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Refractive Indices and Thermo-Optic Coefficients of Aromatic Polyimides Containing Sulfur Atoms

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Aromatic polyimides (PIs) containing thioether (–S–) or disulfide (–S–S–) groups in their molecular structures were prepared to attain high refractive index (n_{av}) and large thermo-optic coefficient (dn_{av}/dT). These PIs exhibit higher n_{av} than the respective ether (–O–) containing PIs, which is due to the large polarizability of sulfur atoms. On the other hand, the values of in-plane/out-of-plane birefringence (Δn) are as small as the other amorphous PIs since the flexible –S– and –S–S– linkages cause small degrees of chain orientation. The values of dn_{av}/dT (−88 to −91 ppm/K) are significantly larger than the other amorphous PIs (−52 to −76 ppm/K). Increases in $|dn_{av}/dT|$ are accounted by high n_{av} and relatively large thermal volume expansion. On the other hand, polarization dependence in thermo-optic coefficients ($d(\Delta n)/dT$) of sulfur-containing PIs are relatively large because of large stress birefringences.

Keywords: sulfur-containing polyimides, refractive index, thermo-optic coefficient

1. Introduction

Thermo-optic (TO) effect (*i.e.* temperature dependent change in refractive index) is frequently utilized for dynamic control of refractive index in active waveguide components [1]. Hence, control of thermo-optic coefficient (temperature gradient of refractive index, dn/dT) is an essential issue for the optical waveguide materials. Although the values of $|dn/dT|$ of polymeric materials are generally larger than those for inorganic waveguide materials, there have been limited numbers of studies on dn/dT of polymers [2,3]. Recently, we have experimentally obtained the values of dn/dT for aromatic polyimide (PI) films formed on Si substrates [4]. The values of dn/dT for average refractive indices (dn_{av}/dT) are in a range of −52 to −70 ppm/K (ppm: 10^{-6}), and the PIs with high n_{av} exhibit large $|dn_{av}/dT|$ as expected from the temperature derivative of Lorentz-Lorenz equation:

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

(β: coefficient of thermal volume expansion).

Since aromatic PIs generally exhibit excellent thermal stabilities, therefore they are good candidates for the active waveguide components utilizing their TO effects. However, the values of $|dn_{av}/dT|$ for PIs are relatively small compared to the other conventional optical polymers such as poly(methylmethacrylate), polystyrene, and polycarbonates. The strong correlation between the values of $|dn_{av}/dT|$ and n_{av} in PIs lead us to extend the relationship to prepare novel PIs showing high n_{av} to obtain large $|dn_{av}/dT|$. In this study, sulfur-containing PIs were prepared to increase and control their n_{av} and dn_{av}/dT.

2. Experimental

The molecular structures of PIs are shown in Fig. 1. All the dianhydrides and 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) were dried under reduced pressure before uses. 4,4′-Diaminodiphenyether (ODA) and 4,4′-diaminodiphenythioether (SDA) were purified by recrystallizations from tetrahydrofuran/hexane followed by sublimations under reduced pressure.

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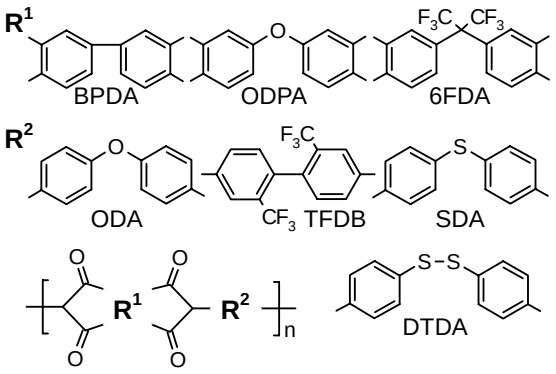

Fig. 1 Molecular structures of polyimides.

4-Aminophenyldisulfide (DTDA) was purified by recrystallization from methanol/water followed by recrystallization from ethanol/hexane.

All PI films (thickness: 8 – 11 μm) were prepared by thermal imidization of their precursor, poly(amic acid)s (PAAs). PAA solutions were prepared by addition polymerizations of equimolar diamine and dianhydride and spin-coated onto 3-inch silicon wafers, followed by drying at 70°C for 30 min and thus thermally imidized at 350°C for 1 h under N_2 flow.

Refractive indices at elevated temperatures were measured using a prism coupler (Metricon, model PC-2000) equipped with a home-built temperature controlling apparatus. Measurements were conducted at a wavelength of 1.32 μm for in-plane and out-of-plane refractive indices (n_{TE} and n_{TM}, respectively). All measurements were conducted on the cooling cycle from 85°C to 35°C in a dried atmosphere (~20% relative humidity) to avoid the influence of moisture sorption/desorption during measurements [4].

