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Properties of organosoluble aromatic polyimides from 3′-trifluoromethyl-3,4′-oxydianiline

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Abstract

A colorless fluorinated diamine, 3′-trifluoromethyl-3,4′-oxydianiline (3′-CF_3-3,4′-ODA) (**II**) was prepared through the nucleophilic substitution reaction of 3-nitrophenol and 2-chloro-5-nitrobenzotrifluoride by catalytic reduction with hydrazine and Pd/C. A series of Polyimides **V** were synthesized from the diamine **II** with various aromatic dianhydrides $\mathbf{III_{a-f}}$ via thermal and chemical imidization. These polyimides had inherent viscosities ranging from 0.88 to 1.12 dl/g. A comparison of **V**, **VI** to analogous polyimides **VII**, **VIII**. **VI**, **VII** and **VIII** was based on 3′4-ODA, 3-CF_3-4,4′-ODA, 4,4′-ODA, respectively. In terms of the color of PI revealed that the color intensity of phenoxy-containing amine of the *meta*-structure and the *para*-structure with the CF_3 group would fell off color intensity. The color intensity of the four polyimide series was lessened in the following order: **V** > **VII** > **VI** > **VIII**. The solubility of **V** is better than **VI, VII** and **VII**. The polyimide **V** films had a tensile strength ranging from 124 to 147 MPa, elongation at break from 9 to 65%, and initial modulus from 2.3 to 2.8 GPa. The glass transition temperature of polymers was recorded at 234–313 °C. They had 10% weight loss at a temperature above 515 °C and left more than 50% residue even at 800 °C in nitrogen. Compared with polyimides **VI**, **V** showed the lower dielectric constants of 2.80–3.50 (40 MHz), and moisture absorptions in the range of 0.44–1.02 wt%.

Keywords: Aromatic polyimides; 3′-trifluoromethyl-3; *meta*-Structure

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1. Introduction

Aromatic polyimides are well known as materials of high performance for their excellent thermal stabilities, chemical resistance and electric properties [1–4]. Polyimides are mainly used in the aerospace and electronic industries in the form of films and moldings. Optical transparency of polyimide films is of special importance in some application such as flexible solar radiation protectors [5], orientation films in liquid crystal display devices [6], optical waveguides for communication interconnects [7], and optical half-waveplates for planar lightwave circuits [8]. However, most polyimides between UV and the visible area have strong absorption, rendering their color close to yellow or brown. And their poor processability in their imidized forms because of high softening temperatures and insolubility.

In the recent study, the polymer of low dielectric constants is used extensive by in the metal dielectric layer of the integrated circuit. The polymer of low dielectric constants and thermal stability has been found and researched [9,10]. As the size of the devices decreases, lower dielectric constants are needed. The best method of reducing the dielectric constant is the introduction of the bulky CF_3 group into aromatic PI, because F is the highest electronegativity and low electric polarity. Beside, the C–F bonding is more close together, and it can increase the space of the interchain to enhance solubility. The fluorinated polymer can enhance the optical transparency [11–15] and lower the moisture absorption. With excellent physical and chemical properties, fluorinated PI can be expected to apply widely to the Electro-Optical and semiconductor industries.

For increasing optical application, a number of very lightly colored to colorless transparent polyimides have been synthesized. Dine-Hart et al. have shown the formation of the charge-transfer complex between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [16]. A lowering of the charge-transfer complexing generally provides polyimides with lighter color. Relevant

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literature shows that flexible groups such as ether groups [17] and the *meta*-structure diamine [18–20] will reduce the PI films' color. We also found that the diamine with the CF_3 group could contribute to PI films' optical transparency and low color [21,22].

In this study, we will discuss the difference in PI films' color intensity, which PI films are synthesized from the *meta*- or *para*-structure of diamine. For this, we synthesize high purity of 3′-trifluoromethyl-3,4′-oxydianiline [23] (**II**) a diamine that contains CF_3, will subsequently polycondensed them with various commercially available aromatic dianhydrides to produce a series of fluorinated polyimides ($\mathbf{V_{a-f}}$). These polymers will be subjected to solubility, moisture absorption, and thermal, optical, and dielectric property measurements and be compared with analogous polyimides ($\mathbf{VI_{a-f}}$) prepared from a non-fluorinated diamine monomer, 3,4′-oxydianiline(**II**′) [24,25]. We also compare **V**, **VI** with that of **VII** (from 3-CF_3-4,4′-oxydianiline) [26] and **VIII** (from 4,4′-oxydianiline) to investigate the structure of diamine and CF_3-containing or not affected coloration.

2. Experimental section

2.1. Materials

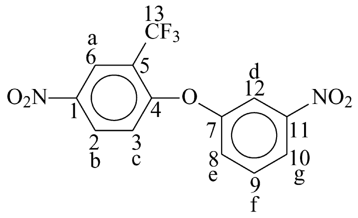
3-Nitrophenol (Acros), 2-chloro-5-nitrobenzotrifluoride (Acros) and 3,4′-diaminodiphenyl ether (TCI) were vacuum-distilled before use. Pyromellitic dianhydride (PMDA) ($\mathbf{III_a}$; Lancaster), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) ($\mathbf{III_b}$; Acros), 4,4′-oxydiphthalic dianhydride (ODPA) ($\mathbf{III_e}$; Chriskev) was recrystallized from acetic anhydride before use. 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) ($\mathbf{III_c}$; Chriskev), diphenylsulfone-3,3′,4,4′-tetracarboxylic dianhydride (DSDA) ($\mathbf{III_d}$; New Japan Chemical Co.), 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) ($\mathbf{III_f}$; Chriskev) were used as received. *N*-methyl-2-pyrrolidone(NMP; Fluka), *N*,*N*-dimethylacetamide(DMAc; Fluka), *N*,*N*-dimethylformamide (DMF; Fluka) and pyridine (Py; Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Synthesis of monomers

2.2.1. 2′-Trifluoromethyl-3,4′-dinitrodiphenyl ether (*I*)

3-Nitrophenol (5.562 g, 0.04 mol) and 2-chloro-5-nitrobenzotrifluoride (0.042 mol) were first dissolved in 20 ml of DMAc in a 100-ml flask with stirring. After the mixture was completely dissolved, potassium carbonate (4.2 g, 0.03 mol) was added to it in one portion. After 30 min of stirring at room temperature, the mixture was heated at 100 °C for 10 h. The obtained mixture was poured into 60 ml of methanol to give a solid, which was collected, washed thoroughly with methanol and hot water, and dried under vacuum at 60 °C. The crude product was recrystallized from ethanol to give fine, pale-cream crystals of 2′-trifluoromethyl-3,4′-dinitrodiphenyl ether (**I**) (11.22 g, 85.7%).

