

Effects of Structural Isomerism and Precursor Structures on Thermo-optic Coefficients of BPDA/PDA Polyimide Films

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The effects of the structural isomerism and the alkyl side-chain lengths in the precursors of BPDA/PDA polyimide (PI) on the temperature dependence of the refractive indices (*i.e.* thermo-optical coefficients) have been investigated. The PIs were formed on Si substrates by thermal curing of a) poly(amic acid)s (PAA) derived from three isomers (*s*-, *a*-, and *i*-) of biphenyltetracarboxylic acid dianhydride (BPDA) and *p*-diminobenzene (PDA) and b) poly(amide alkylester)s (PAEs) having methyl-, *n*-propyl-, *n*-pentyl-, and *n*-octyl side chains. The TO coefficients of PIs increase as the average refractive indices and thermal expansion coefficients increase, which can be well explained with the derivative form of the Lorentz-Lorenz formula. The absolute values of TO coefficients for *s*-BPDA/PDA are smaller than those expected from their refractive indices, which is due to the dense molecular packing and the small coefficient of thermal expansion. Significantly larger TO coefficients were observed for the PI films prepared from PAEs than that from PAA, indicating that the larger volatile components (alcohols) eliminated during thermal imidization cause loose molecular packing in the former PIs. The use of structural isomers and chemical modification of precursors are effective to control the TO coefficients and their anisotropies in BPDA/PDA films.

Keywords / polyimide / optical properties / thermo-optic coefficient / refractive index / molecular packing / structural isomerism / thermal expansion /

1. Introduction

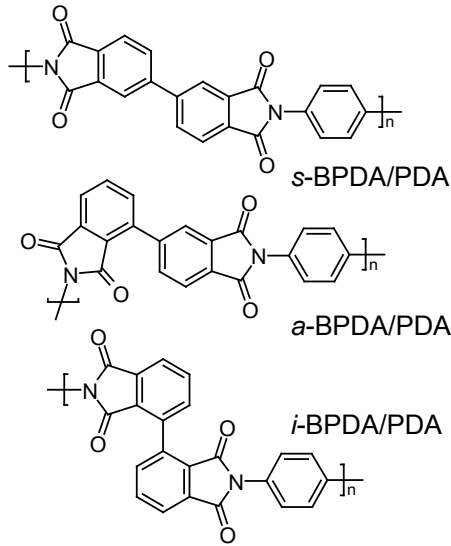
In recent years, research and development for the application of aromatic polyimides (PI) to optical lightwave circuits have been activated.[1] Since the temperature dependence of refractive indices of polymeric materials, that is expressed as 'thermo-optical (TO) coefficient', are more than ten times larger than those of inorganic glasses, applications of polymer optical materials to thermo-optical switches and passive optical filters at variable temperatures attract much attention. In addition, polymer waveguide systems can significantly reduce the power consumption in optical switches and improve the speed of response in the lightwave circuits.

The thermo-optical (TO) coefficient (dn_{av}/dT) of condensed matters can be expressed as the temperature derivative of the Lorentz-Lorenz formula as expressed by

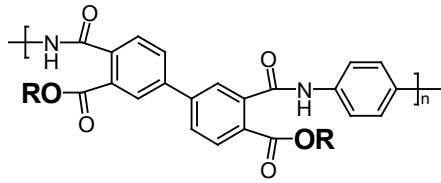
$$\frac{dn_{av}}{dT} = -\frac{(n_{av}^2 - 1)(n_{av}^2 + 2)}{6n_{av}}\beta \quad (1)$$

Eq.(1) indicates that increases in the average refractive index (n_{av}) and/or the thermal expansion coefficient (β) should cause an increase in the absolute value of TO coefficient, $|dn_{av}/dT|$.

Three kinds of structural isomers are known for BPDA/PDA PI as shown in Scheme 1, in which the linearity of polymer chains significantly differs. In addition, large differences have been observed in the coefficients of thermal expansion (CTE) and the glass transition temperatures (T_g) among these isomers.[2,3] When a precursor is changed from a poly(amic acid) (PAA) to a poly(amide alkylester) (PAE), the volatile component eliminated during imidization changes from water to alcohols. Miwa et al.[4] have reported that the CTEs of PI films prepared from PAEs increase as their alkyl chain



Scheme 1. Structures of three isomers of BPDA-PDA polyimides.



