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Colorless and high organosoluble polyimides from 2,5-bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride and aromatic bis(ether amine)s bearing pendent trifluoromethyl groups

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Abstract

A series of polyimides **III**$_{\mathbf{a-h}}$ characterized by colorlessness, high transparency, high solubility, and good mechanical property, was synthesized from the aromatic dianhydride, 2,5-bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride (I), and various aromatic diamines (**II**$_{\mathbf{a-h}}$) with pendent trifluoromethyl group via polyaddition, chemical imidization, and direct cast films. The **III** series showed more colorless than the polyimides (**V** and **VI** series) of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) contained, the **VI** series was synthesized from the **II** with 6FDA. These films **III** had cut-off wavelengths between 371 and 376 nm, as well as *b** value (a yellowness index) ranging from 3.0 to 4.7. In fact, it is so far the most colorless aromatic polyimide in our systematical researches. The **III** series had inherent viscosity ranging from 0.72 to 1.33 dL/g and showed excellent solubility in a variety of organic solvents. They were soluble in a concentration of 5–10% in the amide polar solvent, ether solvent, and chlorinated solvent. These films showed strength tensile of 97–123 MPa, dielectric constants of 2.78–3.28 (1 MHz), and moisture absorptions of 0.11–0.36 wt%. The glass transition temperature of the **III** series was recorded at 214–259 °C, the 10% weight loss temperature was over 468 °C, and the residue was more than 47% at 800 °C in nitrogen.

Keywords: 2,5-Bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride; High organosoluble; Colorless

1. Introduction

Aromatic polyimides are a kind of high performance polymer, that have excellent thermal stabilities, chemical resistance, electric properties and mainly used in the aerospace and electronic industries in the form of films and moldings [1,2]. Depending on the application, optical transparency of polyimide films is of special importance, such as flexible solar radiation protectors [3], orientation films in liquid crystal display devices [4], and optical half-waveplates for planar lightwave circuits [5]. However, most polyimides between UV and the visible area have strong absorption, rendering their color close to yellow or brown. In addition, they have poor processability in their imidized forms because of high softening temperatures and limited solubility.

By introducing the ether chain [6–8] or bulky group [9, 10], the aromatic polyimide can raise the flexibility of polymer, reduce the melting point or the glass transition temperature, and modify solubility while maintaining the thermomechanical properties. For optical applications, a number of very lightly colored to colorless transparent polyimide films have been synthesized and characterized. The optically transparent and colorless polyimides (**V** series) could be synthesized from a dianhydride and a diamine with the hexafluoroisopropylidene group [11]. In addition, a lowering the formation of the charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties provides polyimide with lighter colored [12]. It had been also proved that polyimide with trifluoromethyl or the ether group can enhance the solubility and thermal stability, reduce dielectric constant and moisture absorption, and raise the optical transparency [13–15].

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Our laboratory has been discussing the polyimides prepared from 2,5-bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride (**I**) [16,17], one kind of organosoluble, lower colored, and thermostable material. In this study, polyimides $\mathbf{III_{a-h}}$ were synthesized from **I** with CF_3-contained diamines $\mathbf{II_{a-h}}$. We found that $\mathbf{III_{a-h}}$ were lighter-colored and even colorless. These polymers were investigated in terms of the color and optical transparency of film, solubility, and the mechanical, thermal, and dielectric properties.

2. Experimental

2.1. Materials

Aromatic dianhydride, 2,5-bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride (**I**), was synthesized from *tert*-butylhydroquinone (*t*-BHQ; TCI) and 4-nitrophthalodinitrile (TCI). Acetonitrile (ALPS), *N*,*N*-dimethyl formamide (DMF; Fluka), and acetic anhydride (Ac_2O; Fluka) were used as received. The fluorinated aromatic diamines were synthesized from 2-chloro-5-nitrobenzotrifluoride (Acros) with bisphenols. 1,4-Hydroquinone (Acros), 4,4′-biphenyl (TCI), 3,3′,5,5′-tetramethyl-4,4′-biphenyl (Mitsubishi Petrochemical Co., Japan), 2,5-di-*tert*-butylhydroquinone (Acros), 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A; Acros), 2,2-bis(4-hydroxyphenol)hexafluoropropane (6F-bisphenol-A; Asahi glass Co., Ltd) and 9,9-bis(4-hydroxyphenyl)fluorene (Acros) were used as received. Other solvents included *N*-methy-2-pyrrolidone (NMP; Fluka), *N*,*N*-dimethylacetamide (DMAc; Fluka), and pyridine (Py; Wako).

2.2. Synthesis of 2,5-bis(3,4-dicarboxyphenoxy)-t-butylbenzene dianhydride (I)

Based on the literature [16,17], *t*-BHQ and 4-nitrophthalodinitrile were dissolved in the DMF with potassium carbonate to synthesize bis(ether dinitrile) at room temperature, and then were hydrolyzed to produce bis(ether diacid) before finally adding acetie anhydride to form bis(ether-dianhydride) monomer **I**, yield: 88%, mp: 211–213 °C.

2.3. Synthesis of aromatic bis(ether amine)s bearing pendent trifluoromethyl groups

Take 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene ($\mathbf{II_a}$) as an example. 1,4-Hydroquinone 20 mmol was dissolved in 20 ml of DMAc. Then, 2-chloro-5-nitrotrifluoromethylbenzene 40.5 mmol and potassium carbonate 35 mmol were added, and the mixture was heated at 110 °C for 12 h. The mixture was allowed to cool and poured into methanol/water (volume ratio of 10/1) to give a solid, which was collected, washed thoroughly with hot water and methanol, and dried, under vacuum. The crude product was recrystallized from DMF/CH_3OH to give di(ether-nitro)-compound 1,4-bis(4-nitro-2-trifluoromethylphenoxy)benzene ($\mathbf{II'_a}$) 9.3 g (yield: 95%, mp: 221 °C) ([18] mp: 216 °C). $\mathbf{II'_a}$ and Pd/C (10%) 0.18 g were mixed in ethanol (100 ml), and hydrazine monohydrate 60 mmol was added to the stirred mixture at 80 °C until the evolution of nitrogen had ceased. The filtrate was then condensed to remove the solvent. The crude product was purified by recrystallization from ethanol to give white crystals 7.64 g ($\mathbf{II_a}$), yield: 93.5%, mp: 132–133 °C ([18] mp: 133.9 °C) ([19] mp: 126 °C). Elem. Anal. Calcd for $C_{20}H_{14}N_2O_2F_6$ (428.33): C, 56.08%; H, 3.29%; N, 6.54%. Found: C, 56.21%; H, 3.32%; N, 6.55%.

