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Thermal Expansion Behavior of the Ordered Domain in Polyimide Films Investigated by Variable Temperature WAXD Measurements

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Coefficients of thermal expansion (CTEs) along the main chain direction in the ordered domain of aromatic and semi-aliphatic polyimide (PI) films (α_c) were determined in order to investigate the thermal expansion behaviors of self-standing PI films in the direction parallel to the film plane. Variable temperature wide-angle X-ray diffraction (VT-WAXD) measurements were performed using a synchrotron radiation facility in the temperature range of 60−360°C. All the PI films showed characteristic WAXD profiles to liquid-crystalline-like ordered domain overlapped with broad and intense amorphous halos, and diffraction peaks corresponding to the repeating unit along the main chain (*c*-axis) and the inter-chain ordering (Ch-pack) were clearly resolved. The α_cs along the *c*-axis of PIs having rigid-rod structure are negative, whereas those for PIs containing bent linkages, such as ether (–O–) or methylene (–CH_2–), in the main chains are large and positive. The α_c values coincide well with the in-plane CTEs of the PI films estimated by thermal mechanical analysis (TMA). This indicates that the negative in-plane CTEs observed for the rigid-rod PI films originates from the negative α_c in the ordered domain, which originates from the extended main chains with appreciable orientation in the film plane.

Keyword: Polyimide / WAXD / thermal expansion / in-plane orientation / β-transition

1. Introduction

Polyimides (PIs) have been widely used in electric, electronic, and aerospace applications due to their high thermal and chemical stability, high mechanical strengths, high electric voltage & radiation resistance, flame retardancy, and good flexibility [1,2]. Since PIs are commonly used as buffer coatings, interlayer dielectric, and interconnects in micro- and opto-electronic components, their relatively large coefficients of thermal expansion (CTEs) could lead to problems at interfacial surfaces with inorganic/metallic layers, where thermal stress give rise to cracking, peeling, or breaking.

Numata et al. [3] have reported that aromatic PIs having rigid-rod structures show very small CTEs along the direction parallel to the film surface. For instance, the CTEs of PIs derived from 4,4”-terphenyldiamine are as small as 5.6 ppm/K. Such very small CTEs originate from highly extended PI chains due to their straight and linear structures. This concept was extensively investigated by Hasegawa et al [4]. They reported that a series of rigid-shape PIs which include ester (–COO–) and amide (–CONH–) groups exhibit small CTEs. The aggregation structures of both fully aromatic and semialiphatic PI films are identified as a mixture of a liquid-crystalline (LC)-like ordered domain and an amorphous matrix.[5] Thereby, thermal expansion behaviors in the ordered domain of PI films should be precisely estimated to investigate the in-plane CTEs of their self-standing films. In this study, CTEs in the ordered domain of aromatic and semi-aliphatic PI films were quantitatively estimated using variable temperature (VT)-WAXD measurements, and they are compared with CTEs of PI films measured by TMA, which reflect in-plane thermal expansion of the whole films consisting of LC-like ordered domains and amorphous matrix.

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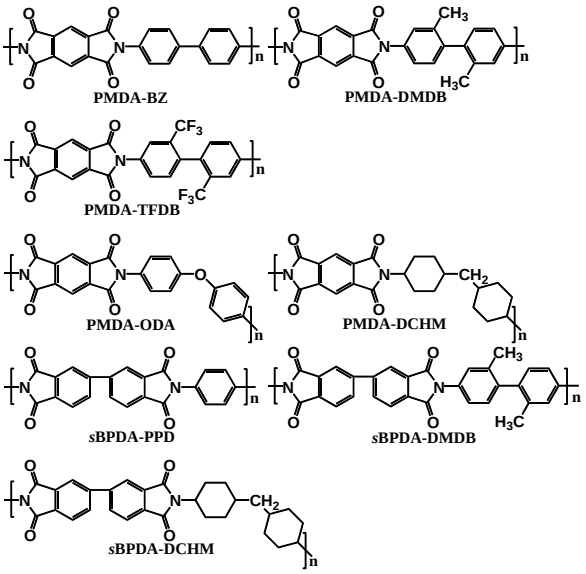


Scheme 1. Structures of polyimides (PIs).