Scheme 2. Structure of a poly(amide alkylester)s (PAEs) prepared as precursors for *s*-BPDA/PDA PI. **R** represents CH₃, *n*-C₃H₇, *n*-C₅H₁₁, or *n*-C₈H₁₇.

lengths increase. In addition, Takeichi et al.[5] have reported that the degree of in-plane/out-of-plane molecular orientation increases with increasing the alkyl chain lengths. These facts suggests that the morphology, packing states, and molecular orientation are appreciably influenced by the isomeric structures of PAA and the alkyl-chain lengths in PAEs. Loose molecular packing increases the proportion of free volume, which should enhance the CTE and dn_{av}/dT . In addition, the present authors reported that the dn_{av}/dT of aromatic PI films formed on Si substrates exhibit significant polarization dependence, whereas little anisotropy is observed for PMMA film.[6,7] Since the birefringence (Δn) and dn/dT are closely related to the anisotropy in TO coefficients ($d(\Delta n)/dT$), a higher degree of molecular orientation causes an increase in the absolute value of $d(\Delta n)/dT$ (denoted as $|d(\Delta n)/dT|$).

The objective of this study is to clarify the mechanisms of the temperature dependence of refractive indices in BPDA/PDA PI films and to control the values of dn_{av}/dT and $d(\Delta n)/dT$ by using isomeric structures of PAA and PAE precursors with different alkyl chain lengths through the concurrent variations in n_{av} and β of PIs.

Table 1. Isomeric PI films of BPDA/PDA prepared under different conditions.

PI	isomer	film formation	T_i [°C]
s-1	<i>s</i> -BPDA/PDA	on substrate	350
s-2	<i>s</i> -BPDA/PDA	substrate free	350
s-3	<i>s</i> -BPDA/PDA	substrate free	400
a-1	<i>a</i> -BPDA/PDA	on substrate	350
a-2	<i>a</i> -BPDA/PDA	substrate free	350
a-3	<i>a</i> -BPDA/PDA	substrate free	400
i-3	<i>i</i> -BPDA/PDA	substrate free	400

2. Experimental

For examining the influence of structural isomerism of PIs, three kinds of isomers, namely, *s*-, *a*- and *i*-isomers of BPDA-PDA were prepared (Scheme 1). DMAc solutions of the corresponding poly(amic acid)s (PAAs) were prepared from *s*-, *a*-, and *i*-isomers of biphenyl tetracarboxylic dianhydrides (BPDA) and *p*-diaminobenzene (PDA) by the conventional two-step method.[1] The solutions were spin-coated onto Si substrates followed by three different procedures, 1) drying in N₂ at 70°C for 2h, and subsequent imidization at 350°C for 1h under nitrogen, 2) drying in N₂, peeled from substrates, and imidized at 350°C for 1h, and 3) processed as 2) followed by additional annealing at 400°C for 1h. The PI films thus prepared are listed in Table 1. A homogeneous film of *i*-BPDA/PDA was only obtained when the PAA film was peeled from substrate and cured under the substrate-free condition, which is due to the hairpin-like bent structure of *i*-BPDA.

Further, five kinds of PI films were prepared from PAA solution of *s*-BPDA/PDA (denoted as **A**) and PAE solutions of methyl- (**E1**), propyl- (**E3**), pentyl- (**E5**), and octyl- (**E8**) esters (Scheme 2) The synthetic procedures of the PAE precursors have been reported elsewhere.[5] The precursor solutions were spin-coated onto Si (denoted as **-c**) or BK-7 glass (**-d**) substrates, followed by drying at 70°C for 1h. The films were thermally imidized stepwise at 160°C for 1h, at 250°C for 1h, and 350°C for 1h. The thicknesses of PI films thus obtained were 8-11 μm. The films **-d** were peeled from substrates and devoted to dn/dT measurements. Variable-temperature measurements of polarization-dependent refractive indices (dn_{TE}/dT and dn_{TM}/dT) were performed at elevated temperatures using a prism coupler (converted Metricon PC-2000) at the wavelength of 1320 nm. The temperature was varied in the range of 35-85 °C at 17-19 % of relative humidity. The values of $d(\Delta n)/dT$ were calculated as $(dn_{TE}/dT) - (dn_{TM}/dT)$.

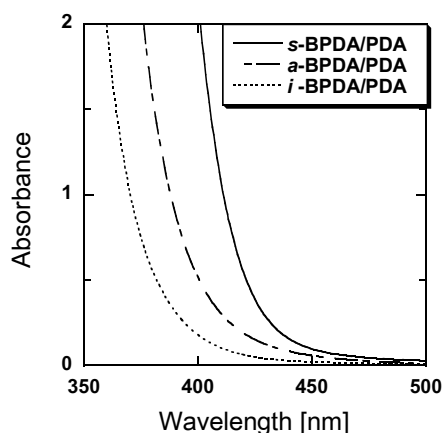


Fig. 1. Optical absorption spectra of three isomers of BPDA/PDA PI films formed on silica substrates.

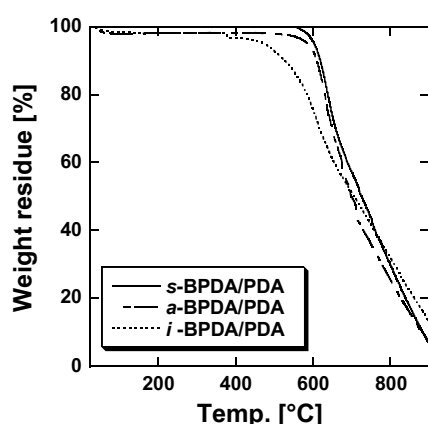


Fig. 2. TGA curves for isomers of BPDA/PDA PIs.

