Effects of Bent Structure and Formation of Hydrogen Bonding on the Thermal Expansion Behaviors of Polyimide Films

Tomohiro Okada, Shinji Ando*

(Depart. of Chem. & Mater. Sci., Tokyo Tech, Tokyo, Japan)

* sando@polymer.titech.ac.jp.

ABSTRACT

Since coefficients of volumetric thermal expansion (CVE)s of polymers are much larger than those of ceramics and metals, thermally stable polymers with controlled volumetric thermal expansion (VTE) would be in high demand as interlayer dielectrics or matrices for polymer/inorganic composites in semi-conductor industries. VTE behavior of polymers is affected by local vibrational or rotational motions of main chains[1]. While *para*-substituted phenyl rings may undergo free rotation in the solid state, *meta*-substituted counterpart, which may kink to some extent, hardly rotate at room temperature or higher. In addition, intra- or intermolecular hydrogen bonds formed by hydroxyl or amide groups may inhibit such local motions of polymer chains. In this study, effects of rigid-bent structure and formation of hydrogen bonds on the VTE behaviors of three kinds of polyimide (PI) films (Fig. 1) were examined using thermal mechanical analysis and near-infrared optical interferometry. Although the difference in CVEs were negligible in the range of 80 to 180 ºC, CVEs varied in decreased order of *s*BPDA-PPD (with rigid-linear structure) > *s*BPDA-HAB (with hydrogen bond) > *s*BPDA-MPD (with rigid-bent structure) in the range of 180 to 280 ºC (Table 1). To clarify these behaviors, dynamical relaxation of the PIs were examined by DMA, and local conformations were evaluated based on Far-IR absorption spectra. Rigid-bent structure in *s*BPDA-MPD effectively inhibit segmental motions just below the glass transition temperature (T_g), and the resultant CVE decreased in the higher temperature region than *s*BPDA-PPD. In case of *s*BPDA-HAB, the CVE increased with increasing temperature due to enhanced local motion around the hydroxyl groups leading to weakening of hydrogen bonds.

References:

[1]K. Hagiwara, T. Ougizawa, T. Inoue, K. Hirata, Y. Kobayashi, *Rad. Phys. Chem.*, **58**, 525 (2000).

[2]M. Kochi, C. Chen, R. Yokota, M. Hasegawa, P. Hergenrother, *High Perform. Polym.*, **17**, 335 (2005).

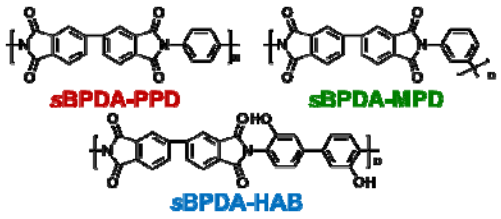

Fig. 1 Structures of PI films.

Table 1. CVEs of PI films.

	CVE (ppm/K)	
	80−180ºC	180−280ºC
sBPDA-PPD	114	150
sBPDA-MPD	115	127
sBPDA-HAB	115	142

(error : ±5%)

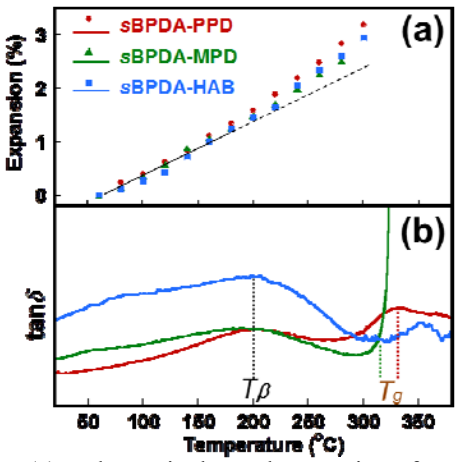

Fig. 2 (a) Volumetric thermal expansion of PI films. (b) Loss tangent (tanδ) curves of PI films.