

Structure Dependence of Linear and Volumetric Thermal Expansion of Polyimide Crystallites 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 volumetric (CVE) thermal expansion of the crystal lattices were analyzed by variable temperature synchrotron wide-angle X-ray diffraction (VT-WAXD). The CTEs along the chain axis (c -axis) are very small for all the PIs, though negative CTEs were observed along the c -axis for PIs having bent linkages. Rigid-rod PIs and PIs having crankshaft structures exhibit nearly isotropic thermal expansion along the a - and b -axes, whereas extraordinarily anisotropic expansion was observed for a PI having an ether linkage (PMDA/ODA) with a large and negative CTE along the a -axis. In addition, the CVE of a PI having an amide linkage in the main chains is significantly smaller than that of a PI having an ester linkage despite their similar skeletons, which is attributable to the intermolecular hydrogen bonds formed between amide groups. A rigid-rod or quasi linear structures accompanied with enhanced intermolecular interactions endow PIs with high thermal stability and reduced CVEs. These knowledge is beneficial for designing novel PIs for next-generation electric and electronic applications.

Keywords: Linear thermal expansion, Volumetric thermal expansion, VT-WAXD, Crystalline lattice, Anisotropic expansion, Aromatic polyimides.

1. Introduction

In the fields of dielectric interlayer and electric packaging materials, not only the coefficients of linear thermal expansion (CTE) but also the coefficients of volumetric thermal expansion (CVE) of thermally stable polymers like polyimides (PIs) are to be controlled. In this study, a series of crystalline powders of aromatic PIs were prepared, and their thermal expansion behaviors of the crystal lattices were precisely analyzed by variable-temperature wide-angle X-ray diffraction (VT-WAXD) using a synchrotron radiation facility. The CTE along each crystal lattice (a -, b -, and c -axis) as well as CVEs were evaluated, and their dependence on the chemical structures is discussed.

2. Sample Preparation and WAXD Analysis

Fig.1 shows the dianhydrides and diamines used for the PI synthesis. Crystalline PI particles were prepared according to the literature [1–4] by heating poly(amic acid) solutions at higher than 200°C. The WAXD experiments were performed using a BL40B2 beamline with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2012B-1307, 2013A-1077). The sample temperature was precisely controlled in the range of 50 and 350 °C by using

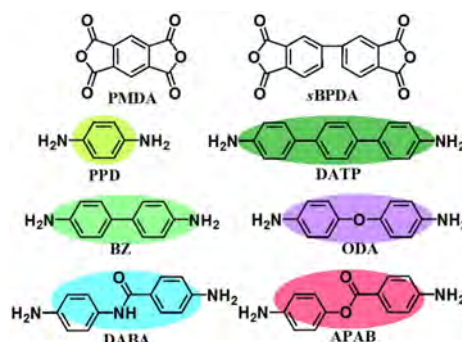


Fig. 1 Structures of dianhydrides and diamines used for the PI synthesis.

Mettler-Toledo high-temp control stage under N₂ atmosphere.

3. Results & Discussion

Fig. 2 shows the VT-WAXD profiles of PMDA/ODA particles. The crystalline particles showed sheaf or coral type morphologies similar to polymer spherulites. The diffraction peaks observed were assigned according to the literature [5]. The lattice system of PIs with unknown crystal structures was assumed as orthorhombic. The relative thermal expansions for each crystal lattice estimated from *d*-spacings are plotted against temperature. Fig. 3 shows the thermal expansion behaviors of the crystal lattices and the unit volume of PMDA/ODA having a bent ether linkage. It should be noted that extraordinarily anisotropic expansions were observed with a large and negative CTE along *a*-axis, which could be due to vigorous librational motion along *b*-axis at elevated temperatures accompanying flip-flop or rotational motion of phenyl rings in the diamine moiety. The CTEs and CVEs of crystal lattices analyzed for PIs derived from PMDA are summarized in Fig. 4. The CTEs along *c*-axis are very small for all the PIs, though small but negative CTEs were observed for the PIs derived from diamines having bent linkages (ODA, DABA and APAB). The PIs derived from rigid-rod diamines (BZ and DATP) and those having crankshaft structures (DABA and APAB) exhibit nearly isotropic thermal expansion along *a*- and *b*-axes. In addition, the CVE of PMDA/DABA is much smaller than that of PMDA/APAB in spite of their similar skeletal structures, which is attributable to the rigidity of crystal lattice along *a*- and *b*-axes of the former originating from the formation of intermolecular hydrogen bond networks between amide linkages. A rigid-rod structure with enhanced intermolecular interactions endows PIs with high thermal stability and reduced thermal expansion. These knowledge is beneficial for designing novel PIs exhibiting controlled CVEs for next-generation electric and electronic applications.

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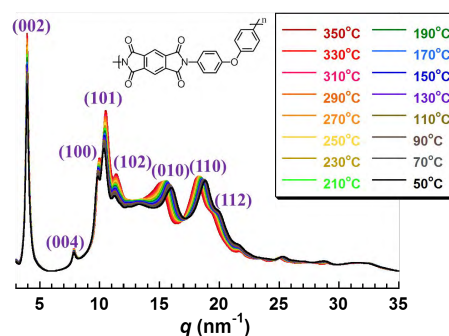


Fig. 2 VT-WAXD profiles of semi-crystalline particles of PMDA/ODA. Diffraction peaks were assigned according to literature [5].

Fig. 3 Thermal expansion behaviors of each crystal axis and unit volume of PMDA/ODA PI.

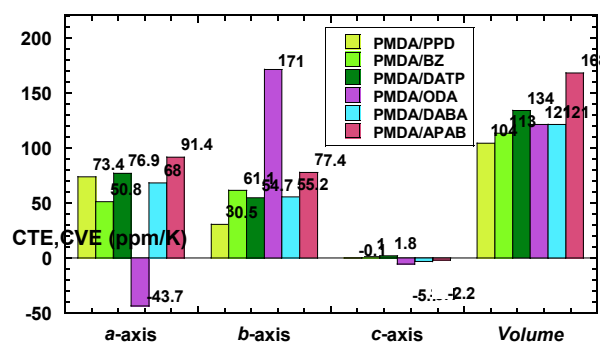
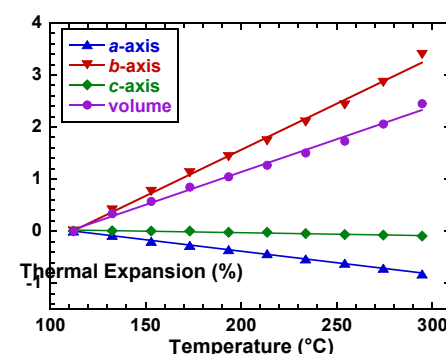


Fig. 4 Comparison of CTEs along *a*-, *b*-, and *c*-crystal axes and CVEs of unit volume for the PIs derived from PMDA.