3. Results and Discussion

3.1 Characterization of *s*-, *a*-, and *i*-Isomeric PIs

The optical absorption spectra of the PI isomers free from substrates are shown in Fig. 1. The absorption edge are located at the longest wavelength for *s*-isomer whereas at the shortest for *i*-isomer. The deepest and shallowest coloration observed for *s*- and *i*-isomers, respectively, are explained in terms of the π -conjugation in the BPDA moieties. The dihedral angles at the biphenyl linkages optimized by the density functional theory (B3LYP/6-311G(d)) are 40.8°, 46.7°, 54.0° for *s*-, *a*-, *i*-isomers, respectively. This clearly indicates that a more planar structure ($s > a > i$) gives a smaller band-gap and a longer absorption edge that cause deep coloration.

The thermo-gravimetric analysis (TGA) curves measured for the three isomers are shown in Fig. 2. The 5-wt% degradation temperatures are 603 °C, 599°C, and 495°C for *s*-, *a*-, and *i*-isomers, respectively. The highest thermal stability observed for *s*-isomer can be attributed to the dense molecular packing stabilized by the intermolecular

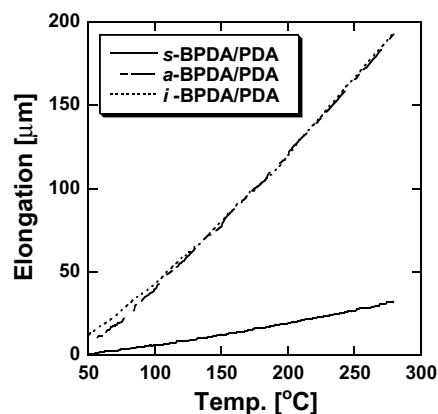


Fig. 3. TMA curves of isomers of BPDA/PDA PIs.

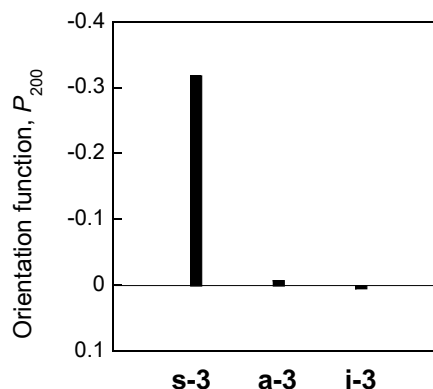


Fig. 4. Herman's 2nd-order orientation function (P_{200}) estimated for three isomers of BPDA/PDA PIs using polarized ATR-IR spectra.

π - π stacking and the least intramolecular steric hindrance. In contrast, the bent polymer chains in *i*-isomer should cause significant intramolecular distortion and intermolecular stress.

The thermo-mechanical analysis (TMA) curves measured for the three isomers are shown in Fig. 3. The coefficients of thermal expansion (CTE) estimated between 50°C and 250°C are 8.8, 53.5, and 51.6 ppm/K for *s*-, *a*-, and *i*-isomers, respectively. The smallest CTE value observed for *s*-isomer is attributed to the fully elongated and well-packed PI chains. In contrast, much larger CTEs observed for *a*-, and *i*-isomers originate from their bent biphenyl linkages.

The Herman's second-order orientation function (P_{200}) of PI main chains, which were estimated from polarized ATR-IR spectra [8,9], are shown in Fig. 4. The P_{200} can be expressed by the following formula, in which θ corresponds to the angle between the main chains and the axis perpendicular to the film plane.

$$P_{200} = (3\langle \cos^2\theta \rangle - 1)/2 \quad (-0.5 < P_{200} < 1) \quad (2)$$