Other bis(ether-amine)s: 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl ($\mathbf{II_b}$) [20], 4,4-bis(4-amino-2-trifluoromethylphenoxy)-3,3′5,5′-tetramethylbiphenyl ($\mathbf{II_c}$) [21], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene ($\mathbf{II_d}$), 1,4-bis[4-amino-2-trifluoromethylphenoxy]-2,5-di-*tert*-butylbenzene ($\mathbf{II_e}$) [22], 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane ($\mathbf{II_f}$) [23], 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane ($\mathbf{II_g}$) [24], 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene ($\mathbf{II_h}$) [25] were prepared in an analogous manner.

2.4. Synthesis of polyimide

Diamine $\mathbf{II_a}$ (0.343 g, 0.8 mmol) was dissolved in 5.5 mL of dried DMAc. After diamine $\mathbf{II_a}$ was completely dissolved, dianhydride I (0.366 g, 0.8 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to obtain poly(amic acid) (PAA) solution. Then a 0.8 mL mixture of Ac_2O and pyridine (the volume ratio 2:1) was added to the PAA solution. The PAA solution was imidized by stirring in oil bath at 80 °C for 1 h, and then the solution was spread on a glass plate and placed in an 80–100 °C oven for 1 h to remove the solvent. Finally, the solution was sequentially heated from 100 to 250 °C at the rate of 20 °C/10 min and 250 °C for 30 min to remove the residual solvent. By soaking in water, a flexible polyimide film of $\mathbf{III_a}$ was self-stripped off the glass surface. Inherent viscosity of $\mathbf{III_a}$ was 0.78 dL/g in DMAc at a 0.5 g/dL concentration at 30 °C.

The typical IR spectrum of $\mathbf{III_a}$ is shown in Fig. 1. As the PAA was converted into the polyimide, the characteristic absorption bands of the imide ring were observed near 1778 (asymmetric C=O stretch) and 1725 (symmetric imide C=O stretch). Others were 1612–1486 (aromatic C=C stretch), 1376 (C–N stretching), 1245 (C–O), 1087, 742 cm^{-1} (imide ring deformation) and some stronger peak of C–O and C–F stretching were in the range 1100–1300 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.98 (2H, s, $H_{c,h}$), 7.91 (2H, s, $H_{a,g}$), 7.72, 7.70 (2H, d, $H_{j,j'}$), 7.50, 7.48 (3H, d, $H_{l,l',i}$), 7.41 (1H, s, H_b), 7.25, 7.23 (2H, s, $H_{m,f}$), 7.21 (2H, d, $H_{k,k'}$), 7.11 (2H, s, $H_{d,e}$), 1.33 (1H, s, H_n). ^{13}C

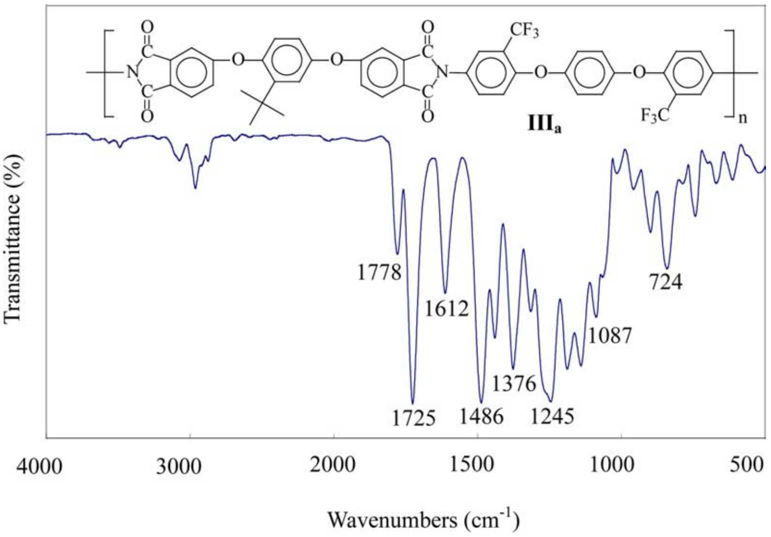


Fig. 1. FTIR spectra of polyimide **III_a**.

NMR (100 MHz, DMSO-d_6, δ, ppm): 166.1, 166.0 ($C^{27,27',27'',27'''}$), 163.0 ($C^{3,13}$), 162.7 (C^{25}), 154.4 (C^{10}), 151.9 (C^{22}), 151.4 (C^{7}), 150.0 (C^{12}), 143.8 (C^{19}), 134.4, 134.2 ($C^{1.,15}$), 133.28 ($C^{5,17}$), 126.7 (C^{24}), 126.2, 126.0 ($C^{6,16}$), 125.5, 125.2 ($C^{4,18}$), 123.4 (C^{23}), 123.0, 122.7 ($C^{2,14}$), 122.9 (C^{28}, quartet, ${}^{1}J_{C\text{–}F}=273$ Hz), 121.6 (C^{26}), 119.7 (C^{8}), 119.3 (C^{21}, doublet, ${}^{2}J_{C\text{–}F}=31$ Hz), 119.1 (C^{20}), 111.8 (C^{9}), 111.3 (C^{11}), 34.62, 34.45 (C^{29}), 30.63, 29.75 (C^{30}) (Fig. 2).

NMR for **III_g**: ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.94–7.98 (2H, t, $H_{c,c'}$), 7.82, 781 (2H, d, $H_{a,a'}$), 7.6–7.62 (2H, dd, $H_{b,b'}$), 7.50 (2H, s, H_g), 7.41–7.45 (6H, $H_{k,h}$), 7.26 (1H, s, H_f), 7.17, 7.15 (2H, d, $H_{d,e}$), 7.11, 7.10 (4H, d, H_j), 6.99 (2H, s, H_i), 1.40, 1.37 (9H, H_l). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 166.2–166.1 ($C^{30,30',30'',30'''}$), 163.8, 163.7 ($C^{3,13}$), 156.7 (C^{25}), 153.7 (C^{22}), 151.5 (C^{10}), 150.7 (C^{7}), 144.8 (C^{28}), 134.1 ($C^{12,24}$), 132.0 (C^{27}), 131.2 (C^{19}), 129.0 (C^{20}), 127 ($C^{5,17}$), 126.1 ($C^{1,15}$), 125.5 ($C^{4,18}$), 124.9 ($C^{6,16}$), 123.3 (C^{23}), 123.2 (C^{31}, quartet, ${}^{1}J_{C\text{–}F}=272$ Hz), 123.1 (C^{8}), 122.4 (C^{21}, quartet, ${}^{2}J_{C\text{–}F}=32$ Hz), 121.1 (C^{32}, quartet, ${}^{1}J_{C\text{–}F}=272$ Hz), 118.4 (C^{29}, doublet, ${}^{2}J_{C\text{–}F}=32$ Hz), 118.7 (C^{26}), 112.3, 112.1 ($C^{9,11}$), 35.13, 35.07 (C^{33}), 30 (C^{34}) (Fig. 3).

