Analysis of Compression Behaviors of a Highly Crystalline Polyimide Prepared from Monomer Salts and Poly(amic acid)

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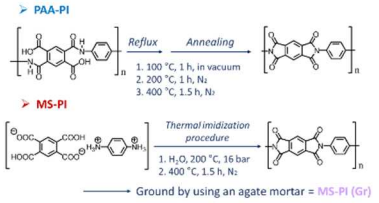
Introduction: Physical properties of aromatic polyimides (PIs) are closely related to their molecular aggregation structures. We have been investigating the relationship between the optical properties and molecular aggregation structures of PIs at elevated pressures.[1] In general, crystalline PI particles are synthesized by thermal imidization of poly(amic acid) (PAA) in high b.p. solvents. Recently, PI particles obtained by hydrothermal polymerization of 'monomer salt' (MS), consisting of co-crystals between dianhydride and diamine, were reported as PIs with very high crystallinity.[2] In this study, compression behaviors of the crystalline and amorphous regions of highly crystalline PI samples prepared from MS and PAA were investigated by wide-angle X-ray diffraction (WAXD) and infrared absorption (IR) spectroscopy under high pressure up to 4 GPa.

Experimental and methods: Highly crystalline PMDA/PPD powder were prepared by hydrothermal polymerization of MS (MS-PI) or by thermal imidization of PAA in a high b.p. solvent (PAA-PI) (**Scheme 1**). Besides, ground MS-PI (MS-PI (Gr)) was prepared by grinding MS-PI with an agate mortar. To apply pressure to the PI samples, a diamond anvil cell (Syntech Co. Ltd.) was used.



Scheme 1 Synthetic scheme of highly crystalline PI samples.

Results and Discussion: The crystallinity (X_c) and density (ρ) at atmospheric pressure for MS-PI (X_c = 0.90, ρ = 1.77 g/cm^3), MS-PI(Gr) (X_c = 0.46, ρ = 1.77 g/cm^3), and PAA-PI (X_c = 0.40, ρ = 1.74 g/cm^3) were estimated based on the WAXD intensity profiles. The volume compression of the crystal lattices of MS-PI, MS-PI (Gr), and PAA-PI at 4.0 GPa were evaluated at 14.0 %, 12.0 % and 9.5 %, respectively (**Fig. 1**). This result demonstrates that MS-PI and MS-PI (Gr) exhibited larger volume compressibility despite their higher densities than PAA-PI. On the other hand, pressure-induced higher-frequency shifts of the IR-band assignable to C=O asym. of the imide ring were analyzed to investigate the compression behaviors of the crystalline and amorphous regions. In general, this shift is attributed to an increase in binding constants (k) caused by shrinkage of covalent bond lengths. The C=O asym. band can be fitted by two Gaussian functions, in which the band at the higher frequency is assignable to C=O groups in the amorphous region. This band exhibits larger shifts than that assigned to the crystalline region in each PI sample (**Fig. 2**). This result indicates that the compressibility of the amorphous region was larger than that of the crystalline region. Consequently, volumetric compression of the crystal lattice in the highly crystalline PIs is dependent on the crystallinity because the compression stress can be preferentially relaxed in the amorphous region.

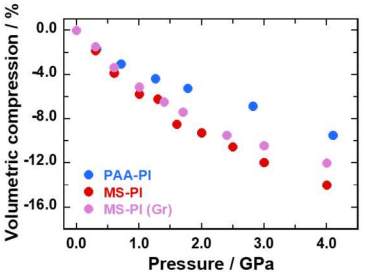


Fig. 1 Volumetric compression of crystalline lattice up to 4 GPa.

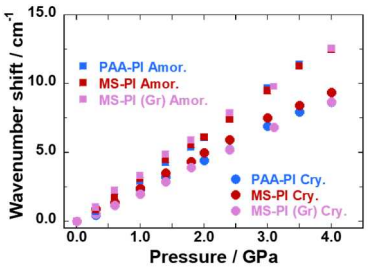


Fig. 2 Peak shifts of C=O asym. mode in crystalline and amorphous regions induced by pressure application.

Reference: [1] E. Fujiwara, S. Ando, *et al.*, *J. Phys. Chem. B*, **122**, 8985 (2018). K. Takizawa, S. Ando, *et al.*, *Macromolecules*, **44**, 49 (2011). *ibid*. **45**, 4764 (2012), *ibid*. **47**, 3951 (2014). [2] B. Baumgartner, *et al.*, *Polym. Chem.*, **5**, 3771 (2014).

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