Extended Abstract

Changes in Aggregation Structures of Polyimides Caused by Intermolecular Photo-crosslinking under Very High Pressure

E.Fujiwara*, H. Fukudome*, K. Murakami*, R. Ishige* and S. Ando*
* Department of Chemistry and Materials Science, Tokyo Institute of Technology, Japan
e-mail: efujiwara@polymer.titech.ac.jp

I. Introduction

Polyimides (PI) are widely known as high-performance engineering plastics exhibiting high thermal stability, radiation resistance, and mechanical strength. It has been reported that not only the chemical and electronic structures of the repeating unit but also the chain packing significantly affect the physical properties of PIs. For instance, density, refractive index, and thermal conductivity of PIs can be enhanced by applying high pressure due to the dense aggregation structures formed under elevated pressures. However, in many cases, the dense aggregation structures and enhanced properties of PIs are reverted to their original state after depressurization. Thereby, a new method is required to fix the dense aggregation structures to maintain their unique properties exerted under high pressure. There are some reports that photo-crosslinking reactions is usable to fix the structures of polymers under high pressure via intermolecular photo-crosslinking reactions [1]. Previously, we reported the effects of photo-crosslinking reactions of benzophonone-containig PIs (BP-PIs), which enables to maintain the dense aggregation structures induced by applying 400 MPa [2]. In the present study, changes in aggregation structures of BP-PI by the photo-crosslinking under very high pressure were investigated by using UV/visible absorption spectra (Fig. 1).

II. Experimental

The molecular structure of BP-PI used in this study is shown in Fig. 2(a). To generate pressure up to 8 GPa, PI films were loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.) (Fig. 2(b)) equipped with culet synthetic diamond anvils with 600 μm diameter (Sumi-crystal type-IIa, Sumitomo Electric Hardmetal Corp.). The ruby fluorescence technique was used to measure the pressure inside the sample chamber. 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, using a Xe lamp (Hamamatsu Photonics Co., Ltd.) as a light source. PI films were irradiated by UV with a UV LED light (λ=350 nm, Hamamatsu Photonics Co., Ltd) under atmospheric pressure and 8 GPa.

III. Result and Discussion

To clarify the changes of aggregation states of BP-PI, UV/visible absorption spectra were measured for BP-PI films at ambient pressure before and after UV irradiation at atmospheric pressure and 8 GPa. The UV/vis spectrum of a PI film irradiated by UV light at 8 GPa showed significant bathochromic shift even after releasing the pressure (Fig. 3(b)). This bathochromic shift is due to the enhanced van der Waals interaction caused by the reduced interchain distances. Therefore, this shift indicates that the dense aggregation structures at 8 GPa was partially maintained by photo-crosslinking reactions. This method potentially enables to maintain the characteristic properties of BP-PI films associated with the highly dense molecular packing formed at very high pressure.

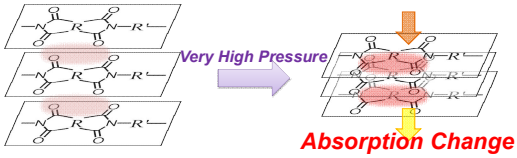

Figure 1. Schematic illustration of change in the aggregation structure and in the optical absorption of PIs under high pressure

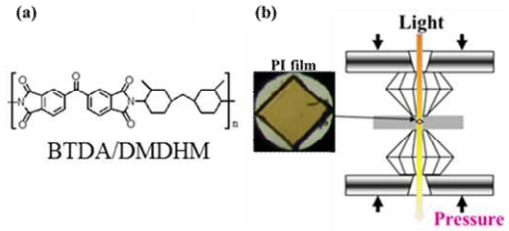

Figure2. (a) Molecular structure of BP-PI and (b) optical microscope image of the PI film in DAC and schematic presentation of cross-section of DAC.

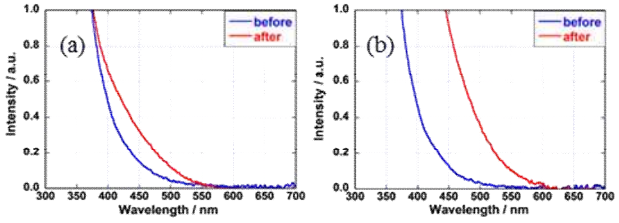

Figure 3. Optical absorption of BP-PIs before and after UV irradiation at (a) atmospheric pressure and (b) 8 GPa.

References

[1] G. Maxein, S. Mayer, R. Zentel, "Structure-Property Relations in Cholesteric Networks from Chiral Polyisocyanates", *Macromolecules*, **32**, pp5747-5754, June 1999

[2] K. Murakami, S. Ando, "Effects of UV Crosslinking under High temperature on the refrective Indices and Agreggation Structures of Benzophenone-containig Polyimides", *Journal of Photopolymer Science and Technology*, **24**, pp277-282, May 2011