Polyimides **$III_{b\text{–}g}$** were synthesized in a similar manner. The elemental analysis results are shown in Table 1.

2.5. Measurements

IR spectra were recorded on a Horiba Fourier-transform infrared spectrometer FT-720 (FTIR). Elemental analyses were run on a Perkin–Elmer model 2400 CHN analyzer. Weight-average molecular weights ($\bar{M}_w$'s) and number-average molecular weights ($\bar{M}_n$'s) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT NMR spectrometer. Inherent viscosities were determined at 0.5 g/dL concentration with an Ubbelohde viscometer at 30 °C. Color intensity of the polymers was evaluated on a Macbeth color-eye colorimeter. Measurements were performed with films, 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 films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. 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 30–60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 9–11 mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20 °C/min. The differential scanning calorimetry (DSC) analyses were measured on a TA Instruments DSC 2010 at a heating rate of 15 °C/min in flowing nitrogen (40 cm^3/min). The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric 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 the weighing of 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. Polymer synthesis

Polyimides **$III_{a\text{–}h}$** were synthesized from dianhydride **I**

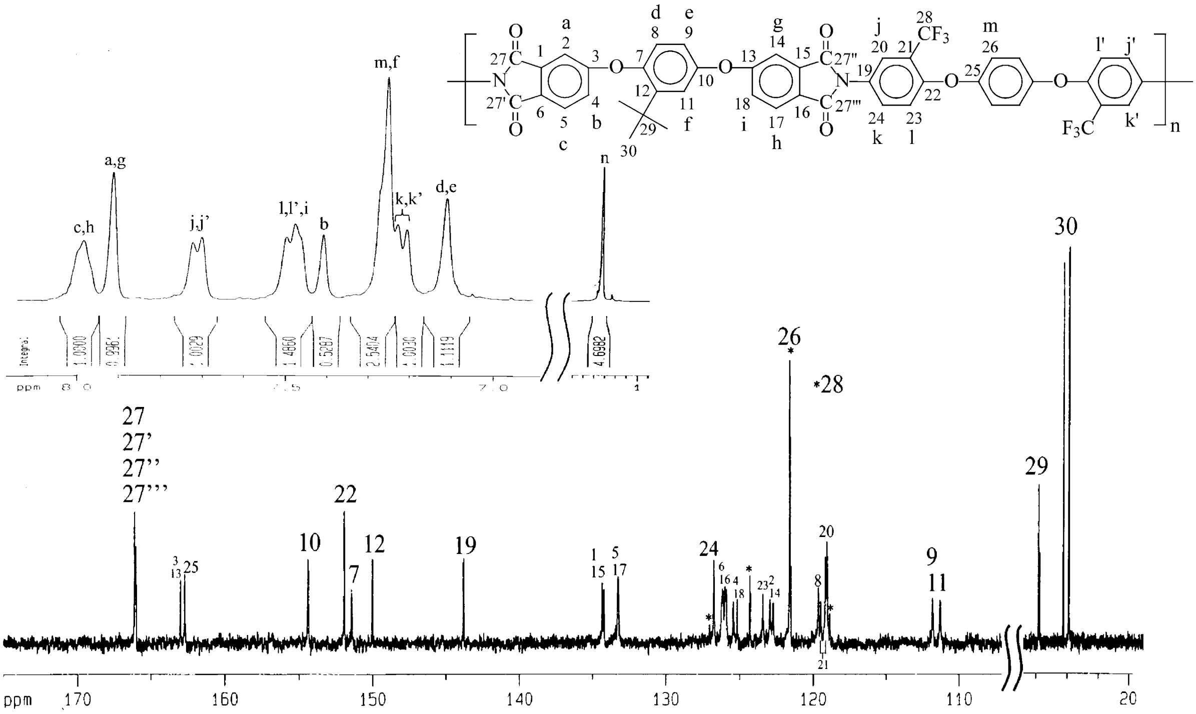


Fig. 2. The ^{1}H and ^{13}C spectra of polyimide $\mathbf{III_a}$ in DMSO-d_6.