The mp is 110–111 °C by differential scanning calorimetry (DSC) at a scan rate of 5 °C/min. IR (KBr): 1531, 1351 ($-NO_2$ stretch), 1261 (C–F stretch), 1197, 1147 cm^{-1} (C–O stretch). ^1H NMR (500 MHz, DMSO-d_6): $\delta = 8.55-8.56$ (1H, H_a), 8.49–8.52 (1H, H_b), 8.20– 8.22 (H, H_g), 8.07–8.08 (H, H_d), 7.82–7.86 (H, H_f), 7.74–7.76 (H, H_c), 7.34, 7.33 (H, H_e). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 158.9$ (C^4), 154.6 (C^7), 149.1 (C^{11}), 142.6 (C^1), 132.1 (C^9), 130.1 (C^2), 126.8 (C^8), 123.4 (C^6, quartet, $^3J_{C-F} = 5$ Hz), 123.2 (C^{13}, quartet, $^1J_{C-F} = 274$ Hz), 120.7 (C^3), 120.2 (C^5, quartet, $^2J_{C-F} = 31$ Hz), 119.4 (C^{10}), 115.2 ppm (C^{12}).

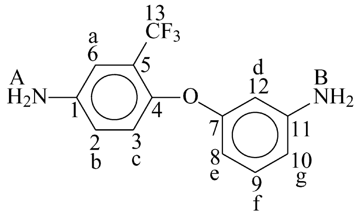


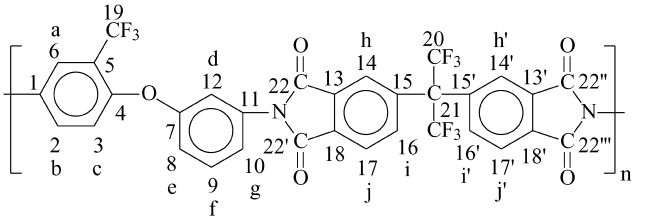
Elem. anal. calcd. for $C_{13}H_7F_3N_2O_5$ (328.20): C, 47.57%; H, 2.15%; N, 8.54%. Found: C, 47.55%; H, 1.88%; N, 8.42%.

2.2.2. 2-Trifluoromethyl-3,4′-diaminodiphenyl ether (3′-trifluoromethyl-3,4′-oxydianiline) (*II*)

To a suspension solution of the purified dinitro compound **1** (9.81 g, 0.03 mol) and 10% Pd/C (0.18 g) in ethanol (100 ml), hydrazine monohydrate (5 ml) was added dropwise to the stirred mixture at 70 °C within 30 min. After complete addition, the mixture was heated at the reflux temperature for another 2 h. The reaction solution was filtered hot to remove Pd/C, concentrated till 20 ml and added 5 ml hot water, then cool and stayed to precipitate white crystal that was dried in vacuum at room temperature to give **II** (7.36 g, 91.5%).

The mp is 66–67 °C (lit. [23] 62.4–64 °C) by DSC (5 °C/min). IR (KBr): 3438, 3359 (NH stretch), 1270, 1106 (C–F stretch), 1222, 1147 (C–O stretch). ^1H NMR (500 MHz, DMSO-d_6): $\delta = 6.95$, 6.93 (1H, H_a), 6.92, 6.91 (1H, H_c), 6.81– 6.86 (2H, $H_{b,f}$), 6.25–6.27 (1H, H_e), 6.08–6.09 (1H, H_d), 6.04–6.06 (1H, H_g), 5.39 (2H, H_A), 5.16 (2H, H_B). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 159.5$ (C^7), 150.2 (C^{11}), 145.4 (C^4), 142.9 (C^1), 129.8 (C^9), 123.6 (C^{13}, quartet, $^1J_{C-F} = 271$ Hz), 123.2 (C^3), 121.6 (C^5, quartet, $^2J_{C-F} = 30$ Hz), 118.6 (C^2), 110.6 (C^6, quartet, $^3J_{C-F} = 5$ Hz), 108.5 (C^{10}), 104.3 (C^8), 102.1 (C^{12}).





Elem. anal. calcd. for $C_{13}H_{11}F_3N_2O$ (268.23): C, 58.21%; H, 4.13%; N, 10.44%. Found: C, 58.20%; H, 3.69%; N, 10.54%.

2.3. Synthesis of polyimides

2.3.1. Thermal cyclodehydration

II (0.268 g, 1 mmol) was dissolved in 4.5 ml of dried DMAc in a 50-ml flask. After the diamine was completely dissolved, 0.444 g (1 mmol) of 6FDA(**III$_f$**) was added in one portion. The mixture was stirred at room temperature for 12 h. Then, the obtained poly(amic acid) solution was spread on a glass plate, which was placed in an 80 °C oven for 1 h to remove the solvent. The semidried poly(amic acid) film was sequentially heated at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min, and 250 °C for 30 min. By soaking in water, a flexible polyimide film of **V$_f$** was self-stripped off from the glass surface. The inherent viscosity of the polymer in DMAc was 0.88 dl/g, measured at a concentration 0.5 g/dl at 30 °C.

The typical IR spectrum of **V$_f$** is shown in Fig. 1. The characteristic absorption bands of the imide ring were observed near 1779, 1725 (asymmetrical and symmetrical C=O stretching vibration), 1375 (C–N stretching vibration), 734 cm^{-1} (imide ring deformation) and 1100–1300 cm^{-1} showed some stronger peak(C–O and C–F stretching).

^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.16–8.22 (2H, $H_{j,j'}$) close to the imide ring appeared at the farthest downfield region; 7.96 (3H, $H_{a,i,i'}$) the H_a ortho-oriented to the CF_3 group shifted to the upfield region; 7.76 (2H, $H_{h,h'}$); 7.74 (1H, H_g); 7.61–7.65 (1H, H_b); 7.37, 7.35 (1H, H_d); 7.26–7.32 (3H, $H_{c,e,f}$), the $H_{c,e,f}$ shifted to a higher field due to the electron donating property of aromatic ether. ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 165.9, 165.9, 165.6, 165.6 ($C^{22,22',22',22'''}$); 155.6 (C^7); 153.7 (C^4); 137.5; 137.4 ($C^{15,15'}$) showed different shifts as the result of the asymmetric phenyl group; 135.8 (C^2); 133.6 (C^{11}); 133.4 (C^1); 133.0 ($C^{13,13'}$); 132.6 ($C^{16,16'}$); 130.6 ($C^{18,18'}$); 127.1 ($C^{17,17'}$); 126.5 (C^9); 124.4 ($C^{14,14'}$); 123.6 (C^{10}); 123.4 (C^{19}, quartet, $^1J_{C-F} = 286$ Hz) and 122.8 (C^{20}, quartet, $^1J_{C-F} = 273$ Hz) of the hexafluoroisopropylidene group. 121.5 (C^3), 120.2 (C^5, quartet, $^2J_{C-F} = 31$ Hz), 120.1 (C^6), 119.0 (C^8), 118.1 (C^{12}), 64.6 (C^{21}).

