Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 7021–7033
polymer
www.elsevier.com/locate/polymer

Highly optically transparent/low color polyimide films prepared from hydroquinone- or resorcinol-based bis(ether anhydride) and trifluoromethyl-containing bis(ether amine)s

Chin-Ping Yang[✠], Yu-Yang Su, Shiou-Jung Wen, Sheng-Huei Hsiao[*]

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, ROC

Received 29 May 2006; received in revised form 11 July 2006; accepted 15 July 2006
Available online 17 August 2006

Dedicated to Prof. Chin-Ping Yang, who cherished research and publications as his lifetime joys.

Abstract

Two series of novel polyimides (**5a–g** and **6a–g**) containing flexible ether linkages and pendent trifluoromethyl (CF_3) groups were synthesized from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**3a**) and 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**3b**) with various CF_3-substituted aromatic bis(ether amine)s (**4a–g**) via ring-opening polyaddition to poly(amic acid)s, followed by thermal or chemical imidization. These polyimides were readily soluble in a variety of organic solvents and could be solution-cast into flexible and tough films. The cast films exhibited high optical transparency and almost no color, with a UV–vis absorption edge of 368–382 nm and a very low b^* value (a yellowness index) of 6.2–15.5. They had good thermal stability with glass-transition temperatures of 186–288 °C, and most of them did not show significant decomposition before 500 °C. Moreover, these polyimide films also possessed low dielectric constants of 2.79–3.49 (at 1 MHz) and low water uptakes (<0.65 wt%).

Keywords: Fluorinated polyimides; Low color; Low dielectric constant

1. Introduction

Linear aromatic condensation polyimide film is a material of choice for use in many aerospace as well as commercial applications where long term thermal stability is needed [1,2]. Because of their inherent toughness and flexibility, low density, remarkable thermal stability, radiation resistance and mechanical strength, aromatic polyimide films have excellent potential for applications in microelectronics and aerospace fields. However, aromatic polyimides are generally insoluble in organic solvents, exhibit low optical transparency, and have intense yellow color. These facts may restrict their practical applications in some fields. Therefore, much effort has been concentrated on synthesizing soluble and colorless polyimides while retaining their desired properties [3–9]. Although soluble and colorless polyimides can be obtained from alicyclic dianhydride or diamine monomers [5–9], these materials may have limited long term thermal stability because of less stable aliphatic segments.

The coloration of aromatic polyimides is mainly caused by the intra- and intermolecular charge transfer (CT) interactions between alternating electron-donating diamine and electron-accepting dianhydride components [10]. Incorporation of large, bulky groups such as *tert*-butyl group into either the diamine or dianhydride monomers reduces the amount of interchain electronic interactions and lessens CT complex formation, thereby leading to soluble and colorless polyimides [11,12]. Recently,

---

[*] Corresponding author. Tel.: +886 2 25925252x2977; fax: +886 2 25861939.

E-mail address: shhsiao@ttu.edu.tw (S.-H. Hsiao).

[✠] Chin-Ping Yang deceased on August 17, 2005, at the age of 75.

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.07.066

much effort has been spent on synthesizing fluorinated aromatic polyimides, especially the trifluoromethyl (CF_3)-containing polyimides [13–22]. It has been demonstrated that the introduction of bulky CF_3 group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which was attributed to low polarizability of the C–F bond and the increase in free volume. Another approach to enhance solubility and/or melt processability is to incorporate flexible linkages along the backbones, either into the diamine or into the dianhydride component. Polyimides containing ether linkages prepared through phenoxy derivatives via nitro-displacements, especially General Electric's poly(ether imide), Ultem 1000 resin, have achieved great commercial success [23–25].

Several papers and patents disclose nitro-displacement reactions with hydroquinone and resorcinol and subsequent conversion of the intermediates to bis(ether anhydride)s [24–28], which are readily reacted with aromatic diamines to form polyimides with 1,4- and 1,3-linked, main-chain, phenylene–ether units. The polyimides so formed exhibit reduced T_g as compared to the conventional polyimides because of the incorporation of flexible ether linkages into the backbone, but the solubility is still not satisfactory. This work reports the synthesis and basic characterization of two series of new fluorinated polyimides derived from hydroquinone bis(ether anhydride) **3a** and resorcinol bis(ether anhydride) **3b** with several CF_3-containing bis(ether amine)s. In addition to the steric effect contributed by the bulky $-CF_3$ group, the obtained polyimides should exhibit reduced intra- and intermolecular CT interactions because of the decrease in both the electron-donating property of the diamine moiety (caused by the electron-withdrawing CF_3 pendents) and the electron-accepting property of the dianhydride moiety (caused by the electron-donating ether group). By comparative studies of these polymers with their non-fluorinated analogs, we confirmed that the introduction of electron-withdrawing $-CF_3$ groups and electron-donating ether linkages into the polyimide structures rendered the new polymers better solution processability, less color and lower dielectric constants, and comparable thermal and mechanical properties with non-fluorinated polyimides.

