論文 / 著書情報
Article / Book Information

Title	Polarization Dependence of Thermo-Optic Coefficients in Polyimide Films Originating from Chain Orientation and Residual Thermal Stress
Authors	Yoshiharu TERUI, Shinji ANDO
Citation	Journal of Applied Physics, Vol. 116, Issue 5,
Pub. date	2014, 8
Note	This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. The following article appeared in Journal of Applied Physics, Vol. 116, Issue 5, and may be found at http://dx.doi.org/10.1063/1.4891998 .

Polarization dependence of thermo-optic coefficients in polyimide films originating from chain orientation and residual thermal stress

Yoshiharu Terui and Shinji Ando

Citation: [Journal of Applied Physics](#) **116**, 053524 (2014); doi: 10.1063/1.4891998

View online: <http://dx.doi.org/10.1063/1.4891998>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/116/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Morphology and chain aggregation dependence of optical gain in thermally annealed films of the conjugated polymer poly\[2-methoxy-5-\(2-ethylhexyloxy\)-p-phenylene vinylene\]](#)
J. Appl. Phys. **113**, 233509 (2013); 10.1063/1.4811532

[Anisotropy in thermo-optic coefficients of polyimide films formed on Si substrates](#)
Appl. Phys. Lett. **83**, 4755 (2003); 10.1063/1.1631744

[Measurement of the thermo-optic coefficients in sol-gel derived inorganic–organic hybrid material films](#)
Appl. Phys. Lett. **81**, 1438 (2002); 10.1063/1.1501448

[Thermal stress and glass transition of ultrathin polystyrene films](#)
Appl. Phys. Lett. **77**, 2843 (2000); 10.1063/1.1322049

[Structure, chain orientation, and properties in thin films of aromatic polyimides with various chain rigidities](#)
J. Appl. Phys. **81**, 698 (1997); 10.1063/1.364210

AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Polarization dependence of thermo-optic coefficients in polyimide films originating from chain orientation and residual thermal stress

Yoshiharu Terui and Shinji Ando^{a)}

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

(Received 11 March 2014; accepted 22 July 2014; published online 7 August 2014)

Control of polarization dependences of thermo-optic (TO) coefficients, i.e., the temperature dependence of birefringence ($d(\Delta n)/dT$), is critical issue for optical materials. Especially in active optical components like TO switches, polarization dependent behaviors are caused by $d(\Delta n)/dT$ of materials. Origins of polarization dependence of TO coefficient were investigated for seven kinds of polyimide (PI) films in terms of main chain orientation and residual thermal stress. The values of $d(\Delta n)/dT$ of PI films originated from chain orientation vary from nil to negative as the degrees of in-plane orientation increase. Magnitudes of $d(\Delta n)/dT$ depend on intrinsic birefringences, second order orientation coefficients, and their temperature dependence. On the other hand, those of $d(\Delta n)/dT$ originated from residual stress are negative for PI films exhibiting large in-plane coefficients of thermal expansion (CTE) and vary to zero as their CTE decreases due to reduced residual stress. $d(\Delta n)/dT$ originating from chain orientation decreases as the degree of chain orientation increases, but that from residual thermal stress increases, which is the reason that no apparent trend was observed for the $d(\Delta n)/dT$ of PI films adhering to Si substrates. Based on these examinations, the $d(\Delta n)/dT$ of on-substrate PI films were successfully decreased to the levels of peeled PI films by incorporation of alicyclic structures in the main chains and/or the use of PI substrates whose CTEs are close to those of PI films. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4891998>]

I. INTRODUCTION

The thermo-optic (TO) effect (i.e., temperature-dependent change in the refractive index) in optical polymers has recently attracted much attention because this phenomenon is essential for all optical materials and can be utilized to fabricate active optical waveguide components such as TO optical switches and tunable wavelength-division multiplexers.^{1,2} In particular, the temperature gradient of the refractive index (dn/dT) of transparent polymeric materials^{3–11} is one order of magnitude larger ($\sim -1 \times 10^2$ ppm/K) than that of silica glass¹² (+10 ppm/K). By using polymeric materials, power consumptions of such active waveguide components can be significantly reduced due to their large $|dn/dT|$. Thereby, quantitative estimations and control of dn/dT s and their polarization dependence of polymers are crucial for fabricating active waveguide components using optical polymers.

For optically transparent polymers, the relationship between their average refractive indices (n_{av}) and their temperature gradients (dn_{av}/dT) can be expressed by the temperature derivative of the Lorentz-Lorenz formula

$$\frac{dn_{av}}{dT} = -\frac{(n_{av}^2 - 1)(n_{av}^2 + 2)}{6n_{av}}\beta, \quad (1)$$

where T is the temperature, and β is the volumetric thermal expansion coefficient of materials. This is because the temperature dependence of molecular polarizability is negligibly

small compared with the large β s of polymers.^{13,14} According to Eq. (1), the values of dn_{av}/dT of polymers are always negative due to their positive β , and a large n_{av} and/or a large β give a large $|dn_{av}/dT|$.

Among a number of polymeric materials for optical applications, we focused on the TO effects in aromatic polyimides (PIs) due to their favorable properties for thermally stable optical waveguide applications.^{15–17} We have been developing a variety of passive optical devices and components such as single-mode waveguides,¹⁸ waveplates,^{19–21} and polarizers^{22–24} using partially fluorinated and perfluorinated PIs. In addition, regarding to TO effects in PIs, we have reported that the dn_{av}/dT of aromatic PIs can be controlled by introducing sulfide (–S–) and disulfide (–S–S–) linkages into the main chains, which is effective to endow large $|dn_{av}/dT|$ to optical polymers.²⁵ On the other hand, we have also reported that PI films formed on Si substrates exhibit significant polarization dependence in dn/dT ,²⁶ which indicates that the absolute values of dn/dT observed for transverse electric (TE) polarization (parallel to the film plane) are significantly larger than those for transverse magnetic (TM) polarization (perpendicular to the film plane). This polarization dependence may cause undesirable instability in the performance of active waveguide components such as TO switches.

