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Pressure-Induced Variations in Fluorescence Properties of Polyimide Films Displaying Excited-state Intramolecular Proton Transfer

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ABSTRACT:

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, fluorescent emission properties of PIs have been widely studied. [1, 2] Semi-aliphatic PIs consisting of pyromellitic dianhydride having a −OH group at the benzene ring and alicyclic diamines exhibited reddish orange fluorescence with extraordinary large Stokes shift via excited-state intramolecular proton transfer (ESIPT) mechanism where the proton at the −OH group is transferred from the enol to the keto form. It is known that not only the chemical structures of the repeating unit but also the aggregation structures significantly affect the optical properties of PIs. Recently, we have reported the pressure-induced variations of fluorescence property caused by reduction in inter-chain distances under high pressure.[3] In this study, the ESIPT fluorescence property of PI film was investigated by using fluorescence lifetime measurement under very high pressure up to 8 GPa.

The molecular structure of a semi-aliphatic PI prepared from 3HPMDA and alicyclic diamines (3HPMDA/DCHM) is shown in Fig. 1. To generate pressure up to 8 GPa, the PI film was loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.) (Fig.2) equipped with 600 μm-culet synthetic diamond anvils (Sumi-crystal type-IIa). Daphne 7474 (Idemistu) was used as a pressure medium. The standard ruby fluorescence technique was used to determine the pressure inside the sample space.[4] The streak images of the PI films were measured with streak camera system (Hamamatsu, C5680).

The streak image of 3HPMDA/DCHM measured at atmospheric pressure by excitation at 343 nm is shown in Fig. 3. The PI exhibited an enol emission around 400 nm as well as a keto emission around 570 nm generated by ESIPT. In addition, a fluorescence observed around 500 nm is attributable to that from the aggregated-chains excited via the Förster resonance energy transfer (FRET) process. We have reported that this FRET process is competitive with the ESIPT process in 3HPMDA/DCHM film.[3] Based on the photo-physical process of the PI, the fluorescence intensity decay curves observed in the ranges of 400-420 nm and 570-590 nm were analyzed by double exponential functions, in which each decay component was fitted by $F_n(t) = I_n \cdot \exp(-t/\tau_n)$ (τ_n : lifetime, I_n: relative intensity). Two decay components in the former wavelength region are attributable to the ESIPT and the FRET process (component 1) and the enol emission (component 2), respectively. On the other hand, the two decay components in the latter wavelength region are assignable to the emission from aggregated form (component 3) and the keto emission (component 4), respectively. In addition, the fluorescence intensity ratio of each component (A_n) was defined as $A_n = I_n/\Sigma I_n$ (ΣI_n : the summation of two components in one wavelength region) at each pressure. As shown in Fig. 4, A_1 is almost constant in all the pressure range, indicating that the number of excited moieties taking the enol form is independent from pressure. On the other hand, A_3 is gradually increased and A_4 is decreased with increasing the pressure up to 4 GPa. This result is explainable by an increase in the efficiency of FRET due to the reduction of inter-molecular chain distances. In conclusion, the FRET process which generates the fluorescence of aggregated form of PI chains became dominant compared with the ESIPT process which gives the keto emission at elevated pressures.

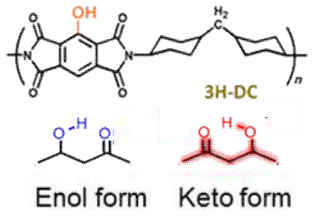

Fig. 1 Molecular structure of 3HPMDA/DCHM.

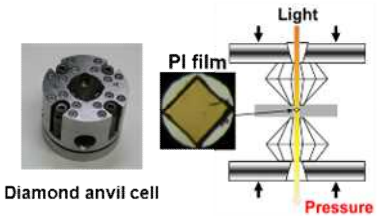

Fig. 2 Photo images and cross-sectional drawing of diamond anvil cell (DAC).

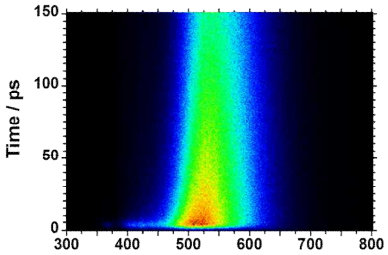

Fig. 3 Streak image of 3H-DC at atmospheric pressure.

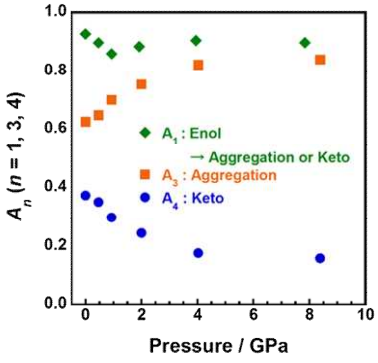

Fig. 4 Pressure dependence of A_n of components 1, 3 and 4.

[1] J. Wakita, *et al.*, *J. Phys. Chem. B*, **19**, 15212 (2009). [2] K. Kanosue, *et al.*, *Macromolecules*, **48**, 1777 (2015). *ibid.* **49**, 1848 (2016). [3] K. Takizawa, *et al.*, *Macromolecules*, **47**, 3951 (2014). [4] G. J. Piermarini, *et al.*, *J. Appl. Phys.*, **44**, 5377 (1973).

Keywords: Polyimide, Excited-state intramolecular proton transfer, Fluorescence lifetime, High pressure