In case that the principal axes of PI chains are

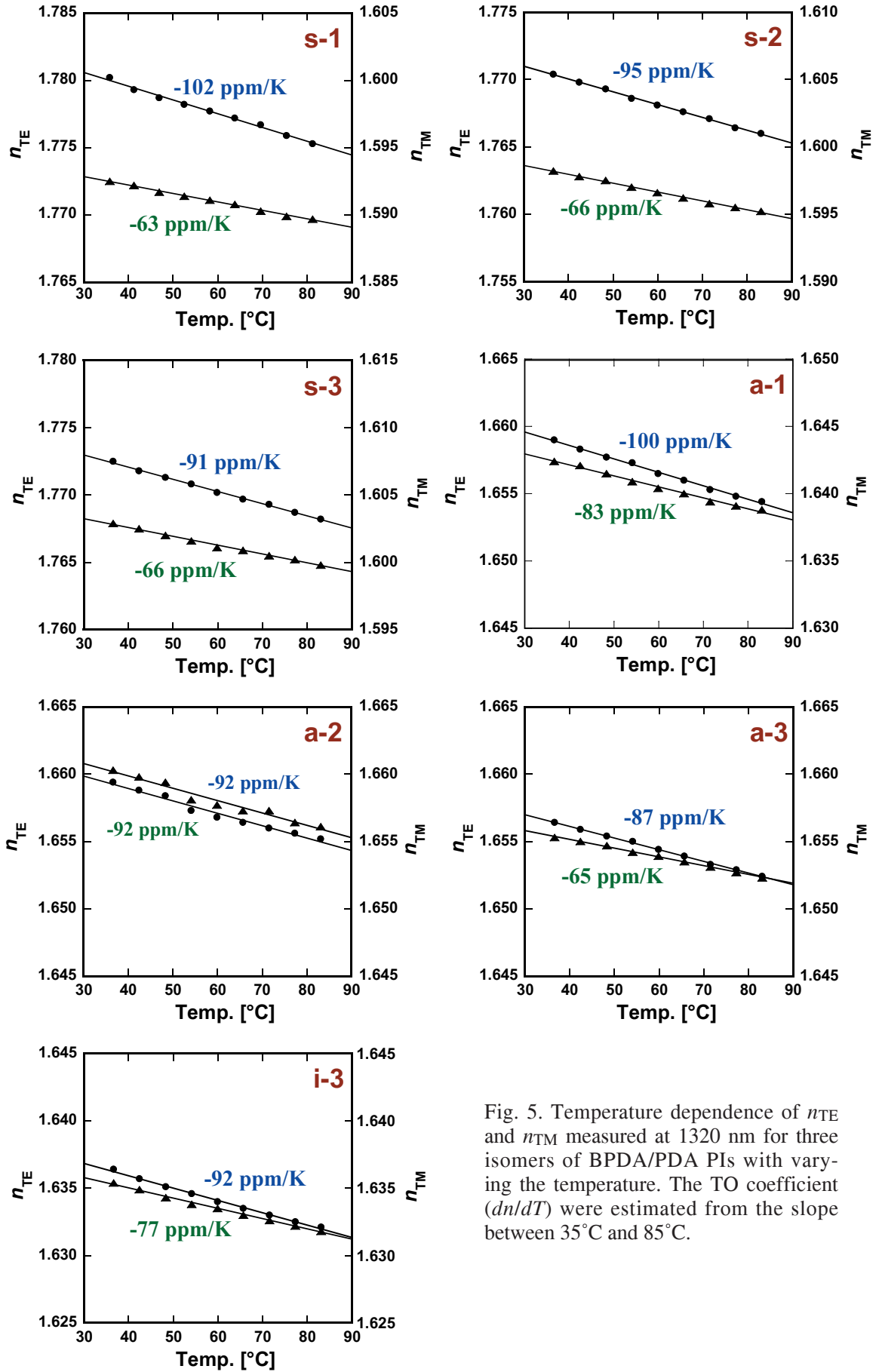


Fig. 5. Temperature dependence of n_{TE} and n_{TM} measured at 1320 nm for three isomers of BPDA/PDA PIs with varying the temperature. The TO coefficient (dn/dT) were estimated from the slope between 35 °C and 85 °C.

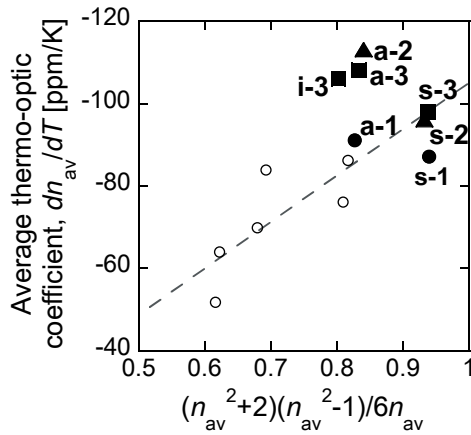


Fig. 6. Plots of dn_{av}/dT against the term appearing in Eq.(1) for isomers of BPDA/PDA PIs. The open circles correspond to the data for amorphous PIs [6].

perfectly orientated along the film plane, the value of P_{200} becomes -0.5 , whereas it becomes null for the random distribution of orientations.

As clearly indicated in Fig. 4, the polymer chain of *s*-isomer demonstrates a high degree of orientation onto the film plane, which accords with the rigid and linear molecular structure. In contrast, *a*- and *i*-isomers exhibit little molecular orientation, which corresponds to highly isotropic distribution of polymer chains. These trend are similar to that observed for TMA measurements.