In this study, we define the polarization dependence of dn/dT as the difference between the values of dn/dT for in-plane and out-of-plane refractive indices (n_{TE} and n_{TM} , respectively), which are equal to the temperature dependence of in-plane/out-of-plane birefringence (Δn)

^{a)}Author to whom correspondence should be addressed. Electronic mail: sando@polymer.titech.ac.jp. Tel.: +81-3-5734-2137. Fax: +81-3-5734-2889.

$$\frac{dn_{\text{TE}}}{dT} - \frac{dn_{\text{TM}}}{dT} = \frac{d(n_{\text{TE}} - n_{\text{TM}})}{dT} = \frac{d(\Delta n)}{dT}, \quad (2)$$

$d(\Delta n)/dT$ causes polarization dependence in the properties of active waveguide components.¹ Figure 1 shows schematic views of a TO switch made by polymer waveguides and the influence of polarization dependence of dn/dT on the switching performance. If the $|dn_{\text{TM}}/dT|$ of the waveguide core is significantly smaller than the $|dn_{\text{TE}}/dT|$, the refractive index change needed for complete switching of TM-polarized signals is not achieved, a critical condition for TE signals, which leads to additional heating of the waveguide core. Thereby, $d(\Delta n)/dT$ is expected to be minimized or optimally eliminated in most waveguide applications. The present authors have been exploring methods to control the dn/dT and $d(\Delta n)/dT$ of PI films formed on Si substrates and have reported that some PI films having very small Δn , representing small degrees of chain orientation, exhibit negative values of $d(\Delta n)/dT$ due to the temperature dependence of stress-birefringence originating from a mismatch of coefficients of linear thermal expansion (CTE) between PI films and Si substrates.²⁷ Based on these findings, we have achieved a 30%–50% decrease in $d(\Delta n)/dT$ of PI films by replacing aromatic rings with alicyclic structures, which is attributable to the effective reduction of the stress-optical coefficient. However, these semi-alicyclic PI films still exhibit appreciable $d(\Delta n)/dT$, which are two or more times larger than those for PI films peeled off from the substrates. We would like to develop new and facile methods for the effective reduction of the $d(\Delta n)/dT$ of PI films.

Apart from such approaches to control $d(\Delta n)/dT$, there remains an important issue to be clarified: the reason why $d(\Delta n)/dT$ values do not exhibit simple correlations with other properties such as Δn , residual stress, or anisotropy in CTE, when PI films are formed on Si substrates.²⁶ In this study, we investigate the effects of chain orientation and residual thermal stress on $d(\Delta n)/dT$ and propose a theoretical basis that

quantitatively explains the origins of $d(\Delta n)/dT$ for PI films formed on substrates. In addition, we demonstrate two facile and effective approaches to reduce the $d(\Delta n)/dT$ for on-substrate PI films to the levels of those for off-substrate ones.

II. EXPERIMENTAL

A. Sample preparation

Thin films of poly(methyl methacrylate) (PMMA) obtained from Sumitomo Chemical Co. Ltd. (Sumipex-MGSS, optical grade) were prepared by spin-coating of a toluene solution. The spin-coated PMMA solution was dried at 40 °C/20 min, 65 °C/20 min, and 80 °C/20 min in a convection oven, followed by annealing at 120 °C under reduced pressure. Aromatic PI films were prepared by thermal imidization of their precursors, poly(amic acid)s (PAAs). The molecular structures of aromatic PIs used in this study are shown in Figure 2. The PAA solutions were prepared by polycondensations of equimolar dianhydrides and diamines in *N,N*-dimethylacetamide (DMAc). Alicyclic PI films were prepared from corresponding poly(amic acid trimethylsilyl ester) (PASE) solutions using the *in situ* silylation method.²⁸ These precursor solutions were spin-coated on Si substrates (4-in. diameter, 380 μm thick, (001) surface) and dried at 70 °C for 30 min, followed by thermal imidization for 1 h under nitrogen flow. The imidization temperatures were 350 °C for aromatic PIs and 300 °C for alicyclic PIs. The values of $d(\Delta n)/dT$ were measured for films in two conditions, (1) films formed on Si substrates (on-substrate films) and (2) those peeled off from the substrates prior to measurement (off-substrate films). The residual stress in the off-substrate PI films was effectively released by annealing at above the imidization temperature. The thicknesses of PMMA and PI films used for measurements were controlled in a range of 12–15 μm . Thick substrates made of Kapton-type aromatic PI with a 4-in. diameter and 0.7-mm thickness were kindly supplied by NTT Advanced Technology Corp.

FIG. 1. Possible influence of the temperature dependence of in-plane/out-of-plane birefringence ($d(\Delta n)/dT$) on the switching properties of polymer optical waveguides. When one of the cores in the Y-branched waveguides is heated by a metallic heater, the refractive index is decreased to shut off optical signals. However, if $|dn_{\text{TM}}/dT|$ of the core material is significantly smaller than the $|dn_{\text{TE}}/dT|$, a refractive index change needed for complete switching of TM-polarized signals is not achieved, even though TE-polarized signals are completely switched without crosstalk.

FIG. 2. Molecular structures of aromatic PIs used in this study.

B. Variable temperature measurements of refractive indices

A prism coupler (Metricon, PC-2010) equipped with a home-made temperature-control apparatus (See the Appendix) was used for refractive index measurements at elevated temperatures.^{25–27} Linearly polarized CW laser beams with TE (transverse electric) and TM (transverse magnetic) polarization were used for the measurements of n_{TE} (refractive index in the in-plane direction of films) and n_{TM} (out-of-plane direction, normal to film surface), respectively. The average refractive index and in-plane/out-of-plane birefringences of polymer films were calculated according to the following equations:

$$n_{av} = \sqrt{\frac{2n_{TE}^2 + n_{TM}^2}{3}}, \quad (3)$$

$$\Delta n = n_{TE} - n_{TM}. \quad (4)$$

A near-infrared laser at a wavelength of 1.324 μm was used as the light source to avoid anomalous dispersion of refractive indices near the absorption edges. The refractive index (n) of the coupling prism made of gallium gadolinium garnet at each temperature was estimated using the values of $n = 1.9387$ at 25 $^{\circ}\text{C}$ and $dn/dT = +17.2$ ppm/K at 1.324 μm .²⁹ The measurements were carried out under a dry atmosphere ($\sim 20\%$ relative humidity) and in a temperature range of 85 $^{\circ}\text{C}$ to 35 $^{\circ}\text{C}$. The sample temperature was controlled in descending order to prevent moisture absorption. A very small amount of silicone oil was used as a lubricant for the off-substrate films/heating plate and the film/prism surfaces in order to suppress thermal stress caused by the CTE mismatch among the substrates, a prism, and PI films. Prior to the variable temperature experiments, the accuracy of temperature control was checked for this measurement system. The reliability of temperature control of the prism and the sample were $\pm 3^{\circ}\text{C}$ in the worst case. The experimental errors in the refractive indices and $d(\Delta n)/dT$ were estimated as ± 0.0003 and ± 5 ppm/K, respectively.

C. Residual thermal stress and its temperature dependence

Residual stresses (σ) in polymer films supported by Si substrates are estimated from the curvatures of the PI films and the biaxial modulus of silicon crystal parallel to the (001) surface.^{30–32} The curvatures of the samples were measured using a depth profiler (Veeco Instruments, Dektak 3). The temperature dependence of σ ($d\sigma/dT$) was estimated in a temperature range of 80–140 $^{\circ}\text{C}$ using a home-made heating attachment for the profiler. The measurements were carried out under a dry atmosphere ($\sim 20\%$ relative humidity) to avoid the stress relaxation derived from moisture absorption. The experimental errors for the values of σ and $d\sigma/dT$ were estimated as ± 5 MPa and ± 0.05 MPa/K, respectively.