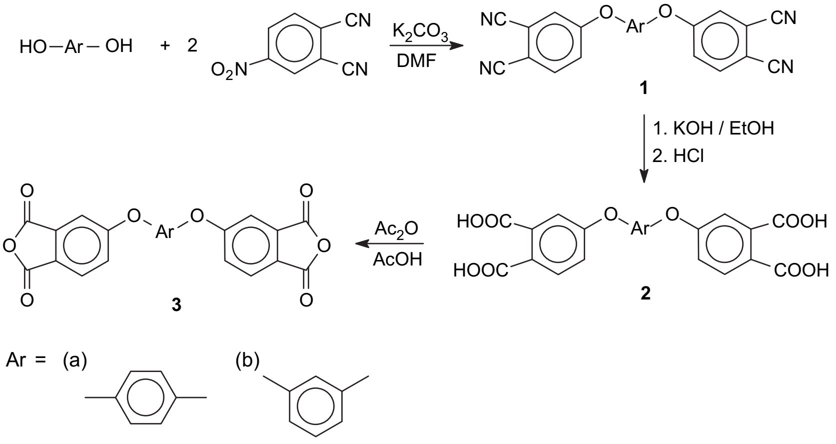
2. Experimental

2.1. Materials

According to a well-developed synthetic method [29–35], the trifluoromethylated aromatic bis(ether amine)s were prepared from the chlorodisplacement of 2-chloro-5-nitrobenzotrifluoride with corresponding aromatic diols in the presence of potassium carbonate in dimethyl sulfoxide (DMSO), followed by Pd/C-catalyzed hydrazine reduction; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**4a**; mp = 132–133 °C) [29], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene (**4b**; mp = 164–165 °C) [30], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2,5-di-*tert*-butylbenzene (**4c**; mp = 215–216 °C) [31], 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**4d**; mp = 155–156 °C) [32], 4,4′-bis(4-amino-2-trifluoromethylphenoxy)-3,3′,5,5′-tetramethylbiphenyl (**4e**; mp = 256–257 °C) [33], 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**4f**; mp = 131–132 °C) [34], and 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (**4g**; mp = 65–66 °C) [35]. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Synthesis of bis(ether anhydride)s **3a** and **3b**

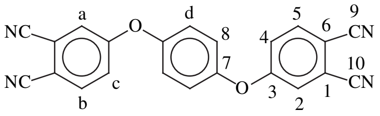
As shown in Scheme 1, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**3a**; mp = 270–271 °C, 72% yield) and 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**3b**; mp = 169–170 °C, 65% yield) were synthesized starting from the nitro-displacement reaction of 4-nitrophthalodinitrile with hydroquinone and resorcinol, respectively, in *N*,*N*-dimethylformamide (DMF) in the presence of potassium carbonate as the base, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile)s (**1a**, mp = 261–262 °C, 80% yield; **1b**, mp = 186–187 °C, 75% yield) and the cyclodehydration of the resulting bis(ether diacid)s (**2a**, 92% yield; **2b**, 87% yield). The synthetic details have been described in a previous article [28]. The spectroscopy and elemental analysis data of



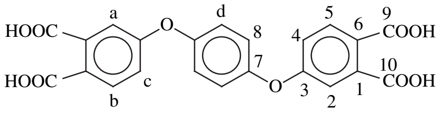
Scheme 1. Synthetic route to bis(ether anhydride)s **3a** and **3b**.

the intermediate tetranitriles and tetracarboxylic acids and the target bis(ether anhydride)s are listed as follows.