The average refractive indices (n_{av}) decrease in the order of $s > a > i$ -isomer as shown in Figs. 5 and 6. In general, refractive index of a condensed matter is expressed by the Lorentz-Lorenz equation

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

where N_A , M , ρ , α are the Avogadro's number, molecular weight, density, and polarizability, respectively. The higher n_{av} observed for *s*-isomer can be explained by the higher density and the larger polarizability. The polarizabilities calculated by the DFT are 31.4, 30.5, and 29.7 ($\text{\AA}^3$) for *s*-, *a*-, and *i*-BPDA dianhydrides, respectively. In addition, the coefficients of molecular packing (K_p), which were estimated from the calculated values of α and the observed values of n_{av} of PIs, are 0.574, 0.558, and 0.562 for *s*-, *a*-, and *i*-isomers, respectively. These facts support that the dense molecular packing in *s*-BPDA/PDA films and the relatively loose packing in *a*- and *i*-isomers, which also coincides with the trend observed in the TMA and the polarized ATR-IR. Although *i*-isomer exhibits a slightly larger value of K_p than *a*-isomer, their similarity is noticeable.

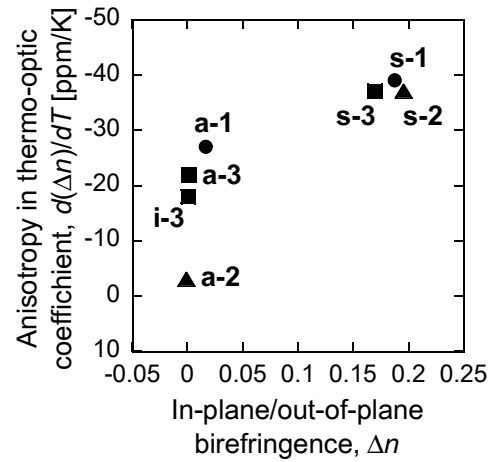


Fig. 7. Plots of $d(\Delta n)/dT$ against Δn for isomers of BPDA/PDA PIs.

3.2 Analysis of TO Coefs. and Their Anisotropy for *s*-, *a*-, and *i*-isomers of PI films

The plots of the measured values of dn_{av}/dT against the term related to n_{av} for the PIs listed in Table 2 are shown in Fig. 6. For the PI films formed on substrates (-1) the plot of **a-1** is located on the linear relations reported for several amorphous PIs [6], but that of **s-1** is deviated from the linearity. The relatively smaller value of $|dn_{av}/dT|$ than that expected from the n_{av} for **s-1** is owing to the decreased β as demonstrated by the smaller value of CTE. This also originates from the dense molecular packing and linear structure of *s*-isomer.

In addition, the values of $|dn_{av}/dT|$ observed for the PI films thermally imidized without substrates (substrate-free, -2, -3) are larger than that for the PIs imidized on substrates (-1) regardless of the imidization temperature. The CTE mismatch between PI film and silica substrate causes molecular orientation and dense molecular packing in the PIs on substrates (-1) during cooling, which should reduce the $|dn_{av}/dT|$. In contrast, it is noteworthy that substrate-free imidization provides loose molecular packing with larger values of β and CTE due to the absence of thermal stress.

Furthermore, the values of in-plane/out-of-plane birefringence (Δn) also decrease in the order of $s > a > i$ -isomers as shown in Fig. 7. The larger values of Δn for *s*-isomer agree well with the higher degree of orientation as evidenced by the P_{200} value estimated by the ATR-IR measurements.

The plots of the measured values of $d(\Delta n)/dT$ against those of Δn are shown in Fig. 7. In general, a larger value of Δn provide a larger value of $|d(\Delta n)/dT|$. The higher degrees of molecular orientation of *s*-isomers, which is demonstrated by the larger value of P_{200} and Δn , should cause

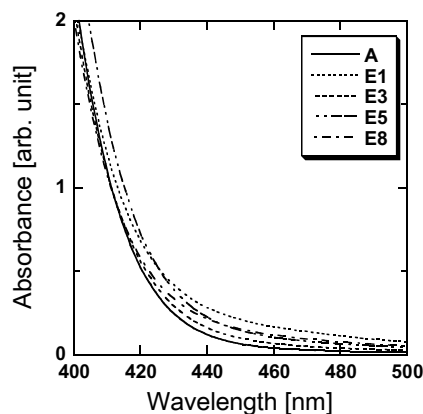


Fig. 8. Optical absorption spectra of *s*-BPDA/PDA PI films prepared from various precursors.

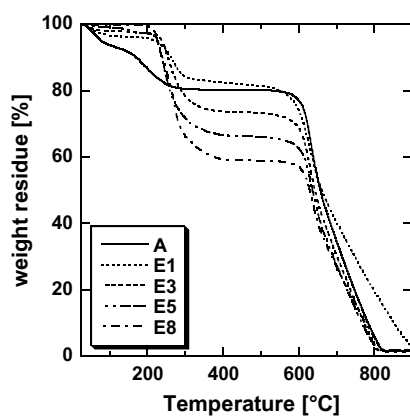


Fig. 9. TGA curves of the precursor films (PAA and PAEs) for *s*-BPDA/PDA PI.

considerable anisotropy in CTE along the in-plane (TE) and the out-of-plane (TM) directions, which should increase the values of $|d(\Delta n)/dT|$. In addition, the reason of the positive values of $d(\Delta n)/dT$ for the PI films whose Δn values are almost null is that the $d(\Delta n)/dT$ can be generated not only by the molecular orientation but also by the residual stress. The absence of the anisotropy in dn/dT (i.e. $|d(\Delta n)/dT|=0$) as observed for **a-2** can be explained by the released internal stress due to the brittleness of the film.