D. Biaxial stress-optical coefficients

Biaxial stress-optical coefficients (C'_G) of polymers in the glassy state were estimated from stress-birefringence

(Δn_s ; difference in Δn for PI films before and after peeling from the substrates) divided by stress σ

$$C'_G = \frac{\Delta n_s}{\sigma} = \frac{\Delta n_{\text{supported}} - \Delta n_{\text{peeled}}}{\sigma}. \quad (5)$$

E. Linear thermal expansion coefficients

The in-plane CTEs for off-substrate PI films were measured with a thermo-mechanical analyzer (ULVAC, TM 7000) as average values in a range of 50–300 $^{\circ}\text{C}$. The out-of-plane CTEs were estimated from temperature shifts of interferences of transmitted light caused by temperature variations of the optical path, i.e., a product of thickness and the in-plane refractive index of the films. The temperatures of sample films were precisely controlled by a hot-stage (Mettler Toledo, Model FP82HT).

III. RESULTS AND DISCUSSION

A. TO coefficients of polymer films formed on Si substrates

Figure 3 shows the temperature dependence of n_{TE} and n_{TM} of a PMMA film formed on a Si substrate. The film was optically isotropic because both the birefringence ($\Delta n = n_{TE} - n_{TM}$) and its temperature dependence ($d(\Delta n)/dT = dn_{TE}/dT - dn_{TM}/dT$) were very small, which are comparable to the experimental error range. The refractive index of PMMA decreases as the temperature increases owing to its volumetric thermal expansion (β). It should be noted that the dn_{av}/dT for PMMA film formed on a Si substrate (-88 ppm/K) is smaller than that for a PMMA bulk prism⁴ (-120 ppm/K) in their absolute values. The smaller $|dn_{av}/dT|$ value for the on-substrate film is attributed to restrained thermal expansions due to very small CTE of Si(001) substrates ($+2.6$ ppm/K). The restraint leads to small apparent thermal volume expansion (β') of polymer films attached to substrates, which result in small $|dn_{av}/dT|$ s according to Eq. (1). In case the polymer films are formed on substrate having negligibly small CTE, the TO coefficient of polymer films can be estimated as follows:¹

$$\left. \frac{dn_{av}}{dT} \right|_{\text{on substrate}} = \frac{1}{3} \left(\frac{1+\nu}{1-\nu} \right) \left. \frac{dn_{av}}{dT} \right|_{\text{bulk}} \quad (6)$$

FIG. 3. Temperature dependence of in-plane and out-of-plane refractive indices (n_{TE} and n_{TM} , respectively) of PMMA film formed on Si substrate.

where ν is the Poisson ratio of the polymer. Using the values of ν for PMMA³³ (0.365) and dn_{av}/dT for bulk PMMA (-120 ppm/K), the dn_{av}/dT for on-substrate PMMA film is estimated at -86 ppm/K, which is very close to the experimental dn_{av}/dT in the present study. This result confirms the reliability of our measurement system of TO coefficients.

The temperature dependence of in-plane and out-of-plane refractive indices of a fluorinated aromatic PI 1a (6FDA/ODA) film formed on a Si substrate is shown in Figure 4. Unlike the case of PMMA, aromatic PI films exhibited significantly large polarization dependence of TO coefficients ($d(\Delta n)/dT$). In order to investigate the molecular-structure dependence, the polarization dependences of dn/dT were measured for seven kinds of aromatic PI films formed on Si substrates, and the estimated values of $d(\Delta n)/dT$ are listed in Table I. Investigation of the molecular-structure dependence of dn_{av}/dT is made in this section, and that of $d(\Delta n)/dT$ will be discussed in Sec. III B.

To analyze the relationship according to Eq. (1), the values of $(n_{av}^2 - 1)(n_{av}^2 + 1)/6n_{av}$ are plotted against dn_{av}/dT for the PI films formed on Si substrates (Figure 5). Because the term of $(n_{av}^2 - 1)(n_{av}^2 + 1)/6n_{av}$ is nearly proportional to n_{av} in the range of $1.4 < n_{av} < 1.8$, the absolute values of dn_{av}/dT ($|dn_{av}/dT|$) tend to increase as the n_{av} increases. However, the correlation in Figure 5 is unclear due to the differences in volumetric expansion among PIs. Coefficients of apparent volumetric thermal expansion (β'), estimated from n_{av} and dn_{av}/dT according to Eq. (1), are in a range of 100 ± 20 ppm/K. In cases of PI films exhibiting small birefringence with lower degrees of in-plane orientation of main chains (PI 1a, 1b, 2a, 2b), the PIs derived from ODA diamine (PI 1a and 2a), which includes a bent and flexible ether (-O-) linkage, exhibit larger β' than those derived from a linear and rigid TFDB diamine (PI 1b and 2b). This suggests that a bent and flexible structure in the main chain leads to an increase in β' . On the other hand, the PI films exhibiting large birefringence with higher degrees of in-plane orientation (PI 3a, 3b, 4c) did not necessarily demonstrate small β' values despite their rigid structures. These PIs should exhibit small CTEs parallel to the film plane, and the restraint of thermal expansions caused by a CTE mismatch between PI film and the Si substrate should be small compared to the PI films with lower degrees of orientation.

FIG. 4. Temperature dependence of in-plane and out-of-plane refractive indices (n_{TE} and n_{TM} , respectively) of fluorinated PI 1a (6FDA/ODA) film formed on Si substrate.

TABLE I. Average refractive indices (n_{av}), in-plane/out-of-plane birefringence (Δn), thermo-optic coefficients (dn/dT , ppm/K), and their polarization dependence ($d(\Delta n)/dT$, ppm/K) for aromatic PI films formed on Si substrates. dn_{TE}/dT , dn_{TM}/dT , and dn_{av}/dT represent in-plane, out-of-plane, and average TO coefficients in a range of 35–85 °C.

Polyimide	n_{av}	Δn	dn_{TE}/dT	dn_{TM}/dT	dn_{av}/dT	$d(\Delta n)/dT$
1a (6FDA/ODA)	1.5604	0.0074	-76.3	-56.8	-69.8	-19.5
1b (6FDA/TFDB)	1.5180	0.0076	-57.1	-41.0	-51.7	-16.1
2a (ODPA/ODA)	1.6425	0.0099	-87.5	-53.1	-76.0	-34.4
2b (ODPA/TFDB)	1.5797	0.0097	-63.4	-37.9	-54.9	-25.5
3a (PMDA/ODA)	1.6469	0.0693	-99.2	-58.8	-86.1	-40.4
3b (PMDA/TFDB)	1.5691	0.1151	-86.6	-77.9	-83.8	-8.8
4c (BPDA/PDA)	1.7191	0.1874	-98.9	-59.9	-86.8	-39.0

B. Origins of polarization dependence of TO coefficient

As described above, significant polarization dependence has been observed for the TO coefficients of PI films formed on Si substrates.²⁷ The experimental values of $d(\Delta n)/dT$ are plotted against Δn in Figure 6. For the off-substrate films (squares), the $|dn_{av}/dT|$ values increase as the Δn increase, which readily indicates that a higher degree of chain orientation leads to a large value of $|d(\Delta n)/dT|$. In contrast, those for the on-substrate films (triangles) do not exhibit clear correlations to Δn .