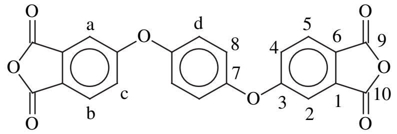
Compound **1a**: IR (KBr): 2233 (CN), 1245 cm^{-1} (C–O). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.12 (d, $J = 8.8$ Hz, 2H, H$_b$), 7.85 (d, $J = 2.3$ Hz, 2H, H$_a$), 7.50 (dd, $J = 8.8$, 2.3 Hz, 2H, H$_c$), 7.33 (s, 4H, H$_d$). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 161.41 (C^3), 151.21 (C^7), 136.47 (C^5), 122.92 (C^8), 122.51 (C^4), 122.30 (C^2), 116.91 (C^1), 116.13 (C^{10}), 115.64 (C^9), 108.45 (C^6). Elemental analysis: Calcd. for $C_{22}H_{10}N_4O_2$ (362.35): C, 72.92%; H, 2.78%; N, 15.46%. Found: C, 72.42%; H, 2.93%; N, 15.26%.



Compound **2a**: IR (KBr): 2540–3440 (O–H), 1714 (C=O), 1272 cm^{-1} (C–O–C). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 13.42 (br, 4H, –COOH), 7.76 (d, $J = 8.5$ Hz, 2H, H$_b$), 7.41 (dd, $J = 8.5$, 2.2 Hz, 2H, H$_c$), 7.18 (d, $J = 2.2$ Hz, 2H, H$_a$), 7.15 (s, 4H, H$_d$). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 168.76 (C^{10}), 168.44 (C^9), 158.52 (C^3), 155.62 (C^7), 136.64 (C^1), 136.60 (C^5), 131.57 (C^6), 128.96 (C^8), 119.57 (C^4), 117.52 (C^2).



Compound **3a**: IR (KBr): 1845 (asym. C=O str.), 1770 (sym. C=O str.), 1268 cm^{-1} (C–O–C). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.77 (d, $J = 8.6$ Hz, 2H, H$_b$), 7.21 (s, 4H, H$_d$), 7.15 (d, $J = 1.8$ Hz, 2H, H$_a$), 7.14 (dd, $J = 8.6$, 1.8 Hz, 2H, H$_c$). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 168.73 (C^{10}), 167.67 (C^9), 159.59 (C^3), 151.75 (C^7), 136.77 (C^1), 131.62 (C^5), 125.97 (C^6), 122.00 (C^8), 118.81 (C^4), 116.68 (C^2). Elemental analysis: Calcd. for $C_{22}H_{10}O_8$ (402.32): C, 65.68%; H, 2.51%. Found: C, 65.46%; H, 2.67%.



FTIR, ^{1}H NMR, and ^{13}C NMR spectra of compounds **1–3b** are shown in Figs. 1–3, respectively, and the spectroscopic data are listed as follows.

Compound **1b**: IR (KBr): 2231 (C≡N), 1247 cm^{-1} (C–O). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.11 (d, $J = 8.8$ Hz,

