IL3-11

A Comprehensive Study on Anisotropic Thermal Expansion Behaviors of Crystal Lattice of Aromatic Polyimides Analyzed by VT-WAXD

S. Ando*, Y. Kozaki, T. Masuda, and R. Ishige
Department of Chemical Science and Engineering, Tokyo Institute of Technology, Japan
E-mail: sando@polymer.titech.ac.jp

To gain insight into the anisotropic thermal expansion behaviors of aromatic polymers and to obtain design principles for new materials exhibiting low thermal expansion as well as high thermal and mechanical stability, highly crystalline μm-sized particles of thirteen kinds of aromatic polyimides (PIs) were synthesized, and their coefficients of linear (CTE) and volumetric (CVE) thermal expansion of crystal lattices were precisely analyzed by variable temperature synchrotron wide-angle X-ray diffraction (VT-WAXD). The CTEs and CVEs of PIs having flexible main chains have been reported by Brillhart et al. [1]. PI particles were prepared by heating of NMP solutions of poly(amic acid) at 200°C for 2 h, followed by annealing of precipitated particles at 400°C for 2 h. The particle morphology was sheaf or coral type, similar to polymer spherulites. Transmission VT-WAXD profiles were measured at BL40B2 beamline at JASRI/SPring-8 and 11C beamline at Photon Factory/KEK in the temperature range of 50~350°C. Diffraction peaks observed in the profiles were assigned according to literature, and relative thermal expansion estimated from *d*-spacing were plotted against temperature. The CTEs along *c*-axis are small for all the PIs, though negative CTEs were observed for PIs having a bent linkage or bulky side groups (−CF_3). Moreover, the CVE of PMDA/TFDB is the largest despite its rigid-rod structure. The CVEs of rigid-rod PIs without side chains (PMDA/PPD, /BZ, /DATP) increase with increasing the phenyl rings at the diamine moieties. This could be associated with rotational motion of the phenyl rings. PIs having bulky side groups (PMDA/DMDB, /TFDB) exhibit nearly isotropic thermal expansion along *a*- and *b*-axes, whereas highly anisotropic expansion was observed for a PI having a bent ether linkage (PMDA/ODA) with an extraordinarily negative CTE along the *a*-axis (−44.2 ppm/K). This could be due to vigorous librational motion along the *b*-axis associated with 'flip-flop' of phenyl rings at the diamine moiety, which also induces a negative CTE along the *c*-axis. These experimental findings are beneficial for designing and developing novel thermally stable polymers exhibiting very low CTEs and CVEs.

[1] M.V. Brillhart, P. Cebe, *J. Polym. Sci. Part B Polym. Phys.* **33** 927–936 (1995).

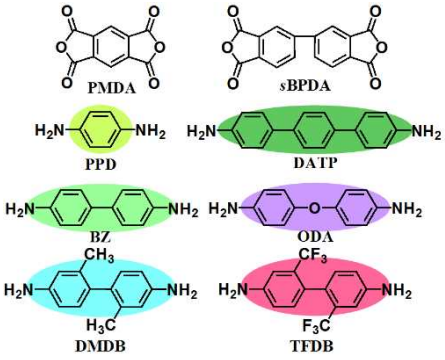

Figure 1. Monomers for PI particles.

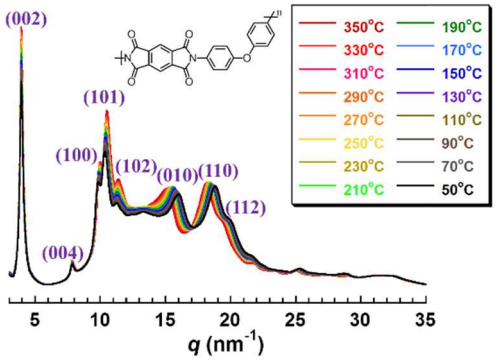

Figure 2. VT-WAXD profiles of crystalline PI powder of PMDA/ODA.

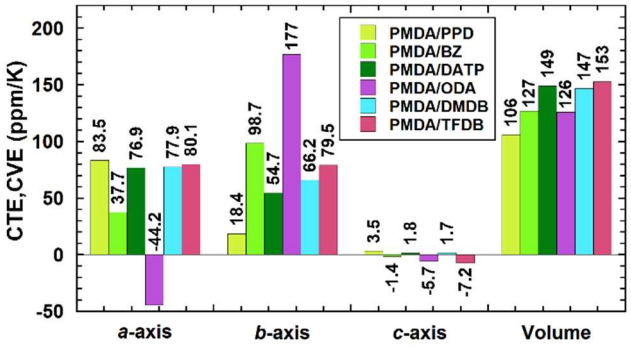

Figure 3. Comparison of CTEs along *a*-, *b*-, and *c*-axes, and CVEs for six kinds of PIs derived from PMDA.