3.3 Characterization of *s*-BPDA/PDA films prepared from Different Precursors (PAA and PAEs)

The optical absorption spectra of the *s*-BPDA/PDA PI films prepared on silica substrates from PAA and four different PAEs are shown in Fig. 8. The absorption edges are observed at almost the same positions with slight differences depending on the film thicknesses. This indicates that the precursors do not affect the coloration of PI films.

The thermo-gravimetric analysis (TGA) curves observed for the PAA and PAE films are shown in Fig. 9. Significant weight-losses caused by imidization are observed around 150-230°C for

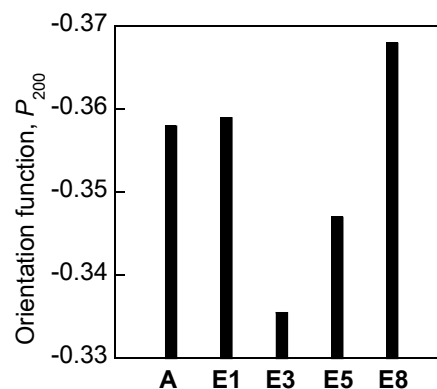


Fig. 10. Herman's 2nd-order orientation function (P_{200}) estimated for *s*-BPDA/PDA PIs prepared from PAA and PAE precursors.

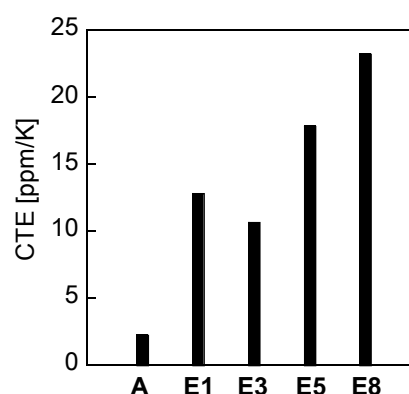


Fig. 11. CTEs observed for *s*-BPDA/PDA PIs prepared from PAA and PAE precursors.

PAA and 230-300°C for PAEs. These curves clearly indicate that the elimination of alcohols from PAEs during imidization occurs at much higher temperatures than that of H₂O from PAA, which should affect the molecular packing of aromatic PIs.

3.4 Analysis of TO Coefs. and Their Anisotropy for *s*-Isomers Prepared from Different Precursors.

The P_{200} values estimated for the PI films using polarized ATR-IR spectra are shown in Fig. 10. Compared with the P_{200} value for the PI from PAA, the smaller P_{200} values are obtained for the PIs from PAEs having short chains but larger P_{200} values are observed for those with long chains. These results agree with that reported by Takeichi et al.[5] who estimated the degrees of molecular orientation using polarized monochromated light. They demonstrated that the molecular orientation is effectively randomized with eliminated alcohols for PAEs having short alkyl chains, whereas the orientation is enhanced in the PAEs having long alkyl chains because eliminated alcohols behave as plasticizers which enhance the in-plane molecular orientation.

In addition, the CTEs within the film plane for all

Table 2. Film thickness, polarization-dependent refractive indices, in-plane/out-of-plane birefringence, polarization-dependent TO coefficients, and their anisotropies observed for three isomers of BPDA/PDA PI films. *s*-BPDA/PDA film was only obtained for substrate-free condition.

PI	<i>d</i> [μm]	<i>n</i> _{TE}	<i>n</i> _{TM}	<i>n</i> _{av}	Δ <i>n</i>	<i>dn</i> _{TE} / <i>dT</i> [ppm/K]	<i>dn</i> _{TM} / <i>dT</i> [ppm/K]	<i>dn</i> _{av} / <i>dT</i> [ppm/K]	<i>d</i> (Δ <i>n</i>)/ <i>dT</i> [ppm/K]
s-1	8.8	1.7802	1.5925	1.7199	0.1877	-102	-63	-90	-39
s-2	6.9	1.7704	1.5982	1.7149	0.1722	-95	-66	-86	-29
s-3	7.1	1.7725	1.6029	1.7178	0.1696	-91	-66	-83	-25
a-1	12.3	1.6590	1.6424	1.6535	0.0166	-100	-82	-94	-8
a-2	8.6	1.6594	1.6603	1.6597	-0.0009	-92	-92	-92	0
a-3	7.3	1.6564	1.6553	1.6560	0.0011	-87	-65	-80	-22
i-3	10.3	1.6364	1.6454	1.6361	0.0010	-102	-3	-90	-9

