

# Synthesis and Properties of Cost-effective Light-color and Highly Transparent Polyimide Films from Fluorine-containing Tetralin Dianhydride and Aromatic Diamines

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A novel fluoro-containing tetralin dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-6-fluoro-1-naphthalene succinic dianhydride (FTDA) was successfully prepared via a cost-effective route with maleic anhydride and *p*-fluorostyrene as the starting materials. A series of semi-alicyclic polyimides (PIs) have been synthesized from FTDA and aromatic diamines, including 4,4'-oxydianiline (ODA) for PI-a, 1,4-bis(4-aminophenoxy)benzene (APB) for PI-b, 2,2'-bis[(4-aminophenoxy)phenyl]propane (BAPP) for PI-c, and 2,2'-bis[(4-aminophenoxy)phenyl]hexafluoropropane (BDAF) for PI-d via a one-step high-temperature imidization procedure. The derived PI resins are easily soluble in polar aprotic solvents, such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). Flexible and tough PI films were cast from their solutions in NMP at a solid content of 15 wt%. The prepared PI films exhibited good optical transparency in the visible light region with the transmittance higher than 80% at the wavelength of 450 nm. In addition, the PI films exhibited good thermal stability with the 5% weight loss temperatures >402 °C and glass transition temperatures >230 °C.

**Keywords:** tetralin dianhydride, fluoro, polyimide, optical properties, thermal properties

## 1. Introduction

Colorless or light-color and transparent polymer optical films have been finding various applications in optoelectronic fabrications, such as substrates for flexible display devices, substrates for flexible photovoltaic devices, substrates for flexible and transparent printing circuit boards, alignment layers for liquid crystal display devices, and so on [1]. Conventional light-color polymer optical films, such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) are facing great challenge in practical optoelectronic applications due to their inferior thermal resistance. For instance, in the fabrication of flexible active matrix organic light emitting display devices (AMOLEDs), the processing temperature on the flexible polymer optical film substrates is usually higher than 250 °C [2]. Most of the common polymer optical films, such as PET or PEN will lose their optical and mechanical properties at such a high processing temperature. Thus, light-color and optically

transparent high-temperature-resistant polymer optical films have attracted great attentions from both of the academic and engineering aspects. This driving force has greatly promoted the development of polymer optical films with outstanding thermal stability.

Polyimide (PI) films represent a class of high performance films with excellent combined properties, including outstanding thermal stability, good mechanical properties, and admirable dielectric properties [3]. Conventional wholly-aromatic PI films exhibit a deep color from deep-brown to brown-yellow due to the presence of charge transfer complexes (CTC) in their molecular structures [4]. It has been now well-established that the formation of CTC can be efficiently prohibited by cutting or weakening the conjugation interactions between the electron-donating amino moiety and electron-withdrawing anhydride moiety [5]. Thus, various endeavors, including introduction of non-conjugated aliphatic or alicyclic units,

substituents with strong electron-negativities, such as fluoro-containing groups, sulfone groups, etc. have been performed to develop light-color PI optical films [6]. Among various light-color PI films, the semi-alicyclic ones derive from alicyclic dianhydrides and aromatic diamines usually possess the best comprehensive properties, including good optical transparency, good thermal stability, and acceptable mechanical properties [7]. For instance, recently, Hasegawa and coworkers developed a series of colorless and transparent semi-alicyclic PI optical films from hydrogenated pyromellitic dianhydride (HPMDA) and aromatic diamines [8,9]. The derived PI films showed excellent optical transmittance in the ultraviolet and visible light regions, high thermal stability up to 450 °C, and good tensile properties. Although semi-alicyclic PIs have been paid much attention in high-tech applications, several obstacles, especially the high cost and synthetic difficulties for alicyclic dianhydrides have to be overcome in the further development of functional semi-alicyclic PIs. Matsumoto reviewed the synthetic pathways for alicyclic dianhydrides [10]. Usually, severe reaction conditions, such as photoirradiation or high-pressure oxidation with nitric acid or ozone are often used in the synthesis of such dianhydrides. Thus, a low-cost synthetic route for alicyclic dianhydride monomers is highly desired to develop high performance and cost-effective semi-alicyclic PI optical films.

