Aggregation Structures and Optical Properties of Polyimides Having Rigid or Bent Structures under High Pressure

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Polyimides (PI) are known as high-performance engineering plastics exhibiting high thermal stability, mechanical strength, and good flexibility. PIs having a bent linkage in the main chains have attracted interests because of their good thermal properties and high optical transparency. Since intermolecular interactions significantly affect the physical properties of PIs, aggregation structure is a key to understand their properties. We have reported that the relationships between the molecular aggregation structures and optical properties of PIs as analyzed by synchrotron wide-angle X-ray diffraction (WAXD) and UV/visible absorption spectroscopy at very high pressure [1]. In this study, the aggregation structures of PIs having bent linkages were investigated using UV/visible spectra under very high pressure up to 8 GPa (Fig. 1). The molecular structures of PIs having rigid (*s*BPMD) and bent (*a*BPMD) structures are shown in Fig. 2(a). To generate pressure, PI films were loaded into an anvil cell (DAC, Syntech) (Fig. 2(b)) equipped with synthetic diamond anvils having a 600 μm culet (Sumi-crystal type-IIa). The ruby fluorescence technique was used to determine the pressure inside. The UV/Vis absorption spectra of *s*BPMD and *a*BPMD PIs under high pressure are shown in Fig. 3(a). Pressure-induced bathochromic shifts are observed in the absorption bands of PIs, which is related to enhanced van der Waals interactions caused by reduced interchain distances. The pressure-induced energy shifts for the PIs are plotted as a function of pressure (Fig. 3(b)). The absorption energies were gradually shifted to lower energy by applying pressure, and the energy shifts for *a*BPMD is larger than *s*BPMD at all pressures, which indicates that the former may have looser aggregation structure with enlarged interchain distances. In addition, changes in the slopes of plots are observed at ca. 1 GPa. Easily compressible volume was preferentially compressed below 1 GPa, and then hardly compressible volume was gradually compressed up to 8 GPa.

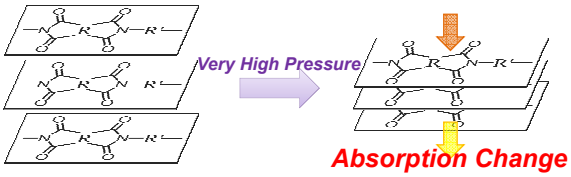

Figure 1. Schematic illustration of compressed inter-molecular distance under high pressure

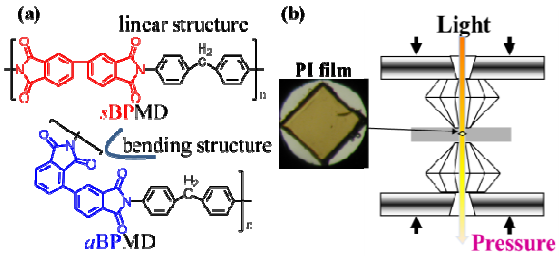

Figure 2. (a) Molecular structures of rigid and bent PIs and (b) views of a PI film and DAC.

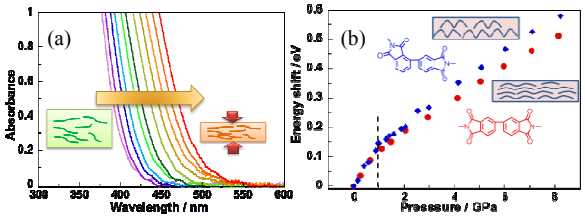

Figure 3. Variations in (a) optical absorption of *s*BPMD and (b) energy shifts of rigid and bent PIs as a function of pressure up to 8 GPa.

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