

Highly Fluorescent Blue-Light Emitting Polyimides Derived from Dianhydrides Containing Diphenylether Linkages

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Introduction

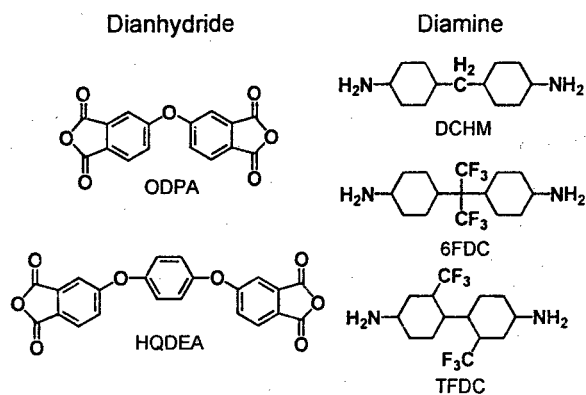
We have been investigating the enhancement of fluorescence intensity of semi-aromatic polyimides (PIs). We have recently reported that the effective suppression of charge-transfer (CT) fluorescence and the enhancement of locally excited (LE) fluorescence are essential for strong emission in the visible region [1]. With the help of molecular design using density functional theory (DFT) calculations, we have found that the use of perfluorinated dianhydrides (P2FDA and 10FEDA) and alicyclic diamines is a very effective way to enhance the fluorescence intensity of PIs [2]. In particular, a dianhydride having a flexible structure gives PIs whose fluorescence is >100 times as high as that of conventional aromatic PIs. However, since the electron affinities of such perfluorinated dianhydrides are high, the excitation of absorption peaks appearing in the visible region give fluorescence peaks at longer wavelengths (550-800nm). In this study, we intended that the fluorescence peaks should be shifted to shorter wavelengths by using non-fluorinated dianhydrides having low electron affinities. In addition, good optical transparency should be attained at shorter wavelengths (400-500nm) in these PIs. We investigated the fluorescence properties of PIs derived from non-fluorinated dianhydride (HQDEA) having the same main skeletal structure as 10FEDA with two ether (-O-) linkages. Furthermore, another dianhydride having an ether linkage (ODPA) was used to investigate the fluorescent behaviors of PIs derived from a non-fluorinated less-flexible dianhydride.

Experimental

Materials and Synthesis

Poly(amic acid silyl ester)s (PASE) were synthesized as precursors of PIs by the *in situ* silylation method [3] using 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDEA), 3,3',4,4'-diphenylether tetracarboxylic dianhydride (ODPA) and

4,4'-diamino-dicyclohexylmethane (DCHM), 2,2'-bis(4-aminocyclohexyl)hexafluoropropane (6FDC), or 2,2'-bis(trifluoromethyl)-4,4'-diaminobicyclohexyl (TFDC) (Scheme 1) in *N,N*-dimethyl



Scheme 1

acetamide (DMAc). HQDEA was synthesized and supplied by Dr. Mengxian Ding at Changchun Institute of Applied Chemistry. 6FDC and TFDC were supplied by Dr. K. Maeda at Central Glass Co. Ltd. DMAc solutions of PASE thus obtained were spin-coated onto fused silica substrates and dried at 70°C for 1h followed by heating at 300°C for 1.5 h, and then cooled to room temperature. Tough and flexible, colorless transparent PI films with thickness of 4–8 μm were obtained.

Measurements and Calculation

Thermogravimetric analysis (TGA, Shimadzu TGA-50 analyzer) was conducted for a small amount (ca. 10mg) of PI films peeled from the substrates. Glass transition temperatures (T_g) were determined using Seiko SSC / 5200 DSC 220. Refractive indices of PI films were measured using a prism coupler (Metricon PC-2000) at a wavelength of 1320 nm. The incident light is linearly polarized in the transverse-electric (TE) or transverse-magnetic (TM) polarizations. Average refractive index was calculated as $(2n_{TE} + n_{TM})/3$. The in-plane/out-of-plane birefringence was calculated as $n_{TE} - n_{TM}$. UV-vis absorption spectra were measured with a Hitachi U-3500 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorescence photometer by the front-face setup. Electron affinities of dianhydrides and Ionization potentials of diamines were calculated using by DFT with the hybrid functional of B3LYP and the 6-311G* basis set. The program package of Gaussian-98 (Rev.A11) was used for the calculations.

