Analysis of Pressure-induced Variations in Aromatic Polyimides based on WAXD Measurements at Very High Pressure

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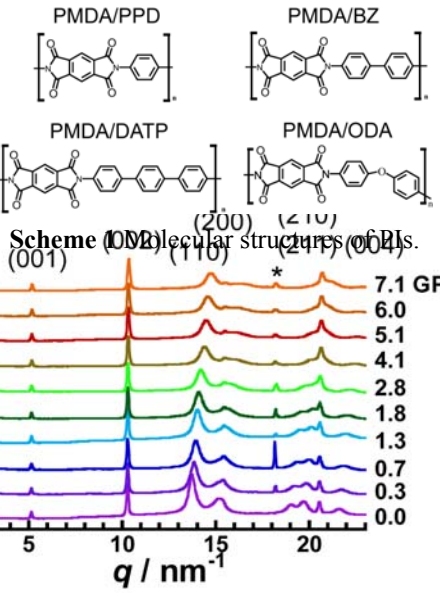
For investigation of the mechanisms of thermal expansion and thermal conductivity of aromatic polymers at the molecular level, pressure-induced variations in the ordered structures of semi-crystalline powders and films of aromatic polyimides (PIs) were examined at elevated pressures up to 8 GPa using synchrotron wide angle x-ray diffraction (WAXD) (Fig.1). Strains (ε) along *a*-, *b*-, and *c*-axes of PIs caused by pressure were evaluated as well as volumetric compression. A PI having *p*-terphenyl in the diamine moiety (PMDA/DATP, Scheme 1) exhibited a larger ε compared to that having *p*-phenyl (PMDA/PPD) (Fig.2), which indicates that an increase in *p*-phenyl groups leads to an increase in ε at high pressure. Interestingly, the lattice parameter along *c*-axis ($d_{c\text{-axis}}$) of PMDA/ODA film having a bent linkage increased by applying pressure up to 0.4 GPa (Fig.3), which is attributable to variations in bond angles. Moreover, the $d_{c\text{-axis}}$s of a solvent-annealed film and a powder of PMDA/ODA with higher crystallinity are larger than that of a spin-coated film, and they showed more significant increases in $d_{c\text{-axis}}$ up to 0.8 GPa. This indicates that pressure-induced structural changes depends on the packing state of ordered structure. High pressure WAXD experiments provide useful information for controlling the properties of PIs.

REFERENCE: K. Takizawa, J. Wakita, K. Sekiguchi, and S. Ando, *Macromolecules*, **43**, 2115- 2117 (2010), *ibid.* **44**, 349-359 (2011), *ibid.***45**, 4764-4771 (2012).



Scheme 1 Molecular structures of PIs.

Fig. 1 Variations in WAXD patterns of crystalline powder of PMDA/PPD PI caused by applying pressure up to 7.1 GPa.

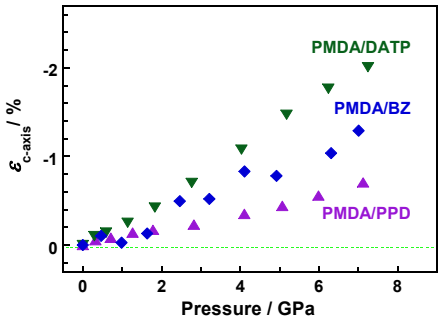


Fig. 2 Pressure dependence of strain along *c*-axis for crystalline powders of rigid PIs.

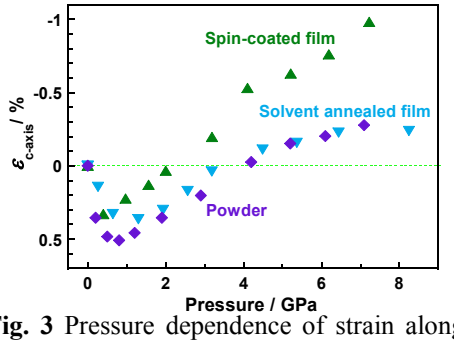


Fig. 3 Pressure dependence of strain along *c*-axis for a PI having a bent linkage.