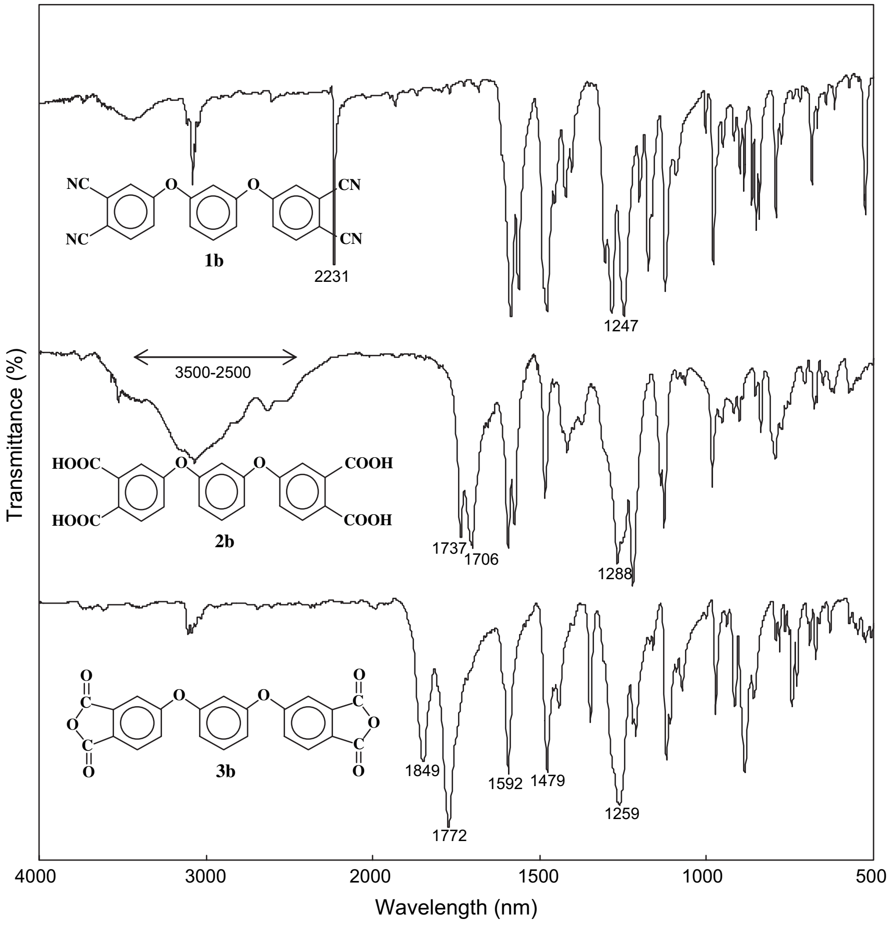


Fig. 1. FTIR spectra of bis(ether dinitrile) **1b**, bis(ether diacid) **2b**, and bis(ether anhydride) **3b**.