2. Experimental

2.1. Materials for Polyimide Synthesis

Pyromellitic dianhydride (PMDA) purchased from Kanto Chemical Co., Inc. was purified by sublimation under reduced pressure (SubRP). 3,3',4,4'-Biphenyltetracarboxylic dianhydride (sBPDA) from Wako Pure Chemical Industries, Ltd., was dried at 170 °C for 12 h under reduced pressure. *p*-Phenylenediamine (PDA) and 4,4'-diaminodiphenylether (ODA) from Wako Pure Chemical Industries, Ltd were recrystallized from THF followed by SubRP. 2,2'-Dimethyl-4,4'-diamino-biphenyl (DMDB) kindly supplied by Seika Corp. (Wakayama, Japan) was recrystallized from ethylacetate followed by SubRP. 2,2'-Bis (trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) kindly supplied by Central glass Co., Ltd. was used as received. 4,4'-Diaminocyclohexylmethane (DCHM) from Tokyo Kasei Kogyo Co. Ltd. was recrystallized from *n*-hexane followed by SubRP. *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and *N*,*N*-dimethylacetamide (anhydrous, DMAc) from Aldrich were used as received.

2.2. Preparation of PI films

The structures of PIs used in this study are shown in Scheme 1. The precursors of aromatic PIs, poly(amic acid)s (PAAs), were prepared by mixing equimolar amounts of dianhydride and diamine in DMAc under dry nitrogen. The PAA solutions were stirred at room temperature for 48 h. The precursors of PMDA/DCHM and BPDA/ DCHM, poly(amic acid) silyleter (PASE), were prepared by the *in-situ* silyation method.[6] PAA and PASE solutions become viscous after stirring for several hours depending on the degree of polymerization and the rigidity of structures. PI films were prepared by thermal imidization of the corresponding PAA or PASE films. The solutions were spin-coated onto Si substrates, followed by soft-baking at 70 °C for 1 h and subsequent thermal imidization by one-step imidization protocol: the final curing conditions were 300 °C / 1.5 h for PMDA/DCHM and BPDA/DCHM films and 350 °C / 1.5 h for the other PI films. The heating rate was 4.6 °C/min from 70°C to the final curing temperature, and all the procedures were performed under nitrogen (N_2) flow.

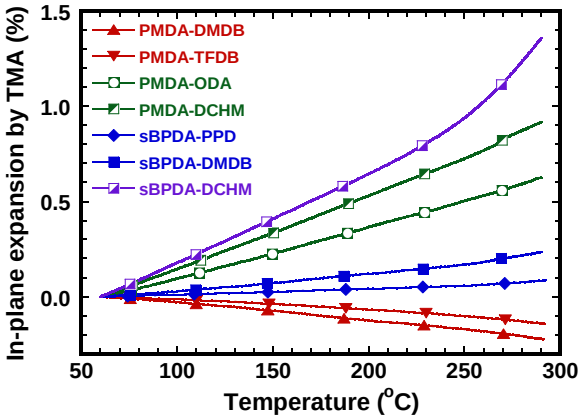


Fig. 1 Thermal expansion behavior in the film plane of PI films measured by TMA.