In our previous work, a series of alicyclic dianhydrides containing tetralin (or tetrahydronaphthalene) units have been successfully developed via a low-cost route using cheap maleic anhydride and *para*-substituted styrene compounds as the starting materials [11-13]. A series of semi-alicyclic PI films with good optical properties and thermal properties were developed. As one of our continuous work developing PI optical films with enhanced optical and thermal properties for advanced optical applications, a novel tetralin dianhydride containing fluorine substituent in the structure was developed in the current work. The synergic effects of tetralin and fluorine groups on the optical and thermal properties of the derived PI films were investigated in detail.

## 2. Experimental

### 2.1. Materials

*p*-Fluorostyrene (Fst) was purchased from Sigma-Aldrich and used as received. It was unnecessary to remove the inhibitor containing in the chemical. The

aromatic diamines, 4,4'-oxydianiline (ODA), 1,4-bis(4-aminophenoxy) benzene (APB), 2,2-bis[(4-aminophenoxy)phenyl]-propane (BAPP) and 2,2-bis[(4-aminophenoxy)-phenyl]hexafluoropropane (BDAF) were all purchased from Tokyo Chemical Industry Co., Ltd., Japan (TCI) and were purified by recrystallization from ethanol and dried in vacuum at 80 °C overnight prior to use. Maleic anhydride was purchased from Beijing Yili Fine Chemicals, China and used as received. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc),  $\gamma$ -butyrolactone (GBL) and butyl cellosolve (BC) were purified by distillation prior to use. The other commercially available reagents were used without further purification.

### 2.2. Measurements

Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g/dL NMP solution at 25 °C. Absolute viscosity was measured using a Brookfield DV-II+ Pro viscometer at 25 °C. Gel permeation chromatography (GPC) measurements were performed using a Waters 1515 HPLC pump equipped with a Waters 2414 refractive index detector. Two Waters Styragel HR 4 columns kept at 35°C±0.1°C were used with HPLC grade NMP as the mobile phase at a flow rate of 1.0 mL/min. Number average weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) were then determined with polystyrene as a standard. Fourier transform infrared (FT-IR) spectra were obtained with a Tensor 27 Fourier transform spectrometer. Ultraviolet-visible (UV-vis) spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The cutoff wavelength was defined as the point where the transmittance drops below 1% in the spectrum. Prior to test, PI samples were dried at 100 °C for 1 h to remove the absorbed moisture. Yellow index (YI) and haze values of the PI films were measured using an X-rite color i7 spectrophotometer with PI film samples at a thickness of 20-40  $\mu$ m. The color parameters were calculated according to a CIE Lab equation.  $L^*$  is the lightness, where 100 means white and 0 implies black. A positive  $a^*$  means a red color, and a negative one indicates a green color. A positive  $b^*$  means a yellow color, and a negative one indicates a blue color. Nuclear magnetic resonances ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) were performed on a AV 400 spectrometer operating at 400 MHz in DMSO- $d_6$  or  $\text{CDCl}_3$ . Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a TA-Q series thermal analysis system

at a heating rate of 10 °C/min in nitrogen. The tensile properties were performed on an Instron 3365 Tensile Apparatus with 80 mm×10 mm×0.05 mm specimens in accordance with GB1447-83 at a drawing rate of 2.0 mm/min. At least six test specimens were tested for each PI film and results were averaged.

Solubility was determined as follows: 1.5 g of the PI resin was mixed with 8.5 g of the tested solvent at room temperature (15 wt% solid content), which was then mechanically stirred in nitrogen for 24 h. The solubility was determined visually as three grades: completely soluble (++), partially soluble (+), and insoluble (-). The complete solubility is defined as a homogenous and clean solution is obtained, in which no phase separation, precipitation or gel formation is detected.