Isotropic values of molecular polarizabilities (α_{av}) were calculated using GAUSSIAN package (version 98 Rev. A9 or later) with a basis set of B3LYP/6-31+G(d). Packing coefficients (K_p) for PIs were calculated from the values of n_{av} and α_{av} using the previously reported method [5].

Thermal stabilities of PIs were estimated using thermogravimetric analyzer (Shimadzu, TGA-50) with a heating rate of 10 °C/min under N_2 flow.

Glass transition temperatures of PI samples (15 mm length / 5 mm width) were obtained using thermal mechanical analyzer (UNVAC, TM-7000) under N_2 with a heating rate of 5 °C/min and a constant load (5 g).

Residual stresses on the PI films were estimated from the curvatures of the samples [6] measured using a depth profiler (Dektak-3).

3. Results

3.1. Refractive Indices and Birefringence of PIs

The PIs derived from sulfur-containing diamine and ODPA dianhydride exhibit significantly higher average refractive indices (n_{av}) than the other aromatic PIs (Table 1) as expected, since the sulfur atoms in thioether (–S–) and disulfide (–S–S–) groups have larger polarizabilities than the other atoms (*e.g.* oxygen in –O–), which is clearly shown in Fig. 2. Note that the values of molecular polarizabilities per volume (α_{av}/V_{vdw}) for the repeating unit of ODPA/SDA are very close to that of ODPA/DTDA despite the difference in the sulfur contents. Although molecular polarizability (α_{av}) of ODPA/DTDA is slightly larger than that for ODPA/SDA, significantly long S–S bond (2.12

Table 1 In-plane, out-of-plane, average refractive indices[a] (n_{TE}, n_{TM}, and n_{av}, respectively), and in-plane/out-of-plane birefringence[b] (Δn) for polyimide films formed on Si substrates.

Polyimide	n_{TE}	n_{TM}	n_{av}	Δn
ODPA/DTDA	1.6718	1.6632	1.6689	0.0086
ODPA/SDA	1.6695	1.6597	1.6662	0.0098
BPDA/DTDA	1.6982	1.6892	1.6952	0.0090
ODPA/ODA	1.6458	1.6359	1.6425	0.0099
ODPA/TFDB	1.5829	1.5732	1.5797	0.0097
6FDA/ODA	1.5629	1.5555	1.5604	0.0074
6FDA/TFDB	1.5205	1.5129	1.5180	0.0076

[a] $n_{av}^2 = (2n_{TE}^2 + n_{TM}^2)/3$ [b] $\Delta n = n_{TE} - n_{TM}$

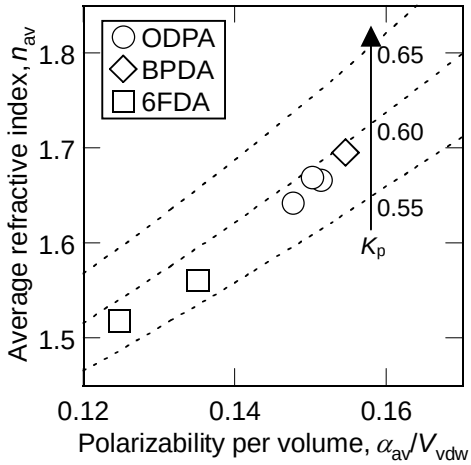

Fig. 2 Relationship between the values of polarizabilities per volume (α_{av}/V_{vdw}) and average refractive indices (n_{av}) for polyimide films formed on Si substrates. Dotted lines represent the relations between α_{av}/V_{vdw} and n_{av} with constant packing coefficients (K_p; large K_p represents dense molecular packing).

Å from the DFT calculation) leads to a large van der Waals volume (V_{vdw}) of ODPA/DTDA repeating units. On the other hand, packing coefficients (K_p) of flexible PIs are smaller (*i.e.* looser molecular packing) than those of the conventional rigid PIs [5] since the bent linkages hinder dense packing of molecular chains.

Further, the values of in-plane/out-of-plane birefringence (Δn) for the sulfur-containing PIs are almost same as those for the other flexible PIs, hence, the degrees of chain orientation for sulfur-containing PIs are very small due to the flexible –S– or –S–S– groups in the main chain structures of PIs. This indicates that the sulfur-containing PIs can be candidates for non-birefringent optical materials.

