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Effect of Molecular Structure on Thermal Volume Expansion of Fully Aromatic Polyimides

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Introduction

Fully aromatic polyimides (PI) are important insulating materials for electronic devices due to not only the high insulating property but also the good mechanical property, high chemical and thermal stabilities, and high processability of the poly(amic acid) precursor. Such electronic devices have been increasingly downsized and denser. As a result, the larger thermal expansion of insulating layers potentially causes warpages from conducting metal layer and induces various failures in the devices. In this study, thermal expansion behaviors of highly crystalline PIs were analyzed by synchrotron wide-angle X-ray diffraction (SR-WAXD) measurement and discussed on the basis of the chemical structure. Coefficients of thermal volume expansion (CVE) of the crystalline region can be precisely evaluated from the lattice parameters, in which the effect of the non-crystalline region can be totally eliminated.

Results and Discussion

The CVE values for rod-shaped PIs consisting of PMDA unit and linear para-linked multi-phenyl diamine units, PMDA-PPD, PMDA-BZ, and PMDA-DATP, were compared in **fig. 1**. The CVE value increased with the number of rotatable phenyl ring in the diamine unit. Generally, the CVE can be related to thermally-activated local molecular motion, and the rotational fluctuation of the aromatic rings could be related to the thermal expansion for the rigid rod PIs. Interestingly, PMDA-BZ showed the same CVE as PMDA-DATP. This characteristic behavior could be attributable to the lowest density (largest free volume) and specific coplanar conformation of the BZ unit[1)], which may allow the largest rotational fluctuation for PMDA-BZ. Consequently, not only the number of mobile units per unit length but also the packing structure of main chains is the dominant factor of CVE. In other words, if the crystal of PI contains less free volume, thermally induced fluctuations are not sufficiently activated, and thus the CVE can be reduced. The effects of flexible linkages and side groups on CVEs will be also discussed in the presentation.

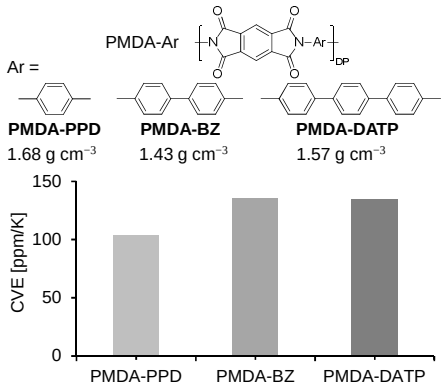

Fig. 1 Chemical structures of rigid-rod PIs derived from PMDA with their CVE values. Crystal density values are inset.

References

1) Okuyama, et al. *Macromolecules* **1995**, *28*, 1547.