2.3. Measurements

Thermal mechanical analyses (TMA) of PI films were conducted with a Shimadzu TM-60 analyzer. The size of specimen was 5 mm-wide and 12 mm-long, the tensile load was 3 g, and the heating rate was 10 °C/min. Variable temperature wide angle X-ray diffraction (VT-WAXD) were performed with the BL40B2 beam line at the Japan Synchrotron Radiation Research Institute (JASRI / SPring-8) using an image-plate as the detector. The wavelength of X-ray was 0.8 Å, and temperature of PI films was controlled with a hot stage (Metler Toledo, FP82HT). WAXD patterns were obtained at each temperature after 5 min intervals in the elevating temperature process. The polarization-dependent refractive indices (n_{TE} and n_{TM}) of PI films were measured with a prism coupler (Metricon, PC-2010) at a wavelength of 1310 nm.

3. Results and Discussion

3.1 Thermal Mechanical Analysis of PI films

The TMA curves observed for the PI films are shown in Fig. 1, and the CTE values estimated from the slopes between 80 °C to 180 °C are listed in Table 1. The in-plane/out-of-plane birefringence ($\Delta n = n_{TE} - n_{TM}$) of the films are listed in Table 1.

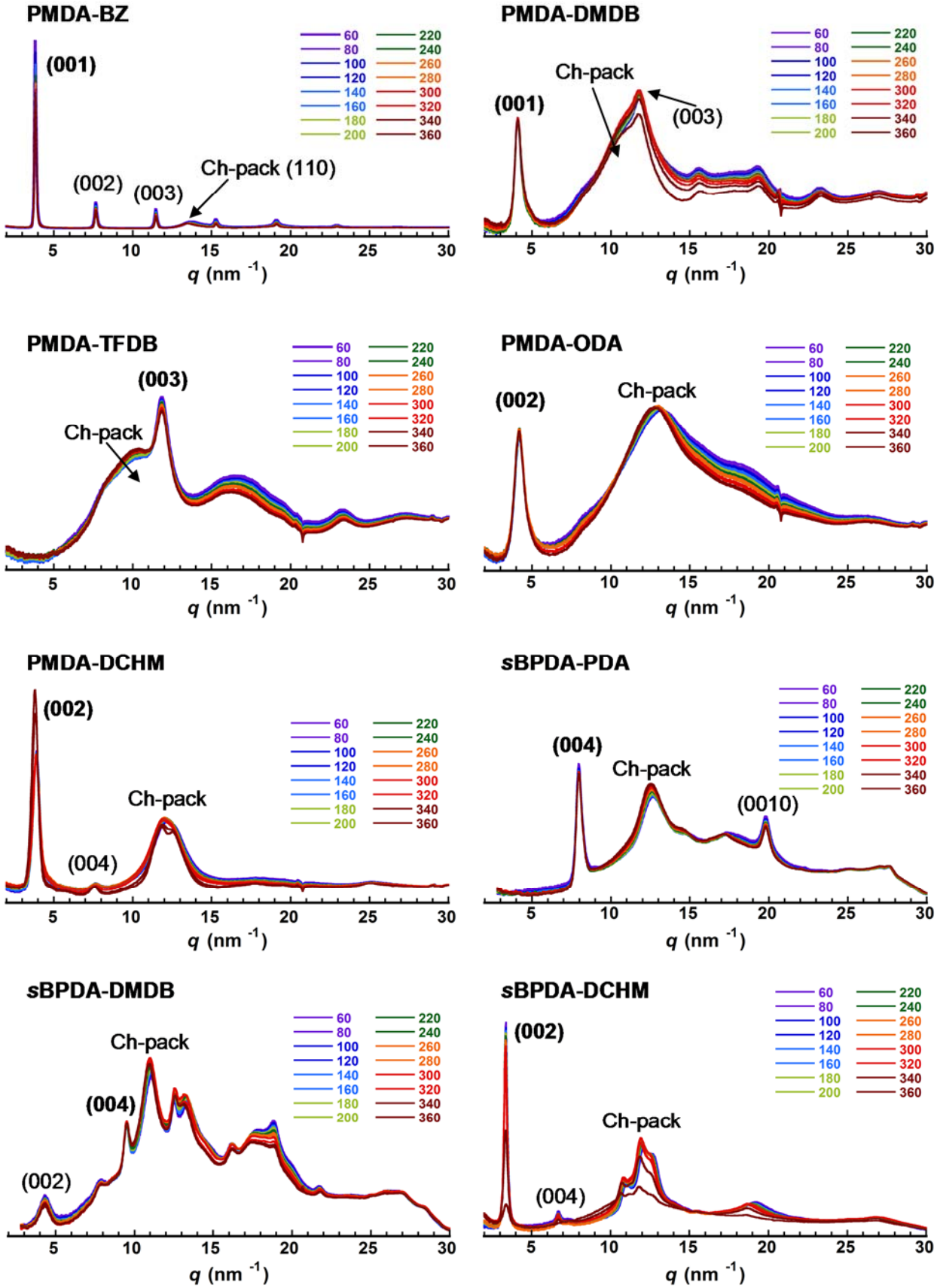


Fig. 2 Variable temperature WAXD profiles of PI films. Assignments of the diffraction peaks used for estimation of α_c values are indicated by boldface.

Table 1. In-plane/out-of-plane birefringence, and CTE values estimated by TMA and VT-WAXD of PI films.

Polyimides	Birefringence Δn	CTE values / ppm·K^{-1}	
		in-plane by TMA	α_c by WAXD
PMDA-BZ	–	–	–3.8
PMDA-DMDB	0.1427	–10.9	–10.7
PMDA-TFDB	0.1104	–5.2	–5.4
PMDA-ODA	0.0632	+26.4	+17.9
PMDA-DCHM	0.0275	+38.1	+9.0
*s*BPDA-PPD	0.1849	+3.1	–1.9
*s*BPDA-DMDB	0.1343	+8.7	–6.6
*s*BPDA-DCHM	0.0131	+48.1	+18.7