### 2.3. Monomer synthesis

*3,4-Dicarboxy-1,2,3,4-tetrahydro-6-fluoro-1-naphthalene succinic dianhydride (FTDA)*. Into a 500-mL three-necked flask equipped with a mechanical stirrer, a gas inlet and a condenser, 43.75 g (0.446 mol) of maleic anhydride, 108.90 g (0.892 mol) of *p*-fluorostyrene, and 0.1 g (0.446 mmol) of 2,5-di-*tert*-butyl hydroquinone were added. Nitrogen was introduced to remove the air in the system. Then, nitric oxide (NO) gas was introduced from a gas inlet placing under the surface of the reaction solution. The reaction mixture were heated to 120°C and maintained for 6 h under an atmosphere of nitric oxide. The produced red-brown nitrogen oxide gas was trapped by passing through an aqueous solution of 20 wt% sodium hydroxide. An orange precipitate formed during the reaction. After the reaction, the mixture was cooled to room temperature and 60 ml of acetonitrile was then added. The reaction mixture was heated to reflux for another 0.5 h. Then, 60 ml of toluene was added and the reaction mixture was cooled to temperature. The produced white needle crystals were collected by filtration and the solid was washed with toluene and petroleum ether in succession. After being dried in vacuum at 80 °C for 24h, the pure FTDA was obtained as white crystals. Yield: 54.9 g (77.3%).

Melting point: 201 °C (DSC peak temperature). FT-IR (KBr, cm<sup>-1</sup>): 2912, 1864, 1782, 1664, 1441, 1376, 1304, 1262, 1211, 1151, 1080, 1027, 967, 914, 870, 819, 754, 633, 594, 558, and 498. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 7.51-7.49 (*d*, 1H), 7.29-7.27 (*m*, 2H), 7.17-7.14 (*m*, 1H), 4.69-4.68 (*d*, 1H), 3.75-3.71 (*m*, 1H), 3.60-3.57(*m*, 1H), 3.44-3.43(*m*, 1H), 2.85-2.83 (*m*, 2H), 2.57-2.53(*m*, 1H), and 2.10-2.06 (*m*,

1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm): 173.9, 172.3, 171.2, 162.3, 160.7, 133.1, 131.3, 130.6, 116.2, 114.9, 43.3, 42.4, 37.3, 36.7, 33.2, and 26.5. MS (EI): 146 (M<sup>+</sup>-172, 100). Elemental analysis: calculated for C<sub>16</sub>H<sub>11</sub>FO<sub>6</sub>: C, 60.38%, H, 3.48%; Found: C, 59.90%, H, 3.53%.

### 2.4. Polyimide synthesis

The general procedure for the synthesis of PIs can be illustrated by the preparation of PI-d. Into a 1000 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet, BDAF (46.6605 g, 0.09 mol) was dissolved in *m*-cresol (100 g) to give a clear diamine solution. Then, FTDA (28.6425 g, 0.09 mol) was added in one batch and an additional volume of *m*-cresol (201 g) was added to wash the residual dianhydride, and at the same time to adjust the solid content of the reaction system to be 20 wt%. After stirring in nitrogen for 1 h at room temperature, a mixture of toluene (320 ml) and isoquinoline (catalytic amount) was then added. The reaction mixture was heated to 180 °C and maintained for 6 h. During the reaction, the toluene-water azeotrope was distilled out of the system and collected in the Dean-Stark trap. After cooling to room temperature, the viscous solution was slowly poured into an excess of ethanol to yield a pale-yellow fibrous resin. The resin was collected and dried at 80 °C in vacuo for 24 h. Yield: 66.0 g (96%).

PI-d resin (15 g) was dissolved in NMP (85 g) at room temperature to afford a 15 wt% solution. The solution was filtered through a 0.45 μm Teflon syringe filter to remove any undissolved impurities. Then, the solution was spin-coated on a clean silicon wafer or quartz substrate. The thickness of the PI film was controlled by regulating the spinning rate. PI-d films with thicknesses ranged from 10~100 μm were obtained by thermally baking the solution in a flowing nitrogen according to the following heating procedure: 80 °C/3 h, 150 °C/1 h, 200 °C/1 h, 250 °C/1 h, and 280 °C/1 h.

The other PI resin and films, including PI-a (FTDA-ODA), PI-b (FTDA-APB), and PI-c (FTDA-BAPP) were prepared according to a similar procedure as mentioned above.