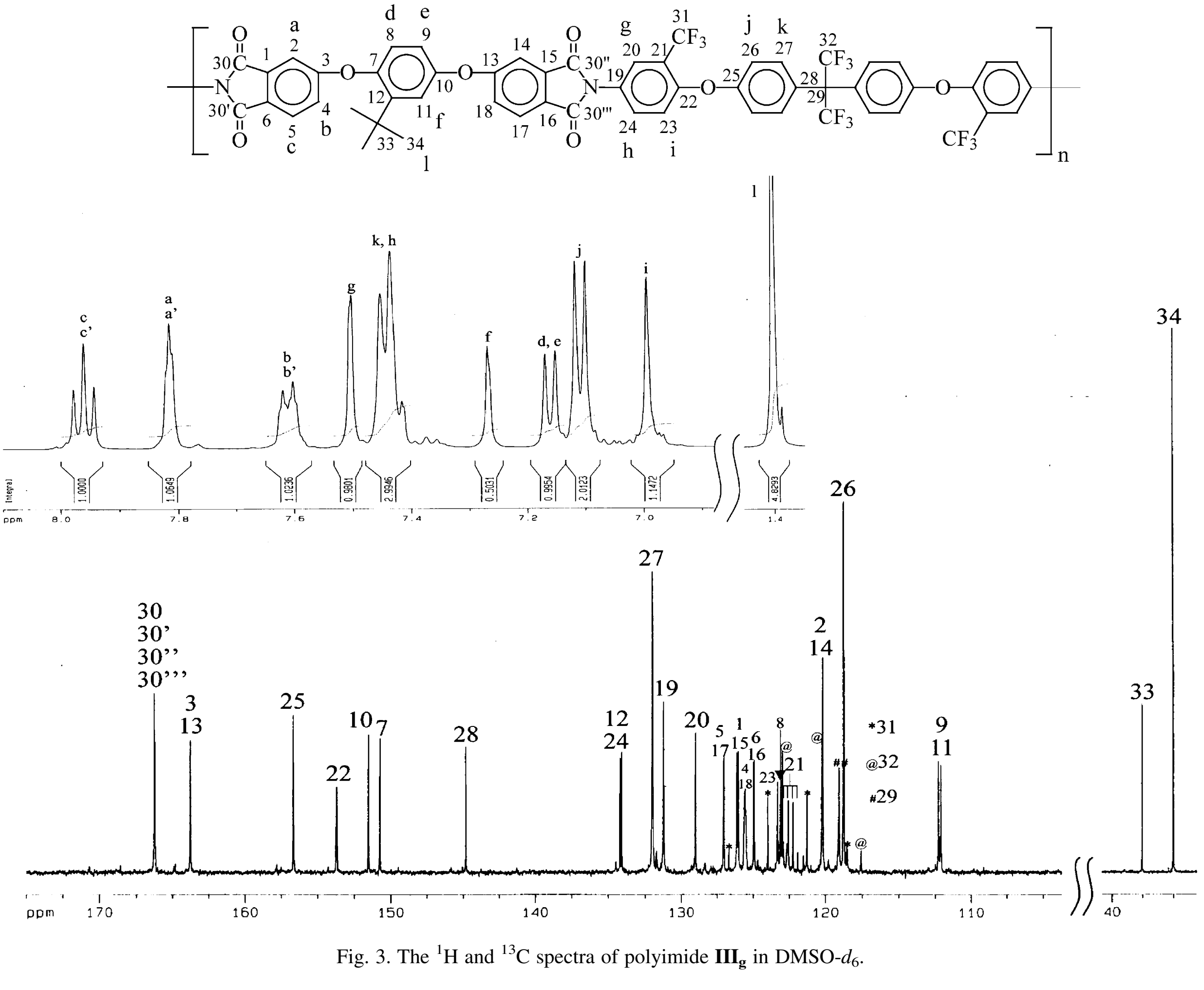


Fig. 3. The ^{1}H and ^{13}C spectra of polyimide $\mathbf{III_g}$ in DMSO-d_6.

Table 1
Elemental analysis of polyimides **III**

Polymer code	Formula of PEI (formula weight)		C	H	N
III$_a$	$(C_{46}H_{28}F_6N_2O_8)_n$	Calcd	64.95	3.32	3.29
	$(850.73)_n$	Found	64.63	3.24	3.22
III$_b$	$(C_{52}H_{32}F_6N_2O_8)_n$	Calcd	67.39	3.48	3.02
	$(926.83)_n$	Found	67.18	3.37	2.92
III$_c$	$(C_{56}H_{40}F_6N_2O_8)_n$	Calcd	68.43	4.10	2.85
	$(982.93)_n$	Found	68.17	4.10	2.85
III$_d$	$(C_{50}H_{36}F_6N_2O_8)_n$	Calcd	66.22	4.00	3.09
	$(906.83)_n$	Found	66.17	3.89	3.00
III$_e$	$(C_{54}H_{44}F_6N_2O_8)_n$	Calcd	67.36	4.61	2.91
	$(962.94)_n$	Found	67.17	4.59	2.81
III$_f$	$(C_{55}H_{38}F_6N_2O_8)_n$	Calcd	68.18	3.95	2.89
	$(968.91)_n$	Found	68.07	3.82	2.77
III$_g$	$(C_{55}H_{32}F_{12}N_2O_8)_n$	Calcd	61.35	3.00	2.60
	$(1076.85)_n$	Found	60.39	2.92	2.49
III$_h$	$(C_{65}H_{40}F_6N_2O_8)_n$	Calcd	71.56	3.70	2.57
	$(1091.03)_n$	Found	71.32	3.66	3.51

and various CF_3-contained bis(ether-amine)s **II$_{a\text{–}h}$** via a conventional two-step procedure of ring-opening polyaddition at room temperature to form PAA, followed imidization by a mixture of Ac_2O/Py to obtain the corresponding polymers, as shown in Scheme 1. The **III** series had inherent viscosity ranging from 0.72 to 1.33 dL/g. The elemental analysis of **III$_{a\text{–}h}$** is listed in Table 1, showing that the measured values are close to the calculated ones. The GPC curves of the **III** series indicated that the $\bar{M}_w$ and $\bar{M}_n$ values were available in the range of $7.19\times10^4-10.6\times10^4$ and $4.70\times10^4-9.62\times10^4$, respectively, relative to polystyrene standard. The polydispersity index (PDI) $\bar{M}_w/\bar{M}_n$ values of the **III** series were 1.3–1.5 (Table 2). ^1H and ^{13}C NMR spectra of **III$_a$** are shown in Fig. 2. In case of ^1H NMR spectrum, all the aromatic protons of **III$_a$** resonated in the region of 7.11–7.98 ppm and H_h of the *t*-butyl group appeared in upfield. $H_{c,h}$ close to the imide ring appeared at the farthest downfield, and H_b, $H_{m,f}$, $H_{k,k'}$ and $H_{d,e}$ shifted to a higher field due to the electron donating property of aromatic ether. In case of ^{13}C NMR spectrum, there should be 30 peaks for **III$_a$**, but the carbon C^3 overlapping with C^{15} and C^5 overlapping with C^{17}, 28 main signals appeared and the number of C was still consistent with the structure. The aromatic carbons $C^{22,22',22'',22'''}$ were carbonyl group and evidenced in the downfield. The one-carbon C–F coupling constant in this case was 273 Hz of the carbon C^{28} of the hexafluoroisopropylidene group. The CF_3-attached carbon (C^{21}) also showed a quartet centered at about 120 ppm with a smaller coupling constant of about 31 Hz due to the two-bond C–F coupling.