In general, birefringence Δn in polymer depends on polymer chain orientation and residual stress. At first, we clarify the relationships between the experimental values of Δn and $d(\Delta n)/dT$ and the degree of chain orientation for the off-substrate PI films to investigate the orientation-driven $d(\Delta n)/dT$. The Δn in a rotationally symmetric system is proportional to the second order orientation coefficient (P_{200}) of polymer chains. In the case of uniaxially drawn films or fibers, chain orientation direction coincides with the axis of symmetry, and Δn can be expressed as³⁴

$$\Delta n = \Delta n^0 \times P_{200}, \quad (7a)$$

where Δn^0 is the intrinsic birefringence. In contrast, spin-coated films can be treated as biaxially drawn films, in which the axis of symmetry is normal to the film plane, and the polymer chains are oriented perpendicular to the axis of

FIG. 5. Thermo-optic coefficients of average refractive indices (dn_{av}/dT) for aromatic PI films formed on Si substrates. Numbers in the figure correspond to those in Fig. 2.

FIG. 6. Comparison between the polarization dependence of the refractive index (birefringence Δn) and its temperature dependence ($d(\Delta n)/dT$) for aromatic PI films. The values of $d(\Delta n)/dT$ for the off-substrate films and the on-substrate ones are plotted by filled squares and open triangles, respectively.

symmetry. Thereby, the relationship between Δn ($=n_{TE} - n_{TM}$) and P_{200} for spin-coated films is expressed as follows:

$$\Delta n = -\Delta n^0 \times P_{200}. \quad (7b)$$

By taking the temperature derivative of Eq. (7b), the relationship between $d(\Delta n)/dT$ and the chain orientation is expressed as follows:

$$\frac{d(\Delta n)}{dT} = -P_{200} \frac{d(\Delta n^0)}{dT} - \Delta n^0 \frac{dP_{200}}{dT}. \quad (8)$$

According to Eq. (8), the influence of chain orientation on $d(\Delta n)/dT$ can be divided into two factors; (a) the temperature dependence of Δn^0 (product of P_{200} and $d(\Delta n^0)/dT$) and (b) the temperature dependence of P_{200} (product of Δn^0 and dP_{200}/dT). For quantitative investigation of $d(\Delta n)/dT$, the values of P_{200} , Δn^0 , and their temperature dependences are to be evaluated. We have previously reported P_{200} for PI films prepared by spin-coating³⁵ and uniaxial drawing³⁶ using polarized ATR/FT-IR spectroscopy, and their Δn^0 values were determined.³⁷ However, the origins of their temperature dependence have not been investigated yet.

First, we investigate the temperature dependences of Δn^0 . Intrinsic birefringence Δn^0 can be estimated according to the Vuks equation³⁸

$$\frac{n_i^2 - 1}{n_{av}^2 + 2} = \frac{4\pi}{3} \frac{\rho N_A}{M} \alpha_i, \quad (9)$$

where n_i , α_i , ρ , M , and N_A are the refractive index, the molecular polarizability for a direction i , the density of a polymer, the molecular weight of the repeating unit, and the Avogadro's number, respectively. From the temperature derivative of Eq. (9), the temperature dependence of n_i can be written as follows:

$$\frac{2n_i}{n_i^2 - 1} \frac{dn_i}{dT} - \frac{2n_{av}}{n_{av}^2 + 2} \frac{dn_{av}}{dT} = \frac{1}{\rho} \frac{d\rho}{dT} = -\beta. \quad (10)$$

In the derivation of Eq. (10), the temperature dependence of polarizability (dx_i/dT) was neglected because dx_i/dT is much smaller than $d\rho/dT$ for polymers.⁴ In accordance with Eqs. (1) and (10), the temperature dependence of Δn^0 is approximated as

$$\frac{d(\Delta n^0)}{dT} = \left(1 + \frac{1}{n_{||}^0 n_{\perp}^0}\right) \frac{n_{av}}{n_{av}^2 - 1} \Delta n^0 \frac{dn_{av}}{dT}, \quad (11)$$

where $n_{||}^0$ and $n_{\perp}^0$ are the refractive indices parallel and perpendicular to the axis of symmetry under perfect uniaxial orientation, in which P_{200} becomes unity. The values of $d(\Delta n^0)/dT$ estimated from the experimental values of $n_{||}^0$, $n_{\perp}^0$, and Δn^0 , and those of dn_{av}/dT measured for the off-substrate PI films are listed in Table II. Among the four kinds of aromatic PIs, 4c (BPDA/PDA) exhibited exceptionally large $d(\Delta n^0)/dT$ due to its high n_{av} and large Δn^0 values.

Second, we investigate the temperature dependences of P_{200} . P_{200} represents a degree of orientation of polymer chains to the axis of symmetry, which is defined as:

$$P_{200} = \frac{3\langle \cos^2 \theta \rangle - 1}{2}, \quad (12)$$

where θ is the angle between a polymer main chain and the axis of symmetry, and the value in the angle bracket means the average over all polymer segments. In cases of spin-coated films, the main chains of aromatic PIs tend to orient perpendicular to the axis of symmetry due to their rigid and quasi-linear skeletal structures. Thereby, the values of P_{200} vary from 1 ($\theta = 0$, isotropic) to $-1/2$ ($\theta = \pi/2$; all chains are oriented parallel to the film plane) as the degree of chain orientation increases. PI films exhibiting anisotropic CTEs will cause changes in θ with temperature. According to Eq. (12), changes in θ will cause temperature dependences of P_{200} . The CTEs parallel to the orientation direction usually take positive values, but they become negative in some cases of rigid-rod polymers. In addition, it decreases by increasing the degree of in-plane chain orientation. The variation of θ originating from the anisotropy in CTE is schematically shown in Figure 7. It can be assumed that an angle $\Delta\theta$, which represents the change in θ caused by elevated temperature ΔT , suffices in the following relation:

$$\tan(\theta + \Delta\theta) = \frac{1 + k_{||}\Delta T}{1 + k_{\perp}\Delta T} \tan \theta \approx (1 - \Delta k \Delta T) \tan \theta, \quad (13)$$

where $k_{||}$ and $k_{\perp}$ are the CTEs parallel and perpendicular to the axis of symmetry, respectively, and Δk ($=k_{||} - k_{\perp}$) is the anisotropy in CTE. According to Eqs. (12) and (13), the change in the orientation coefficients (ΔP_{200}) after a temperature change (ΔT) can be estimated as follows:

$$\Delta P_{200} = 3\Delta k \Delta T (\langle \cos^2 \theta \rangle - \langle \cos^4 \theta \rangle) \quad (14)$$

TABLE II. Average refractive indices (n_{av}), intrinsic birefringence (Δn^0), average thermo-optic coefficients (dn_{av}/dT , ppm/K), and estimated temperature dependence of intrinsic birefringence ($d(\Delta n^0)/dT$, ppm/K) of the peeled PI films.