## 3. Results and discussion

### 3.1. Synthesis of FTDA

The original purpose of our molecular design for the new dianhydrides is to introduce fluoro-containing substituents, including fluorine (-F) or trifluoromethyl (-CF<sub>3</sub>) groups. In our experiments,

introduction of -F group by the well-established synthesis route for tetralin dianhydride was successful (Figure 1). However, the endeavor of introduction of more electron-withdrawing  $-\text{CF}_3$  was fruitless. Generally, the reaction of maleic anhydride (MA) and *p*-substituted styrene (St) compounds occurs with mainly three ways, as shown in Figure 2 [14,15]. The first reaction is the self-polymerization or copolymerization of MA or St monomers, resulting in the formation of oligomer or polymer side-products (reaction a in Figure 2). This side-reaction can be prohibited by addition of 2,5-di-*tert*-butyl hydroquinone polymerization inhibitor. When MA and St starting materials reacted by a Diels-Alder addition reaction, the intermediate (i) formed. Then, two addition reactions might occur. One is the Wagner-Jauregg [4+2] addition reaction between (i) and MA affording the side-product (ii) according to the route (b) shown in Figure 2. Another is the second Diels-Alder ene [2+2] addition reaction between (i) and MA affording the target compound according to the route (c) shown in Figure 2. The former side reaction can be prohibited by the catalyst of reductive nitrogen oxide (NO) gas; thus the reaction proceeded mainly by route (c) to produce the substituted tetralin dianhydride with good yields. However, the formation of intermediate (i) via Diels-Alder reaction of MA and *p*-substituted styrene is highly dependent on the feature of the *R* substituents in the starting St monomers. In the case of electron-donating ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ , or other alkyl groups), the target tetralin dianhydrides can usually be obtained. For instance, tetralin dianhydrides with hydrogen (-H) or  $-\text{CH}_3$  [11], *tert*-butyl [12], or chloromethyl ( $-\text{CH}_2\text{Cl}$ ) [13] have been successfully prepared in our previous work. However, for substituents with strong electron-withdrawing feature, such as  $-\text{CF}_3$ ,  $-\text{CN}$ ,  $-\text{NO}_2$ , etc., the reaction cannot occur, which might be due to the low electron densities in the double bonds caused by the groups mentioned above. In the current work, it was proven that the tetralin dianhydride with the *R* substituent with weak electron-withdrawing fluorine group can also be obtained. This is quite beneficial for the following PI films development, because fluorine substituent can usually provide various desirable properties for the applications in optoelectronic fabrications.

The chemical structure of FTDA was confirmed by FT-IR, NMR and elemental analysis measurements. Figure 3 shows the FT-IR spectra of FTDA and the derived PI films. The characteristic

absorptions at 1859 and 1780  $\text{cm}^{-1}$  assigned to the asymmetric and symmetric stretching vibration of the carbonyl groups ( $\nu_{\text{C=O}}$ ) in FTDA were clearly observed. In addition, the characteristic absorptions at 2960 and 2928  $\text{cm}^{-1}$  due to the asymmetric and symmetric stretching vibrations of saturated C-H bonds in tetralin group and 1224  $\text{cm}^{-1}$  for  $\nu_{\text{C-F}}$  were also clearly observed.

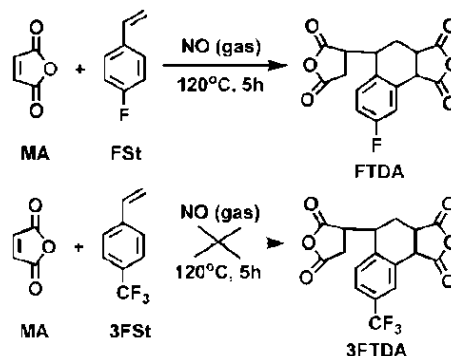


Fig. 1. Synthesis of FTDA dianhydride.

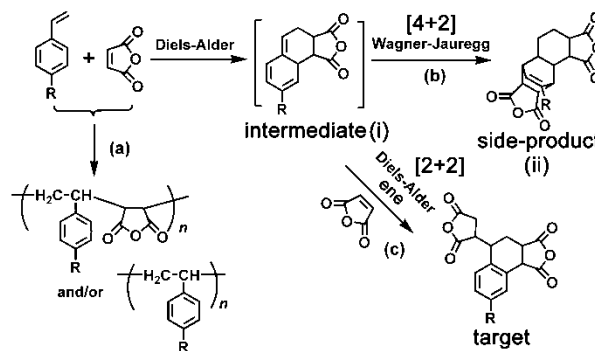


Fig. 2. Reaction mechanism for the synthesis of FTDA.