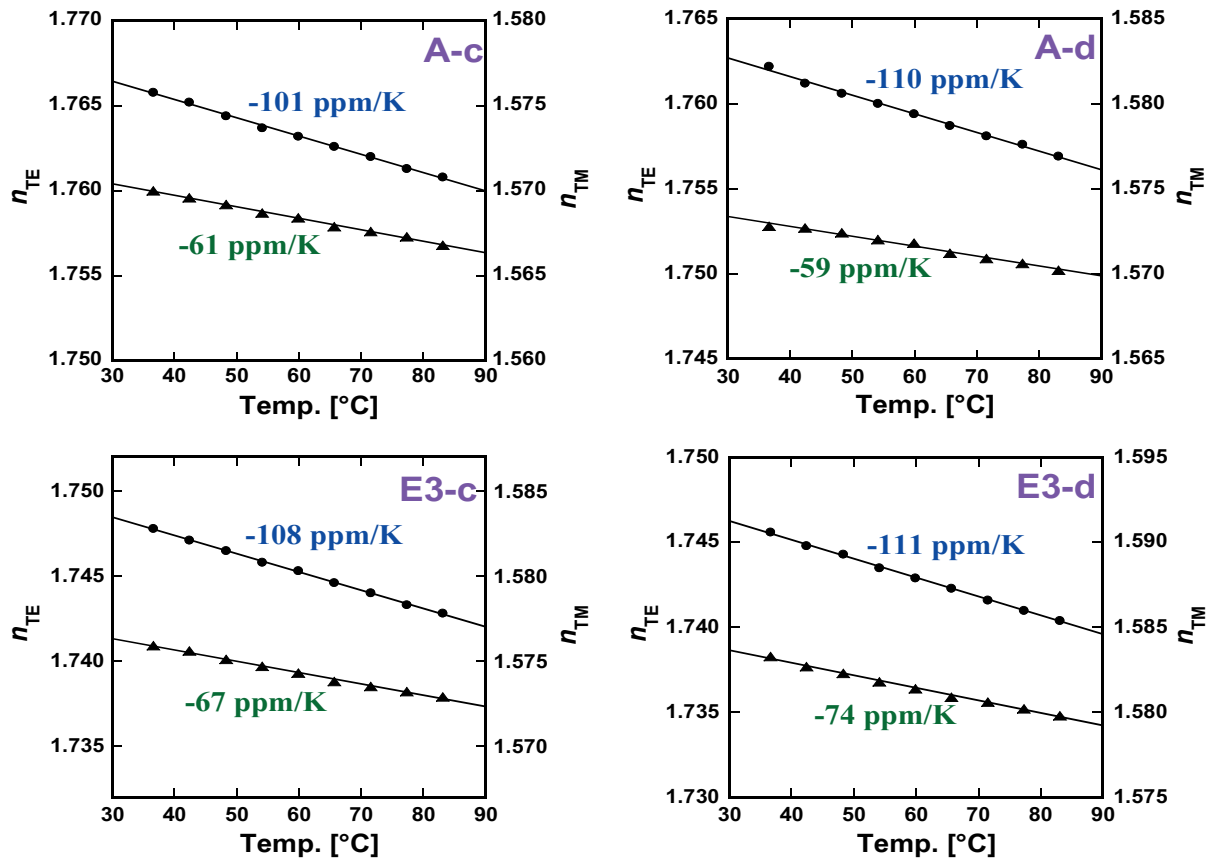


Fig. 12. Temperature dependence of *n*_{TE} and *n*_{TM} measured at 1320 nm for *s*-BPDA/PDA PIs prepared from PAA and E3-PAE. The materials of substrates cause slight variations in *dn/dT*.

Table 3. Precursors, material for substrate, average refractive indices, in-plane/out-of-plane birefringence, film thickness, polarization-dependent TO coefficients, and their anisotropies observed for the PI films prepared from PAA and PAE precursors having different alkyl chain lengths.

	precursor	substrate	<i>n</i> _{av}	Δ <i>n</i>	<i>d</i> [μm]	<i>dn</i> _{TE} / <i>dT</i> [ppm/K]	<i>dn</i> _{TM} / <i>dT</i> [ppm/K]	<i>dn</i> _{av} / <i>dT</i> [ppm/K]	<i>d</i> (Δ <i>n</i>)/ <i>dT</i> [ppm/K]
A-c	PAA	Si	1.7144	0.1835	8.9	-101	-61	-88	-40
A-d	PAA	BK-7	1.7014	0.1894	8.4	-110	-59	-94	-51
E1-d	PAE-methyl	BK-7	1.6975	0.1691	7.8	-107	-73	-96	-34
E3-c	PAE-propyl	Si	1.6924	0.1719	10.3	-108	-67	-95	-41
E3-d	PAE-propyl	BK-7	1.6932	0.1664	8.9	-111	-74	-100	-37
E5-c	PAE-pentyl	Si	1.7040	0.1664	10.2	-109	-68	-96	-41
E5-d	PAE-pentyl	BK-7	1.7042	0.1679	11.1	-106	-67	-94	-38
E8-d	PAE-octyl	BK-7	1.7008	0.1745	7.9	-112	-80	-102	-32