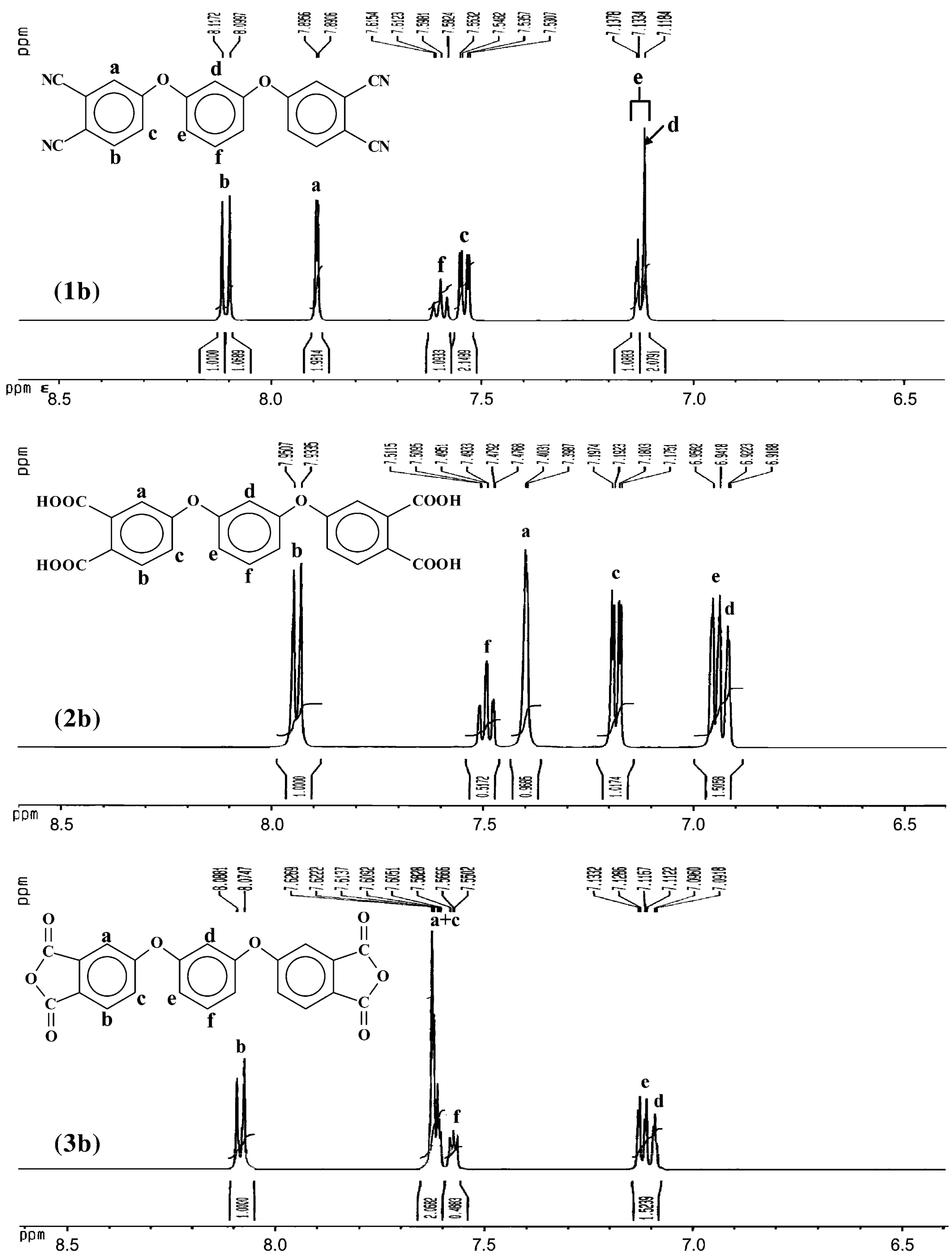


Fig. 2. ^1H NMR spectra of **1b**, **2b** and **3b** in DMSO-d_6.

2H, H_b), 7.89 (d, $J = 2.5$ Hz, 2H, H_a), 7.60 (t, $J = 7.8$ Hz, 1H, H_f), 7.54 (dd, $J = 8.8$, 2.5 Hz, 2H, H_c), 7.13 (dd, $J = 7.5$, 2.2 Hz, 2H, H_e), 7.12 (d, $J = 2.2$ Hz, 1H, H_d). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 160.61 (C^3), 155.36 (C^8), 136.23 (C^5), 132.25 (C^{10}), 122.85 (C^4), 122.60 (C^2), 117.42 (C^1), 116.73 (C^9), 115.81 (C^{11}), 115.33 (C^{12}), 112.72 (C^7), 108.64 (C^6).

Compound **2b**: IR (KBr): 2500–3500 (O–H), 1706 (C=O), 1288 cm^{-1} (C–O–C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.94 (d, $J = 8.6$ Hz, 2H, H_b), 7.51 (t, $J = 8.2$ Hz, 1H, H_f), 7.40 (d, $J = 2.2$ Hz, 2H, H_a), 7.19 (dd, $J = 8.6$, 2.2 Hz, 2H, H_c), 6.95 (dd, $J = 8.2$, 1.8 Hz, 2H, H_e), 6.92 (d, $J = 1.8$ Hz, 1H, H_d). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 168.18 (C^{11}), 167.61 (C^{12}), 158.58 (C^3), 156.83 (C^8), 137.00 (C^1), 132.93 (C^{10}), 131.82 (C^5), 127.63 (C^6), 119.50 (C^4), 118.65 (C^9), 115.64 (C^2), 111.45 (C^7).

Compound **3b**: IR (KBr): 1849 (asym. C=O str.), 1772 (sym. C=O str.), 1479–1592 (arom. C=C), 1259 cm^{-1} (C–O–C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.08 (d, $J = 8.4$ Hz, 2H, H_b), 7.62 (dd, $J = 8.4$, 2.3 Hz, 2H, H_c), 7.61 (d, $J = 2.3$ Hz, 2H, H_a), 7.57 (t, $J = 8.2$ Hz, 1H, H_f), 7.12 (dd, $J = 8.2$, 2.3 Hz, 2H, H_e), 7.09 (t, $J = 2.1$ Hz, 1H, H_d). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 163.20 (C^{11}), 162.50 (C^{12}), 162.38 (C^3), 155.94 (C^8), 134.05 (C^1), 132.25 (C^{10}), 127.84 (C^5), 125.28 (C^6), 125.16 (C^4), 117.00 (C^9), 113.49 (C^2), 112.36 (C^7).

