Effects of Bent Main Chain on the Thermal Expansion Behaviors of Polyimide Films

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Introduction

Polyimides (PIs) have been widely used in aerospace, electric, and electronic industries because of their high thermal stability and chemical resistance. Especially, PIs exhibiting reduced coefficients of linear thermal expansion (CTEs) has been demanded for electric insulators to avoid deformation or delamination due to CTE mismatch between PI and metallic substrate. Although many studies were reported to reduce the in-plane CTEs ($CTE_{//}$) of PIs, there were few studies for reducing the coefficient of volumetric thermal expansion (CVE). Control of relaxation behaviors of polymer chains, such as β and γ relaxations, are crucial to reduce the CVEs of polymers [1]. In this study, we investigate the difference of CVEs in PIs having isomeric structures (Fig. 1). We have reported that *s*BPDA/PPD exhibits a small CVE because of its rigid main chain and semi-crystalline nature [2], though the rotational barriers between heterocyclic rings seem to be unchanged among the isomeric PIs. In this study, we investigate the effect of rotational barriers in the PI main chains on their thermal expansion behaviors.

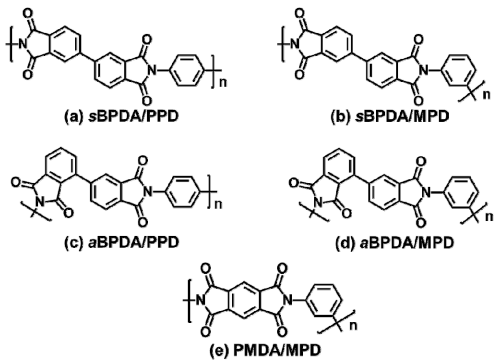

Figure 1; Chemical structures of PIs.

Experimental

Precursors of PIs, poly(amic acid)s (PAAs), were prepared by mixing equimolar amounts of dianhydride and diamine in DMAc. The PAA solutions were spin-coated onto Si substrates, followed by prebaking at 70 ºC for 1 h and subsequent thermal imidization at 350 ºC for 1.5 h. $CTE_{//}$ was measured by thermomechanical analyses (TMA) conducted by TMA-60 (Shimadzu), and those of out-of-plane CTEs ($CTE_{\perp}$) were estimated by optical interferometry [2]. CTEs were measured in the range of 80 and 280 ºC. Dynamic mechanical analyses (DMA) were conducted with a DMS-7100 (Hitachi High-Tech). The density functional theory (DFT) with B3LYP functional and 6-311G(2d, p) basis set were utilized for geometry optimization and steric energy calculations.

Table 1 $CTE_{//}$ & $CVE_{\perp}$ of PI films (ppm/K).

	$CTE_{//}$	$CTE_{\perp}$	CVE
*s*BPDA/PPD	5.4	119.6	130.4
*s*BPDA/MPD	38.5	40.6	117.6
*a*BPDA/PPD	51.2	45.7	148.1
*a*BPDA/MPD	45.0	48.2	138.2
PMDA/MPD	32.2	52.6	117.0

Result & Discussion

As listed in Table 1, the $CTE_{//}$ of *s*BPDA/PPD is much smaller than those of the other PIs. The semi-crystalline nature of this PI may promote molecular chain orientation in the in-plane direction of film. Except for *s*BPDA/PPD, $CTE_{//}$s of the PI films are comparable to their $CTE_{\perp}$s. This is explainable by nearly isotropic orientation of PI chains with their amorphous nature. These are supported by the absence of apparent diffraction peaks in the wide angle X-ray diffraction patterns and the very small in-plane/out-of-plane birefringence. For both of *s*BPDA- and *a*BPDA-PIs, the CVEs of PIs derived from MPD are smaller than those from PPD. In addition, for both of the PPD- and MPD-PIs, *a*BPDA-PIs exhibit larger CVEs than *s*BPDA-PIs. To explain the thermal expansion behaviors of these PIs, DMA analyses were performed to investigate their relaxation behaviors. Fig. 2 shows the loss elastic moduli of the PI films, in which β-relaxations are observed in the range of temperature between 0 and 250 ºC. These relaxations could be closely related to their volumetric thermal expansion behaviors. The β relaxations of *s*BPDA- and *a*BPDA-PIs were attributed to the rotational relaxation at the 4,4'-diphthalimide and 3,4'-diphthalimide moieties, respectively [3]. However, *s*BPDA/PPD and *s*BPDA/MPD exhibit different CVEs despite their same dianhydride structures. Fig. 3 shows the variations of conformational energies between phenylene and phthalimide rings, which indicates that the rotational barriers of PPD-PIs are lower than those of MPD-PIs. Thereby, the β relaxations could be also related to the rotational motions between the phenylene and phthalimide rings. Kochi et al. [3] have reported that *a*BPDA-PIs exhibited lower β relaxation temperatures with smaller activation energies compared with *s*BPDA-PIs. The lower β relaxation temperatures lead to vigorous molecular motion and increase in CVEs for *a*BPDA-PIs compared to *s*BPDA-PIs. As a consequence, a combination of 4,4'-diphthalimide and *m*-phenylene linkages in the repeating unit of PI can effectively reduce the CVE than those for PIs containing 3,4'-diphthalimide and/or *p*-phenylene linkages.

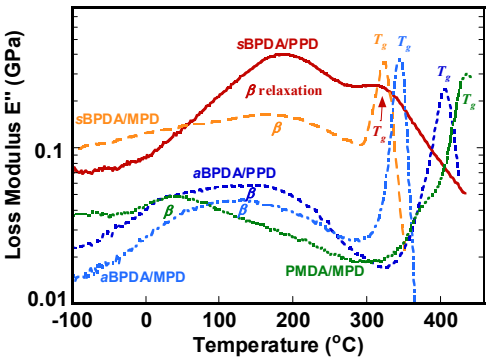

Figure 2; Loss elastic moduli of PI films operated at 10 Hz.

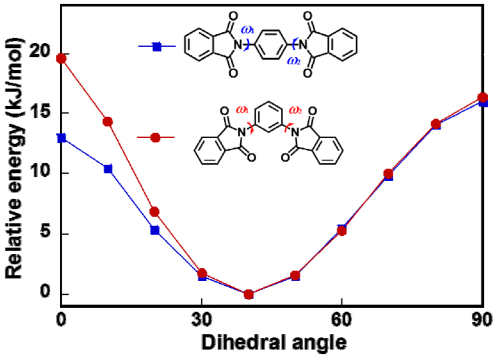

Figure 3; Conformational energies of the dihedral angle between phenylene-phthalimide rings in PI structure (square: *p*-phenylene, circle: *m*-phenylene).

References

[1] Wittmann, J. C.; Kovacs, A. J. *J. Polym. Sci. C*, **1969**, *16*, 4443-4452. [2] Sekiguchi, K.; Ando, S. *Polym. Prep. Jpn.*, **2011**, 60(1), 665. [3] Kochi, M.; Chen, C.; Yokota, R.; Hasegawa, M.; Hergenrother, P. *High Perform. Polym.*, **2005**, *17*, 335-347.