

# Optical Properties of Polyimides Derived from A Perfluorinated Flexible Dianhydride

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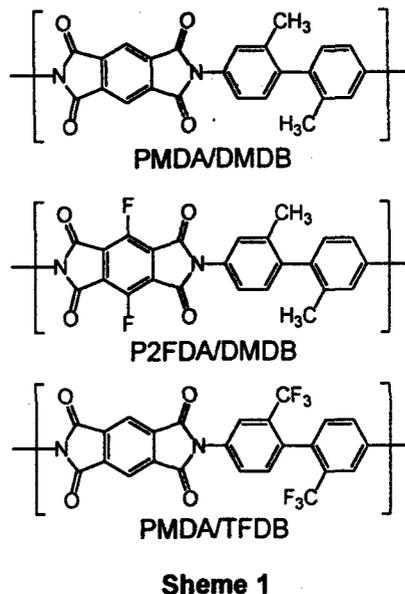
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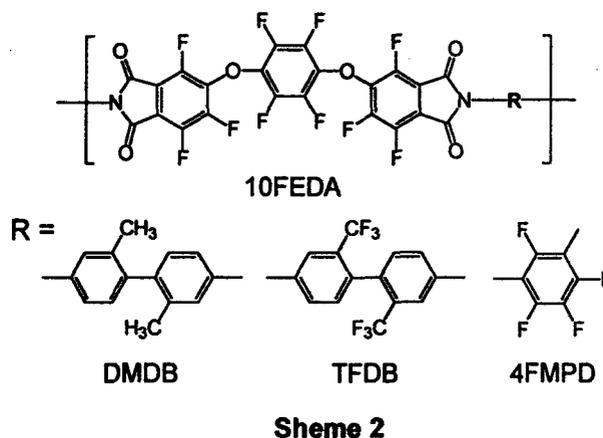
## Introduction

We have been investigated the effects of introduction of fluorines into rod-like polyimides [1]. P2FDA/DMDB (Scheme 1) derived from a perfluorinated dianhydride (P2FDA) has high charge-transfer (CT) interactions due to the increased electron-accepting ability of the dianhydride. PMDA/TFDB derived from a fluorinated diamine (TFDB) has low CT interactions due to the decreased electron-donating ability of the diamine. Further, PMDA/TFDB and P2FDA/TFDB exhibit two fluorescence processes which may be caused by  $-\text{CF}_3$  groups that weaken intermolecular interactions. Hence, the electronic states of PIs depend on the electronic properties of dianhydrides and diamines and intermolecular interactions between polymer chains [2, 3]. In this study, the effect of fluorination and that of introduction of flexible ether linkages into polyimides were investigated using a perfluorinated dianhydride, 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzendianhydride (10FEDA).



## Experimental

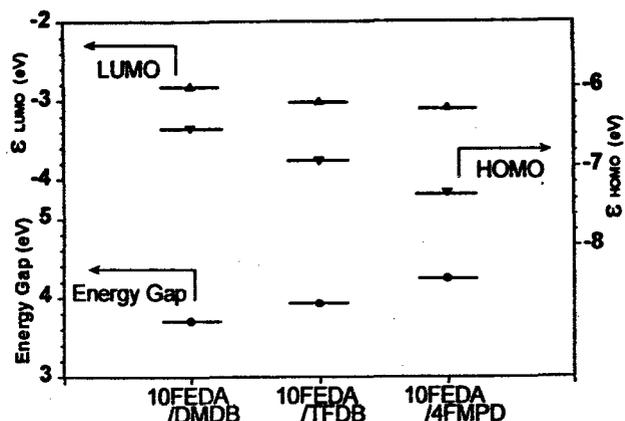
Three kinds of PIs were synthesized from 10FEDA [4] as a dianhydride and 2,2'-dimethyl-4,4'-diaminobenzene (DMDB), 2,2'-bis(trifluoromethyl)-4,4'-diaminobenzene (TFDB), or tetrafluoro-*m*-phenyldiamine (4FMPD) as a diamine (Scheme 2). The DMAc solutions of poly(amic acid) (PAA) (30-40 wt%) were spin-coated onto quartz substrates (2.5 mm-thick) and thus heated to 350°C at a heating rate of 10°C/min, kept for 1h, and then cooled to room temperature. The average thicknesses of PI films were 4 μm for UV-Vis absorption spectra and 8 μm for fluorescence spectra. Thermogravimetric analysis (TGA) was conducted for a small amount (ca. 10 mg) of PI films peeled from substrates using a Shimadzu TGA-50 analyzer. The PI films were heated to 900°C at 10°C/min under nitrogen. UV-Vis absorption spectra were measured using a Hitachi U-3500 spectrophotometer, and fluorescence spectra were measured using a Hitachi F-4500 fluorescence photometer. The refractive