The data for PMDA-BZ were unavailable due to its fibrous nature. It should be noted that negative CTEs were observed for two rigid-rod PIs derived from PMDA dianhydride (–10.9 ppm/K for PMDA-DMDB and –5.2 ppm/K for PMDA-TFDB), which corresponds to significant in-plane shrinkage of the films upon heating. It has been reported that negative CTEs are observed for highly orientated rigid fibers such as Aramid (–4.0 ppm/K) [7], which is attributed to molecular motion perpendicular to the elongated main chains at elevated temperatures. As evidenced by the large Δn values (0.1427 and 0.1104, respectively), main chains of these PIs are highly extended and oriented in the film plane. This could be a reason for their negative CTEs.

In contrast, two rigid-rod PIs derived from *s*BPDA show small but positive CTEs (+3.1 ppm/K for sBPDA-PPD, and +8.7 ppm/K for *s*BPDA-DMDB). These PI films exhibit very large birefringence (Δn = 0.1849 and 0.1343), which are comparable to those of PMDA-derived rigid-rod PIs, demonstrating highly orientated chains in the film plane. The slightly bent *s*BPDA structure would cause expansion along the chain axis upon heating. The other three PIs having bent linkages in the diamine moieties (PMDA-ODA, PMDA-DCHM, *s*BPDA-DCHM) exhibit positive and large CTEs in the range of 26.4–48.1 ppm/K. Their small Δn values (0.013–0.063) apparently indicates isotropic and nearly random orientation of PI chains. In particular, *s*BPDA-DCHM, which has bent structures both in the dianhydride and diamine moieties, show the largest CTE with the smallest Δn. These facts clearly indicates that the thermal expansion behaviors of PI films are closely related to the structural rigidity/linearity and the degree of in-plane orientation of PI chains. However, most of

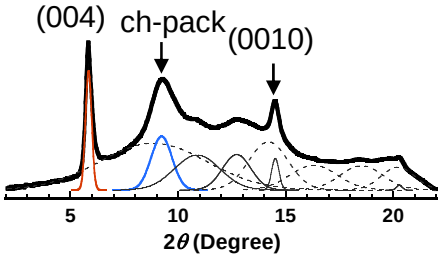


Fig. 3 WAXD profile of *s*BPDA-PPD PI film. Thin solid and dotted lines represent Gaussian components used for fitting.