Polyimide	n_{av}	$n_{ }^0$	$n_{\perp}^0$	Δn^0	dn_{av}/dT	$d(\Delta n^0)/dT$
1a (6FDA/ODA)	1.5259	1.771	1.472	0.322	-82.5	-42.2
3a (PMDA/ODA)	1.6469	1.887	1.513	0.374	-86.1	-41.8
3b (PMDA/TFDB)	1.5719	1.793	1.447	0.346	-74.4	-38.1
4c (BPDA/PDA)	1.7181	2.016	1.544	0.472	-95.5	-52.4

FIG. 7. Schematic model for temperature dependent change of chain directions derived from the anisotropy in CTE.

and

$$\frac{dP_{200}}{dT} \approx \frac{\Delta P_{200}}{\Delta T} = 3\Delta k(\langle \cos^2\theta \rangle - \langle \cos^4\theta \rangle). \quad (15)$$

The values of $\langle \cos^4\theta \rangle$ can be estimated from the 4th order orientation coefficients obtainable from polarized Raman spectroscopy or the wide-angle X-ray diffraction pattern, although such measurements are difficult to employ for amorphous PIs. In this study, we approximated $\langle \cos^4\theta \rangle$ by $\langle \cos^2\theta \rangle^2$, which corresponds to a case where all polymer chains take the same θ value on average. The experimental Δk , P_{200} , and the dP_{200}/dT estimated using Eq. (15) for the off-substrate PI films are listed in Table III. The PIs exhibiting large Δk represent relatively large dP_{200}/dT . In general, a higher degree of chain orientation leads to a large Δk , but PI 4c exhibits an intermediate Δk value (119 ppm/K) because its rigid structure with a higher degree of molecular aggregation leads to smaller volumetric thermal expansion. Hence, the dP_{200}/dT of PI 4c is not so large despite the highest degree of chain orientation ($P_{200} = -0.330$).

Temperature dependences of $d(\Delta n)/dT$ for PI films are estimated using Eqs. (8), (11), and (15). Both of the estimated and experimental values of $d(\Delta n)/dT$ for the off-substrate PI films are always negative, as listed in Table IV, and their absolute values are significantly large for films exhibiting higher degrees of orientation (3b and 4c). As shown in Figure 8, the estimated values of $d(\Delta n)/dT$ well reproduce the experimental ones, which apparently demonstrates that the experimental values of $d(\Delta n)/dT$ observed for the off-substrate PI films are explainable as a sum of the two factors (a) and (b).

We start investigation on residual stress effect on Δn and $d(\Delta n)/dT$. The values of $d(\Delta n)/dT$ measured for the on-substrate PI films are noticeably different from those for the

TABLE III. Coefficients of linear thermal expansion coefficients (CTE, ppm/K), anisotropy in CTE (Δk , ppm/K), second order orientation coefficient P_{200} of peeled PI films, and the estimated dP_{200}/dT . $k_{||}$ and $k_{\perp}$ represent out-of-plane and in-plane CTEs (parallel and perpendicular to the axis of rotational symmetry).

Polyimide	$k_{ }$	$k_{\perp}$	Δk	P_{200}	$\langle \cos^2\theta \rangle$	dP_{200}/dT
1a (6FDA/ODA)	85	60	25	-0.015	0.323	16.4
3a (PMDA/ODA)	106	27	79	-0.141	0.239	43.1
3b (PMDA/TFDB)	169	-4.2	173	-0.281	0.146	64.7
4c (BPDA/PDA)	119	0.2	119	-0.330	0.113	35.8

TABLE IV. The estimated and experimental values of polarization dependence in TO coefficient ($d(\Delta n)/dT$, ppm/K) derived from the chain orientation.

Polyimide	$P_{200} \cdot d(\Delta n^0)/dT$	$\Delta n^0 \cdot dP_{200}/dT$	$d(\Delta n)/dT$ (estimated)	$d(\Delta n)/dT$ (experimental)
1a (6FDA/ODA)	0.6	5.3	-5.9	-4
3a (PMDA/ODA)	5.9	16.1	-22.0	-22
3b (PMDA/TFDB)	10.7	22.4	-33.1	-34
4c (BPDA/PDA)	17.3	16.9	-34.2	-39

off-substrate PI films (see Figure 6). Based on the experimental results, we have reported that the difference in $d(\Delta n)/dT$ between the off- and on-substrate films is caused by the temperature dependence of stress birefringence ($d(\Delta n_s)/dT$) for the PI films exhibiting lower degrees of chain orientation, and this term can be represented as follows:^{1,27}

$$\frac{d(\Delta n_s)}{dT} = C'_G \frac{d\sigma}{dT}, \quad (16)$$

where C'_G is the in-plane/out-of-plane stress-optical coefficient for biaxial stress, and σ is the residual stress (positive for expansion stress). The temperature dependence of σ can be expressed as

$$\frac{d\sigma}{dT} = \frac{E_f}{1 - \nu_f} (k_f - k_s), \quad (17)$$

where E_f , ν_f , k_f , and k_s are Young's modulus, the Poisson ratio, the in-plane CTEs of PI film and substrate, respectively.^{39,40} The values of $d(\Delta n_s)/dT$ for the oriented PI films were estimated according to Eq. (16) using the experimental values of C'_G and $d\sigma/dT$ as listed in Table V. Since residual stress is induced in the on-substrate PI films during cooling from the highest imidization temperature (300–350 °C) to room temperature,⁴¹ the value of $d\sigma/dT$ becomes small (close to zero) when k_f is similar to k_s (2.6 ppm/K at 20 °C), and they become negative when the values of k_f are negative. On the other hand, the estimated C'_G for the PI films are in a range of 100–280 ppm/MPa, which are much larger than those for conventional optical polymers such as PMMA and polystyrene. This is due to the higher content of benzene and imide rings in the molecular structures of PIs.⁴² As shown in

FIG. 8. Comparison between the experimental values of $d(\Delta n)/dT$ for the off-substrate PI films (open circles) and the estimated values of $d(\Delta n)/dT$ derived from the chain orientation (filled circles).

TABLE V. Residual stress (σ ; MPa), temperature dependence of σ ($d\sigma/dT$; MPa/K), stress-optical coefficients for biaxial stress (C'_G), and estimated values of temperature dependence of stress birefringence ($d(\Delta n_s)/dT$; ppm/K) with respect to the difference between the values of $d(\Delta n)/dT$ for the off- and on-substrate PI films ($\Delta[d(\Delta n)/dT]$; ppm/K). Values in the parenthesis indicate error ranges.