2.3.2. Chemical cyclodehydration

The method of synthesis polyamic acid was similar to the thermal cyclodehydration. Then a 1 ml mixture of Ac_2O and pyridine (volume ratio 2:1) was added to the polyamic acid solution. The polyamic acid solution was imidized by stirring in oil bath at 80–100 °C for 1 h, and obtained solution was spread on a glass plate, which was placed in an 80 °C oven for 1 h to remove the solvent. And then sequentially heated at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 200 °C for 30 min. By soaking in water, a flexible polyimide film of **V$_f$** was self-stripped off from the glass surface. The inherent viscosity of the polymer in DMAc was 0.76 dl/g.

2.4. Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a PerkinElmer model 2400 CHN analyzer. Weight-average molecular weights (M_ws) and number-average molecular weights (M_ns) were obtained via Gel permeation chromatography (GPC) on the basis of polystyrene calibration using Water 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. ^1H and ^{13}C NMR spectra were measured on a JEOL EX-500 spectrometer. The inherent viscosities were determined at a 0.5 g/dl concentration with an Ubbelohde viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements carried out on 9–11 mg and heated in flowing nitrogen or air (40 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen at a heating rate of 15 °C/min. Mechanical properties of the films were measured on an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 cm/min on strips approximately 30–70 μm thick, 0.5 cm wide, and 2 cm in gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated on a Macbeth color-eye colorimeter. Measurements were performed of films 20–60 μm thick with an observational angle of 10° and a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer

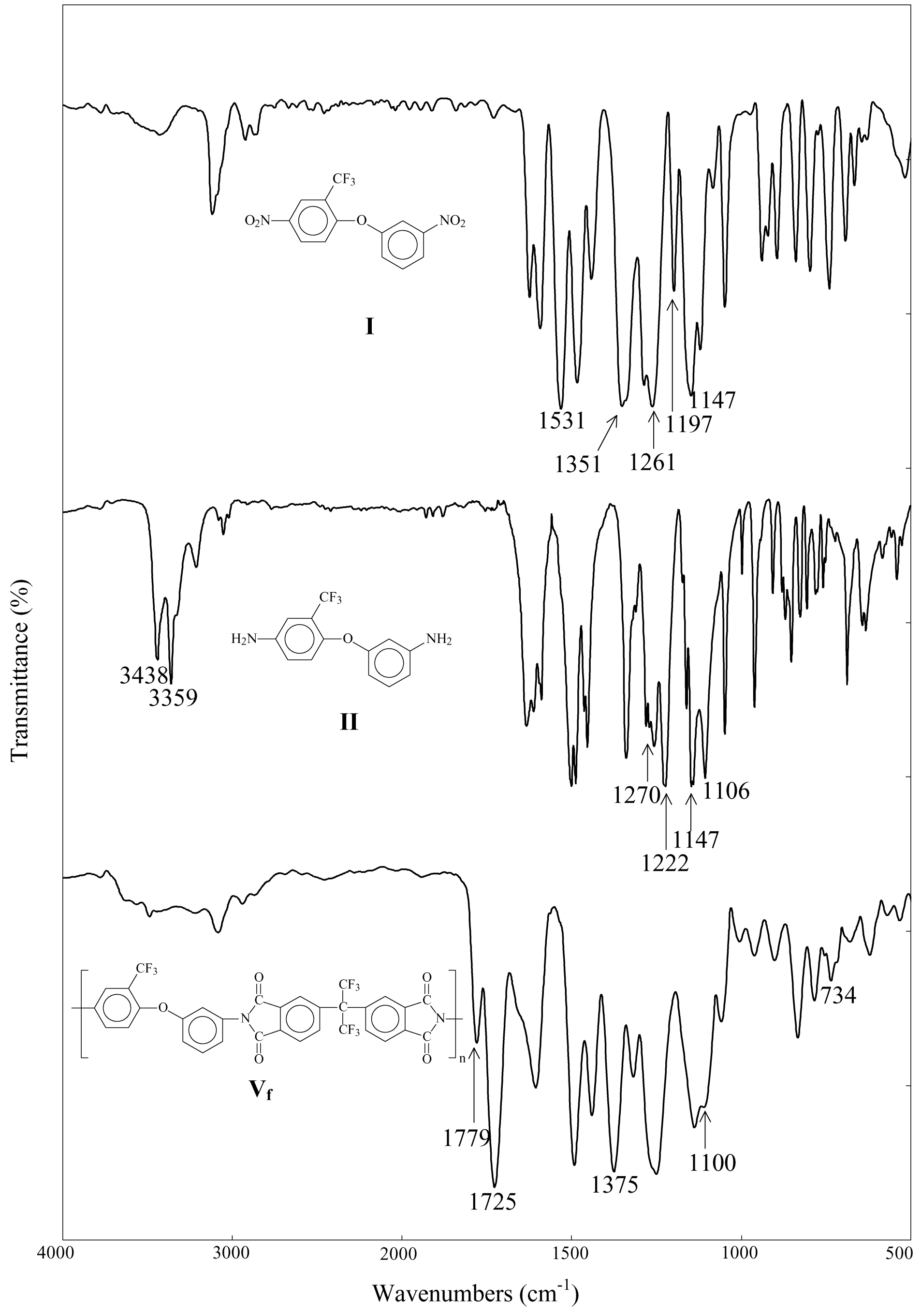


Fig. 1. FT-IR spectra of dinitro compound **I**, CF_3-diamine **II** and polyimide $\mathbf{V_f}$.

films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a HP 4194A Impedance/Gain Phase Analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. The equilibrium moisture absorption was determined by weighing the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

3. Results and discussion

3.1. Monomer synthesis

In order to compare the color intensity and other properties of the PI which were affected by the structure of the aromatic diamine with one phenoxy, we need to synthesize the high purity and colorless $3'$-CF_3-$3,4'$-ODA(**II**) to compare the color intensity of PI from $3,4'$-ODA($\mathbf{II'}$), 3-CF_3-$4,4'$-ODA($\mathbf{II''}$) and $4,4'$-ODA($\mathbf{II'''}$). **II** was prepared by a nucleophilic chloro-displacement reaction of 2-chloro-5-nitrobenzotrifluoride with 3-nitrophenol or 3-aminophenol to synthesize the dinitro compound **I** and the amine–nitro compound **I′**, and the subsequent reduction of the intermediate **I** or **I′** to get **II** (Scheme 1). **II** from **I′** was pale yellow solid and the mp was 62–64 °C by One et al. [23]. We used the former method to get high purity of **II** by reducing **I**, **II** was close to colorless crystal and the mp was 66–67 °C. We attributed our results to the amine compound **I′**, which is easily colored by heating nucleophilic chloro-displacement reaction.