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

Polymer code/η_{inh} (dL/g)		GPC data of poly(ether-imide)s[a]		
PEI	η_{inh}[b] (dL/g)	$\bar{M}_n\times10^4$	$\bar{M}_w\times10^4$	$\bar{M}_w/\bar{M}_n$
III$_a$	0.78	7.31	9.84	1.4
III$_b$	1.16	8.40	10.60	1.3
III$_c$	1.33	7.67	10.06	1.3
III$_d$	0.79	5.91	8.48	1.4
III$_e$	0.75	6.80	9.34	1.4
III$_f$	0.79	7.42	9.75	1.3
III$_g$	0.72	4.70	7.19	1.5
III$_h$	0.73	6.79	9.14	1.4

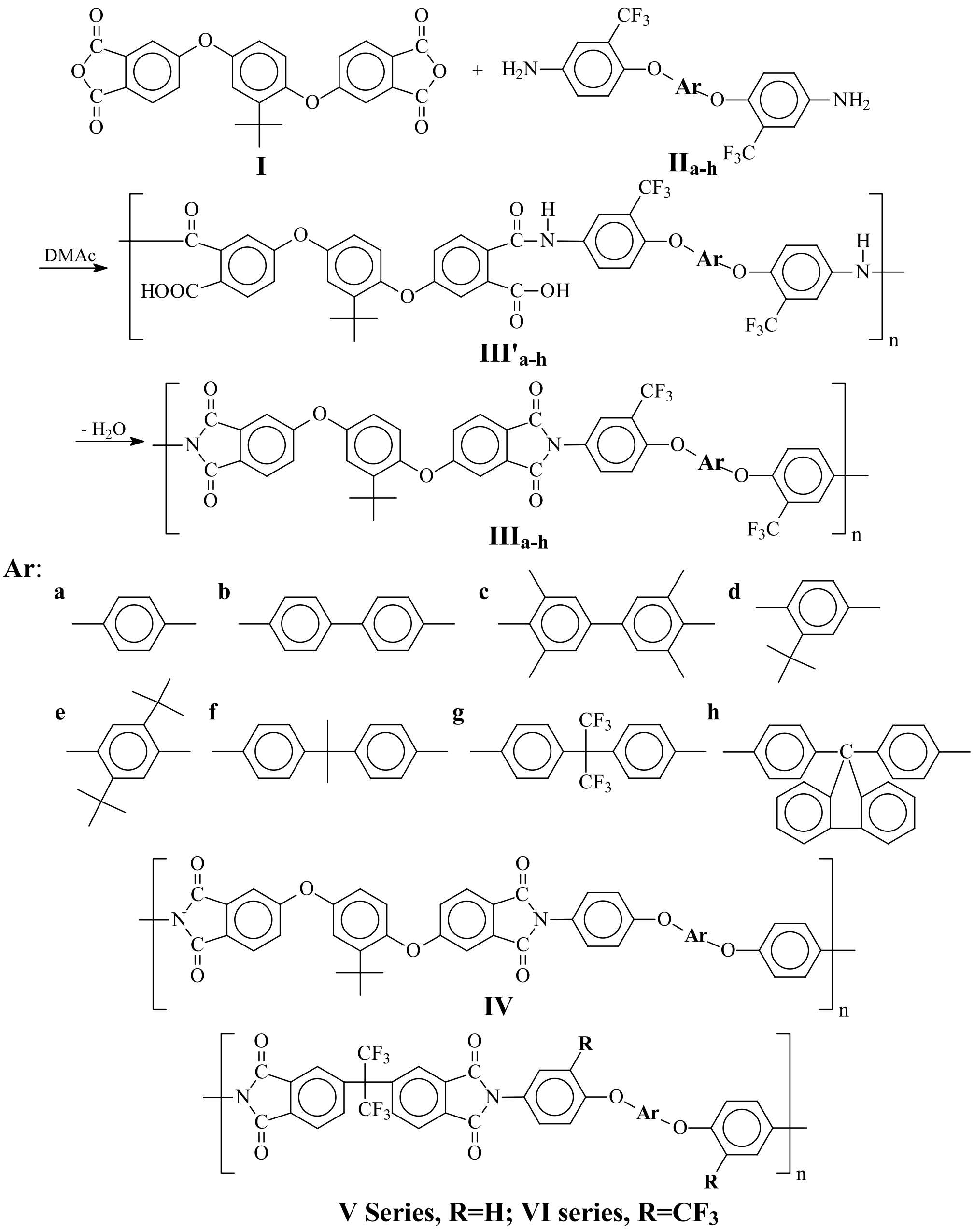
[a] Relative to polystyrene standard, using THF as the eluent.

[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

Fig. 3 shows ^1H and ^{13}C NMR spectra of **III$_g$**. All the aromatic protons of **III$_g$** resonated in the region of 6.99–7.98 ppm. Like **III$_a$**, the H_h of the *t*-butyl group appeared in upfield and the $H_{c,c'}$ is at the farthest downfield, and H_f, $H_{d,e}$, H_j, and H_i in a higher field. There are 34 main peaks for **III$_g$** in ^{13}C NMR spectrum and the number of carbons was conformed to **III$_g$**. The aromatic carbons $C^{30,30',30'',30'''}$ were carbonyl group and evidenced in the downfield. The C^{31} and C^{32} showed clear quartet and the one-carbon C–F coupling constants were 272 Hz. The CF_3-attached carbon C^{21} and C^{29} also showed a quartet centered with a smaller coupling constant of about 32 Hz due to the two-bond C–F coupling. The above-cited results evidence that the **III** series has been synthesized successfully.

3.2. Properties of polymer

The color intensities of the polymer were elucidated from the yellowness (b^*), redness (a^*) and lightness (L^*) indices observed by a Macbeth color-eye colorimeter. In this case, we base our judgment of the degree of yellowness on the b^* value. Table 3 shows that all polyimides **III$_{a\text{–}h}$** with a lower b^* value range from 3.0 to 4.7. The insignificant difference of b^* value in the **III** series arose from either the purity and colorness of diamines or the thickness of polyimide films. Polyimide film would be lighter-colored while the purity of



Scheme 1. Synthesis of polyimides.