Results and discussion

Thermal Properties of PIs

Figures 1 and 2 show the 5% weight loss temperatures (T_d^5) and the glass transition temperatures (T_g) of the PIs. These PIs exhibit reasonable values of T_d^5 ($> 420^\circ\text{C}$) and T_g ($> 200^\circ\text{C}$) as thermally stable optical polymers. In particular, the PIs derived from TFDC exhibit the highest heat-resistance because TFDC has more rigid structure, in which two cyclohexane rings are directly bonded, compared with DCHM and 6FDC.

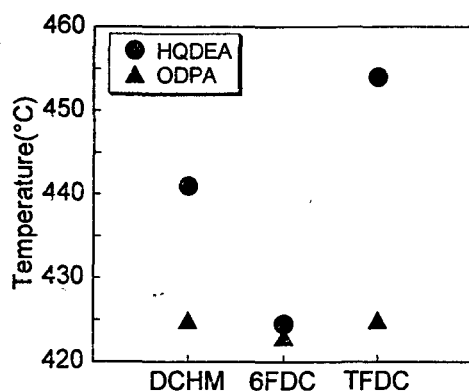


Fig. 1 5% weight loss temperature.

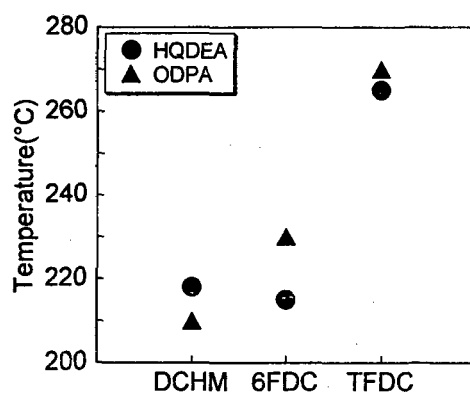


Fig. 2 Glass transition temperature.

Refractive Indices and Birefringence

Figure 3 shows the refractive indices and birefringence of the PIs. The refractive indices decrease with increasing the fluorine contents in the repeating units. The birefringence is remarkably

smaller than conventional aromatic PIs due to the small intrinsic polarizability anisotropy and the lower degree of chain orientation originated from alicyclic diamines. The PIs derived from TFDC exhibit relatively large birefringence than those from DCHM or 6FDC because TFDC has a rigid structure, and the degree of chain orientation becomes relatively high.

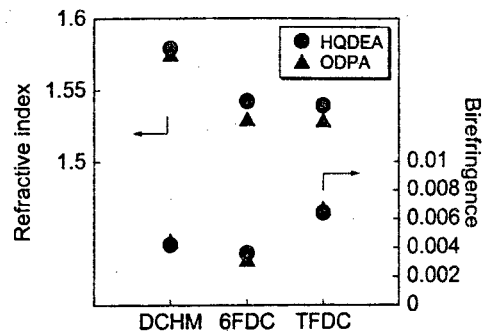


Fig. 3 Refractive indices and birefringences of PIs.

UV-Vis Absorption Spectra

Figure 4 shows the UV-vis absorption spectra of PI films (ca. 4 μ m-thick). The lower electron affinities of ODPA and HQDEA (1.59 and 1.41 eV) compared with those of conventional dianhydrides (1.8–2.1 eV) increases the energy gaps between HOMO and LUMO, which provide high optical transparency in the whole visible region. According to the previous studies, intermolecular and intramolecular CT absorption bands appear near absorption edges [4,5]. Hence, absorption edges strongly reflect the electron-donating ability of diamine and the electron-accepting ability of dianhydride. However, this is not the case for the PIs of this study because the CT nature is effectively suppressed by the combination of aliphatic diamines and the aromatic dianhydrides having low electron-accepting ability. The characteristic absorption peak originating from imide rings solely appears at ca. 320nm [6,7] but no distinct CT bands are observed.