3.2. Polymer synthesis

Polyimides were synthesized from diamine **II** and dianhydrides $\mathbf{III_{a-f}}$ in a conventional two-step procedure: ring-opening polyaddition at room temperature to poly(amic acid)s, followed by sequential heating to 250 °C or mixture of Ac_2O/Py to obtain the corresponding polymers, as shown in Scheme 2. Transformation from poly(amic acid) to polyimide was possible via the thermal or chemical cyclodehydration; merits of the former were easy to handle and to cast into thin film, and the latter was suited to prepare soluble polyimides. In this study, brittle polyimides $\mathbf{V_a(C)}$ were improved on the ability to form film through copolymerization.

Fig. 2 shows the variation curves of inherent viscosities of the poly (amic acid)s obtained from BPDA with CF_3-containing diamine **II** or 3,4′-ODA at various times. The reaction of BPDA with fluorinated **II** proceeded relatively slow and its inherent viscosity reached 0.3 dl/g after 30 min. After this point, inherent viscosity increased slowly and reached 1.05 dl/g in 9 h; polymerization nearly ceased and no increase in inherent viscosity was observed after 12 h. The reaction of BPDA with 3,4′-ODA proceeded relatively fast and its inherent viscosity increased fast within 30 min; inherent viscosity reached 0.95 dl/g after 2 h and then decreased gradually.

The results of elemental analysis of $\mathbf{V_{a-f}}$ are listed in Table 1. $\mathbf{V_a}$ and $\mathbf{V_c}$ could not dissolve in THF, but others can dissolve and measure the GPC curves of the polyimide. M_w and M_n values were available in the range of 5.78–9.81 × 10^4 and 3.76–7.58 × 10^4, respectively, relative to standard polystyrene. The polydispersity index M_w/M_n of **V** is in the range of 1.3–1.5 (Table 2).

Table 1
Elemental analysis (%) of the polyimides

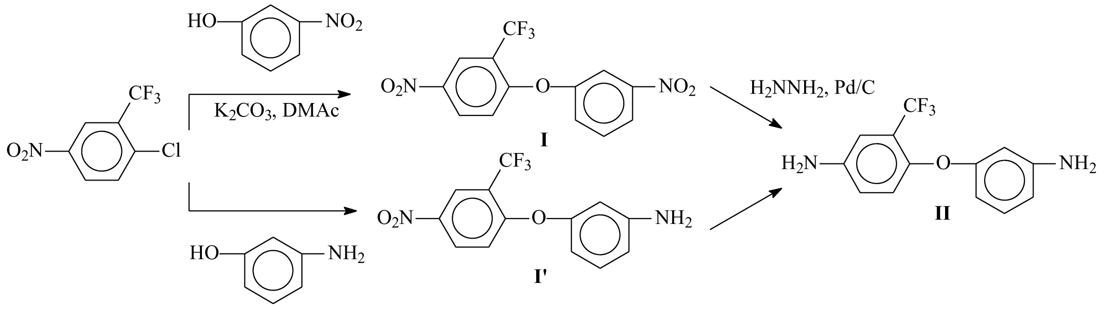
Polymer code	Formula of PI (formula weight)		C	H	N
$\mathbf{V_a}$	$(C_{23}H_9N_2O_5F_3)_n$	Calcd	61.34	2.01	6.22
	$(450.33)_n$	Found	60.24	1.93	6.27
$\mathbf{V_b}$	$(C_{30}H_{13}N_2O_6F_3)_n$	Calcd	64.99	2.36	5.05
	$(554.44)_n$	Found	63.97	2.26	5.25
$\mathbf{V_c}$	$(C_{29}H_{13}N_2O_5F_3)_n$	Calcd	66.17	2.49	5.32
	$(526.43)_n$	Found	65.31	2.41	5.42
$\mathbf{V_d}$	$(C_{29}H_{13}N_2O_7F_3S)_n$	Calcd	58.99	2.22	4.74
	$(590.49)_n$	Found	58.35	2.24	5.06
$\mathbf{V_e}$	$(C_{29}H_{31}N_2O_6F_3)_n$	Calcd	64.21	2.42	5.16
	$(542.42)_n$	Found	63.58	2.29	5.34
$\mathbf{V_f}$	$(C_{31}H_{13}N_2O_5F_9)_n$	Calcd	56.02	1.97	4.22
	$(664.44)_n$	Found	56.26	1.85	4.30

3.3. Optical properties

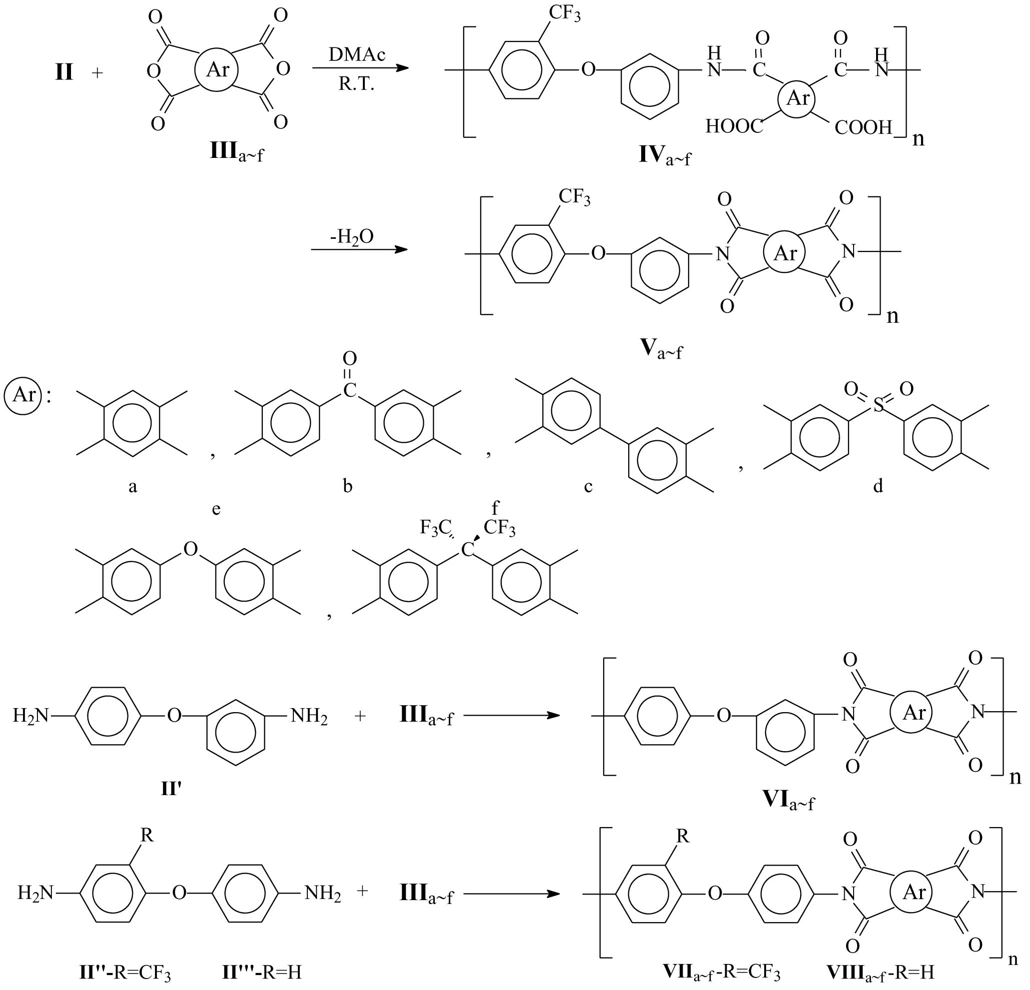
The color coordinates of polyimides **V** and corresponding polyimides **VI**, **VII** and **VIII** are given in Table 3.

