

Molecular Aggregation Structures and Optical Properties of Polyimide Films Analyzed by Synchrotron Wide-Angle X-ray Diffraction, Infrared Absorption, and UV/visible Absorption Spectroscopies at Very High Pressure

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The molecular aggregation structures of polyimide (PI) chains have been investigated using wide-angle X-ray diffraction (WAXD) and UV/visible absorption spectroscopy. In general, PI films do not exhibit definitive crystalline diffraction peaks, which indicates the absence of large domains with three-dimensional positional order. Hence, the ordered domains with mesomorphic order between crystalline and amorphous phase in the film can be interpreted as liquid-crystalline-like (LC-like) ordered domains. We have recently

reported the variations in the aggregation structures of PI chains in the ordered domains up to 8.0 GPa. (~80,000 atm) [1] On the other hand, two kinds of optical absorption bands are observed for fully aromatic polyimides. The first one is 'locally excited' (LE) transition that occurs between the molecular orbitals located around the dianhydride moiety of PIs. The second one is 'charge transfer' (CT) transition originating from the CT complexes formed between the dianhydride and diamine moieties. Recently, we have reported the pressure-induced variations in the absorption spectra of fully aromatic and semi-aliphatic PIs up to 400 MPa (~4,000 atm).[2] A pressure-induced bathochromic shift was observed in the LE band, and a pressure-induced increase in absorbance was observed for the intermolecular CT band. These findings were very beneficial for developing highly fluorescent PIs [3], whereas the relationships between the pressure-induced variations in the molecular aggregation structures and optical properties of PI films have not been examined so far.

In this study, the relationship between the molecular aggregation structures and the optical properties of fully-aromatic and semi-aliphatic PI films (Fig.1) were analyzed by synchrotron wide-angle X-ray diffraction (WAXD), infrared (IR) absorption, and UV/visible absorption spectroscopies at very high pressures up to 8.2 GPa. To generate high pressures, PI

films (size : 180 x 180 μm) were loaded into diamond anvil cell (DAC, Syntech Co. Ltd) equipped with 600 μm culet synthetic diamond anvils (Sumi-crystal type-IIa).

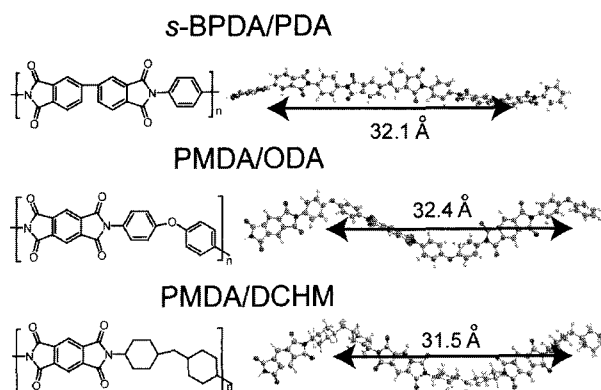


Fig.1 Molecular structure of polyimides (PIs) and geometries of their trimers optimized by DFT.

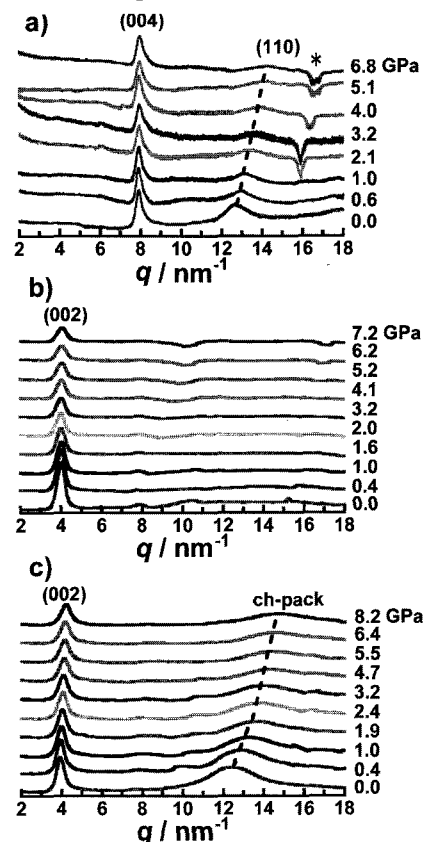


Fig.2 Variations in X-ray scattering patterns for (a) s-BPDA/PDA, (b) PMDA/ODA, and (c) PMDA/DCHM

The standard ruby fluorescence technique was used to determine the pressure inside the sample room. The transmission X-ray diffraction measurements were performed with a BL-40B2 beam line at the Japan Synchrotron Radiation Research Institute (SPring-8) using an image-plate as the detector, and silicone oil as the pressure medium. As shown in Figs. 2 and 3, the PIs showed significant reduction in the interchain distances as represented by ch-pack and (110) peaks in the first stage of compression up to GPa, which resulted in an appreciable decrease in the interchain free volume. In addition, an apparent reduction the C-C bond lengths of aromatic rings was also confirmed by the pressure-induced high wavenumber shifts of the IR stretching vibration of the PIs with the help of DFT calculations. Moreover, pressure-induced bathochromic shifts were clearly observed in the LE

absorption band of PIs, which is related to the enhanced van der Waals interaction caused by the reduced interchain distances. (Fig.4) The intensity of the CT absorption band of *s*-BPDA/PDA was reduced up to 0.3 GPa, indicating that local conformational changes affect the intramolecular CT interactions. In contrast, the CT absorptions of PMDA/ODA and PMDA/DCHM were enhanced with increasing the pressure, which was caused by an enhancement of the intermolecular CT interactions. The significant variations observed in the LE and intermolecular CT bands below 1 GPa accord with the significant decrease in the interchain distances as indicated by the synchrotron

