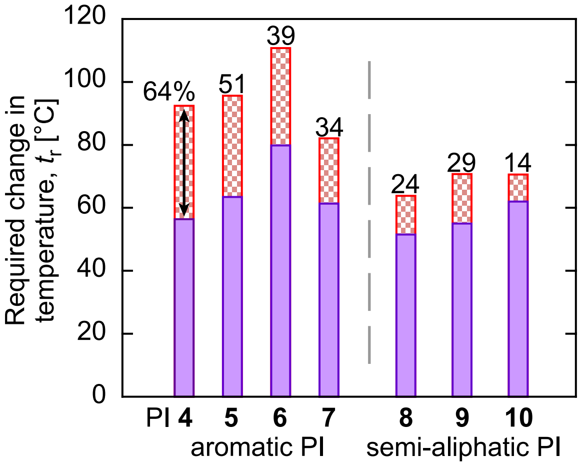


Fig. 6 Polarization dependence in the calculated values of required temperature changes t_r for 0.3% decreases in refractive indices. Filled (blue) bars and hashed (red) bars represent the values of t_r for TE- and TM-polarized light, respectively. Numbers placed above the bars represent the excess of t_r^{TM} compared to t_r^{TE}.

Thermal properties are also important for waveguide materials utilizing TO effect. The values of glass transition temperatures (T_g) for the semi-aliphatic PIs were above 200°C, which are smaller than those for aromatic FPIs[12] (323°C and 304°C for PI 6 and 7, respectively). The use of flexible and kinked DCHM causes reduction of the intermolecular interactions. Since the values of t_r for the semi-aliphatic PIs are smaller than those for the aromatic PIs, relatively low T_g will not make a severe problem for practical use. On the other hand, the values of thermal decomposition temperautre (T_d^5; temperature at which the thermal decomposition loss of the sample weight reaches 5%) is above 390°C, hence, the semi-aliphatic PIs should endure reperating temeprature changes in active waveguide components.

4. CONCLUSIONS

In the former part of the paper, we investigated the molecular structure dependence of thermo-optic coefficients dn/dT and the origins of their polarization dependence using the experimental data for the aromatic PIs. As shown in Fig. 3, amorphous PIs with high n_{av} exhibited large average thermo-optic coefficient dn_{av}/dT. However, all PI did not exhibited larger $|\ dn_{av}/dT\ |$ than PMMA, which reflects the PIs' small thermal volume expansion β derived from strong intermolecular interactions. On the other hand the amorphous PI films having very small Δn exhibited significant $d(\Delta n)/dT$ in the same order as the highly oriented PI films. The large $d(\Delta n)/dT$ for un-oriented PI films were caused by the temeprature dependence of residual stress (see Eqs. 4 and 5).

Based on the relations between the molecular structures and the thermo-optic properties of the PI films, we proposed some strategies for obtaining large $|dn_{av}/dT|$ and small $d(\Delta n)/dT$. Since the increase in n_{av} is difficult for aromatic PIs, increase β by the introduction of flexible and kinked structure was chosen to enlarge $|dn_{av}/dT|$. On the other hand, there are three approaches to achieve small $d(\Delta n)/dT$; (a) small CTE mismatch between the substrates and the PIs, (b) small C_G', and (c) small modulus of PI film. In this study, we used alicyclic diamine DCHM to realize (b) and (c). Resultant semi-aliphatic PIs exhibited cleary large $|dn_{av}/dT|$ and small $d(\Delta n)/dT$ compared to the aromatic PIs. As shown in Fig. 6, polarization dependence of the properties of active waveguide components using semi-aliphatic PIs will be significantly reduce. Furthermore, therse semi-aliphatic PIs exibited small residual stress, high thermal stability, and acceptably high T_gs. Hence, we can conclude that the introduction of alicyclic moieties into the main chains of PIs is an effective approach to acheice favorable thermo-optic properties in polymeric waveguide materials.

