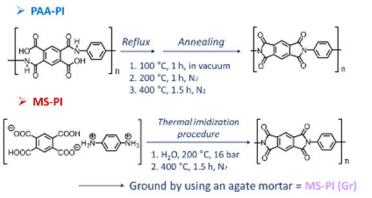
Analysis of Compression Behaviors of a Highly Crystalline Polyimide Prepared from Monomer Salts and Poly(amic acid)

Eisuke FUJIWARA[1], Ryohei ISHIGE[1], D. Alonso Cerron-Infantes[2], Michael J. Taubländer[2], Mariam M. Unterlass[2], and Shinji Ando[1]

([1]Dep. Chem. Sci. Eng., Tokyo Institute of Technology, [2]Inst. Mater. Chem., Technische Universität Wien)

Introduction: Physical properties of aromatic polyimides (PIs) are related to their molecular aggregation structures. We have recently investigated 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 boiling-solvents, though PI particles obtained by hydrothermally polymerization of 'monomer salt' (MS), which is co-crystal between dianhydride and diamine, demonstrated higher 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 samples were obtained by hydrothermal polymerization of MS (MS-PI) and from PAA by thermal imidization in a high boiling-solvent (PAA-PI) (**Scheme 1**). Besides, ground MS-PI (MS-PI (Gr)) was prepared by using an agate mortar. To generate pressure, PI samples were loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.).



Scheme 1 Synthesis method 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 compressibility of the crystal lattices of MS-PI, MS-PI (Gr), and PAA-PI at 4.0 GPa were estimated as 14.0 %, 12.0 % and 9.5 %, respectively (**Fig. 1**). This result demonstrates that the volumetric compression is suppressed with a decrease in crystallinity. On the other hand, pressure-induced higher-frequency shifts of IR-band derived from C=O asymmetric vibration of the imide ring (C=O asym.) were analyzed for investigating the compression behaviors of the crystalline and amorphous region. In general, this shifts 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 PI chain in the amorphous region. This band exhibits lager higher-frequency shifts than that assigned to PI chain in crystalline region in each PI sample (**Fig. 2**). This indicates that the stress relaxation with free volume compression was more significant in the amorphous region than in the crystalline region. In conclusion, the volumetric compression of the crystal lattice in the highly crystalline PIs is dependent on the crystallinity because the compression stress is relaxed significantly in the amorphous region.

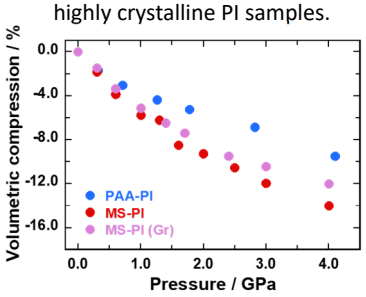


Fig. 1 Volumetric compression of crystalline lattice up to 4 GPa.

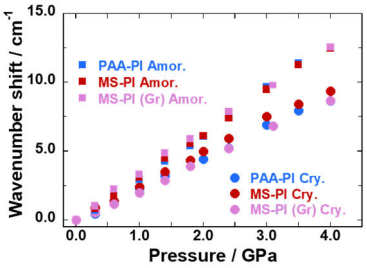


Fig. 2 Peak shifts of C=O asym. at crystalline and amorphous region with pressure application.

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

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