

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

Sho-hei AZAMI and Shinji ANDO*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology (Tokyo Tech)
Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

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

[Experimental] The structures of PIs used in this study are shown in Fig.1. The thicknesses of thin and thick films are 1 μm and 10 μm , respectively. Pressure in the sample cavity was estimated from peak shifts of ruby fluorescence [1]. The pressure was gradually raised up to ca.10 GPa, and absorption spectra of PI films (0.2 mm square) were 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], this variation indicates an increase in the PI segments incorporated in the CT formation. 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 was not 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 remained after depressurization. P6FDA/DMDB shows no distinct band before pressurization, but it exhibits a distinct residual absorption band. These facts demonstrate that such perfluoro-dianhydrides with high electron affinity may cause strong intermolecular CT attractions. The two $-\text{CF}_3$ groups in P6FDA/DMDB are bulkier than the fluorines in P2FDA, which may interfere the intermolecular CT interactions at 0 GPa. However, strong CT formation could be induced by a reduction of inter-molecular distance between polymers, and the packing state thus formed was remained after depressurization.

[1] G. J. Piermarini, S. Block, J. D. Barnett, *J. Appl. Phys.*, **44**, 5377 (1973).

[2] M. Hasegawa, M. Kochi, I. Mita, R. Yokota, *Eur. Polym. J.*, **25**, 349 (1989).

[3] M. Hasegawa, I. Mita, M. Kochi, R. Yokota, *J. Polym. Sci., Part C, Polym. Letts.*, **27**, 263 (1989).

[4] K. Uetake, S. Ando. *Polym. Prep. Japan*, **54**, 1334 (2005)

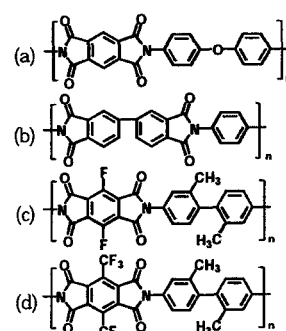


Fig.1 Molecular structures of (a) PMDA/ODA, (b) *s*-BPDA/PDA, (c) P2FDA/DMDB, and (d) P6FDA/DMDB.

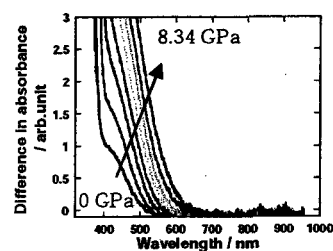


Fig.2 Variations in the difference spectra for PMDA/ODA by pressurization.

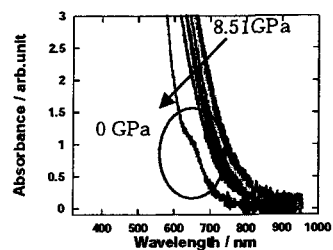


Fig.3 Variations in the absorption spectra for P2FDA/DMDB by depressurization.