3.2. Thermal Properties

As shown in Table 2, the sulfur-containing PIs exhibit high thermal degradation temperatures (T_d^5: 5% weight-loss temperature) and relatively low softening temperatures (T_g). The significant decreases in their moduli over T_s (Fig. 3) indicate that the PIs derived from DTDA forms a group of thermo-plastic PIs.

It is well known that the residual stress exists in PI films formed on inflexible substrates (*e.g.* Si, inorganic glasses), that is generated from the difference in coefficients of thermal expansion (CTE). The sulfur-containing PIs exhibit large values of residual stress (σ) (Table 2), which is due to the very small degrees of chain orientation and large CTEs.

Table 2 Five-percent thermal weight loss temperature (T_d^5), softening temperature (T_s), and residual stress (s) for sulfur-containing PI films.

Polyimide	T_d^5 [°C]	T_s [°C]	σ [MPa]
ODPA/DTDA	536	166	42.6
ODPA/SDA	538	262	47.2
BPDA/DTDA	531	213	26.9

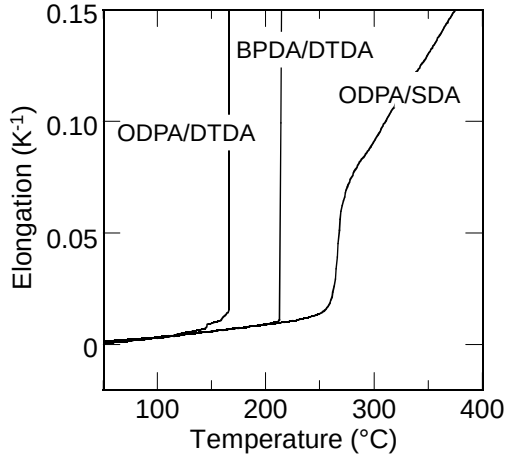

Fig. 3 Temperature–elongation curves for sulfur-containing PI films.

3.3. Thermo-Optic Coefficients

The thermo-optic coefficients and their anisotropies (the polarization dependences) measured for the PI films are listed in Table 3. The temperature dependences in n_{av} (dn_{av}/dT) for sulfur-containing PIs are significantly larger than those for the other amorphous PIs. In addition, increases in $|dn_{av}/dT|$ for the sulfur-containing PIs (ca. 20% from that of ODPA/ODA) are too large as estimated from the increases in n_{av} according to Eq. 1 (Fig. 4). This indicates that the sulfur-containing PIs should have larger β (thermal volume expansion coefficients) than the other PIs. Although the estimated values

Table 3 Thermo-optic coefficients and their anisotropies[a] for polyimide films formed on Si substrates.

Polyimide	dn_{TE}/dT [ppm/K]	dn_{TM}/dT [ppm/K]	dn_{av}/dT [ppm/K]	$d(\Delta n)/dT$ [ppm/K]
ODPA/DTDA	–101	–69	–91	–32
ODPA/SDA	–102	–67	–90	–34
BPDA/DTDA	–100	–63	–88	–38
ODPA/ODA	–88	–53	–76	–34
ODPA/TFDB	–63	–38	–55	–26
6FDA/ODA	–76	–57	–70	–20
6FDA/TFDB	–57	–41	–52	–16

[a] $d(\Delta n)/dT = dn_{TE}/dT - dn_{TM}/dT$

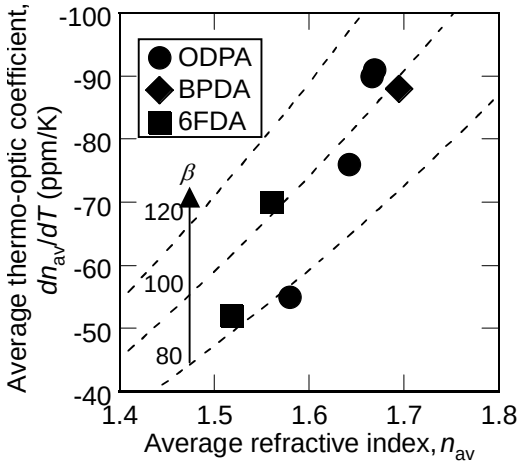

Fig. 4 Relationship between average thermo-optic coefficients (dn_{av}/dT) and average refractive indices (n_{av}) for polyimide films formed on Si substrates. Dotted lines represent the relation between dn_{av}/dT and n_{av} according to Eq. 1.