Polyimide	σ	$d\sigma/dT$	C'_G	$d(\Delta n_s)/dT$	$\Delta[d(\Delta n)/dT]$
1a (6FDA/ODA)	49.9	-0.200	140 (34)	-28 (14)	-16 (5)
3a (PMDA/ODA)	20.4	-0.082	279 (70)	-23 (20)	-18 (5)
3b (PMDA/TFDB)	-26.9	0.106	245 (60)	26 (19)	25 (5)
4c (BPDA/PDA)	-13.4	-0.041	97 (47)	4 (7)	-2 (5)

Figure 9, the estimated $d(\Delta n_s)/dT$ values agree well with the difference in the experimental values of $d(\Delta n)/dT$ between the off- and on-substrate PI films. This result clearly certifies that the temperature dependence of stress birefringence $d(\Delta n_s)/dT$ causes the substrate effect on $d(\Delta n)/dT$ for PI films.

C. Control of polarization dependence of TO coefficients

The reduction of polarization dependence of dn/dT in polymer films is an essential issue to improve the performance of active waveguide components. Since the structures of optical materials applicable to waveguides are more or less isotropic with low degrees of chain orientation and exhibit negligibly small Δn , the dominant origin of $d(\Delta n)/dT$ could be “stress-driven” polarization dependence of the TO coefficient ($d(\Delta n_s)/dT$). According to Eqs. (16) and (17), $d(\Delta n_s)/dT$ can be effectively reduced by (i) elimination of the mismatch between the CTEs of substrates and PI films ($k_f - k_s$) and (ii) reduction of the stress-optical coefficients (C'_G s) of PI films.

At first we investigate an approach to reduce CTE mismatch by using PI substrates. The CTEs of conventional inorganic substrate materials (e.g., silicon, sapphire, and silica glass) are generally much smaller than those of polymers. If we can choose substrates from other than inorganic materials, the CTE of substrate k_s becomes more controllable for reducing the CTE mismatch with polymers. For instance, several kinds of polymeric substrates have been proposed for

FIG. 9. Comparison between the $d(\Delta n)/dT$ induced by the use of Si substrate (open symbols) and the estimated values of temperature dependence of stress birefringence $d(\Delta n_s)/dT$ for the on-substrate PI films on Si substrates (filled symbols).

optical waveguide applications.^{43,44} Since the k_s s of these substrates could be close to the k_f of optical PIs, the $d(\Delta n_s)/dT$ spontaneously generated in PI films should be significantly reduced by using polymeric substrates. Therefore, in this study, we employed a polyimide substrate with k_s of 60 ppm/K, which is almost same as the k_f s of the fluorinated PIs developed for waveguide applications (PI 1a and 1b, see Table III). The values of dn_{av}/dT and $d(\Delta n)/dT$ measured for the PI films formed on PI substrates are shown in Table VI. As we had expected, the $d(\Delta n)/dT$ for the PI films formed on the PI substrates were effectively reduced, as small as those for the off-substrate PI films. In addition, the PI films on PI substrates exhibited almost the same dn_{av}/dT as the off-substrate films, which obviously confirm that the thermal expansion of PI films was not restrained by the PI substrates due to the absence of a CTE mismatch (cf. Sec. III). The major advantage of this approach is that the significant $d(\Delta n)/dT$ in the current PIs developed for waveguide applications can be effectively reduced without any modifications of the molecular structures.

Second, we investigate an approach to reduce C'_G of PIs. In photonic and telecommunication applications, the selection of substrate materials for optical waveguides has been limited to inorganics such as Si, sapphire (Al_2O_3), or fused silica glass (SiO_2). Although the k_f of PI films can be reduced to as small as k_s of inorganic materials through enhancement of the degrees of chain orientation,^{45–47} it readily induces significantly large Δn and orientation-driven $d(\Delta n)/dT$, which inevitably deteriorates the performance of waveguides, i.e., polarization dependent optical losses and phase shift between TE and TM signals. Therefore, in case optically isotropic PI films are formed on inorganic substrates, their large CTE mismatch and accompanying large $d\sigma/dT$ s are to be minimized. According to Eq. (16), C'_G could be reduced to achieve a small $|d(\Delta n)/dT|$ for PI films which exhibit large $d\sigma/dT$ values. Although the origins of the molecular-structure dependence of C'_G have not been quantitatively clarified, a large anisotropy in molecular polarizability along the chain axis should lead to a large C'_G .⁴² Hence, introductions of flexible and non-planer aliphatic structures could effectively reduce the $d(\Delta n)/dT$ of PIs. In order to verify this concept, two series of aliphatic PIs were prepared (Figure 10); (a) semi-alicyclic PIs derived from alicyclic diamines (d: DCHM, e: 6FDC, f: TFDC) and aromatic dianhydrides (1: 6FDA and 2: ODPa), and (b) wholly alicyclic PIs derived from the same alicyclic diamines and alicyclic

TABLE VI. Substrate effect on refractive indices (n_{av}), birefringence (Δn), TO coefficients (dn_{TE}/dT , dn_{TM}/dT , and dn_{av}/dT , respectively; ppm/K), and their polarization dependences ($d(\Delta n)/dT$, ppm/K) of aromatic PI films.

Polyimide	Condition	n_{av}	Δn	dn_{av}/dT	$d(\Delta n)/dT$
1a (6FDA/ODA)	On Si	1.5604	0.0074	-70	-20
	On PI	1.5657	0.0026	-80	-5
	Off-substrate	1.5640	0.0004	-83	-4
1b (6FDA/TFDB)	On Si	1.5180	0.0076	-52	-16
	On PI	1.5207	0.0022	-58	-4
	Off-substrate	1.5263	0.0000	-56	-2

FIG. 10. Molecular structures of the alicyclic PIs used in this study.

dianhydride 5 (CBDA). The experimental values of $d(\Delta n)/dT$ for these alicyclic PI films formed on Si substrates are shown in Figure 11. The absolute values of $d(\Delta n)/dT$ for the semi-alicyclic PIs (PI 1d–1f and 2d–2f) are significantly reduced by 30%–50% compared to the aromatic PIs derived from the same dianhydrides. Furthermore, the wholly alicyclic PIs (PI 5d–5f) exhibited very small $d(\Delta n)/dT$ (–3––9 ppm/K), despite the use of Si substrates. The $d(\Delta n)/dT$ for these PI films are as small as those for the off-substrate aromatic PI films without residual stress. The kinked and stiff structure of the CBDA moiety provides additional reduction in anisotropy of polarizability.