All the $\mathbf{V_{a-f}}$ fluorinated polyimides have a lower b^* (a yellowness index) value (the difference ranges from 2.7 to 19.0) by contrast with the corresponding non-fluorinated polyimides $\mathbf{VI_{a-f}}$. The arrangements of dianhydride moieties in the order of the color intensity of polyimides from deep (PMDA) to pale (6FDA) when the diamine structures are fixed. Moreover, the color intensities of the polyimides could also be elucidated from the cutoff wavelength (λ_0) observed in UV–vis absorption spectra. Fig. 3 shows the UV–visible spectra of the polyimide $\mathbf{V_{a-f}}$ and $\mathbf{VI_{a-f}}$ films. The λ_0 from these spectra is listed in Table 3. Consistent with the results obtained from the colorimeter, all the fluorinated polyimides show a lower λ_0 than that of their respective non-fluorinated analogs.

6FDA and ODPA produced fairly transparent and almost colorless polyimide films in contrast to other dianhydrides. These results are attributed to the ether group of ODPA and the hexafluoroisopropylidene group of 6FDA. They reduce the intermolecular charge transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [16].



Scheme 1. Synthesis of 3F-diamine **II**.



Scheme 2. Synthesis of the polyimides.

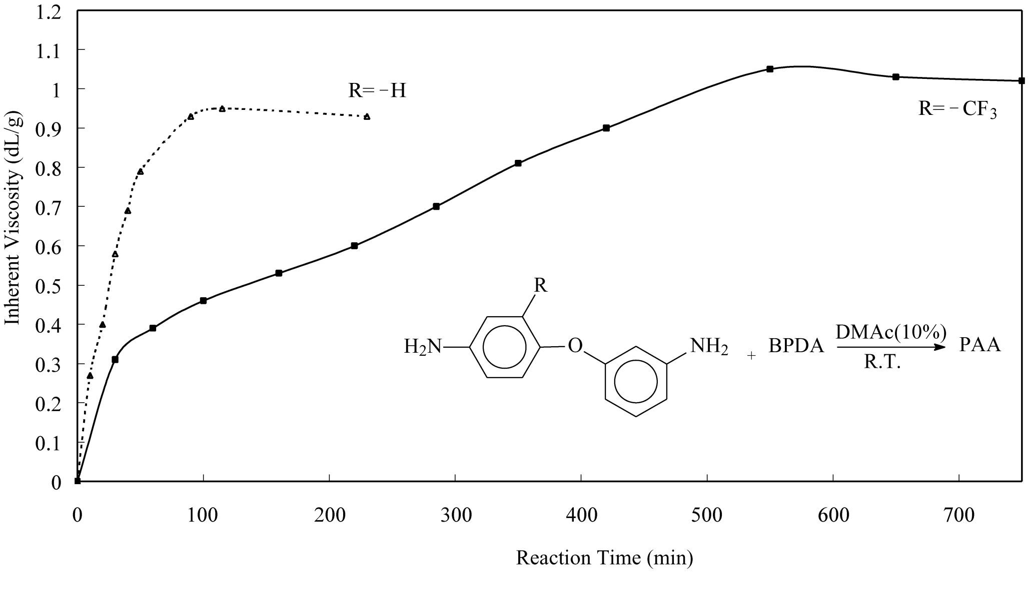


Fig. 2. Viscosity change of poly(amic acid)s prepared in DMAc at 10% solid content at room temperature.

Table 2
Inherent viscosity of polyimides **V** and GPC data of polyimides **V**

Polymer code/η_{inh} (dl/g)		GPC data of polyimides[a]			
PI	η_{inh}[b] (dl/g)	$M_n \times 10^4$	$M_w \times 10^4$	$M_p \times 10^4$	M_w/M_n
$\mathbf{V_a}$	1.12	–	–	–	–
$\mathbf{V_b}$	0.88[c]	4.36	6.83	7.21	1.5
$\mathbf{V_c}$	0.95	–	–	–	–
$\mathbf{V_d}$	1.10	5.34	7.68	8.17	1.4
$\mathbf{V_e}$	0.86	3.76	5.78	5.94	1.5
$\mathbf{V_f}$	0.88	7.58	9.81	–	1.3

[a] Relative to polystyrene standard, using THF as the eluent.
[b] Measured at a polymer concentration of 0.5 g/dl in DMAc at 30 °C.
[c] Measured at a polymer concentration of 0.5 g/dl in H_2SO_4 at 30 °C.

Table 3
Color coordinates and the cut-off wavelength (λ_0) from UV–visible spectra for polyimide films

Polymer code[a]	Film thickness (μm)	Color coordinates[b]				λ_0 (nm)
		b^*	a^*	L^*	Δb^*[c]	
$\mathbf{V_a(H)}$	34	60.8	−11.4	96.3		409
$\mathbf{V_b(H)}$	30	56.4	−10.9	96.1		405
$\mathbf{V_c(H)}$	39	33.7	−8.2	97.7		398
$\mathbf{V_d(H)}$	56	49.1	−8.5	95.8		399
$\mathbf{V_e(H)}$	25	26.2	−8.2	99.2		370
$\mathbf{V_f(H)}$	36	11.3	−5.0	98.9		368
$\mathbf{V_b(C)}$	52	25.0	−9.0	99.0	−31.4	395
$\mathbf{V_c(C)}$	51	18.5	−7.0	98.9	−15.2	399
$\mathbf{V_d(C)}$	63	21.2	−8.1	99.2	−27.9	386
$\mathbf{V_e(C)}$	61	8.7	−2.9	99.7	−17.5	374
$\mathbf{V_f(C)}$	57	8.6	−3.3	99.9	−2.7	366
$\mathbf{V_b(C)}$[d]	81	50.2	1.4	87.4	6.2	404
$\mathbf{V_c(C)}$[d]	44	32.2	−3.8	93.3	1.5	400
$\mathbf{VI_a(H)}$	39	76.6	−1.8	89.3	15.8	420
$\mathbf{VI_b(H)}$	32	71.6	−9.7	94.2	15.2	414
$\mathbf{VI_c(H)}$	52	52.7	−6.9	90.4	19	416
$\mathbf{VI_d(H)}$	53	55.1	−7.4	92.4	6	410
$\mathbf{VI_e(H)}$	44	29.1	−10.5	95.0	2.9	388
$\mathbf{VI_f(H)}$	56	23.8	−7.0	97.0	12.5	383
$\mathbf{VII_a(H)}$	25	75.5	−8.4	93.8	14.7	421
$\mathbf{VII_b(H)}$	25	63.0	−13.5	97.0	6.6	408
$\mathbf{VII_c(H)}$	62	44.9	−9.2	94.9	1.12	411
$\mathbf{VII_d(H)}$	69	50.2	−9.2	94.5	1.1	409
$\mathbf{VII_e(H)}$	42	28.7	−11.4	98.0	2.5	381
$\mathbf{VII_f(H)}$	43	14.6	−4.9	98.8	3.3	369
$\mathbf{VIII_a(H)}$	41	83.9	5.1	88.1	23.1	444
$\mathbf{VIII_b(H)}$	31	78.0	−9.1	94.2	21.6	424
$\mathbf{VIII_c(H)}$	30	58.5	−13.3	95.7	24.8	421
$\mathbf{VIII_d(H)}$	48	60.2	−11.1	93.5	11.1	416
$\mathbf{VIII_e(H)}$	31	31.7	−11.0	98.0	20.4	386
$\mathbf{VIII_f(H)}$	52	37.3	−7.4	94.2	26	387

