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THERMAL EXPANSION BEHAVIORS OF POLYIMIDES ANALYZED BY VARIABLE TEMPERATURE WIDE ANGLE X-RAY DIFFRACTION

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1. Introduction

Polyimides (PIs) are class of super engineering plastics. Because of their high thermal stability, mechanical strength and chemical resistance, they are widely used in various applications, such as an insulator in electrical circuits. For these applications, control of coefficients of volumetric thermal expansion (CVE) is crucial for the dimensional stability of polymeric insulating layers in integrated components.

It has been understood that the expansion of free volume play important roles in thermal expansion of polymers[1]. Because free volume fraction of crystal phase of polymer is less than that of amorphous phase, CVE of crystal phase is expected to be less than amorphous phase. Therefore it is important that clarify thermal expansion behavior of crystal phase to control thermal expansion of polymer.

In general, PI films show low crystallinity and it is difficult to investigate the property of the crystals. Recently, the synthesis methods of highly-crystalline PIs powder were developed[2]. Furthermore, crystal structures of PIs were investigated by wide-angle x-ray diffraction (WAXD) measurement of uniaxial drawing fibers or films[3].

In this study, CVE of highly-crystalline aromatic PI powders or uniaxial drawing films were evaluated by WAXD measurements at variable temperatures.

2. Experimental

The molecular structures of PIs used in this study are shown in Fig. 1. Highly-crystalline powder samples of PMDA-PPD, PMDA-DATP and PMDA-DMDB are synthesized by thermal imidization method[2]. On the other hand, uniaxial drawing fiber was used for measurement of PMDA-BZ, because PMDA-TFDB powder showed very low crystallinity and it is difficult to investigate the crystal structure. The uniaxial drawing film was prepared by thermal imidization during uniaxial drawing of the poly(amic acid) precursor .

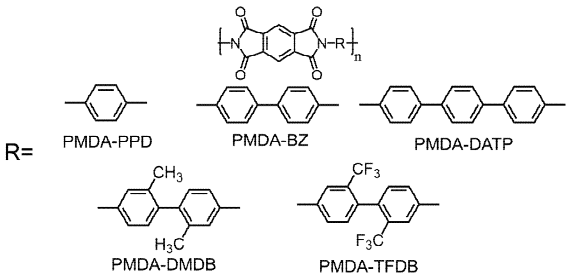

Fig. 1 Molecular structures of PIs.

WAXD measurements were performed at BL-10C beamline in High Energy Accelerator Research Organization (KEK). The detector was a PILATUS 300K and the wavelength of the X-ray was 0.89 Å. Diffraction patterns were obtained at preset temperatures in cooling proces from 290 to 110°C.

3. Results and Discussion

1D WAXD intensity profiles of PMDA-PPD and 2D WAXD pattern of PMDA-BZ are shown in Fig.2. The crystal structures of the all PIs were assigned as orthorhombic. From the indexed diffraction peaks, the temperature dependence of the lattice parameters *a*, *b*, *c* and volume were evaluated as presented in Fig. 3. The lattice parameters of PMDA-PPD is presented as a typical example in Fig. 3 and the lattice parameters and CVE increased linearlly with temperature. The CVE were evaluated from the slope of volume against temperature. The CVE values of all the PIs in Fig. 1 are shown in a diagram of Fig. 4.

