Variations in Optical Absorption Spectra of PI Thin Films under Very High Pressure

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[Introduction] Intra- and intermolecular charge transfer (CT) interactions play important roles in polyimides (PI). The intermolecular CT depends on the packing states of PI, and it affects the solid-state properties (e.g., transparency, fluorescence, and refractive index). Hence, it is important to understand the relations between the CT and the packing state of PIs. In this study, optical absorption spectra of PI thin films have been observed at high pressure using a diamond anvil cell (DAC) with silicone oil as pressure medium.

[Experimental] The structures of PIs are shown in Fig. 1. The thicknesses of thin and thick films are 1 µm and 10 µm, respectively. The pressure in the sample cavity was estimated from the peak shifts of ruby fluorescence [1]. The pressure was raised up to ca. 10 GPa. The optical absorption spectrum of thin PI films was measured at each pressure.

[Results and Discussion] The absorption spectra measured for PMDA/ODA thin films are shown in Fig. 2. A significant increase in absorbance are observed at 400~500 nm with pressurization (Fig. 2). Since this band is related to the CT interactions [2], the variation indicates an increase in the PI segments that form the CT packing. In contrast, no increase in absorbance was observed for s-BPDA/PDA at the CT band (460 nm) [3]. Since the CT band of s-BPDA/PDA is located at much shorter wavelengths than that of PMDA/ODA, the variation in the CT state could not be observed. For a thick film of P2FDA/DMDB, a distinct hysteresis (a residual absorption band [4]) was observed at 650 nm (Fig. 3), which indicates that the CT state generated by pressurization was remained after depressurization. P6FDA/DMDB shows no distinct band before pressurization, but it exhibited a distinct residual absorption band. These facts demonstrate that such perfluoro-dianhydrides with high electron affinity can generate strong intermolecular CT attractions. The two –CF₃ groups in P6FDA/DMDB are bulkier than P2FDA, which may interfere the intermolecular CT interactions at 0 GPa. But, the CT could be induced by a decrease in inter-molecular distance between polymers, and the packing state thus formed was remained after depressurization.


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