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Structure Dependence of Linear and Volumetric Thermal Expansion Coefficients of the Crystal Lattice of Aromatic Polyimides

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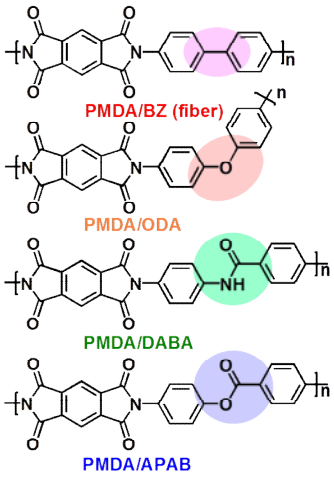
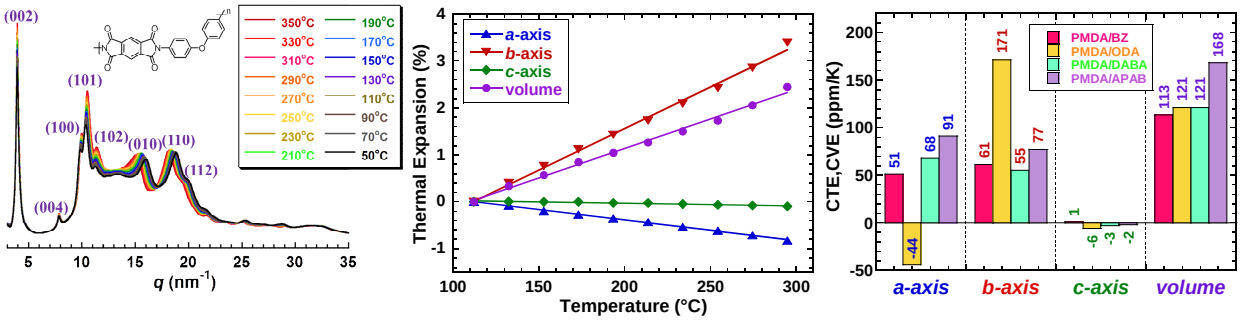


Introduction: For the development of dielectric materials exhibiting high thermal stability and low thermal expansion, a series of crystalline powders of aromatic polyimides (PIs) were prepared, and thermal expansion behaviours of their crystal lattices and were analysed by variable temperature wide-angle X-ray diffraction (VT-WAXD). Coefficients of linear thermal expansion of the crystal lattice along *a*-, *b*-, and *c*-axes (CTEs) as well as those of volumetric thermal expansion (CVE) were precisely evaluated.

Methods: Highly crystalline PI particles were prepared by heating of NMP solutions of poly(amic acid) at 200°C for 2 h.[1] The particles morphology was sheaf or coral type which was similar to polymer spherulites. Transmission VT-WAXD profiles of the PI powders were measured with a BL40B2 beamline at Japan Synchrotron Radadiation Res. Inst. (JASRI/SPring-8) [2012B1317].

Results & Discussion: The diffraction peaks observed in WAXD profiles were assigned according the literature, and the relative thermal expansions estimated from *d*-spacings are plotted against temperature. The CTEs and CVEs of the crystal lattices of PIs are also shown in the figure. 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) and PIs having crankshaft structures (PMDA/DABA and PMDA/APAB) exhibit nearly isotropic thermal expansion along *a*- and *b*-axes. However, it should be noted that highly anisotropic expansions were 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 at elevated temp. accompanying flip-flop or rotational motion of phenyl rings in the diamine moiety. In addition, the CVE of PMDA/DABA is much smaller than that of PMDA/APAB despite the similar skeletons, which is attributable to the structural rigidity along *a*- and *b*-axes of the former due to formation of intermolecular hydrogen bond network between amide linkages. A rigid-rod structure with enhanced intermolecular interactions endows PIs with high thermal stability and small thermal expansion.



(*Left*) Variable temperature WAXD profiles of crystalline powder of PMDA/ODA, (*Middle*) Variations of the crystal lattice (*a*-, *b*-, and *c*-axes) of PMDA/ODA caused by heating, and (*Right*) Comparison of coefficients of linear (CTE) and volumetric thermal expansion (CVE) of four kinds of PIs.

References

[1] Y. Nagata, Y. Ohnishi and T. Kajiyama, **Highly Crystalline Polyimide Particles**, *Polymer J.*, 1996, 28, 980-985.