**Table 1** Calculated electron affinities (EA) of dianhydrides and ionization potentials (IP) of diamines

	P2FDA	PMDA	10FEDA	BPDA <sup>a</sup>
EA (eV)	2.48	2.13	2.04	1.78
	DBDB	TFDB	4FMPD	
IP (eV)	6.76	7.14	7.65	

a, 3,3',4,4'-biphenyltetracarboxylic dianhydride



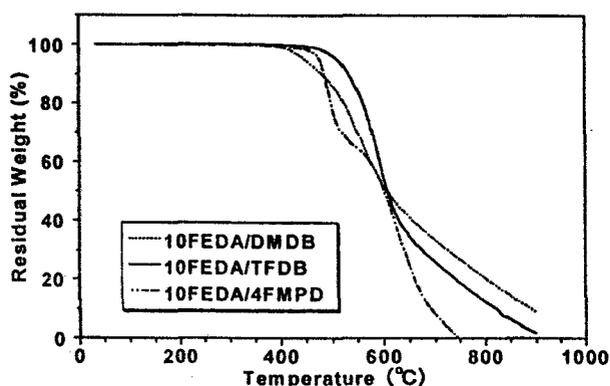
**Fig. 1** Calculated energy gaps and MO energies of HOMO and LUMO for the model compounds of polyimides

indices of PI films spin-coated and cured on quartz substrates were measured with 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. The in-plane/out-of-plane birefringence was calculated as  $(n_{TE} - n_{TM})$ . DFT theory (B3LYP/6-31G\*\*) was used for the calculations of molecular orbital energies, ionization potentials, and electron affinities. All the calculations were performed using the program of Gaussian-98 [5] (Rev. A9).

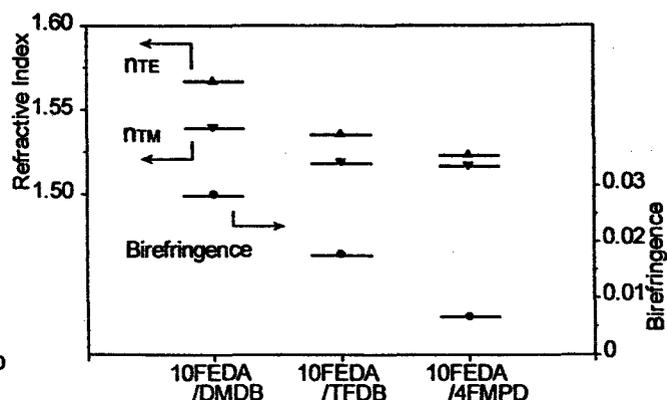
## Results and Discussion

**Calculation of Molecular Orbital Energies :** Table 1 shows the calculated values of electron affinities (EA) of dianhydrides and ionization potentials (IP) of diamines. The EA of 10FEDA is lower than that of non-fluorinated PMDA, which means that 10FEDA has lower electron-accepting ability than that of PMDA. On the other hand, the calculated IPs of diamines decrease with increasing the fluorine content. This means that the decrease in electron-donating ability of diamines is caused by the introduction of fluorines [6]. Fig. 1 shows the molecular orbital (MO) energies and the energy gaps between HOMO and LUMO for model compounds of PIs. The LUMO levels are roughly constant, whereas, the HOMO levels are significantly displaced to lower energies with decreasing the electron-donating ability of diamines. This agrees well with the fact that the LUMOs of PIs are located on dianhydride moiety, while the HOMOs are located on diamine moiety and imide nitrogen. The energy gaps increase with decreasing the electron-donating ability of diamines, indicating the reduction of CT interactions.