[a] (H): Polyimides were obtained by the thermal imidization method. (C): Polyimides were obtained by the chemical imidization method with DMAc as solvent.
[b] The color parameters were calculated according to a CIE LAB equation, using paper as a standard. L^* is lightness; 100 means white, while 0 implies black. A positive a^* means red color, while a negative a^* indicated green color. A positive b^* means yellow color, while a negative b^* implies blue color.
[c] Δb is the value of camparing **V(H)** difference.
[d] Polyimides were obtained by the chemical imidization method with NMP as solvent.

On comparing thermal imidization polymers with chemical imidized ones, **V(C)** showed a lower b^* value than **V(H)** did (the difference ranged from 1.7 to 31.4). Because $\mathbf{V_a(C)}$ cannot synthesize film in DMAc directly, we used copolymer to get film $\mathbf{V_{a/e}}$. It is also colorless via chemical imidization. On chemical imidization, colorlessness is related to the solvent. For example, when $\mathbf{V_b}$ and $\mathbf{V_c}$ form films by DMAc, they were colorless than they do by NMP.

Generally, PI films were synthesized by pure 3,4′-ODA(**II**′), which were more colorless than 4,4′ODA(**II**‴) due to the phenoxy-containing in *meta*-structure which can reduce color intensities. We considered the PI-**V** from **II** would be light color than 3-CF_3-4,4′-ODA(**II**″), so we synthesized **VII** and **VIII** to compare color intensities. **V** showed a lower b^* value than **VII** did (the difference ranged from 1.1 to 14.7). Because of the phenoxy-containing in *meta*-structure can reduce the electron-conjugation on the imide ring and these results were attributed to the reduction of the intermolecular CTC effect. Thus **V** is more colorless than **VII**.

Fig. 4 shows that all the fluorinated polyimides are more colorless than their respective non-fluorinated analogues. The light colors of the polyimides with the CF_3 groups in their diamine moieties could be explained by the decreased intermolecular interactions. The bulky and electron-withdrawing CF_3 group in diamine **II** and **II**″ were effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). And the *meta*-structure can also reduce the degree of resonance and color intensities. So the colorlessness of four series polyimides is in the following order: 3′-CF_3-3,4′-ODA(**V**) > 3-CF_3-4,4′-ODA(**VII**) > 3,4′ -ODA(**VI**) > 4,4′-ODA(**VIII**).

3.4. Solubility

The solubility of these polyimides was tested in various organic solvents, and the results are summarized in Table 4. Besides $\mathbf{V_b(H)}$, all polyimides **V** obtained via thermal or chemical cyclization were soluble in NMP, DMAc, DMF, DMSO, *m*-cresol, and Py. However, the solubility of $\mathbf{V_b}$ via thermal imidization was poor. This might be attributed to the formation of some intermolecular links of the C=O group of BTDA during the thermal imidization [27]. It can be proved by soluble $\mathbf{V_b(C)}$ through chemical imidization.

Compared with non-fluorinated polyimides **VI**, we find that the solubility of **V** is better than **VI**. This difference in solubility can be attributed to the molecular asymmetry and

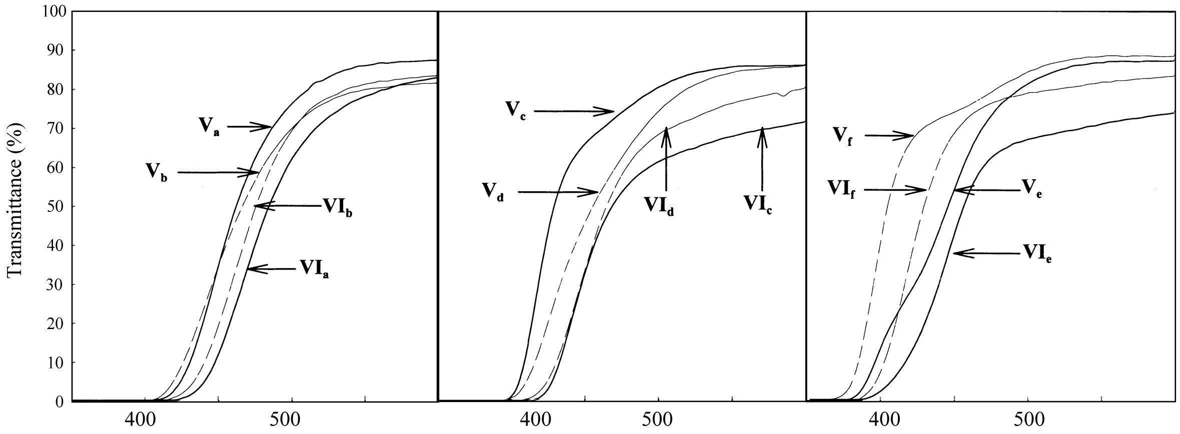


Fig. 3. UV–visible spectra of polyimide films prepared via thermal cyclization.

the presence of bulky CF_3 groups, which inhibit close packing and reduce the interchain interaction to enhance solubility.

Comparison of **V** with **VII** and **VI** with **VIII** show the different position of phenoxy-containing amine. The solubility of the *meta*-structure **V** and **VI** are better than the *para*-structure **VII** and **VIII**, which can be attributed to the *meta*-structure that inhibits close packing and enhances solubility.