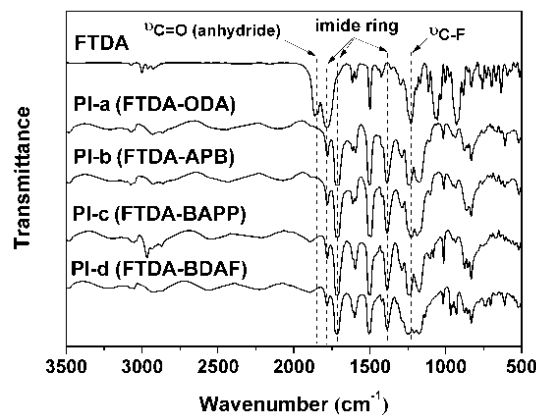


Fig. 3. FT-IR spectra of FTDA and the PI films.

The  $^{13}\text{C}$  NMR spectrum of FTDA was presented in Figure 4 together with the assignments of the observed resonances. In the figure, 16 signals are

clearly revealed; among which, 9 carbons induce signals in the embedded Distortionless Enhancement by Polarization Transfer (DEPT-135) measurements due to their attached protons. This result is consistent with the proposed structure. In addition, elemental analysis results also revealed the successful preparation of the target dianhydride. The characterization results demonstrated that the alicyclic dianhydride FTDA was successfully synthesized and the obtained monomer possessed high purity for the following polymerization.

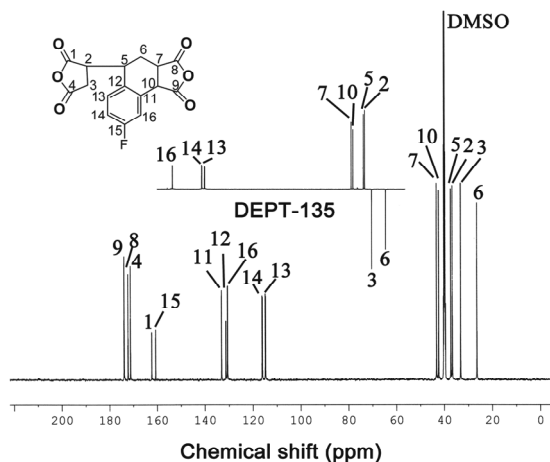


Fig. 4.  $^{13}\text{C}$ -NMR and DEPT-135 spectrum of FTDA dianhydride.

### 3.2. PI synthesis

A series of semi-alicyclic PIs were synthesized from FTDA and various aromatic diamines via a one-step high temperature polycondensation procedure, as shown in **Figure 5**. All the reaction mixtures maintained homogeneous during the polymerization process in *m*-cresol solvent,

indicating good solubility of the obtained polymers. The intrinsic viscosities of the resulting PIs were in the range of 0.65 to 1.02 dL/g measured at 25 °C in NMP (Table 1). This result reveals that the FTDA possessed good reactivity when polymerizing with aromatic diamines. The obtained PI resins have a numerical average molecular weight ( $M_n$ ) of 24500~41400 g/mol determined by GPC measurements (Table 1). This high  $M_n$  values further reflect the good reactivity of FTDA. Flexible, tough and clear PI films could be cast from their NMP solutions. All the PI films exhibited a light-color from very pale-yellow to palr-brown at a thickness of 40~50  $\mu\text{m}$ . Meanwhile, the PI films were fingernail creasable, indicating good toughness. According to the tensile properties measurements (Table 1), the PI films exhibited tensile strength ( $T_s$ ) values of 82-90 MPa and elongations at break higher than 7.3%.