REFERENCES

1. W. S. Rodney and R. J. Spindler, "Index of Refraction of Fused-quartz Glass for Ultraviolet, Visible, and Infrared Wavelength", *J. Res. Natl. Bur. Stand.*, **53**, 185-189 (1954).
2. J. M. Cariou, J. Dugas, L. Martin, and P. Michel, "Refractive-Index variations with temperature of PMMA and polycarbonate", *Appl. Opt.*. **25**, 334-336 (1986).
3. P. Michel , J. Dugas, J. M. Cariou, and L. Martin, "Thermal Variations of Refracive Index of PMMA, Polystyrene, and Poly(4-methyl-1-pentene)", *J. Macromol. Sci. Phys.*, **B25**, 379-394 (1986).
4. T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, "Polyimide derived from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl. 1. Synthesis and characterization of polyimides prepared with 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride or pyromellitic dianhydride", *Macromolecules*, **24**, 5001-5005 (1991).
5. S. Ando, T. Matsuura, and S. Sasaki, "Perfluorinated polyimide synthesis", *Macromolecules*, **25**, 5858-5860 (1992).
6. T. Matsuura, S. Ando, S. Sasaki, and F. Yamamoto, "Polyimides Derived from 2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl. 4. Optical Properties of Fluorinated Polyimides for Optoelectronic Components", *Macromolecules*, **27**, 6665-6670 (1994).
7. D. W. Smith, Jr., S. Chen, C. M. Topping, J. Jin, G. Nordin, J. Cardenes, J. Ballato, and S. Foulger, "PERFLUOROCYCLOBUTYL COPOLYMERS FOR MICROPHOTONICS: THERMO-OPTICS AND WAVE-GUIDE MICROMOLDINGS", *Polym. Prepr. (Am. Chme. Soc. Div. Polym. Chem.)*, **43**, 505 (2002).
8. E. E. Gürel, J. S. Rodgers, L. T. Seals, F. R. Williams, G. E. Williams, G. T. Warren, and Q. L. Williams, "NOVEL TECHNIQUE FOR MEASURING THE THERMO-OPTIC COEFFICIENT OF THIN POLYMER FILMS", *Polym. Prepr. (Am. Chme. Soc. Div. Polym. Chem.)*, **43**, 592-593 (2002).
9. T. Matsuura, S. Ando, S. Matsui, S. Sasaki, and F. Yamamoto, "Heat-resistant singlemode optical waveguides using fluorinated polyimides", *Electron. Lett.*, **29**, 2107-2109 (1993).
10. S. Ando, T. Sawada, and Y. Inoue, "Thin, flexible waveplate of fluorinated polyimide", *Electron. Lett.*, **29**, 2143-2144 (1993).

11. S. Ando, T. Sawada, and S. Sasaki, “A rod-like fluorinated polyimide as an in-plane birefringent optical material 2: Control of optical retardation using spontaneous molecular orientation”, *Polym. Adv. Technol.*, **10**, 169-178 (1999).
12. S. Ando, T. Sawada, and S. Sasaki, “In-plane birefringence and elongation behavior of uniaxially drawn aromatic polyimide films” , *Polym. Adv. Technol.*, **12**, 319-331 (2001).
13. T. Sawada, S. Ando, and S. Sasaki, “Optical anisotropy of uniaxially drawn and silver-dispersed polyimide films”, *Appl. Phys. Lett.*, **74**, 938-940, (1999)
14. S. Matsuda, S. Ando, and T. Sawada, “Thin flexible polariser of Ag-nanoparticle-dispersed fluorinated polyimide”, *Electron. Lett.*, **29**, 2143-2144 (2001).
15. Y. Terui and S. Ando, “Anisotropy in thermo-optic coefficients of polyimide films formned on Si substrates”, *Appl. Phys. Lett.*, **83**, 4755-4757 (2003).
16. Y. Oishi, K. Ogasawara, H. Hirahara, and K. Mori, “Synthesis of alicyclic polyimides by the silylation method”, *J. Photopolym. Sci. Technol.*, **14**, 37-40 (2001).
17. D. L. Wood and K. Nassau, “Optical properties of gadolinium gallium garnet”, *Appl. Opt.*, **29**, 3704-3707 (1990).
18. J. C. coburn, M. T. Pottiger, S. C. Noe, and S. D. Senturia, “Stress in Polyimide Coatings”, *J. Polym. Sci. Part B: Polym. Phys.*, **32**, 1271-1283 (1994).
19. S. Ando, Y. Watanabe, and T. Matsuura, “Wavelength Dependence of Refractive Indices od Polyimides in Visible to Near-IR regions”, *Jpn. J. Appl. Phys. Part 1*, **41**, 5254-5258 (2002).
20. D. P. Malladi, J. R. Scherer, S. Kint, and G. F. Bailey, “Water in polymer membranes. Part III. Water sorption and pore volume in cellulose acetate films”, *J. Membrane Sci.*. **19**, 209-231 (1983).
21. H. Franke, D. Wagner, T. Kleckers, R. Reuter, H. V. Rohitkumar, and B. A. Blech, “Measuring humidity with planar polyimide lightguides”, *Appl. Opt.*, **32**, 2927-2935 (1993).
22. J. C. coburn, M. T. Pottiger, and C. A. Pryde, “structure development in polyimide films”, *Mater. Res. Soc. Symp. Proc.*, **308** 475-487 (1993).
23. M. F. Vuks, “DETERMINATION OF THE OPTICAL ANISOTROPY OF AROMATIC MOLECULES FROM THE DOUBLE REFRACION OF CRYSTALS”, *Opt. Spectrosc.*, **20**, 361-364 (1964).
24. M. Ree, K. Kim, S. H. Woo, and H. Chung, “Structure, chain orientation, and properties in thin films of aromatic polyimides with various chain rigidities”, *J. Appl. Phys.*, **81**, 698-708 (1997).
25. M. B. J. Diemeer, “Polymeric thermo-optic space switches for optical communications”, *Opt. Mater. (Amsterdam, Neth.)*, **9**, 192-200 (1998).
26. K. Osaki, T. Inoue, E.-J. Hwan, H. Okamoto, and O. Takaguchi, “Dynamic birefringence of amorphous polymer”, *J. Non Crystal. Solid*, **172-174**, 839-849 (1994).