3.5. Mechanical properties

The mechanical properties for all the **V** polymers were obtained in the form of thin films. The results are

Table 4
Solubility behavior of polyimides

Polymer	Solvents[a]								
	NMP	DMAc	DMF	DMSO	*m*-Cresol	Py	Dioxane	THF	CH_2Cl_2
$\mathbf{V_a(H)}$	+	+	+	+	+	+	−	−	−
$\mathbf{V_b(H)}$	−	−	S	−	−	−	−	−	−
$\mathbf{V_c(H)}$	++	++	++	S	+	+	−	−	−
$\mathbf{V_d(H)}$	++	++	++	+	+	++	+	−	−
$\mathbf{V_e(H)}$	++	++	++	+	+	++	−	−	++
$\mathbf{V_f(H)}$	++	++	+	+	++	++	++	++	++
$\mathbf{V_a(C)}$	++	++	+	+	+	+	−	−	−
$\mathbf{V_b(C)}$	++	++	++	++	+	++	++	++	++
$\mathbf{V_c(C)}$	++	++	++	++	+	+	+	−	−
$\mathbf{V_d(C)}$	++	++	++	++	+	++	++	++	−
$\mathbf{V_e(C)}$	++	++	++	++	++	++	++	++	++
$\mathbf{V_f(C)}$	++	++	++	++	++	++	++	++	++
$\mathbf{VI_a(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VI_b(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VI_c(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VI_d(H)}$	+	+	−	++	+	+	−	−	−
$\mathbf{VI_e(H)}$	+ −	−	−	−	−	S	−	−	−
$\mathbf{VI_f(H)}$	++	++	++	+	+	+	+	−	+
$\mathbf{VII_a(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VII_b(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VII_c(H)}$	−	−	−	−	+	−	−	−	−
$\mathbf{VII_d(H)}$	++	+	++	+	+	+	+ −	−	−
$\mathbf{VII_e(H)}$	+	+	+	+	+	+	+	−	−
$\mathbf{VII_f(H)}$	++	++	+	+	+	++	++	++	++
$\mathbf{VIII_{a-c}(H)}$	−	−	−	−	−	−	−	−	−
$\mathbf{VIII_d(H)}$	+	−	−	−	+	+	−	−	−
$\mathbf{VIII_e(H)}$	+	−	−	−	+	−	−	−	−
$\mathbf{VIII_f(H)}$	++	+	++	+	+	+	+	−	−

Qualitative solubility was determined with 10 mg of polymer in 1 ml of solvent. ++ = Soluble at room temperature; + = soluble on heating; + − = partial soluble on heating; S = swelling; − = insoluble even on heating.

[a] DMSO:dimethylsulfoxide; Py: pyridine; THF: tetrahydrofuran.

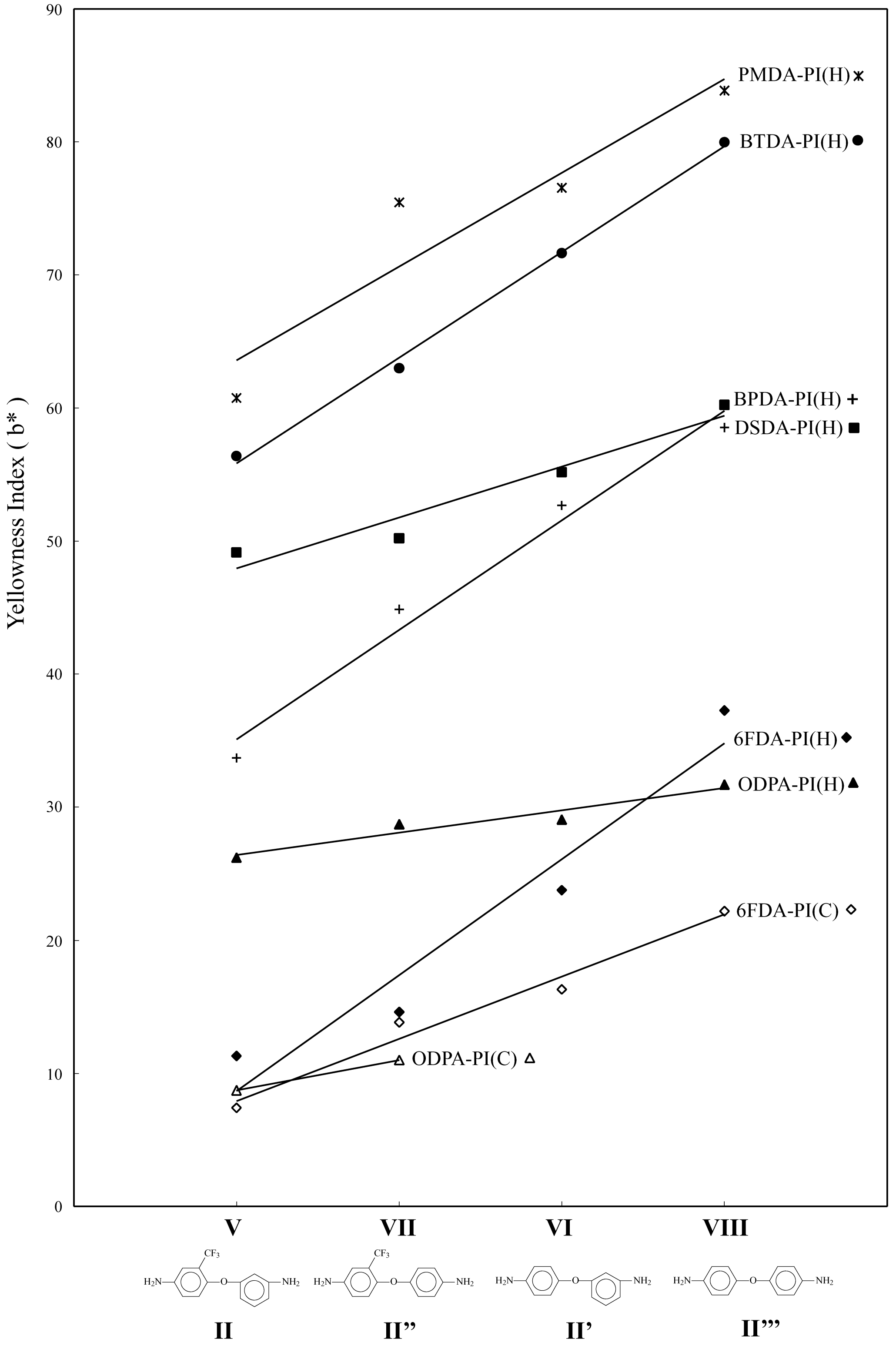


Fig. 4. Comparison of the yellowness index (b^* value) between polyimides **V**, **VI**, **VII**, **VIII**.

summarized in Table 5. Films $\mathbf{V_{a-f}(H)}$ had strengths at break of 124–147 MPa, elongations to break of 9–65%, and initial moduli of 2.3–2.8 GPa. $\mathbf{V_a(H)}$, $\mathbf{V_c(H)}$ and $\mathbf{V_e(H)}$ showed distinct yield points on stress–strain curves and moderate elongations to break, indicating of high toughness.