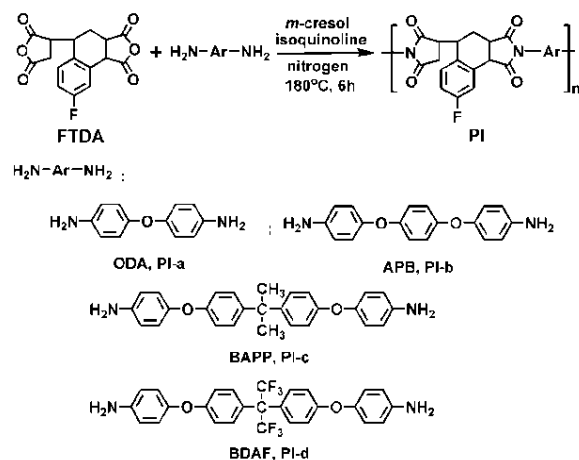


Fig. 5. Synthesis of FTDA-PIs.

**Table 1.** Inherent viscosities, molecular weights, mechanical and optical properties of the FTDA-PIs.

PI	$[\eta]_{\text{inh}}^a$ (dL/g)	Molecular weight (g/mol)			Film quality	Tensile properties			Optical properties			
		$M_n$	$M_w$	$M_w/M_n$		$T_s^c$ (MPa)	$T_M^c$ (GPa)	$E_b^c$ (%)	$\lambda^c$ (nm)	$T_{450}^c$ (%)	$d^e$ ( $\mu\text{m}$ )	$YI^e$ (b $^*$ )
PI-a	0.90	25700	47800	1.86	F&T <sup>b</sup>	82	2.4	7.3	287	82	25	21.1
PI-b	1.02	24500	52200	2.13	F&T	86	2.3	8.1	294	91	25	14.4
PI-c	0.97	30700	75500	2.46	F&T	88	2.3	8.3	289	89	25	9.6
PI-d	0.65	41400	92500	2.23	F&T	90	2.2	7.8	285	94	25	3.3

<sup>a</sup> Inherent viscosities measured with a PI resin at a concentration of 0.5 g/dL in NMP at 25 °C; <sup>b</sup> Flexible and tough; <sup>c</sup>  $T_s$  : Tensile strength;  $T_M$  : Tensile modulus;  $E_b$  : Elongation at break; <sup>d</sup> Not detected; <sup>e</sup>  $\lambda$  : Cutoff wavelength;  $T_{450}$  : Transmittance at 450 nm;  $d$  : Film thickness for yellow index measurements; YI : yellow index.

**Table 2.** Solubility of the PIs.

PI	Solvents <sup>a</sup>						
	NMP	DMAc	GBL	THF	CH <sub>2</sub> Cl <sub>2</sub>	BC	<i>m</i> -cresol
PI-a	++ <sup>b</sup>	++	++	+	++	—	++
PI-b	++	++	++	+	++	—	++
PI-c	++	++	++	++	++	—	++
PI-d	++	++	++	++	++	—	++

<sup>a</sup> NMP: *N*-methyl-2-pyrrolidinone; DMAc: *N,N*-dimethylacetamide; GBL:  $\gamma$ -butyrolactone; BC: butyl cellosolve;

<sup>b</sup> ++: Wholly soluble at room temperature; +: Partially soluble; —: Insoluble;

The FT-IR spectra of the FTDA-PI films are illustrated in Figure 1. It can be clearly observed that the asymmetric stretching vibration of the carbonyl groups absorptions in FTDA at 1859 cm<sup>-1</sup> disappeared in the spectra of PI films. Instead, the characteristic absorptions of imide groups were observed at about 1780 cm<sup>-1</sup> ( $\nu_{\text{s,C=O}}$ ), 1720 cm<sup>-1</sup> ( $\nu_{\text{as,C=O}}$ ) and 1386 cm<sup>-1</sup> ( $\nu_{\text{as,C-N}}$ ), respectively. Meanwhile, the characteristic absorptions around 1500~1600 cm<sup>-1</sup> (aromatic C=C) and 1224 cm<sup>-1</sup> ( $\nu_{\text{C-F}}$ ) were also detected in the FT-IR spectra of the PIs. These peaks indicated the successful preparation of the current PIs with one-step high temperature polycondensation route.