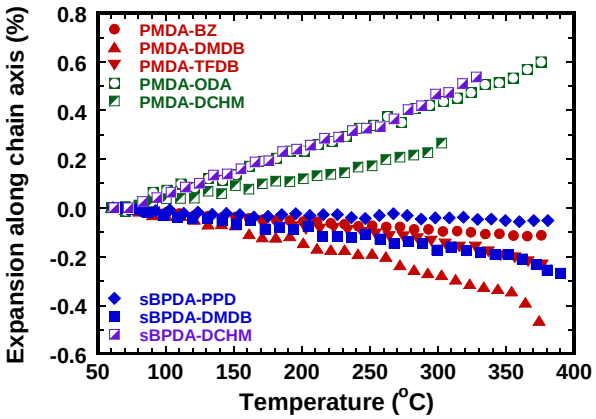


Fig. 4 Thermal expansion behaviors along the *c*-axis in the ordered domain of PIs estimated by VT-WAXD.

PI films consist of LC-like ordered domains and amorphous matrix, and thus their TMA curves reflect thermal expansion behaviors of mixture of the both components. In order to clarify the origin of these CTE values, specific measurements for thermal expansion behaviors of the ordered domains in PI films is strongly expected.

3.2. VT-WAXD Patterns of PI films

The transmission-mode VT-WAXD profiles observed for eight kinds of PIs are shown in Fig. 2. Sample temperature was elevated from 60 to 360 °C at a 20 °C interval. Only the highly crystalline PMDA-BZ fibers demonstrate sharp and periodic diffraction peaks along *c*-axis (00*l*) with a wide but small (110) peak. The other PI films show relatively featureless profiles due to their semi-crystalline or nearly amorphous nature. However, diffraction peaks attributable to (00*l*) and 'Ch-pack' which reflects the intermolecular ordering perpendicular to the main chains [2] are clearly observed for all films. Fig. 3 shows peak decomposition applied for the profile of *s*BPDA-PDA film. Gaussian broadening functions were used to fit the whole profile including wide amorphous halos. The variations in q values for (00*l*) diffractions, which reflect temperature changes in the ordered structures along PI chains,

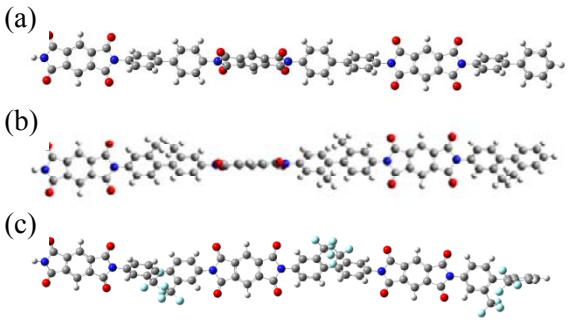


Fig. 5 Optimized geometries of rigid-rod PIs.
(a) PMDA-BZ, (b) PMDA-DMDB, (C) PMDA-TFDB.

were used to estimate the CTE value along the *c*-axis (α_c) via converting to *d*-values. The thermal expansion behaviors estimated from the variations of (00*l*) peaks in the VT-WAXD profiles are shown in Fig. 4, and the α_c values estimated from the slopes between 60 and 240 °C are listed in Table 1. Note that the α_c values estimated from VT-WAXD profiles reflect only the thermal expansion along the main chain in the ordered domain of PI films. The negative α_c values for two rigid-rod PIs derived from PMDA dianhydride (–10.7 ppm/K for PMDA-DMDB, and –5.4 ppm/K for PMDA-TFDB) agree well with the respective CTE values obtained from TMA. Based on the relatively featureless WAXD profiles, significant amounts of less-ordered or amorphous domains should be included. However, the good agreement between CTE and α_c values readily indicates that the negative in-plane CTEs mainly originate from the shrinkage along the *c*-axis in the ordered domain. Meanwhile, amorphous domain exerts little influences on the in-plane shrinkage of these films.