In addition to the very small $|d(\Delta n)/dT|$, the values of dn_{av}/dT of the alicyclic PI films can also be controlled through their molecular structures. As shown in Figure 12, the $|dn_{av}/dT|$ for the PIs derived from fluorinated alicyclic diamines 6FDC (PI 1e, 2e, and 5e) and TFDC (1f, 2f, and 5f) are reduced further than those of the PIs derived from DCHM (1d, 2d, and 5d) by 25%–50%. According to Eq. (1), a small $|dn_{av}/dT|$ is attributable to small values of n_{av} and/or β . Although the n_{av} of the PIs derived from 6FDC and TFDC are smaller than those of the PIs from DCHM by 0.02–0.04, the differences in n_{av} cause only 5%–10% decreases in dn_{av}/dT . Therefore, the PIs derived from 6FDC- and TFDC-

FIG. 11. Molecular structure dependence of $d(\Delta n)/dT$ for the alicyclic PI films formed on Si substrates. FIG. 12. Molecular structure dependence of dn_{av}/dT for the alicyclic PI films formed on Si substrates.

should possess smaller β than the PIs from DCHM. In the case of TFDC-derived PIs, small β may be attributable to the relatively linear structure of the TFDC moiety, whereas the difference between the molecular structures of the DCHM and 6FDC moieties is the only flexible linkages connecting the two cyclohexyl units (the methylene unit $-\text{CH}_2-$ and the hexafluoroisopropylidene unit $-\text{C}(\text{CF}_3)_2-$, respectively) as shown in Figure 10. In the case of 6FDC-derived PIs, the bulky and heavy trifluoromethyl ($-\text{CF}_3$) side groups cause steric hindrance and make the main-chain rotations more difficult. This assumption is supported by the molecular-structure dependence of glass transition temperatures (T_g) shown in Table VII. The 6FDC-derived PIs (1e and 2e) exhibit noticeably higher T_g s than the DCHM-derived ones (1d and 2d). In addition, a similar trend is observed in the dianhydride-structure dependence of T_g s. The 6FDA-derived PIs, containing $-\text{C}(\text{CF}_3)_2-$ linkages, exhibit significantly higher T_g s than the ODPA-derived PIs (containing $-\text{O}-$ linkages). This trend demonstrates that, among the three kinds of flexible linkages, $-\text{C}(\text{CF}_3)_2-$ leads to more restricted main-chain motions compared to $-\text{CH}_2-$ and $-\text{O}-$ linkages.

IV. CONCLUSIONS

The relationships between the polarization dependence of TO coefficients ($d(\Delta n)/dT$) and other properties (e.g., birefringence Δn , orientation coefficient P_{200} , or residual stress σ) were extensively examined for the on-substrate and off-substrate PI films, and the origins of $d(\Delta n)/dT$ were clarified. It was demonstrated that the $d(\Delta n)/dT$ can be divided into two factors, that is, (a) chain orientation-driven and (b) stress-driven ones. The former factor (a) consists of two terms, the temperature dependence of Δn^0 and P_{200} , as

TABLE VII. Molecular structure dependence of glass transition temperatures ($^\circ\text{C}$) of alicyclic PIs.

Dianhydride	Diamine		
	c (DCHM)	d (6FDC)	e (TFDC)
1 (6FDA)	262 ^a	326 ^a	335 ^a
2 (ODPA)	210	230	270

^aValues are from Ref. 25.

shown in Eq. (8). The value of $d(\Delta n)/dT$ derived from this factor is always negative and significantly large for films exhibiting higher degrees of chain orientation. On the other hand, the latter factor (b) is caused by the temperature dependence of stress birefringence ($d\sigma_s/dT$). The value of $d(\Delta n)/dT$ derived from this factor is also negative for films exhibiting large in-plane CTEs, which is the case with lower degrees of chain orientation. However, the $d(\Delta n)/dT$ becomes small and close to zero as the in-plane CTE decreases because the $d\sigma_s/dT$ depends on the CTE mismatch between the PI films and Si substrates, as shown in Eqs. (16) and (17). The experimental values of $d(\Delta n)/dT$ are affected only by factor (a) for off-substrate films, so those values exhibit a clear correlation with Δn . On the other hand, the values of $d(\Delta n)/dT$ for on-substrate PI films are determined by the sum of factors (a) and (b). As schematically shown in Figure 13, the $d(\Delta n)/dT$ originating from factor (a) exhibits an opposite dependence on the degree of chain orientation to that originating from factor (b). This is the essential reason that the behaviors of $d(\Delta n)/dT$ observed for on-substrate PI films could not be straightforwardly investigated with respect to other structural properties (see Figure 6).

Based on the above investigations, we demonstrated two approaches which effectively reduce the significantly large $d(\Delta n)/dT$ observed for the on-substrate PI films. The first approach is the reduction of the CTE mismatch by using “polyimide substrates” of which the CTE is well matched to that of the PI films. As expected, the $d(\Delta n)/dT$ for the PI films formed on polyimide substrates are as small as those for off-substrate PI films (see Table VI). This approach is advantageous in the availability of current optical waveguide PI materials. The second approach is the reduction of C_G' by changing the skeletal structures of PIs by using alicyclic monomers. As shown in Figure 11, the values of $d(\Delta n)/dT$ for the newly synthesized semi-alicyclic PI films range from -9 to -19 ppm/K, which are 30%–50% smaller than those of aromatic PIs. Moreover, the wholly alicyclic PI films formed on Si substrates exhibit $d(\Delta n)/dT$ values in a range of -3 – -9 ppm/K. These values are as small as those for the off-substrate fluorinated aromatic PI films without residual thermal stress. This approach is facile and advantageous if we have to use Si substrates. In this study, we have demonstrated that the polarization dependence of TO coefficients

FIG. 13. Schematic representation of the origins of $d(\Delta n)/dT$ for the PI films formed on Si substrates.

FIG. 14. Schematic figure for the temperature control apparatus for a prism coupler. Point (a): laser-incident position. Point (b): thermocouple for feed-back temperature control is glued on this position.

$d(\Delta n)/dT$ of PI films can effectively suppressed or reduced by choosing an appropriate approach with consideration for the design and fabrication conditions of optical devices and components.

APPENDIX: MEASUREMENT OF TO COEFFICIENT USING PRISM COUPLER

A prism coupler (Metricon, PC-2010) equipped with a home-made temperature-control apparatus (Figure 14) was used for refractive index measurements at elevated temperatures. The ceramic heater ~ 100 V/A, 10×20 mm) glued on a silicon wafer was driven by AC power. The temperature was controlled by adjustable voltage. Conductive silver paste was used as an adhesive between this apparatus and the sample substrate to achieve good thermal contact. Sample and prism temperature was monitored by a K-type thermocouples glued on the film and prism surface with small amounts of silver paste. A laser beam with TE or TM polarization was used for the measurements. The refractive index of the coupling prism (gallium gadolinium garnet) at each temperature was calculated using the values of $n = 1.9390$ at 25°C and $dn/dT = 17.2$ ppm/K at a wavelength of $1.32 \mu\text{m}$.