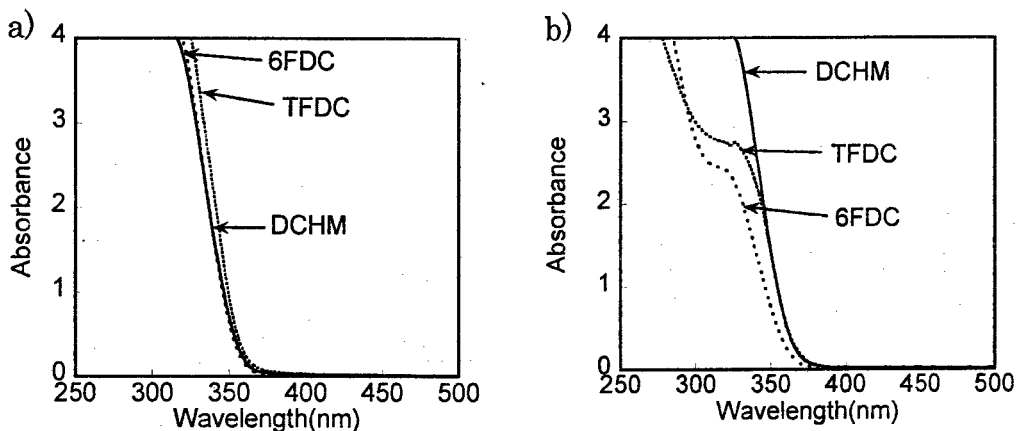


Fig. 4 Absorption spectra of PIs (a : ODPA / diamine, b : HQDEA / diamine).

Fluorescence Excitation / Emission spectra

Figure 5 shows the excitation/emission spectra of PI films (ca. 10 μ m-thick). Fluorescence peaks appear at ca. 415nm for all PIs derived from HQDEA and at ca. 397nm for all PIs from ODPA. Note that the wavelengths of the fluorescence are irrespective of diamines despite a distribution of ionization potentials (7.96, 8.04, 8.25 eV for DCHM, 6FDC, and TFDC, respectively). As described above, the absence of the influence of diamines also indicates that the CT fluorescence mechanism is effectively suppressed. In addition, the fact that the excitation peak coincides well with the absorption peak originating from imide rings (ca. 320nm) strongly support that the observed

strong fluorescence is assigned to the LE fluorescence.

As long as using nonfluorinated dianhydrides containing ether-linkages (ODPA and HQDEA), the bandwidths of fluorescence are narrow (395~420 nm). In contrast, the PIs derived from perfluorinated dianhydrides with flexible ether linkages emit strong fluorescence at longer wavelengths around 480 nm [2], indicating that the fluorescence wavelength is greatly dependent on the degree of fluorination on the phenyl ring adjoining the imide ring as well as the skeletal structures.

Quantum Yields of Fluorescence

Figure 6 shows the quantum yields (Φ) of fluorescence of the PIs estimated using anthracene-doped PMMA as a reference [8]. The quantum yields of the PIs prepared in this study are 0.06 ~ 0.18, which are significantly high compared with the conventional PIs. (e.g. the Φ for BPDA/PDA PI, which is known as a fluorescent aromatic PI is ca.0.005.) In conclusion, we succeeded in developing a series of highly fluorescent blue-light emitting PIs using dianhydrides containing diphenylether linkages.

Acknowledgement

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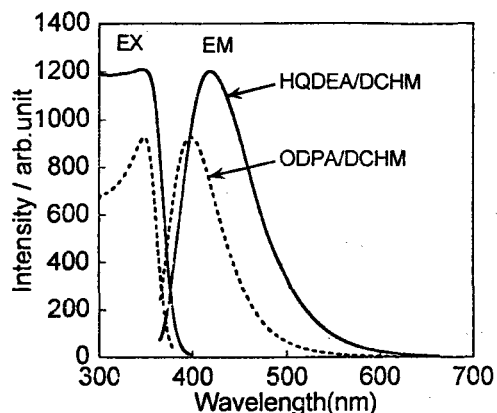


Fig. 5 Excitation/emission spectra.

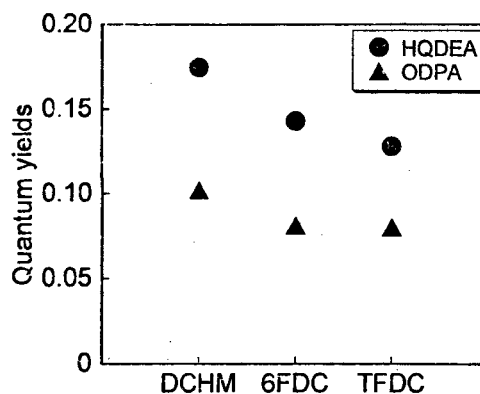


Fig. 6 Fluorescence quantum yields. Reference : Anthracene (10^{-2} M) doped in PMMA.