Fig. 5 displays the optimized geometries of the rigid-rod PIs calculated using the density functional theory (DFT, B3LYP/6-311G(d,p)). The lengths of the repeating units of PIs are 16.7 ± 0.2 Å, whereas the *d*-values along the *c*-axis increase in the order of PMDA-DMDB (15.4 Å) < PMDA-TFDB (15.9 Å) < PMDA-BZ (16.4 Å). This fact demonstrates that the PI chains included in the ordered domain of PMDA-BZ are fully extended, though those in the other two are not, rather shrunken from the extended state. Furthermore, as listed in Table 1, the rod-like PIs having the common skeletal structure exhibit different α_c values in the order of PMDA-DMDB (–10.7) < PMDA-TFDB (–5.4) < PMDA-BZ (–3.8 ppm/K). It should be noted that the PI with the shortest repeating unit (PMDA-DMDB) exhibits the largest negative α_c value in the three. Bruno et al. [8] have investigated the anisotropic thermal expansion of

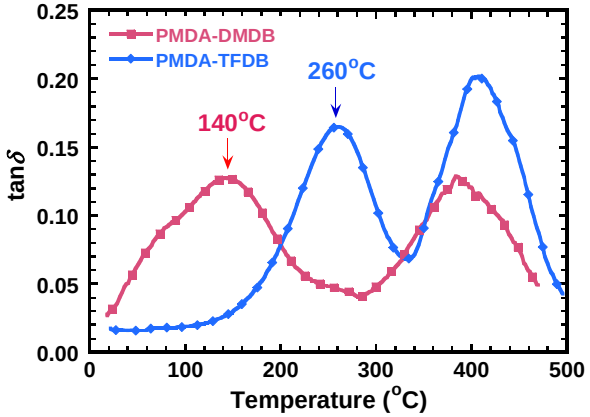


Fig. 6 Temperature dependence of loss factor (*tan* δ) obtained by DMA for PMDA-DMDB and PMDA-TFDB films (*f* =1.0 Hz).

orthorhombic polyethylene, and they concluded that tensions caused by vibrations with components apart from the chain directions are responsible for the negative expansion along the polymer chains, and contribute significantly to the expansion perpendicular to the chains. Based on their explanation, extended rod-like PI chains with bulky side groups, which exert vigorous vibrational motions, should show a negative α_c. Analysis of the WAXD profiles clarified that the *d*-values for Ch-pack diffraction gradually increase in the order of PMDA-BZ (4.6 Å) < PMDA-DMDB (5.4 Å) < PMDA-TFDB (5.8 Å). This indicates that $-CH_3$ and $-CF_3$ side groups effectively expand the intermolecular distances of the PIs. In addition, Fig. 6 shows the temperature dependence of loss factor (*tan* δ) obtained from dynamic mechanical analyses of PMDA-DMDB and PMDA-TFDB PI films. As indicated by arrows in the figure, *β*–relaxation temperature (T_β) of the former PI appeared at 140 °C, which is much lower than the latter PI at 260 °C. This fact strongly suggests that $-CH_3$ side groups with lighter-weight exert vigorous vibrational motion in the less-ordered or amorphous domain below 240 °C. This could be a reason for the largest negative α_c value of PMDA-DMDB. In contrast, biphenyl moieties in PMDA-BZ could commence vigorous vibrational or rotational motions at much lower temperatures, though it does not give significant effects on the thermal shrinkage due to absence of side groups.