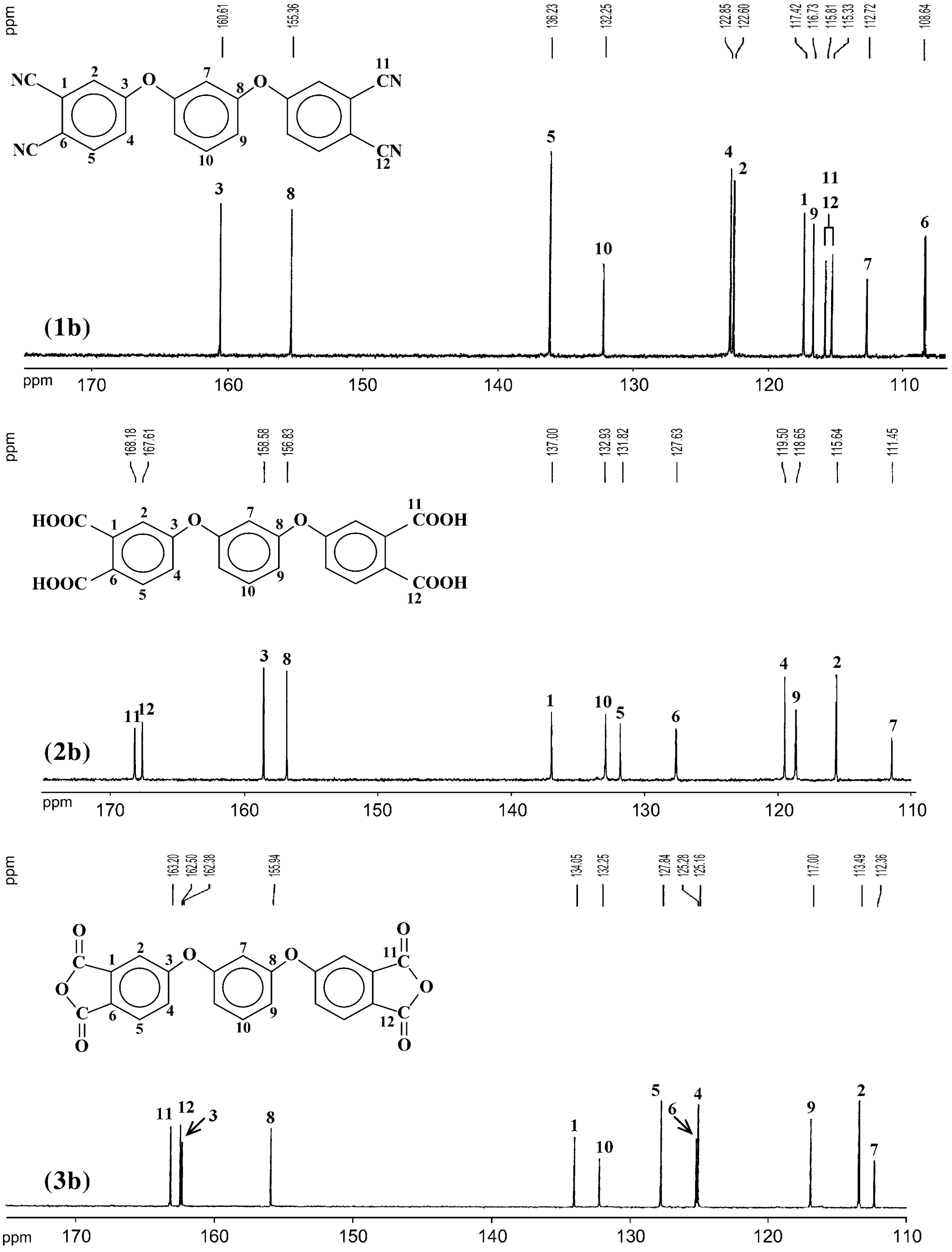


Fig. 3. ^{13}C NMR spectra of **1b**, **2b** and **3b** in DMSO-d_6.

