Anisotropic Thermal Expansion Behaviors of Crystal Lattice of Aromatic Polyimides Analyzed by Variable Temperature WAXD

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ABSTRACT

Highly crystalline μm-sized particles of thirteen kinds of aromatic polyimides (PIs) were prepared, and their coefficients of linear (CTE) and volmetric (CVE) thermal expansion of the crystal lattices were analyzed by variable temperature synchrotron wide-angle X-ray diffraction (VT-WAXD). PI particles were prepared by heating of NMP solutions of poly(amic acid), a precursor of PI, at 200°C for 2 h. The particles morphology was sheaf or coral type, similar to polymer spherulites. Transmission VT-WAXD profiles were measured with a BL40B2 beamline at JASRI/SPring-8 [2012B1317] in the temp range of 50~350°C. Diffraction peaks observed in the profiles were assigned according literature, and relative thermal expansion estimated from *d*-spacings were plotted against temperature. The CTEs along *c*-axis are very small for all the PIs, though small but negative CTEs were observed for the PIs having bent linkages. A rigid-rod PI (PMDA/BZ, PMDA/DATP) and PIs having crankshaft structures (PMDA/DABA, PMDA/APAB) exhibit nearly isotropic thermal expansion along *a*- and *b*-axes, whereas highly anisotropic expansion was observed for a PI having single bent linkage (PMDA/ODA) with a large and negative CTE along *a*-axis. This could be caused by vigorous librational motion along *b*-axis with flip-flop of phenyl rings at the diamine moiety. In addition, the CVE of PMDA/DABA is significantly smaller than that of PMDA/APAB despite the similar skeleton, which is attributable to formation of intermolecular hydrogen bonds between amide linkages. A rigid-rod or quasi linear structure with enhanced intermolecular interactions endows PIs with a small CVE and high thermal stability.

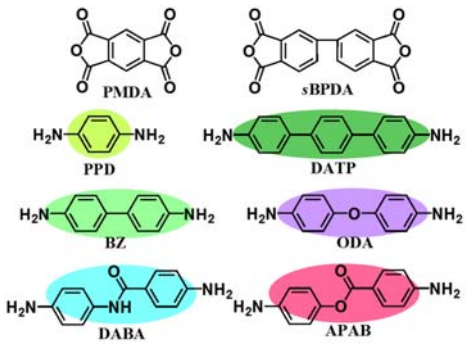

Figure 1. Monomers for PI particles.

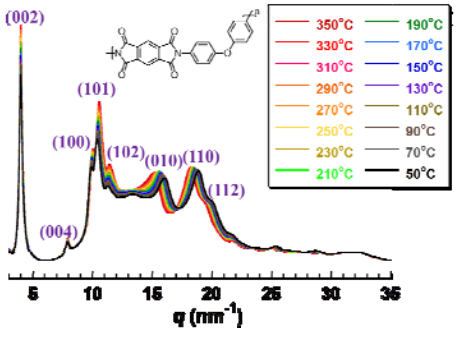

Figure 2. VT-WAXD profiles of crystalline particles of PMDA/ODA.

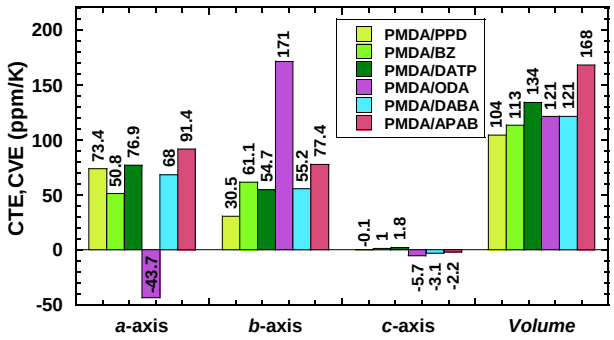

Figure 3. Comparison of CTEs along *a*-, *b*-, and *c*-axes, and CVEs for six kinds of PIs derived from PMDA.