

# Variations in Optical Absorption and Fluorescence Spectra for Polyimide Thin Films Caused by Structural Isomerism

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[Introduction] We have been developing a series of highly fluorescent polyimide (HFPI)s using alicyclic diamines and conventional or perfluoro-dianhydride. The fluorescence wavelength is dominated by their chemical structures: the PIs from unfluorinated dianhydrides emit blue light but those from perfluorodianhydrides emit green or red light [1][2]. To clarify the relationships between the stereo-chemical structures and the optical properties of the HFPIs, we examined the effect of structural isomerism (Scheme 1) on the optical absorption and the fluorescence spectra in an effort to propose a new principle to enhance and control the fluorescence of HFPIs.

[Experimental] PI films and a model compound of *i*-PI(*m*-*i*-PI) were prepared by thermal imidization of their corresponding precursors, poly(amic acid) silyl ester (PASE) and amic acid silylester obtained by *in situ* silylation method [3]. The PI films were formed on quartz substrates (*s*-PI:7  $\mu\text{m}$ -thick, *i*-PI:1  $\mu\text{m}$ -thick). The products were characterized by <sup>13</sup>C-NMR in chloroform-*d* (CDCl<sub>3</sub>), FT-IR, and thermal analyses.

[Results and Discussion] The optical absorption observed below 400 nm and the fluorescence located at 400 nm observed for *s*-PI (Fig.1) are ascribed to the local transition at phthalimide. On the other hand, for *i*-PI, a fluorescence peak is observed around 490 nm with excitation at 420 nm that corresponds to a characteristic absorption peak, and a broad fluorescence consisting of two components (490 nm and 530 nm) is observed with excitation at 320 nm that is ascribed to the transition at the phthalimide (Fig.1). To clarify the photophysical mechanism in *i*-PI, the absorption and fluorescence spectra were measured for *m*-*i*-PI. Since molecules are generally isolated below the concentration of 10<sup>-4</sup> M, the absorption at 420 nm is due to the intramolecular transition of *m*-*i*-PI (Fig.2). In addition, it has been reported that no absorption is observed at 420 nm for phthalimide [4], which indicates that the absorption at 420 nm is originated from the intramolecular dimer formation of phthalimide. Besides, two fluorescence peaks (420 nm/490 nm and 340 nm/530 nm) were observed for *m*-*i*-PI. The former originates from the phthalimide dimer because the excitation wavelength agrees with its absorption. The latter was not observed with excitation above 320 nm, and its excitation peak agrees with the absorption of phthalimide. These features agree with the emission from the excimer formed between phthalimides. In summary, the enhancement of the intra and/or intermolecular interactions caused by the structural isomerism results in the long-wavelength emissions, which suggests that the control of stereo-chemical structures is important for the fluorescence of PIs.

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