monomer was higher, and the color intensity of monomer was lower, or the thickness of polymer film was thinner. As for the influence on color by the chemical or thermal imidization method, the former can avoids oxidization in the air and thus reduces *b** value, such that **III$_a$(C)** is lower than **III$_a$(H)** by 2.2. However, it is not obvious influence on imidization methods in the **III** series. Contrasting the *b** value of the **III** series and common polyimide, Kapton based on PMDA or light-colored polyimide-**V** series based on 6FDA, the *b** value of the **V** series ranging 24.3–33.7 is much smaller than that of Kapton which shows deep yellow to brown. Our laboratory has reported that *b** values were in the range of 6.4–21.2 for the polyimide-**IV** series [26] in 1999, which was much lighter in color than the **V** series. Recently, the diamine with the pendent CF_3 groups and the commercially aromatic dianhydrides was synthesized into fluorinated polyimide [20–25]. One of them was based on 6FDA to form the poylimide VI series, whose *b** values were in the range of 5.4–17.6 and much lighter in color than the **IV** and **V** series. In this study, we synthesized the **III** series, whose *b** values were smaller than the **VI** series'. Fig. 4 shows the comparing results of the **III** and **VI** series. As above-mentioned, the **III** series was the lightest color polyimide. Its degree of colorlessness is almost as the same as that of polyarylate, and was even close to the optical transparency of aliphatic PMMA. The **III** series also shows

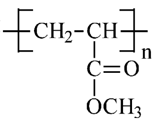
Table 3
Color coordinates and the cut-off wavelength (λ_0) from UV–vis spectra polyimides films

Polymer code	Film thickness (μm)	Color coordinates[a]			λ_0 (nm)	Ref.
		b^*	a^*	L^*		
REF. STD		0.09	−0.02	100.0		
PMMA[b,c]	53	1.2	−0.5	100.0		
Polyarylate[c]	51	3.3	−0.77	98.9		
$\mathbf{III_a}$	36	3.1	−1.7	99.7	374	
$\mathbf{III_b}$	48	3.8	−1.9	99.9	374	
$\mathbf{III_c}$	46	3.6	−1.8	99.8	372	
$\mathbf{III_d}$	63	4.7	−2.0	99.5	376	
$\mathbf{III_e}$	60	4.5	−2.3	99.9	375	
$\mathbf{III_f}$	46	3.1	−1.6	99.8	372	
$\mathbf{III_g}$	62	3.0	−1.5	99.8	371	
$\mathbf{III_h}$	65	3.3	−1.7	99.8	372	
$\mathbf{III_a(H)}$[b]	43	5.3	−2.0	98.4	375	
$\mathbf{IV_a}$		9.85	−5.25	95.9		18
$\mathbf{IV_c}$		21.2	−8.39	94.8		18
$\mathbf{IV_d}$		6.43	−4.16	96.3		18
$\mathbf{IV_f}$		15.4	−2.01	92.0		18
$\mathbf{V_a}$	76	28.7	−10.2	95.0	393	
$\mathbf{V_c}$	42	27.9	−10.6	95	388	
$\mathbf{V_f}$	42	24.3	−8.3	95.6	382	
$\mathbf{VI_b}$	39	14.7	−4.17	99.0	364	21
$\mathbf{VI_c}$	47	17.6	−6.61	99.6	373	22
$\mathbf{VI_d}$	23	7.1	−2.9	99.9	346	
$\mathbf{VI_f}$	36	11.1	−3.8	99.5	365	24
$\mathbf{VI_g}$	25	5.4	−1.9	100.1	343	25
$\mathbf{VI_h}$	38	6.1	−3.2	99.8	348	26
Kapton[c]	38	85.1	0.3	90.1	443	

[a] L^* is lightness. 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.

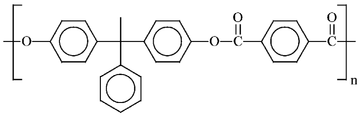
[b] $\mathbf{III_a(H)}$ were obtained by the thermal imidization method with DMAc as solvent. PMMA were obtained with MIBK as solvent.

[c] **PMMA**:

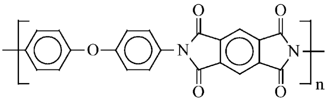


$\left[CH_2-CH(C{=}O)(OCH_3)\right]_n$

; **Polyarylate**:



Kapton:



higher lightness, and their L^* values are over than 99.5%, are lighter than polyarylate and even nearly to PMMA (100%). Moreover, the color intensity of the **III** series could also be elucidated from the cut-off (λ_0) observed in UV–vis absorption spectra. In general, the polyimides are derived from 6FDA (**V** series) with good transmittance than others polyimide already. However, in this study, the λ_0 of the **III** series in the range of 371–376 nm are listed in Table 3. And Fig. 5 shows the UV–vis spectra of the **III** series, which show that the **III** series is the kind of polyimide with high transmittances and are even higher than the **V** series' and kapton's.

To summarize, the colorlessness of the **III** series stems from the structures of dianhydride and diamine. The bis(ether anhydride) with the *t*-butyl group can avoids oxidization and coloration of film, and is effective in preventing the CTC formation between the polymer chain through steric hindrance. In the prior study, this dianhydride had been proven to form colorless polyimides [15]. And bis(ether amine) with the pendent CF_3 group also can reduces CTC formation to form colorless polyimides [21,22]. Therefore, the **III** series combines hindering from CTC formation and reducing oxidization in the synthesis to obtain colorless characteristic.

The solubility of these polymers was tested in various solvents, and the results are summarized in Table 4. $\mathbf{III_{a-h}}$ can be dissolved at 10 wt/v% concentration in the amide type solvents such as NMP, DMAc, and DMF. In dioxane and THF containing the ether group and chlorinated solvents of CH_2Cl_2 and $CHCl_3$, they are all soluble in a 5–10 wt/v% concentration. In the phenolic solvent like *m*-cresol and the basic solvent like Py, the **III** series is also soluble around 5–10 wt/v% concentration except $\mathbf{III_c}$, which swells in *m*-cresol. This series can also be dissolved in arene solvent, for example $\mathbf{III_{a,b,d}}$ and $\mathbf{III_g}$ were souble in toluene and xylene. The solubility of $\mathbf{III_{a-h}}$ is very different in DMSO and ketone solvent. $\mathbf{III_{a,d,e}}$ and $\mathbf{III_g}$ can be dissolved in MIBK, but others cannot. $\mathbf{III_{a,g,h}}$ can be dissolved in DMSO solvent at 10 wt/v% concentration, $\mathbf{III_{c,d,f}}$ can at 1 wt/v%. $\mathbf{III_{g,h}}$ showed the higher solubility