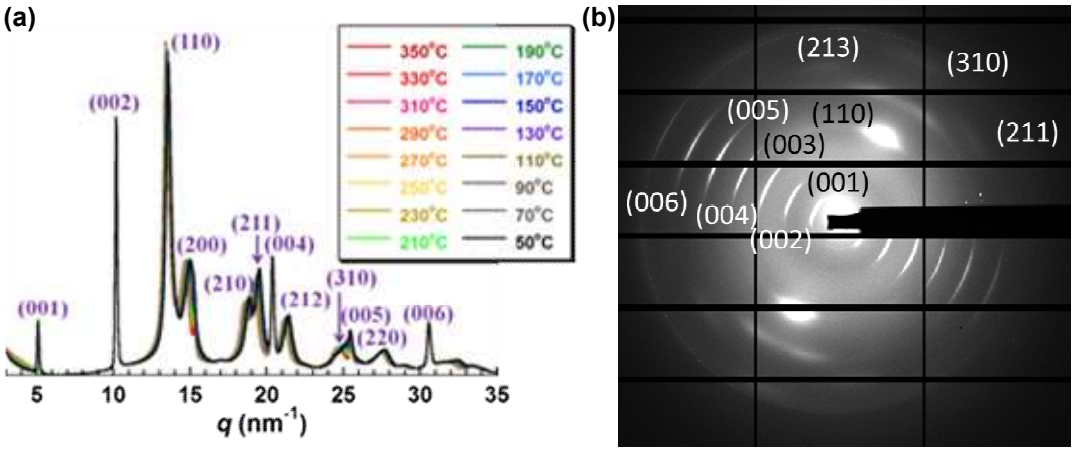

Fig. 2 X-ray diffraction pattern of (a) PMDA-PPD and (b) PMDA-BZ PIs at room temperature.

Firstly, CVE values were compared among PMDA-PPD, PMDA-BZ and PMDA-DATP, which have different nunber of aromatic ring in the repeating unit. PMDA-PPD shows smallest CVE value (104 ppm/K) in these PIs. PMDA-PPD has only one aromatic ring, the molecular motions such as rotation of aromatic ring or imide ring are expected to have no great influence on thermal expansion of free volume to give small CVE. Although PMDA-BZ has fewer number of aromatic ring, CVE value of PMDA-BZ was as large as PMDA-DATP. In the crystal of PMDA-BZ, it has been considered that the biphenyl moiety of PI adapts a coplaner structure[3]. Because torsion structures are more stable than coplaner structure in biphenyl moiety, moleculer rotation of PMDA-BZ is much more vigorous than usual biphenyl rotation. As the result, free volume expansion with temperature can become large and PMDA-BZ shows relatively high CVE value.

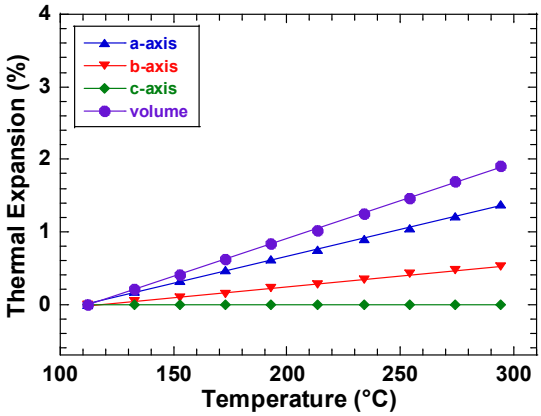

Fig. 3 Variations in crystalline lattice parameters with increasing the temperature.

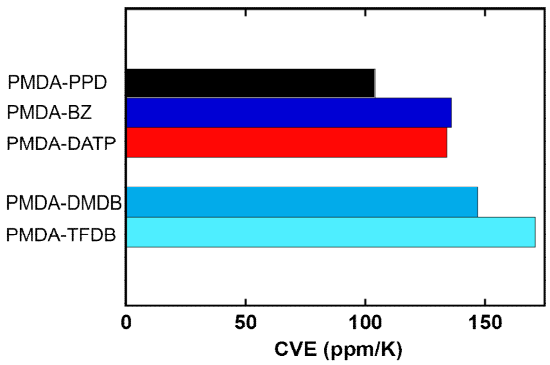

Fig. 4 CVE values of crystalline phases of PIs in the temperature range 110-290°C

Secondly, CVE values are compared among PMDA-BZ, PMDA-DMDB and PMDA-TFDB which have same number of aromatic ring but the subsutituent groups are different. CVE values increased with increasing size of subsutituent group (CVE: PMDA-BZ < PMDA-DMDB < PMDA-TFDB). The bulky substituent group such as trifluoromethyl group causes large free volume. Therefore, PIs with bulky substituent groups show larger CVE than PIs without substituent group.

In conclusion, the effect of chemical structures on the CVE values of a series of aromatic PIs were precisely investigated, and the conformation of the aromatic rings and the substituent side groups are found as a key factor to control the CVE values.

References:

1. K. Hagiwara, T. Ougizawa, T. Inoue, K. Hirata, Y. Kobayashi, *Rad. Phys. Chem.*,2000, **58**, 525. 2. K. Wakabayashi, S. Kohama, S. Yamazaki, and K. Kimura, *Polymer*, 2007, **48**,458. 3. Y. Obata, K. Okuyama, S. Kurihara, Y. Kitano, T. Jinda, *Macromolecules*, 1995, **28**, 1547