The solubility of PIs was tested quantitatively in various organic solvents at a concentration of 15 wt% at room temperature and the results are summarized in Table 2. All the PIs were easily soluble in polar aprotic solvents (NMP and DMAc), *m*-cresol, and  $\gamma$ -butyrolactone (GBL). Among the PIs, PI-c (FTDA-BAPP) and PI-d (FTDA-BDAF) showed the best solubility due to the synergic effects of bulky tetralin moiety, pendant fluoro substituent, and flexible ether and isopropylidene or hexafluoroisopropylidene linkages. They were wholly soluble in tetrahydrofuran (THF) and dichloromethane at room temperature. In the same condition, PI-a (FTDA-ODA) and PI-b (FTDA-APB) were only partially soluble in dichloromethane. The enhancement of the solubility of FTDA-PIs can be attributed to the more loose packing of the molecular chains induced by the lateral fluorine group.

### 3.3. Optical properties

Effects of the fluorine and tetralin moiety in FTDA on the optical properties in FTDA-PI films

were investigated by UV-Vis and yellow index measurements. Figure 6 exhibits the UV-Vis spectra of the PI thin films at a thickness of 10  $\mu\text{m}$ . The cut off wavelengths, transmittances at 450 nm, and yellow indices of the FTDA-PI films are summarized in Table 1.

The PI films showed good optical transparency in the ultraviolet-visible light region with cutoff wavelengths lower than 300 nm and transmittances close or higher than 80% at 450 nm. The good optical transparency of the current PI films is mainly attributed to the asymmetrical alicyclic tetralin structure and the fluorine group in the dianhydride unit. The FTDA-PI films showed yellow index (YI) values of 3.3-21.1, which were much lower than that of all-aromatic PI films, such as Kapton film (YI=108) [16]. Especially, PI-4 film containing both of fluoro substituents in the dianhydride and diamine moieties exhibited a lowest YI value of 3.3 in the series. The light colors for the current FTDA-PI films mainly originate from the absence or inhibition of intra- and/or intermolecular charge-transfer interactions in the PIs due to the non-conjugation tetralin rings. The alicyclic tetralin structure and fluorine unit in FTDA moiety was presumably effective in disrupting the CTC formation in the polymer chains. Similarly, the aliphatic linkages in the diamine moiety, including flexible ether (-O-), propylidene [-C(CH<sub>3</sub>)<sub>2</sub>] or hexafluoroisopropylidene [-C(CF<sub>3</sub>)<sub>2</sub>] groups also are beneficial reducing the formation of CTC in the PI molecular chains.

In summary, the FTDA-PI films, especially PI-4 film possessed good optical properties due to the synergistic effects of alicyclic tetralin moiety, electron-withdrawing fluorine and -C(CF<sub>3</sub>)<sub>2</sub> groups and flexible ether linkages. This low-color feature is

extremely desirable for its application as components for various optoelectronic devices such as TFT-LCDs, flexible display devices or photovoltaic modules.

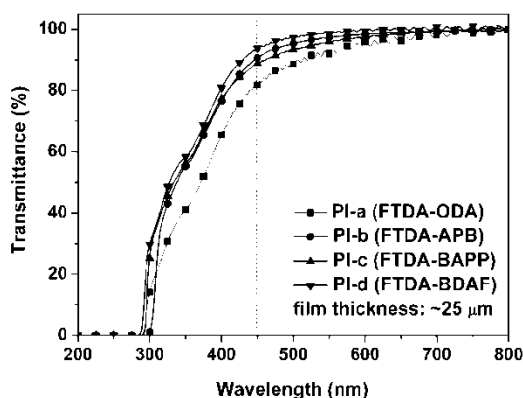


Fig. 6. UV-Vis spectra of FTDA-PI films.

### 3.4. Thermal properties

The thermal stabilities of the FTDA-PI films were investigated by TGA and DSC measurements. Table 3 summarizes the thermal characterization of the polymers. Figure 7 depicts the TGA plots for the films over a temperature range of 50 to 750 °C in nitrogen. It can be seen from the plots that the current PIs possess good thermal stability with no significant weight loss up to approximately 400 °C. After 400 °C, the PIs lose their original weight rapidly, leaving a residual weight ratio in the range 18.6–28.6% at 750 °C. The 5% weight loss temperatures ( $T_{5\%}$ ) of the PI films are all higher than 400 °C in nitrogen. This implies that the fluoro-substituted tetralin moiety has good thermal resistance. Although the thermal stability of the current PIs is lower than that of common wholly aromatic PIs, it is high enough for their applications in optoelectronic applications.

