Analysis of Aggregation Structures and Optical Properties of Polyimides Having Bent Structures in the Dianhydride Moieties under High Pressures

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Polyimides (PI) are known as super engineering plastics exhibiting high thermal stability, excellent physical properties, and environment resistance. Recently, PIs having bent structures have attracted interests because of their good processability and high optical transparency. The investigation of the aggregation structures is important because the intermolecular interactions significantly affect the physical properties of PIs. We have recently reported that the relationship between the aggregation structures and optical properties of PIs analyzed by wide-angle X-ray diffraction (WAXD) and UV/Vis absorption spectroscopy at very high pressure up to 8 GPa.[1] In this study, the aggregation structures of PIs having bent structures in the main chains were investigated by using UV/Vis absorption spectra under very high pressure up to 8 GPa. The molecular structures of the PIs used in this study are shown in Fig.1a. The high pressure experiments were performed using a diamond anvil cell (DAC) with 600 μm-ϕ diamond culets (Fig.1b). The UV/Vis absorption spectra of *s*BPMD and *a*BPMD PIs under high pressures are shown in Fig.2. Pressure-induced bathochromic shifts were observed in the absorption bands of PIs, which is related to enhanced van der Waals interactions due to reduced interchain distances. The energy shifts observed for the absorption bands against pressure are plotted in Fig.3. *a*BPMD PI having bent a main chain forms looser aggregation structure than *s*BPMD because the absorption band of *a*BPMD exhibited more pronounced energy shifts than *s*BPMD. In addition, the slopes of plots show significant changes at 1 GPa, which indicates that free volume was preferentially compressed at lower pressure up to 1 GPa, and structural changes were induced at higher pressure from 1 to 8 GPa.

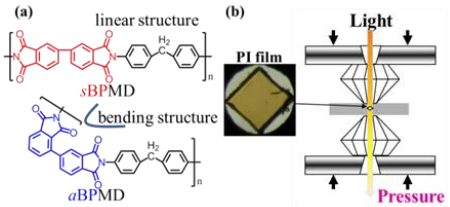

Figure 1. Molecular structure of PIs(a) and schematic illustrate of DAC(b)

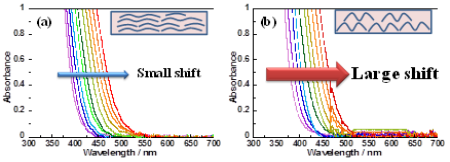

Figure 2. Optical absorption of *s*BPMD(a) and *a*BPMD(b) under high pressure

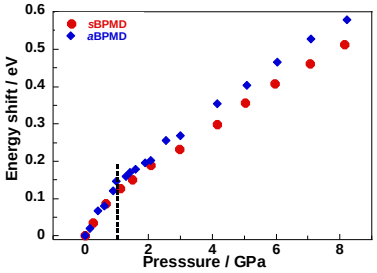

Figure 3. Energy shifts of *s*BPMD and *a*BPMD as a function of pressure

References

[1] K. Takizawa, J. Wakita, S. Azami, S. Ando: *Macromolecules*, **2011**, *44*, 349-359.