WAXD patterns. In summary, the high pressure experiments indicate that the optical properties and the aggregation structure of PIs are closely related in a linear manner.

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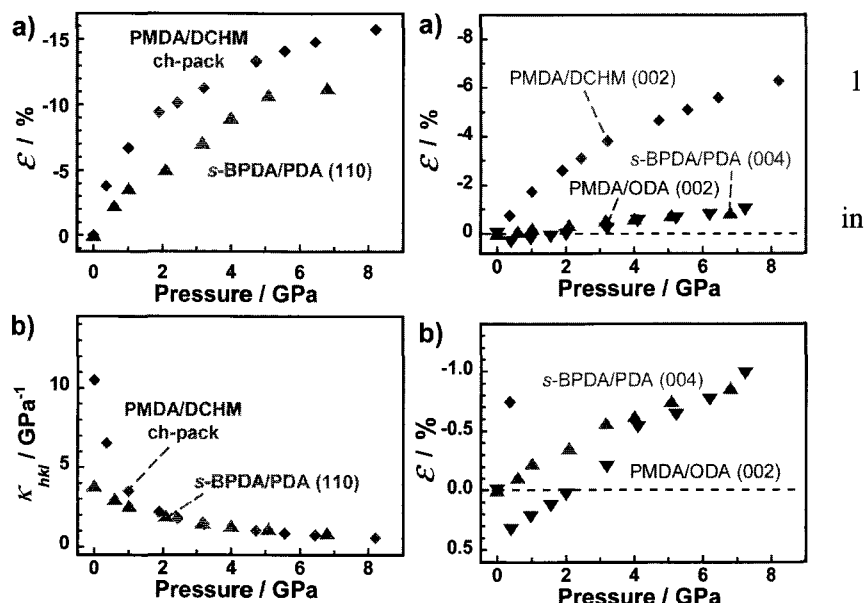


Fig. 3 (Left) Variations in (a) strains (κ) of chain packing peaks and (b) linear compressibilities (ϵ) along the (110) peak of *s*-BPDA/PDA and the ch-pack peak of PMDA/DCHM by applying pressure. (Right) Variations in (a) strains of (00*l*) peaks of PIs by applying pressure, (b) a

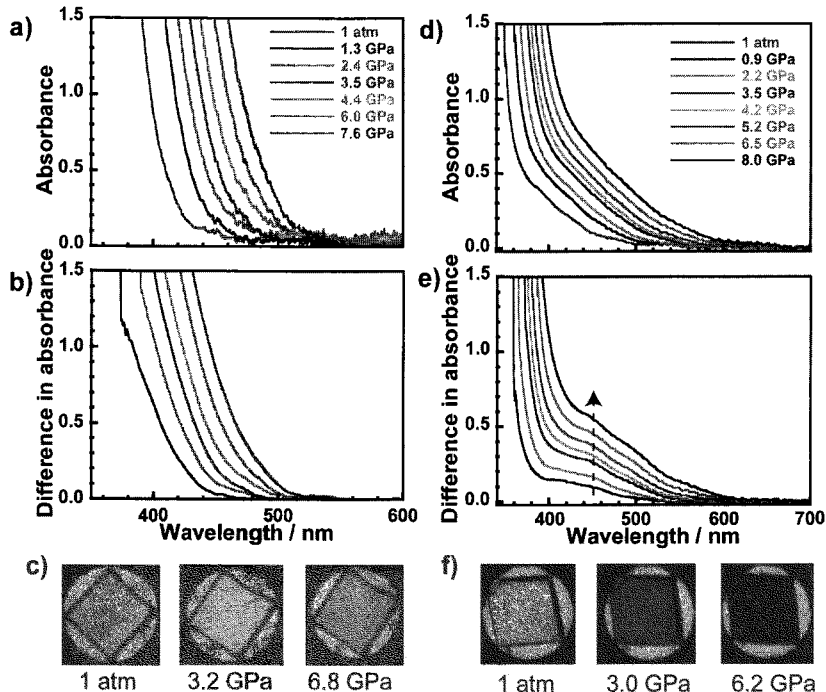


Fig. 4 Pressure dependence of (a) optical absorption spectra, (b) absorption differential spectra of *s*-BPDA/PDA thin film, (c) pressure-induced variations in the color of *s*-BPDA/PDA thick film, pressure dependence of (d) optical absorption spectra and (e) absorption differential spectra of PMDA/ODA thin film, (f) pressure-induced variations in the color of PMDA/ODA thick film.