Pressure-Induced Variations in Luminescence Properties of Polyimides having Fluorescent End-groups

Koichiro Muto*, Eisuke Fujiwara*,Liang Naiqiang*, Ryohei Ishige*, Shinji Ando*
* Department of Chemical Science and Engineering, Tokyo Institute of Technology, Japan
e-mail: kuto@polymer.titech.ac.jp

Ⅰ. INTRODUCTION

Organic luminescent materials have been widely used as displays, light emitting devices, photovoltaic devices, and spectrum convertors. Recently, polyimides (PIs) have been attracted as novel photoluminescence materials because of their high thermal and chemical stability, and mechanical strength. We have developed a variety of photoluminescent PIs exhibiting various colored fluorescence in visible wavelength region, which is controllable by changing its primary structure [1]. On the other hand, photoluminescence properties of PIs strongly depend not only on the primary structure but also on the aggregation state. We have reported that the intensity of main-chain fluorescence in PIs is decreased at high pressures due to the promotion of nonradiative deactivation caused by enhancement of intermolecular energy transfer [2]. However, the effect of applying pressure on photoluminescence properties of PIs with fluorescent end-groups has yet to be investigated.

In this study, the correlation between the aggregation state and the photoluminescent properties in PIs with fluorescent end-groups was examined on the base of photoluminescence spectroscopy under high pressure.

Ⅱ. EXPERIMENTAL

The chemical structures of end-capped PIs, *s*BPDA/DCHM-3HPA (*s*BPDC-3HPA) and 6FDC/DCHM-3HPA (6FDC-3HPA), are shown in **Fig. 1**. To generate high pressure, PI films were loaded into a sample chamber of diamond anvil cell (DAC, Syntech Co. Ltd.) (**Fig. 2**). The ruby fluorescence technique was used to measure the pressure inside sample chamber [3]. The photoluminescence spectra of the PI films at high pressures (from 0.1 MPa to 2.0 GPa) were measured by a multichannel CCD spectrometer (Hamamatsu Photonics), and a LED light (λ_{ex} =365 nm, Hamamatsu Photonics) was used as an excitation light source.

Ⅲ. RESULT AND DISCUSSION

The intensity of the fluorescent peak observed at 550 nm, assignable to the end-groups of *s*BPDC-3HPA, significantly decreased with increasing the pressure. This is explainable by the enhancement of intermolecular energy transfer caused by decrease in the distance between the main-chain and end-groups (**Fig.3(a)**). On the other hand, the intensity of end-group fluorescence of 6FDC-3HPA observed at 550 nm obviously increased at elevated pressures (**Fig.3(b)**). In case of 6FDC-3HPA, the energy transfer between the main-chain and end-groups was suppressed because of the small optical absorbance of 6FDC. Therefore, the increase in fluorescence is attributable to the suppression of local molecular motion by the hydrostatic pressure.

These results clearly indicate that the restraint of intermolecular energy transfer in PIs having fluorescent end-groups is a key factor for novel luminescent materials showing outstanding photoluminesncence properties even in densely aggregated states.

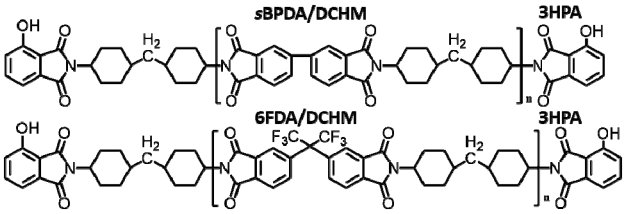

Fig. 1 Chemical structures of End-capped PIs

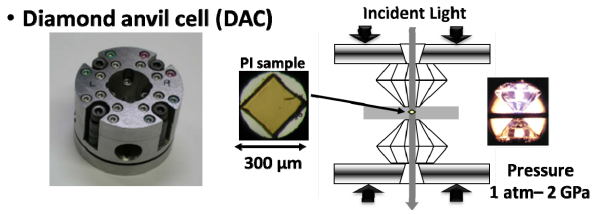

Fig. 2 Schematic illustration of DAC and its cross-section

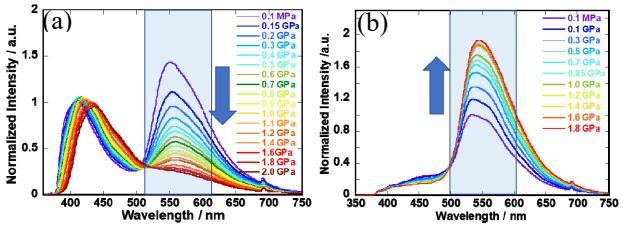

Fig. 3 Variations in emission spectra of (a) sBPDC-3HPA and (b) 6FDC-3HPA by applying pressure up to 2GPa.

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