Films $\mathbf{V_{b-f}(C)}$ had strengths at break of 100–132 MPa, elongations to break of 8–10%, and initial moduli of 2.0–2.6 GPa. From the comparison of $\mathbf{V_{a-f}(H)}$ and $\mathbf{V_{b-f}(C)}$, both kinds showed similar mechanical properties, but thermal imidized polyimides had higher values.

Table 5
Tensile properties of polyimide films

Polymer code[a]	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
V_a(H)	127	124	65	2.3
V_b(H)	–	147	10	2.8
V_c(H)	143	137	40	2.6
V_d(H)	–	129	9	2.5
V_e(H)	141	132	36	2.6
V_f(H)	–	131	9	2.6
$V_{a/e}$(H)	129	126	42	2.3
V_b(C)	–	132	10	2.4
V_c(C)	–	118	8	2.6
V_d(C)	–	100	10	2.0
V_e(C)	–	107	8	2.0
V_f(C)	–	118	9	2.2
$V_{a/e}$(C)	140	136	40	2.6

[a] (H): Polyimides were obtained by the thermal imidization method. (C): Polyimides were obtained by the chemical imidization method.

Though **V_a(C)** had the same degree of polymerization as **V_a(H)**. But **V_a(C)** was brittle after turning into a film, we used copolyimide to improve its mechanical properties. Copolyimides **$V_{a/e}$(H)** and **$V_{a/e}$(C)** also showed good mechanical properties, indicating that the strength and toughness of these films were not affected by copolymerization. They had strengths at yield of 129 and 140 MPa, strengths at break of 126 and 136 MPa, elongations to break of 42 and 40%, and initial moduli of 2.3 and 2.6 GPa.

3.6. Thermal properties

The thermal properties of **V_{a-f}** were evaluated by thermogravimetry (TG) and DSC. The thermal behavior data of all polymers are listed in Table 6.

DSC experiments rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the glass transition temperatures (T_g), of all the polyimides could be easily read in the subsequent DSC heating trace. The T_g values of these polyimides **V_{a-f}** were in the 234–313 °C range, depending on the structure of the dianhydride component, and decreased with the increase in the flexibility of the polymer backbones. As expected, the polyimide (**V_e**) obtained from ODPA showed the lowest T_g because of the presence of a flexible ether linkage between the phthalimide units, and the polyimide (**V_a**) derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit.

The thermal stability of the polyimides **V_{a-f}** was evaluated by dynamic TGA conducted at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA thermograms. The T_{10} values of these polyimides stayed in the range of 515–604 °C in nitrogen and in the range of 545–596 °C in air. They left more than 50% char yield at 800 °C in nitrogen. BPDA polyimide **V_c** containing rigid biphenyl moiety had the highest T_{10} and char yield. DSDA-bearing **V_d** showed a higher T_{10} in air than in nitrogen, and this might be due to the antioxidating actions of the sulfonyl group.

Table 6
Thermal properties of polyimides

Ploymer[a]	T_g (°C)[b]	T_{10} (°C)[c]		Char yield(%)[d]
		In N_2	In air	
V_a	313	596	580	50
V_b	252	586	575	57
V_c	270	604	596	60
V_d	271	515	546	51
V_e	234	591	584	57
V_f	262	555	545	52

[a] Polyimides were obtained by the thermal imidization method.
[b] Baseline shift in the second heating DSC traces, with a heating rate of 15 °C/min.
[c] Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.
[d] Residual weight (%) when heated to 800 °C in nitrogen.

3.7. Dielectric constants and moisture absorption

The dielectric constants results list in Table 7. The fluorinated polyimides **V_{a-f}** showed lower dielectric constants (2.85–3.64 at 1 kHz) than the non-fluorinated polyimides **VI_{a-f}** (3.24–4.41 at 1 kHz). The decreased dielectric constants might be attributed to the presence of bulky 3F groups, which resulted in less efficient chain packing and an increase in the free volume. And the strong electronegativity of fluorine resulted in very low polarizability of the C–F bonds, thereby decreasing the dielectric constant. Polyimides **V_{a-f}** had a lower dielectric constant than commercial polyimides such as kapton films (3.97 at 1 MHz). Besides, the 6FDA derived polyimides **V_f** and **VI_f** exhibited the lowest dielectric constants in two series due to the larger free volume of the CF_3 group.

The moisture absorption of series **V** is summarized in Table 7. The polyimides **V_{a-f}** exhibited lower moisture

Table 7
Moisture absorption and dielectric constants of polyimides

Polymer[a]	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (dry)			
			1 kHz	10 kHz	1 MHz	40 MHz
$\mathbf{V_a}$	32	0.4	3.37	3.34	3.23	3.20
$\mathbf{V_b}$	50	0.32	3.64	3.65	3.50	3.50
$\mathbf{V_c}$	37	0.30	3.45	3.43	3.35	3.20
$\mathbf{V_d}$	38	0.31	3.62	3.60	3.46	3.45
$\mathbf{V_e}$	72	0.26	3.40	3.38	3.30	3.33
$\mathbf{V_f}$	36	0.18	2.85	2.83	2.78	2.80
$\mathbf{VI_a}$	21	0.89	3.52	3.50	3.41	3.41
$\mathbf{VI_b}$	73	0.43	4.37	4.33	4.20	4.18
$\mathbf{VI_c}$	34	0.56	3.68	3.64	3.55	3.55
$\mathbf{VI_d}$	64	0.82	4.41	4.36	4.22	4.16
$\mathbf{VI_e}$	60	0.73	3.67	3.65	3.55	3.55
$\mathbf{VI_f}$	73	0.55	3.32	3.29	3.22	3.22
Kapton	28	0.52	3.89	3.85	3.97	3.69

[a] Polyimides were obtained by the thermal imidization method.

absorptions (0.14–0.44%) than the corresponding non-fluorinated homologs $\mathbf{VI_{a-f}}$ (0.55–0.89%) as a result of the hydrophobicity of the CF_3 group. Moreover, polyimides $\mathbf{V_f}$ and $\mathbf{VI_f}$ exhibited the lowest moisture in the two series due to the higher fluorine content in the repeat unit.

4. Conclusions

3′-Trifluoromethyl-3,4′-oxydianiline (**II**) was prepared through the nucleophilic substitution reaction of 3-nitrophenol and 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate. By catalytic reduction with hydrazine, and Pd/C would be more colorless and high purity than from 3-aminophenol. A series of polyimides **V** was synthesized from diamine **II** with various aromatic dianhydrides via imidization. **V** series exhibited lighter colored, better solubility, good mechanical as well as thermal properties, lower dielectric constants and moisture absorption. On color intensities, four type PI from 3′-CF_3-3,4-ODA(**II**), 3,4-ODA (**II**′), 3-CF_3-4,4-ODA (**II**″), and 4,4-ODA (**II**‴) lowered in the following order is **V** > **VII** > **VI** > **VIII**. The methods of imidization affect the PI film color intensity. Chemical cyclodehydration showed lighter color than thermal one. Color also affected by solvent, using DMAc show lower color intensity than NMP.

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