**TGA Measurement :** The TGA curves in Fig. 2 indicate that the 5 % weight-loss tempera-



**Fig. 2** TGA curves of polyimide films



**Fig. 3** Refractive indices and birefringence of polyimides

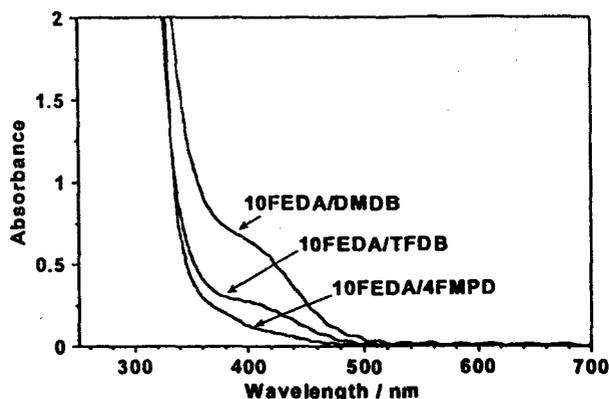


Fig. 4 Absorption spectra of polyimide films

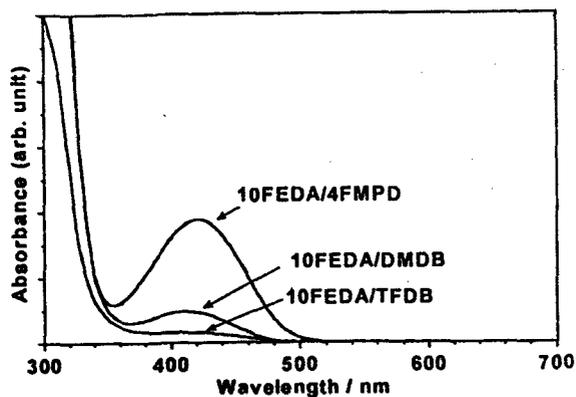


Fig. 5 Absorption spectra of DMSO solutions of polyimides (concentrations are not controlled)

tures of 10FEDA /DMDB, 10FEDA/TFDB, and 10FEDA/4FMPD are 449°C, 512°C, and 477°C, respectively. 10FEDA/TFDB exhibits a higher degradation temperature. This can be attributed to the high thermal stability of  $-CF_2$  group. 10FEDA/4FMPD exhibits a two-step degradation process. At the first step, the fluorines directly bonded to the benzene ring of 4FMPD moiety were eliminated.

**Refractive Indices and Birefringence :** Fig. 3 shows the refractive indices and in-plane/out-of-plane birefringence of PIs. The birefringences decrease with increasing fluorine content [7]. In particular, the birefringence of 10FEDA/4FMPD is significantly small. This can be attributed to the increased dihedral angle between the imide plane and the benzene ring at diamine moiety, due to the steric hindrance between the fluorines at the *o*-position of 4FMPD and the oxygen at carbonyl group of 10FEDA.

**Absorption Spectra :** Fig. 4 shows the UV-Vis absorption spectra of PI films (4  $\mu\text{m}$ -thick). The PIs derived from 10FEDA exhibit distinctive absorption shoulders at ca. 400 nm. In order to identify the shoulders, absorption spectra of PIs dissolved in DMSO were measured (The concentrations could not be controlled due to the low solubility.) (Fig. 5). These spectra show that the wavelengths of the absorption peaks are independent of the structures of diamines. If the absorption peaks and shoulders are closely related to the CT interactions, these should be displaced depending on the diamines. As a result, these shoulders are assigned to the local transitions at the 10FEDA moiety. For the PIs derived from P2FDA, the absorption peaks which are assigned to the local transitions are observed at ca. 500 nm [2]. Fig. 4 shows that the absorption edges of PIs [8] are shifted to long wavelengths in an order of 10FEDA/4FMPD < 10FEDA/TFDB < 10FEDA/DMDB. Since this order agrees well with that of calculated energy gaps, the absorption edges are closely related to the CT interactions.

