# Effects of Isomeric Structures of Main Chain on the Volumetric Thermal Expansion Behaviors of Polyimide Films

(Tokyo Tech) ○Tomohiro Okada, Shinji Ando

Polyimides (PIs) exhibiting reduced coefficients of linear thermal expansion (CTEs) has been demanded for electric insulators to avoid deformation or delamination due to CTE mismatch among PI, metallic wire, and inorganic substrate. Although many studies were reported for reducing in-plane CTEs ($CTE_{//}$) of PIs, only few studies tried to reduce the coefficient of volumetric thermal expansion (CVE). To reduce the CVEs of polymers, control of relaxation behaviors of polymer chains, such as $\beta$ and $\gamma$ relaxations, are crucial [1]. In this study, we examined the differences in CVEs for PIs having isomeric structures (**Fig. 1**).

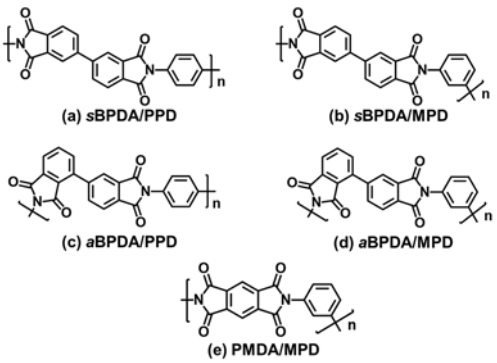


**Figure 1;** Chemical structures of PIs.

The $CTE_{//}$ and $CTE_{\perp}$ values measured by TMA and optical interferometry [2] are listed in Table 1. The $CTE_{//}$ of *s*BPDA/PPD is much smaller than those of the other PIs. Its semi-crystalline nature may promote the chain orientation in the in-plane direction. Except for *s*BPDA/PPD, the $CTE_{//}$s of PI films are comparable to their $CTE_{\perp}$s, which is explainable by the nearly isotropic orientation of PI chains with their amorphous nature. This is supported by the absence of apparent diffraction peaks in their wide angle X-ray diffraction patterns and the very small in-plane/out-of-plane birefringence.

**Table 1** $CTE_{//,\perp}$ & CVE 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 |

It is noteworthy that the CVEs of PIs derived from MPD are smaller than those from PPD for both of *s*BPDA- and *a*BPDA-PIs. In addition, *a*BPDA-PIs exhibit larger CVEs than *s*BPDA-PIs for both of PPD- and MPD-PIs. To explain these thermal expansion behaviors, DMA analyses were performed to investigate their relaxation behaviors. In the loss elastic moduli of PI films, $\beta$-relaxation peaks were observed between 0 and 250 ºC, and these could be closely related to their volumetric thermal expansion behaviors. The $\beta$ relaxations of *s*BPDA- and *a*BPDA-PIs have been attributed to rotational relaxation at 4,4'-diphthalimide and 3,4'-diphthalimide moieties, respectively [3]. However, *s*BPDA/PPD and *s*BPDA/MPD exhibit different CVEs despite their common dianhydride moiety. In addition, the calculated conformational energies between the phenylene and phthalimide rings by DFT indicates that the rotational barriers for PPD-PIs are lower than those for MPD-PIs. Thereby, the $\beta$ relaxations could be closely related to the rotational motions of these rings below the $T_g$ (< 250 ºC). Kochi et al. [3] have reported that *a*BPDA-PIs exhibited lower $\beta$ relaxation temperatures with smaller activation energies compared with *s*BPDA-PIs. The former leads to vigorous molecular motion and increase in CVEs for *a*BPDA-PIs compared to *s*BPDA-PIs. As a consequence, the combination of 4,4'-diphthalimide and *m*-phenylene linkages in the repeating unit of PIs can effectively reduce the CVE than those for PIs containing 3,4'-diphthalimide and/or *p*-phenylene linkages.

References

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Tomohiro Okada, Department of Chemistry & Materials Science, Tokyo Institute of Technology, 2-12-1-E4-5, Oookayama, Meguro-ku, Tokyo 152-8552, Japan
Tel & Fax; +81-3-5734-2889, e-mail: tokada@polymer.titech.ac.jp