On the other hand, two rigid-rod PIs derived from *s*BPDA show small and negative α_c values despite their small but positive CTEs. This difference arises from the fact that α_c values mainly reflect thermal expansion in the ordered domain, though CTE represent behaviors of the whole film. The slightly bent and rotatable *s*BPDA

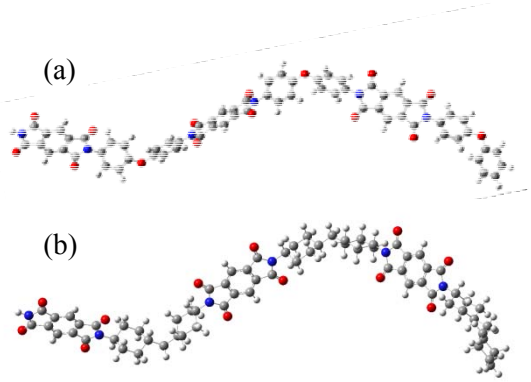


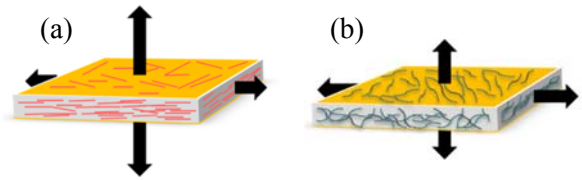
Fig. 5 Optimized geometries of PIs having bent linkages. (a) PMDA-ODA, (b) PMDA-DCHM.

structure would cause a larger extent of expansion along the chain axis upon heating. Harris et al. [9] reported that PIs derived from sBPDA dianhydride exhibit T_β around 170 °C, which suggests that rotational motion around the biphenyl linkage at sBPDA moiety provides an additional source for the shrinkage of PI chains.

Fig. 7 displays the optimized geometries of PIs having bent linkages (–O– or $-CH_2-$) in their diamine moieties. They possess flexible and curvy chain structures, which leads to isotropic and random orientation of PI chains even in solid films. As expected from their structures, the PIs exhibit positive and large α_c values in the range of 9.0–18.7 ppm/K, which agrees with the CTE values in Table 1. It should be noted that their α_c values are not proportional to CTEs. PMDA-ODA which has a relatively rigid structure with an ether linkage exhibits a small difference between α_c and CTE (8.5 ppm/K), whereas PMDA-DCHM and sBPDA-DCHM having bulky and flexible cyclohexane skeletons demonstrate large differences (29.1 and 29.4 ppm/K). This is explainable by the fact that the former includes significant amount of ordered domains in the film, while the latter are highly amorphous and their thermal expansion behaviors are primarily determined by the amorphous domain that contains larger amount of free volume. Scheme 2 represents the typical molecular shapes and thermal expansion behaviors of (a) a rigid-rod PI and (b) a bent and flexible PI, respectively.

4. Conclusion

VT-WAXD measurements were performed for eight kinds of PI films to estimate the CTEs along the main chain direction in the ordered domain (α_c). Most of the films showed liquid-crystalline-like ordered structure including broad amorphous halo, though diffraction peaks from the repeating unit along the main chain (*c*-axis) and the inter-chain



Scheme 2. Schematic representation of molecular shapes and thermal expansion behaviors of (a) rigid-rod PI and (b) flexible PI chains in solid films.

ordering (Ch-pack) were clearly observed. The α_c values of the three PIs having rigid-rod structures derived from PMDA are negative, which agrees well with the in-plane CTEs of the films estimated by TMA. In addition, a PI with the shortest repeating unit in the three (PMDA-DMDB) exhibits the largest negative α_c value. These facts indicate that the negative in-plane CTE of these films essentially originate from the thermal shrinkage of their ordered domain, which is attributable to vibrational motion of $-CH_3$ side groups. In contrast, the α_c values of PIs containing bent linkages in the main chain are positive and large, which also agrees with their in-plane CTEs. In particular, the PIs derived from DCHM diamine demonstrate large differences between α_c and CTE, which could be due to their highly amorphous nature including larger amount of free volume.

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