#### Fluorescence Excitation/Emission Spectra

Fig. 6 shows the absorption, excitation and emission spectra of PI films (8  $\mu\text{m}$ -thick). The excitation and emission peaks are shifted to longer wavelengths and the fluorescence intensity are decreased as (c)10FEDA/4FMPD < (b)10FEDA/TFDB < (a)10FEDA/DMDB. Since the orders of excitation and emission peaks agree well with that of absorption edges, these fluorescence should be related to the CT interactions [9]. Comparing the absorption spectra to the excitation spectra, the excitation peak of (c)10FEDA/4FMPD coincides with the absorption shoulder at ca. 400 nm. This indicates that the fluorescence based on the localized excita-

tion of dianhydride is predominant over the CT fluorescence. Since the dihedral angle between 10FEDA and 4FMPD moieties should be larger than those of other PIs, the CT fluorescence is to be suppressed in 10FEDA/4FMPD. This is supported by the very small birefringence of this PI. The excitation peak of (b)10FEDA/TFDB is located between the absorption edge and the absorption shoulder. In addition, since the half-width of the excitation peak is larger than those of 10FEDA/DMDB and 10FEDA/4FMPD, the fluorescence originating from a localized excitation is overlapped with the CT fluorescence. In contrast, the excitation peak of (a)10FEDA/DMDB coincides well with the absorption edge. Hence, this peak can be assigned to the CT fluorescence. Consequently, an increase in the electron-donating ability of diamine causes an increase in the degree of CT fluorescence and a decrease in the fluorescence based on the localized excitation at the dianhydride. the excitation spectra differ from the absorption spectra for the rod-like PIs derived from P2FDA [2]. This may be related to the strong intermolecular interactions. In contrast, the excitation spectra agree with the absorption spectra for the flexible PIs in which the intermolecular interactions are relatively reduced.

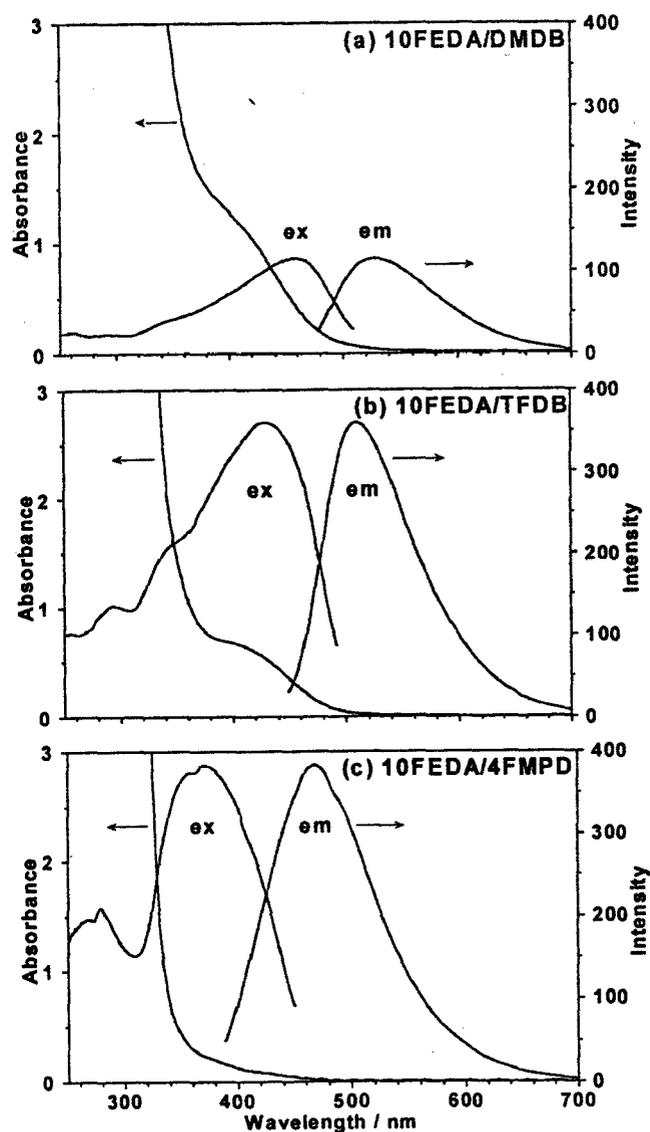


Fig. 6 Absorption, excitation and emission spectra of PI films

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