Temperature- and Pressure-Induced Changes in Crystalline Structures of Polyimides Analyzed by Synchrotron Wide-Angle X-ray Diffraction

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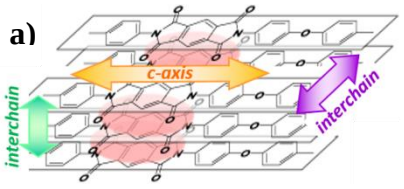
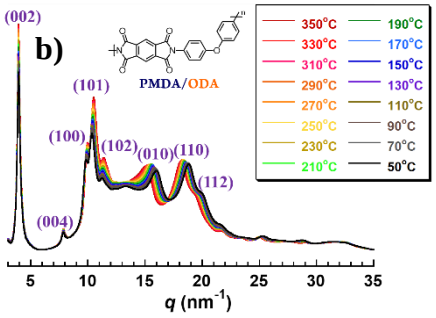
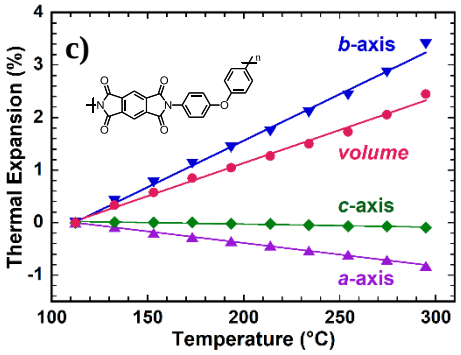
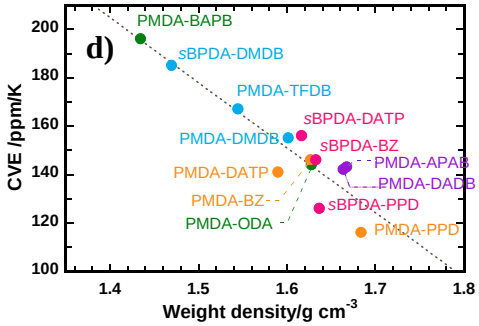
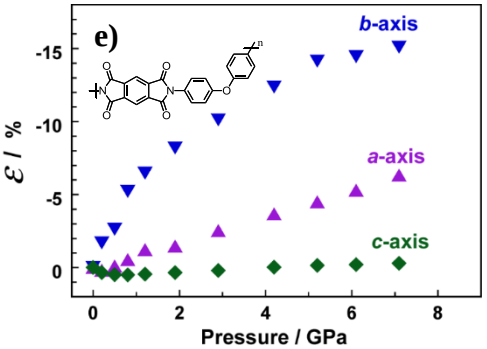
Variations in the crystalline structures of polyimides (PIs, **Fig. a**) were analyzed under variable temperature (80°C−300°C) [1−3] or variable pressures (1 atm−8 GPa) [4−7] using synchrotron wide-angle X-ray diffraction (WAXD). Firstly, coefficients of thermal linear and volumetric expansion (CTE, CVE) of crystal lattice for 13 kinds of fully aromatic crystalline polyimides (PIs) were evaluated from the temperature dependence of lattice parameters measured from VT WAXD patterns (**Fig. b**), and the effects of chemical structure on CTE and CVE are discussed. The smallest CVE (+116 ppm/K) was observed for PMDA-PPD derived from pyromellitic acid dianhydride and *p*-phenylenediamine with the simplest rigid-rod structure, and the largest CTE anisotropy was observed for PMDA-ODA containing an ether linkage (**Fig. c**) with an extraordinarily negative CTE along the *a*-axis (−44 ppm/K). The values and anisotropy of the CTEs strongly depended on the crystalline structure, whereas the CVEs were negatively correlated with the weight density, regardless of the PI type (**Fig. d**). Secondly, variations in the crystalline structures of PIs were analyzed under elevated pressures up to 8 GPa using a diamond anvil cell (DAC). The compressibilities ( ) along the polymer chain axis (*c*-axis) of rigid-rod PIs increased with an increase in the number of phenyl rings in the diamine moiety, which could be due to a pressure-induced deformation of the periodic structure associated with changes in bond angles and dihedral angles. In contrast, PMDA/ODA showed an increase in the lattice parameter along the *c*-axis up to 0.8 GPa (**Fig. e**), which could be due to a widening of the ether bond angle. Moreover, PMDA/PPD showed isotropic compression along interchain directions, whereas PMDA/DATP derived from 4,4'-*p*-terphenylene diamine and PMDA/ODA showed highly anisotropic compression along the cofacial stacking direction, which resulted in the larger volumetric shrinkages of the latter PIs. Consequently, the behaviors of thermal expansion and linear compression of the crystalline lattices of PIs are mutually correlated, and these knowledge can be used to develop novel PIs for electronic and photonic applications, of which the CTE, CVE, compressibility, and their anostropies are precisely controlled.











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