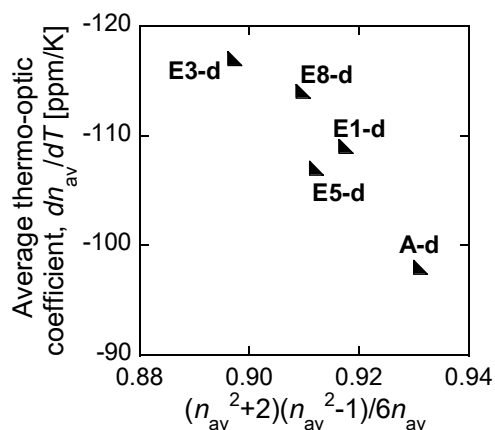


Fig. 13. Plots of dn_{av}/dT against the term appearing in Eq.(1) for *s*-BPDA/PDA PIs prepared from PAA and PAEs. The films were formed on Si substrates.

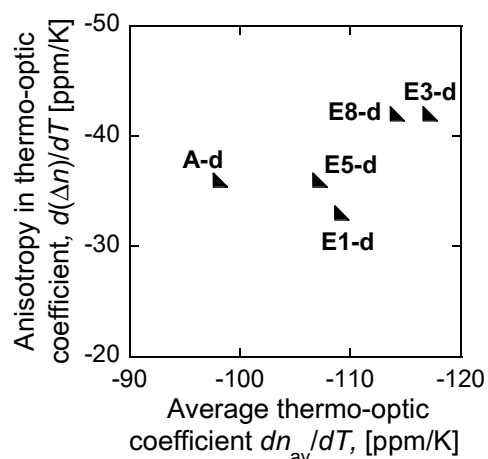


Fig. 14. Plots of $d(\Delta n)/dT$ against dn_{av}/dT for *s*-isomers prepared from different precursors.

PIs from PAEs are larger than that from PAA, and this trend becomes significant with increasing the alkyl chains as shown in Fig. 11. The inconsistency between the order of P_{200} ($E3 < E5 < A < E1 < E8$) and that of CTE ($A < E3 < E1 < E5 < E8$) indicates that the increase in CTE observed for PAEs is not originated from the decrease in molecular orientation but from the loose molecular packing resulting from the elimination of alcohols at higher temperatures (230–300°C). This fact suggests that the order in CTEs is similar to that in volume expansion (β).

The refractive indices (n_{av}) of the PIs prepared from PAEs are significantly smaller than that from PAA as in listed in Table3, Figs.12 and 13. This can be also attributed to the loose molecular packing in the former PIs, which was generated by alcohols eliminated during imidization at the higher temperatures (~50°C) than that from PAA. As seen in Fig. 13, the values of $|dn_{av}/dT|$ for the PIs prepared from PAEs are larger than that from PAA, although the values of n_{av} are smaller. As suggested by the order in CTE, the increase in $|dn_{av}/dT|$ originating from the increase in β accompanied by loose molecular packing is more significant than the influence of the lowering of n_{av} .

Furthermore, larger values of $|dn_{av}/dT|$ tends to provide larger $|d(\Delta n)/dT|$ s for the PIs prepared from PAEs as seen in Fig. 14. In contrast, the value of $|d(\Delta n)/dT|$ for the film from PAA is comparable to those from PAEs despite the smaller value of $|dn_{av}/dT|$. The degrees of molecular orientation (P_{200}) decrease in cases of the short alkyl chains of PAEs. Hence, the anisotropy in thermal expansion (CTE) are relatively large for the PI prepared from PAA than those from PAEs having short chains, which may cause an increase in $|d(\Delta n)/dT|$ in the former PI.

4. Conclusions

The TO coefficients of BPDA/PDA polyimides (PIs) prepared by thermal curing of *s*-, *a*-, and *i*-isomers of PAA and those from four kinds of PAEs having methyl-, *n*-propyl-, *n*-pentyl-, and *n*-octyl side chains were investigated. The values of $|dn_{av}/dT|$ for PIs increase as those of n_{av} and CTEs increase. The $|dn_{av}/dT|$ for *s*-BPDA/PDA is smaller than that expected from its n_{av} due to the dense molecular packing and the small CTE. Significantly larger values of $|dn_{av}/dT|$ are observed for the PIs from PAEs than that from PAA, which indicates that the larger alcohols eliminated during thermal imidization provide loose molecular packing in the former PIs. The control of structural isomerism and chemical modification of precursors are very effective tools to control the TO coefficients and their anisotropies in the PI films.

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