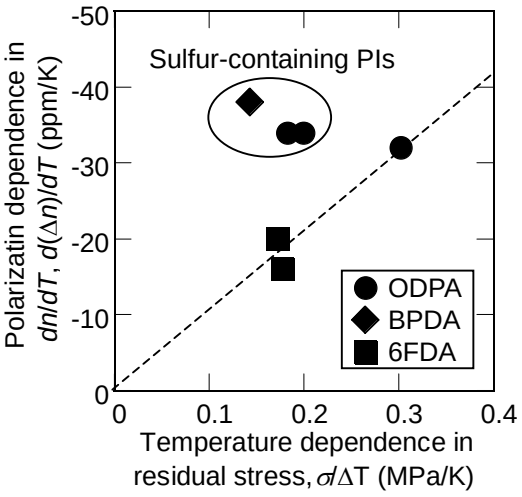

Fig. 5 Relationship between polarization dependences in thermo-optic coefficients ($d(\Delta n)/dT$) and calculated temperature gradient of residual stress ($\sigma/\Delta T$). The parameter ΔT represents the difference between room temperature (25 °C) and softening temperatures of PIs.

of β from Fig. 4 are smaller than those for flexible PI films without substrates [7], small β for the PI films on Si substrates are caused by the restrictions of thermal expansions by hard Si substrates.

Theoretically, polarization dependence in thermo-optic coefficient is identical with temperature dependence of birefringence ($d(\Delta n)/dT$). Since the residual stress in PI films decrease as a temperature increases [8], stress-birefringence in PI films exhibit temperature dependences:

$$\frac{d(\Delta n)}{dT} = C_G \frac{d\sigma}{dT} \approx C_G \cdot \frac{\sigma}{T_g - T_r} \qquad (2)$$

where C_G is stress-optical coefficient and T_r is room temperature. We have experimentally shown that the values of $d(\Delta n)/dT$ of un-oriented PI films are quantitatively accounted by Eq. 2 [9]. As shown in Fig. 5, $d(\Delta n)/dT$ for the sulfur-containing PIs are relatively large despite the small $\sigma/\Delta T$, hence, the sulfur-containing PIs have larger C_G than the other amorphous PIs. The low T_gs observed in the sulfur-containing PIs indicate that their moduli should be small. Hence, the large deformations will be caused by temperature dependence of residual stress, which induce the large stress birefringence.

5. Conclusion

The aromatic PIs containing thioether (–S–) or disulfide (–S–S–) groups exhibit significantly higher n_{av} than the other amorphous PIs originating from the large polarizabilities of sulfur atoms. The value of n_{av} for the former is almost same as the latter because the values of α_{av}/V_{vdw} are close to each other. In contrast, the values of Δn for these PIs are as small as the other amorphous PIs, therefore he sulfur-containing PIs can be candidates for non-birefringent optical materials.

The dn_{av}/dT for the sulfur-containing PIs ranges from –88 to –91 ppm/K, which are significantly larger than those for the amorphous PIs in their absolute values. Firstly, this is ascribed to the high n_{av} of sulfur-containing PIs. Secondly, highly flexible molecular structures of sulfur-containing PIs would large thermal volume expansion. The both effects lead to the large $|dn_{av}/dT|$. In contrast, the similar values of $d(\Delta n)/dT$ for sulfur-containing PIs and ODPA/ODA PI can be explained in terms of the large residual stress on Si substrates and the large stress-optical coefficients of sulfur-containing PIs.

References

1. H. Ma, A. K.-Y. Jen, and L. R. Dalton, *Adv. Mater.*, **19** (2002) 1339.
2. J. M. Cariou, J. Dugas, L. Martin, and P. Michel, *Appl. Opt.*, **25** (1986) 334.
3. P. Michel, J. Dugas, J. M. Cariou, and L. Martin, *J. Macromol. Sci. Phys.*, **B25** (1986) 379.
4. Y. Terui and S. Ando, *Appl. Phys. Lett.*, **83** (2003) 4755.
5. Y. Terui and S. Ando, *J. Polym. Sci. Part B: Polym. Phys.*, **42** (2004) 2354.
6. J. C. Coburn, M. T. Pottiger, S. C. Noe, and S. D. Senturia, *J. Polym. Sci. Part B: Polym. Phys.*, **32** (1994) 1271.
7. J. C. Coburn, M. T. Pottiger, and C. A. Pryde, *Mater. Res. Soc. Symp. Proc.*, **308** (1993) 475.
8. M. Ree, K. Kim, S. H. Woo, and H. Chang, *J. Appl. Phys.*, **81** (1997) 698.
9. Y. Terui and S. Ando, *Proc. SPIE*, **5724** (2005) 336.