

# Analysis of Aggregation Structures of Polyimides Having a Bent Linkage by UV/Vis Absorption Spectra at High Pressures

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## I. INTRODUCTION

Polyimides (PI) are known as high-performance engineering plastics exhibiting high thermal and chemical stability, flame resistance, radiation resistance, mechanical strength, and good flexibility. Recently, PIs having a bent linkage have attracted much interests because of its good thermal properties and high transparency. It is known that not only the chemical and electronic structures of repeating unit but also intermolecular interactions significantly affect the physical properties of PIs, and therefore, knowledge of the aggregation structures is prerequisite for detailed understanding and precise control of the properties of PIs having bent linkages. Previously, we have reported that relationship between the molecular aggregation structures and optical properties of fully aromatic and semialiphatic PI were analyzed by synchrotron wide-angle X-ray diffraction (WAXD), infrared absorption, and UV/visible absorption spectroscopy at very high pressure up to 8 GPa [1]. In this study, the aggregation structures of PIs having bending structures were investigated by using UV/visible absorption spectra under very high pressure up to 8 GPa (Fig.1).

## II. EXPERIMENTAL

The molecular structures of the PIs used in this study are shown in Fig.2. To generate pressure up to 8 GPa, the PI films were loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.) (Fig.3) equipped with 600  $\mu\text{m}$  culet synthetic diamond anvils (Sumi-crystal type-IIa, Sumitomo Electric Hardmetal Corp.). The standard ruby fluorescence technique was used to determine the pressure inside the sample room. The UV/visible absorption spectra of the PI films were measured with multichannel CCD spectrometer (PMA-11, Hamamatsu Photonics Co., Ltd.) in the range of 200-950 nm (C7473-36), using an Xe lamp (Hamamatsu Photonics Co., Ltd.) as a light source.

## III. RESULT AND DISCUSSION

To clarify the effects of a bent linkage in the dianhydride moieties on the aggregation structures of PIs, variations in UV/vis absorption spectra for PI films were examined under very high pressure up to 8 GPa. The UV/Vis absorption spectra of *s*BPMD and *a*BPMD PIs under high pressure are shown in Fig.4. Pressure-induced bathochromic shifts were observed in the absorption band of PIs, which is related to the enhanced van der Waals interactions caused by reduced interchain distances. In the case of *s*BPMD and *a*BPMD PIs, the latter having a bent linkage has looser aggregation structure because its absorption band exhibited more pronounced bathochromic shift compared to the former.

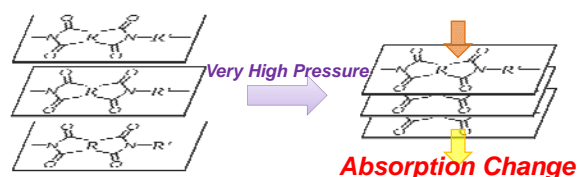


Figure 1. Schematic illustration of optical absorption under high pressure

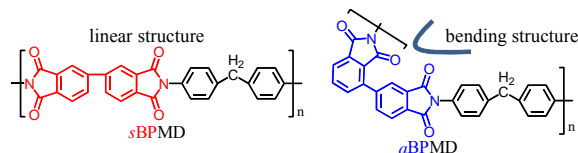


Figure 2. Molecular structure of PIs

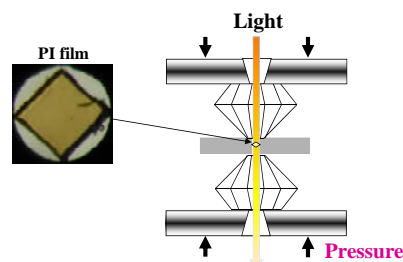


Figure 3. Schematic illustration of DAC

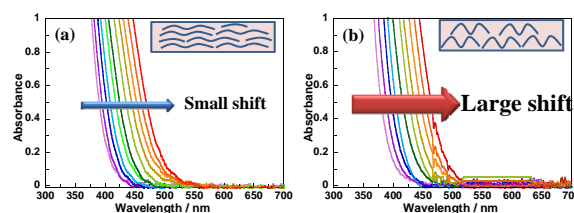


Figure 4. Optical absorption of *s*BPMD(a) and *a*BPMD(b) under high pressure up to 8 GPa

## REFERENCES

- [1] K. Takizawa, J. Wakita, S. Azami, S. Ando, "Relationship between Molecular Aggregation Structures and Optical Properties of Polyimide Films Analyzed by Synchrotron Wide-Angle X-ray Diffraction, Infrared Absorption, and UV/Visible Absorption Spectroscopy at Very High Pressure", *Macromolecules*, **44**, pp349-359, Jan 2011