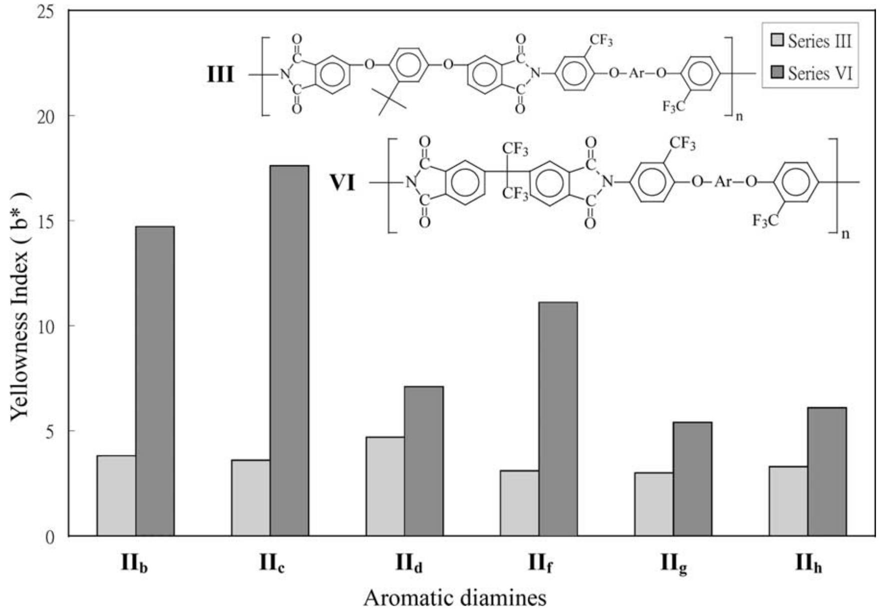


Fig. 4. Comparison of the yellowness index (b^* value) between polyimides **III** and **VI**.

than $\mathbf{III_f}$ in DMSO, it attributed to the bulky or asymmetric substitutive group. The 'Ar' with pare-phenylene of $\mathbf{III_{a,d,e}}$, in DMSO, the solubility is reduced as the *t*-butyl group increases, which is because of the aliphatic *t*-butyl group has difficulty dissolved in DMSO. However, the **III** series is insoluble in alcohol like MeOH and in alkane solvent like heptane. As mentioned above, the **III** series is one kind of highly soluble polyimide, a fact that is attributed to the diamines ($\mathbf{II_{a-h}}$), which contain two flexible phenoxy groups and bear the pendent CF_3 group. In addition, there is a *t*-butyl group and ether groups in the dianhydride (**I**), which can disorder the chains and hinder dense chain stacking, thereby reducing the interchain interactions to enhance solubility. $\mathbf{III_a}$ and $\mathbf{III_g}$ show the excellent solubility in the **III** series because of the more CF_3 group in the repeat unit.

The mechanical properties for all polymers are obtained in the form of thin films and are summarized in Table 5. $\mathbf{III_{a-h}}$ show a distinct yield point on the stress-strain curve, with the yield strength ranging between 103 and 110 MPa except for $\mathbf{III_{c,g,h}}$. These polymer films had strengths at break of 97–123 MPa, elongations to break of 10–56%, and initial moduli of 2.0–2.6 GPa. Although $\mathbf{III_b}$ contains rigid structure of biphenyl, which shows a yield point at 110 MPa, elongation is 18%, and the highest initial moduli of 2.6 GPa in the **III** series, reflecting that $\mathbf{III_b}$ has good

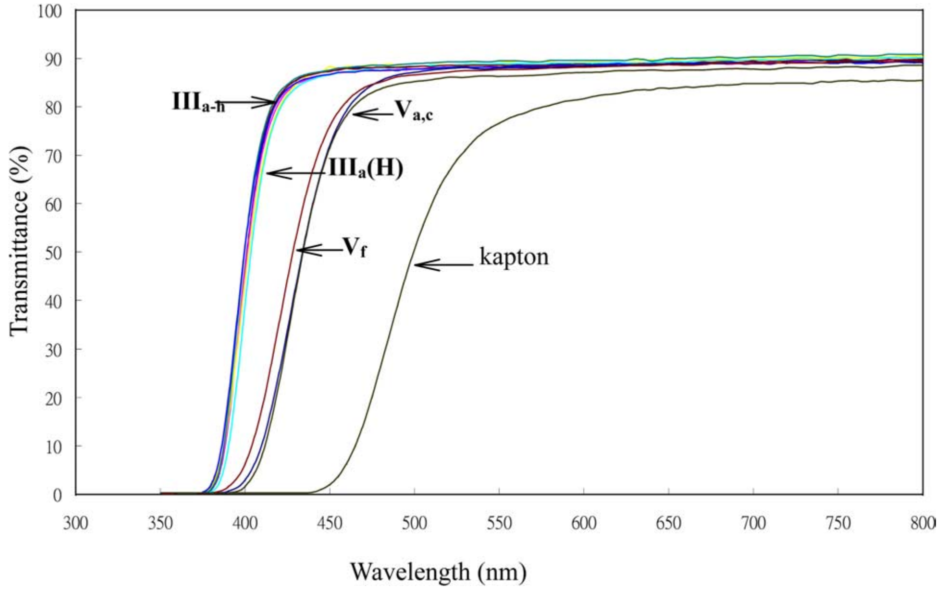


Fig. 5. UV–vis spectra of polyimide films $\mathbf{III_{a-h}}$, $\mathbf{III_a(H)}$, $\mathbf{V_{a,c,f}}$ and Kapton film.

Table 4
Solubility of polyimides **III**

Polymer Code	Solvent[b]											
	NMP DMAc DMF	DMSO	*m*-Cresol	Py	Dioxane	THF	CH_2Cl_2	$CHCl_3$	Aceton	MIBK	Toluene	Xylene	MeOH heptane
$\mathbf{III_a}$	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	−
$\mathbf{III_b}$	+++	−	++	+++	+++	++	+++	+++	S	−	−	−	−
$\mathbf{III_c}$	+++	+	S	++	++	+++	++	+++	−	−	++	S	−
$\mathbf{III_d}$	+++	+	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	−
$\mathbf{III_e}$	+++	−	++	++	++	++	+++	+++	++	+++	++	+++	−
$\mathbf{III_f}$	+++	+	++	+++	++	+++	+++	+++	−	−	++	S	−
$\mathbf{III_g}$	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	−
$\mathbf{III_h}$	+++	+++	+++	+++	+++	+++	+++	+++	−	−	+++	S	−

Qualitative solubility was determined with as: +++, 100 mg of polymer in 1 mL of solvent soluble (10%); ++, 5%; + = soluble, − = insoluble, S = swelling under 1%.