¹M. B. J. Diemeer, *Opt. Mater.* **9**, 192 (1998).

²H. Ma, A. K.-Y. Jen, and L. R. Dalton, *Adv. Mater.* **14**, 1339 (2002).

³R. M. Waxler, D. Horowitz, and A. Feldman, *Appl. Opt.* **18**, 101 (1979).

⁴P. Michel, J. Dugas, J. M. Cariou, and L. Martin, *J. Macromol. Sci. Phys.* **B25**, 379 (1986).

⁵R. S. Moshrefzader, M. D. Radcliffe, T. C. Lee, and S. K. Mohapatra, *J. Lightwave Technol.* **10**, 420 (1992).

⁶T. Watanabe, N. Ooba, Y. Hida, and M. Hikita, *Appl. Phys. Lett.* **72**, 1533 (1998).

⁷R. Blomquist, L. Eldada, M. McFarland, R. Norwood, C. Poga, and L. Shacklett, *Proc. SPIE* **3799**, 266 (1999).

⁸A. Norris, J. DeGroot, Jr., F. Nishida, U. Penisz, N. Kushibiki, and T. Ogawa, *Proc. SPIE* **4798**, 79 (2002).

⁹X. Li, Z.-Q. Cao, Q.-S. Shen, Q.-H. Meng, D.-Y. Huang, K.-P. Guo, L. Qiu, and Y.-Q. Shen, *Chin. Phys. Lett.* **23**, 998 (2006).

¹⁰D. I. Johnson and G. E. Town, *Proc. SPIE* **6038**, 603821 (2006).

¹¹M. R. Saleem, S. Honkanen, and J. Turunen, *Opt. Commun.* **288**, 56 (2013).

¹²W. S. Rodney and R. J. Spindler, *J. Res. Natl. Bur. Stand.* **53**, 185 (1954).

¹³J. M. Cariou, J. Dugas, L. Martin, and P. Michel, *Appl. Opt.* **25**, 334 (1986).

¹⁴H. Gao, D. Yorifuji, Z. Jiang, and S. Ando, *Polymer* **55**, 2848 (2014).

- ¹⁵T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, *Macromolecules* **24**, 5001 (1991).
- ¹⁶S. Ando, T. Matsuura, and S. Sasaki, *Macromolecules* **25**, 5858 (1992).
- ¹⁷T. Matsuura, S. Ando, S. Sasaki, and F. Yamamoto, *Macromolecules* **27**, 6665 (1994).
- ¹⁸T. Matsuura, S. Ando, S. Matsui, S. Sasaki, and F. Yamamoto, *Electron. Lett.* **29**, 2107 (1993).
- ¹⁹S. Ando, T. Sawada, and Y. Inoue, *Electron. Lett.* **29**, 2143 (1993).
- ²⁰S. Ando, T. Sawada, and S. Sasaki, *Polym. Adv. Technol.* **10**, 169 (1999).
- ²¹S. Ando, T. Sawada, and S. Sasaki, *Polym. Adv. Technol.* **12**, 319 (2001).
- ²²T. Sawada, S. Ando, and S. Sasaki, *Appl. Phys. Lett.* **74**, 938 (1999).
- ²³S. Matsuda, S. Ando, and T. Sawada, *Electron. Lett.* **37**, 706 (2001).
- ²⁴S. Matsuda, Y. Yasuda, and S. Ando, *Adv. Mater.* **17**, 2221 (2005).
- ²⁵Y. Terui and S. Ando, *J. Photopolym. Sci. Technol.* **18**, 337 (2005).
- ²⁶Y. Terui and S. Ando, *Appl. Phys. Lett.* **83**, 4755 (2003).
- ²⁷Y. Terui and S. Ando, *Proc. SPIE* **5724**, 336 (2005).
- ²⁸Y. Oishi, S. Onodera, J. Oravec, K. Mori, S. Ando, Y. Terui, and K. Maeda, *J. Photopolym. Sci. Technol.* **16**, 263 (2003).
- ²⁹D. L. Wood and K. Nassau, *Appl. Opt.* **29**, 3704 (1990).
- ³⁰M. Ree, T. L. Nunes, G. Czornyj, and W. Volksen, *Polymer* **33**, 1228 (1992).
- ³¹M. Ree, S. Swanson, and W. Volksen, *Polymer* **34**, 1423 (1993).
- ³²J. C. Coburn, M. T. Pottiger, S. C. Noe, and S. D. Senturia, *J. Polym. Sci. Part B: Polym. Phys.* **32**, 1271 (1994).
- ³³W. Wunderlich, in *Polymer Handbook*, 4th ed., edited by J. Brandrup, E. H. Immergut, and E. A. Grulke (John Wiley & Sons, Inc., NY, 1999), Chap. 5.
- ³⁴I. M. Ward, *Structure and Properties of Oriented Polymers* (Applied Science Publishers, London, 1975).
- ³⁵Y. Terui and S. Ando, *J. Polym. Sci. Part B: Polym. Phys.* **43**, 2109 (2005).
- ³⁶S. Matsuda and S. Ando, *J. Polym. Sci. Part B: Polym. Phys.* **41**, 418 (2003).
- ³⁷Y. Terui and S. Ando, *J. Polym. Sci. Part B: Polym. Phys.* **42**, 2354 (2004).
- ³⁸M. F. Vuks, *Opt. Spectrosc.* **20**, 361 (1964).
- ³⁹M. Ree, K. Kim, S. H. Woo, and H. Chung, *J. Appl. Phys.* **81**, 698 (1997).
- ⁴⁰F. Li, S. Fang, J. J. Ge, P. S. Honigfort, J.-C. Cheng, F. W. Harris, and S. Z. D. Cheng, *Polymer* **40**, 4571 (1999).
- ⁴¹H.-T. Kim, S.-K. Kim, and J.-K. Park, *Polym. J.* **31**, 154 (1999).
- ⁴²K. Osaki, T. Inoue, E.-J. Hwang, H. Okamoto, and O. Takiguchi, *J. Non-Crystal. Solid* **172–174**, 838 (1994).
- ⁴³N. Keil, H. H. Yao, C. Zawadzki, J. Bauer, M. Bauer, C. Dreyer, and J. Schneider, *Electron. Lett.* **37**, 579 (2001).
- ⁴⁴C. L. Callender, J. Jiang, C. Blanchetiere, J. P. Walker, S. J. Mihailov, J. Ding, and M. Day, *Proc. Mater. Res. Soc. Symp.* **817**, 195 (2004).
- ⁴⁵S. Numata and T. Miwa, *Polymer* **30**, 1170 (1989).
- ⁴⁶M. T. Pottiger, J. C. Coburn, and J. R. Edman, *J. Polym. Sci. Part B: Polym. Phys.* **32**, 825 (1994).
- ⁴⁷H.-C. Liou, P. S. Ho, and R. Stierman, *Thin Solid Film* **339**, 68 (1999).