Glass transition temperatures ( $T_g$ ) values were obtained from the second heating scans of PI samples at a heating rate of 10 °C/min (Figure 8 and Table 3). All the polymers exhibit good thermal stabilities with the  $T_g$  values in the range of 226–271 °C, depending on the rigidity of the aromatic diamines. It is observed that for the same dianhydride, the  $T_g$  values of the PIs followed the order as ODA > BDAF > APB > BAPP. The decreasing order of  $T_g$  generally correlated with that of the chain flexibility. PI-c derived from FTDA and BAPP showed the lowest  $T_g$  value due to the increase in flexibility of polymer chains induced by the flexible isopropylidene bridges; whereas the PI-a obtained from ODA had the highest values

because of the least flexible linkages in its molecular chains.

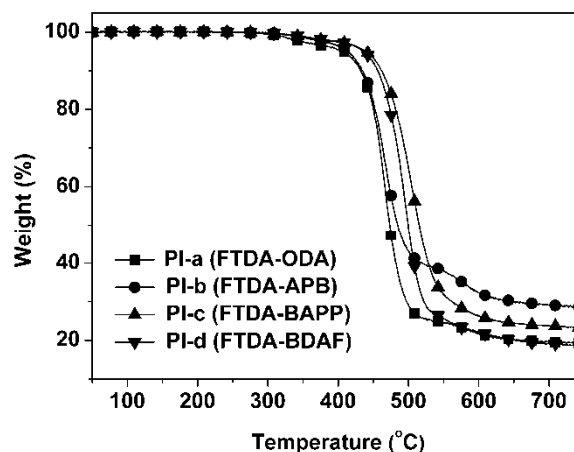


Fig. 7. TGA plots of FTDA-PI films.

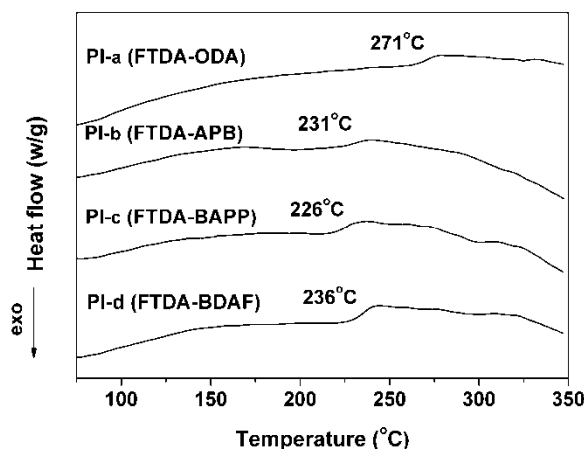


Fig. 8. TGA plots of FTDA-PI films.

Table 3. Thermal properties of PI films.

PI	$T_g^a$ (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^c$ (°C)	$R_{w750}^d$ (%)	CTE <sup>e</sup> (ppm/°C)
PI-a	271	402	431	19.3	-
PI-b	231	412	434	28.6	54.3
PI-c	226	440	462	23.3	60.0
PI-d	236	436	456	18.6	61.5

<sup>a</sup> Glass transition temperature; <sup>b</sup> Temperatures at 5% weight loss; <sup>c</sup> Temperatures at 10% weight loss; <sup>d</sup> Residual weight ratio at 750 °C in nitrogen; <sup>e</sup> Coefficient of thermal expansion.

### 4. Conclusion

FTDA dianhydride containing fluoro-substituted tetralin ring was successfully synthesized via a cost-effective route. A series of semi-alicyclic PI films were prepared from the dianhydride and aromatic diamines. The alicyclic FTDA dianhydride exhibited good reactivity when polymerizing with the diamines. Light-color and transparent PI films

with good optical properties and thermal stability were developed. Good comprehensive properties and relatively low cost make the films good candidates for advanced optoelectronic applications.

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