[b] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran; MIBK, methyl *iso*-butyl ketone.

Table 5
Tensile properties of polyimide films

Polymer code	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
$\mathbf{III_a}$	109	104	28	2.3
$\mathbf{III_b}$	110	107	18	2.6
$\mathbf{III_c}$	–	103	56	2.0
$\mathbf{III_d}$	103	97	16	2.1
$\mathbf{III_e}$	104	98	11	2.1
$\mathbf{III_f}$	108	99	19	2.2
$\mathbf{III_g}$	–	112	10	2.2
$\mathbf{III_h}$	–	123	11	2.4

flexibility. The properties are affected by the structure and molecular weight of the polymer; for instance, $\mathbf{III_c}$ shows the highest inherent viscosity and longest elongation.

The thermal behavior data of all polymers are listed in Table 6. DSC experiments rapidly cooled from 400 °C to room temperature produced predominantly amorphous samples, so the T_g of all the polyimide could be easily read in the subsequent DSC heating trace. The T_g values of these $\mathbf{III_{a–h}}$ were in the range of 214–259 °C, depending on the structure of the diamine component, and decreased with the increase in the flexibility of the polymer backbones. When the 'Ar' of the *p*-phenylene structures of $\mathbf{III_a}$, $\mathbf{III_d}$ and $\mathbf{III_e}$ are compared, the *t*-butyl group of $\mathbf{III_d}$ and $\mathbf{III_e}$ makes chain rotation difficulty than $\mathbf{III_a}$. Especially for the asymmetrical structure, $\mathbf{III_d}$ rotate more difficulty than the symmetrical $\mathbf{III_e}$. Thus, the T_g order is $\mathbf{III_d} > \mathbf{III_e} > \mathbf{III_a}$. When $\mathbf{III_b}$ is compared with $\mathbf{III_c}$, because $\mathbf{III_b}$ contain the rigid structure of biphenyl, the structure of $\mathbf{III_c}$ is looser as a result of the tetramethylbiphenyl. In this case, $\mathbf{III_c}$ shows lower T_g than $\mathbf{III_b}$ does. As the 'Ar' structure containing tetraphenylene-diether, $\mathbf{III_f}$, $\mathbf{III_g}$, and $\mathbf{III_h}$, $\mathbf{III_h}$ uneasily rotate by the asymmetrical bulky group, so the T_g of $\mathbf{III_h}$ is higher than $\mathbf{III_f}$ and $\mathbf{III_g}$.

The thermal stability of $\mathbf{III_{a–h}}$ 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

Table 6
Thermal properties of polyimides

Ploymer	T_g (°C)[a]	T_{10} (°C)[b]		Char yield (%)[c]
		In N_2	In air	
$\mathbf{III_a}$	224	509	497	56
$\mathbf{III_b}$	259	516	490	48
$\mathbf{III_c}$	226	468	527	58
$\mathbf{III_d}$	248	496	478	50
$\mathbf{III_e}$	234	494	485	47
$\mathbf{III_f}$	217	513	506	57
$\mathbf{III_g}$	214	523	516	56
$\mathbf{III_h}$	223	522	504	50

[a] Baseline shift in the second heating DSC traces, with a heating rate of 15 °C/min.

[b] Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.

[c] Residual weight (%) when heated to 800 °C in nitrogen.

Table 7
Moisture absorption and dielectric constants of polyimides

Polymer	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (Dry)			
			1 kHz	10 kHz	1 MHz	40 MHz
III_a	48	0.36	3.24	3.24	3.18	3.15
III_b	28	0.15	3.15	3.16	3.10	3.10
III_c	82	0.27	3.31	3.30	3.28	3.28
III_d	67	0.17	3.23	3.32	3.27	3.25
III_e	55	0.20	3.17	3.14	3.12	3.11
III_f	66	0.21	3.23	3.21	3.19	3.19
III_g	36	0.11	2.88	2.81	2.78	2.76
III_h	56	0.24	2.93	2.85	2.81	2.77
Kapton	28	0.52	3.89	3.85	3.67	3.69

atmospheres were determined from original TGA thermograms. The T_{10} values of these **III_{a-h}** were recorded in the range of 468–523 °C in nitrogen and 478–527 °C in air. They left more than 47% char yield at 800 °C in nitrogen. **III_c** with tetramethylbiphenyl and **$III_{d,e}$** with the *t*-butyl group show lower T_{10} in nitrogen, but others have values above 509 °C. Among the **III** series, **III_c** shows the lowest T_{10} in nitrogen but the highest one in the air. The side-chain with methyl group is decomposed easily by heating process. However, when **III_c** is heated in the air at high temperature, **III_c** will be easily oxidized to form a free radical, causing cross-linking between intermolecular and delaying the decomposition rate of the polymer.

The dielectric constants results and the moisture absorption of the **III** series are listed in Table 7. **III_{a-h}** showed dielectric constants in the range of 2.88–3.64 at 1 kHz lower than kapton. The decreased dielectric constants might be attributed to the presence of the CF_3 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. Therefore, **III_g** exhibited the lowest dielectric constants because the aromatic contained hexafluoroisopropylidene group and the higher fluorine content in the repeat unit. The **III_{a-h}** also exhibited lower moisture absorptions (0.11–0.36%) as a result of the hydrophobicity of the CF_3 group. Moreover, **III_g** exhibited the lowest moisture in the two series as the above dielectric constants part mentioned, because **III_g** contained the higher CF_3 group in the repeat unit.

4. Conclusions

A series of colorless polyimides **III_{a-h}** are synthesized from 2,5-bis(3,4-dicarboxyphenoxy)-*t*-butylbenzene dianhydride (**I**) with various aromatic bis(ether amine) (**II_{a-h}**) bearing the pendent trifluoromethyl group via a chemical imidization. The **III** series shows lighter color and greater transparence than the analogous non-fluorinated polyimides **IV** series and 6FDA-contained **V** series. The **III** series is even more colorless than **VI** series, which was synthesized from the bis(ether amine) **II** with 6FDA. The transparence of the **III** series is nearly to the well known of PMMA. In addition, the **III** series shows excellent solubility in the organic solvents. They were all soluble in the polar solvent such as NMP, DMAc, DMF, dioxane, THF and chlorinated-solvent of CH_2Cl_2 and $CHCl_3$ in 5–10 wt/v% concentration. The **III** series also shows good mechanical properties, thermal properties, lower dielectric constants and moisture absorptions.

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