The effect of the intermolecular interactions on optical properties of highly Fluorescent Fluorinated Polyimides

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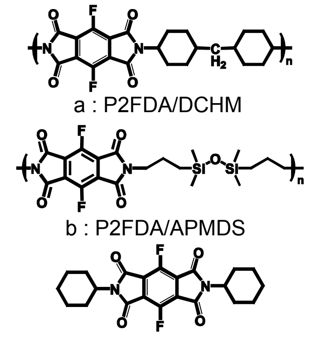
[Introduction] Polyimides (PIs) have been widely used in electronics and aerospace industries due to their excellent thermal, chemical and mechanical properties. Recently, PIs are applied to optical waveguides for optical interconnects due to the high transparency and low dielectric constants. We have investigated the optical absorption and fluorescence properties of PIs. In general, two types of electron transitions are observed in PIs. First one is locally excited (abbreviated as LE) transition that occurs between the molecular orbital located in dianhydride moieties. Second one is charge transfer (abbreviated as CT) transition that occurs between the molecular orbital located in diamine moiety and dianhydride moiety, which means that diamine is the electron-donating moiety and dianhydride is electron-accepting moiety. Although the whole aromatic PIs has very low efficient fluorescence due to the strong intra and intermolecular CT interactions that cause the nonradiative relaxation, we have already developed the highly fluorescent semi-aromatic PIs which emit blue, green and red fluorescence using alicyclic diamine that restrains the CT interaction[1]. However, their photophysical processes have not been clarified. For example, red fluorescence assigned to LE and CT transition was observed in P2FDA/DCHM (scheme1-a) thin film (Fig.1), but these transitions were not calculated by time-dependence density functional (TD-DFT) method for P2FDA/CHA (scheme1-c). This suggests that these transitions do not originate from a single repeating unit of P2FDA/DCHM. In this study, the optical absorption and fluorescence spectra of P2FDA/CHA chloroform solution, P2FDA/APMDS (scheme1-b) thin film, which has the lower static hindrance compared with P2FDA/DCHM, have been observed to examine the effect of intermolecular interactions on the photophysical process of them.



a : P2FDA/DCHM

b : P2FDA/APMDS

c : P2FDA/CHA

Scheme1 Structures of PI and model compound

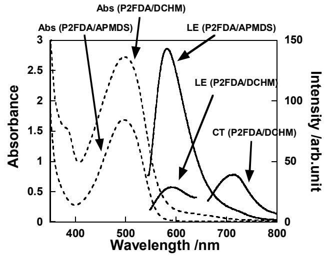


Fig.1 UV-vis and fluorescence spectra of P2FDA/DCHM and P2FDA/APMDS thin film

[Experimental] P2FDA/CHA was prepared by the thermal imidization of amic acid. The product was characterized by solid-state ^{19}F NMR and FT-IR. P2FDA/DCHM and P2FDA/APMDS were prepared by thermal imidization of poly(amic acid) silyl eter (PASE) obtained by *in situ* silyation method[2].

[Results and Discussion] The dependences of optical absorption spectra P2FDA/CHA solution on its concentration were observed as follows. (i) The absorption peaks at 400 ~ 500 nm were observed above 5×10^{-5} M, but they were not observed below 5×10^{-5} M. (ii) The significant dependence of peak shape on concentration was observed (Fig.2). These spectral dependences on concentration suggest that optical absorption at 400 ~ 500 nm does not originate from one molecule of P2FDA/CHA. The TD-DFT calculation for P2FDA/2Ph dimmer demonstrates that the transitions at 400 ~ 500 nm exist in P2FDA/2Ph dimmer. Hence, the absorption peaks at 400 ~ 500 nm observed in P2FDA/CHA originate from the aggregates of P2FDA moieties. Additionally, fluorescence peaks around 500 ~ 600 nm excited at 400 ~ 500 nm were observed. The correspondence of these absorption and fluorescence peak wavelength with LE absorption and fluorescence peak wavelength of P2FDA/DCHM thin film suggests that LE transition of P2FDA/DCHM originates from the aggregates of polymer chains. Although the CT transition is observed for P2FDA/DCHM thin film, no apparent CT transition was observed for P2FDA/APMDS thin film(Fig.1). The calculated ionized potential (Ip) of DCHM (8.21 eV) is smaller than that of APMDS (8.12 eV), which suggests that the electron-donating property of APMDS is more significant than that of DCHM. This indicates that the absence of CT transition in P2FDA/APMDS is not due to the strength of intermolecular CT interaction but to the difference in the aggregation states. In case of P2FDA/APMDS thin film, the P2FDA moieties can be stacked due to the low static hindrance around the imide bond caused by the secondary terminal carbon of APMDS, and thus intermolecular CT complex should not be formed. Meanwhile, in case of P2FDA/DCHM thin film, the mixed layer stacking between P2FDA and DCHM can be partially formed due to the high static hindrance around the imide bond caused by the tertiary terminal carbon atom of DCHM, and thus intermolecular CT complex can be formed. These facts clearly indicate that the difference in the aggregation states induces significant effects on the optical properties of P2FDA PIs.

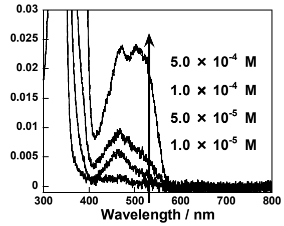


Fig.2 UV-vis and fluorescence spectra of P2FDA/CHA chloroform solution

[1] Y. Urano, Y. Oishi, S. Ando, *Polym. Prep. Jpn.*, **52**, 3480 (2003). [2] Y. Oishi, K. Ogasawara, H. Hirahara, K. Mori, *J. Photopolym. Sci. Technol.*, **14**, 37 (2001). [3] J.Wakita, Y.Urano, K.Uetake, S.Ando.,*Polym. Prep. Jpn.*, **54**(1), 1333 (2005).