2.3. Synthesis of polyimides

2.3.1. Thermal imidization method

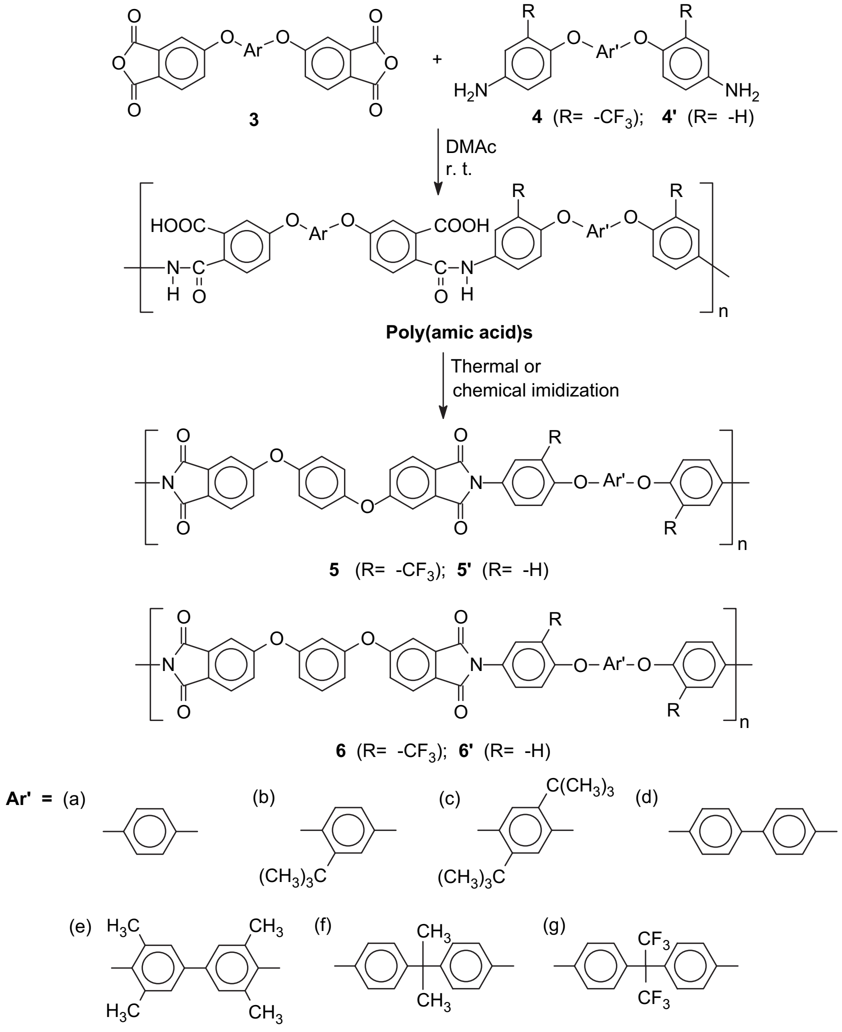
The general polymerization procedure is illustrated by the following example. Into a solution of bis(ether amine) **4a** (0.2998 g, 0.7 mmol) in dried DMAc (4.1 mL) in a 20 mL flask, an equimolar amount of bis(ether anhydride) **3b** (0.2816 g, 0.7 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to afford a highly viscous poly(amic acid) (PAA) solution. Then PAA solution was poured into a glass culture dish, which was placed in an 80 °C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential heating from 120 °C to 250 °C at a heating rate of 3 °C/min and further heated at 250 °C for 1 h. The cured polyimide film was stripped from the glass substrate by immersion in water followed by drying in an oven at 100 °C. Inherent viscosity (η_{inh}) of **6a**(H) was 0.67 dL/g, as measured at a concentration 0.5 g/dL in DMAc at 30 °C.

2.3.2. Chemical imidization method

A pot of 10 wt% PAA solution in DMAc was prepared from each 0.7 mmol of bis(ether amine) **4a** and bis(ether anhydride) **3b** by the same procedure as described above. Then, 2 mL of acetic anhydride/pyridine (volume ratio 2/1) was added to the PAA solution. The mixture was heated at 80 °C for 1 h to effect a complete imidization and then poured into a glass culture dish, which was placed in an oven at 80 °C for 1 h to evaporate the solvent and form a thin solid film. The polyimide film was then heated to 200 °C and held at that temperature for 2 h to remove the residual solvent. Inherent viscosity (η_{inh}) of **6a**(C) was 0.70 dL/g, as measured at a concentration 0.5 g/dL in DMAc at 30 °C.

2.4. Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Elemental analyses were run in a Heraeus VarioEL-III CHN analyzer. Inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30 °C. Weight-average molecular weights ($\overline{Mw}$) and number-average molecular weights ($\overline{Mn}$) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and THF as the eluent. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 8–10-mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20 °C/min. Glass-transition temperatures (T_g) of polymers were determined on a TA Instruments DSC 2010 in flowing nitrogen (40 cm^3/min) at a heating rate of 15 °C/min. Mechanical properties of the films were measured with an Instron model 4400R tensile tester with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 40–60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a GretagMacbeth Color-Eye 3100 colorimeter. Measurements were performed for the films at an observational angle of 10° and with 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. 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 water uptake was determined by the weighing of



Scheme 2. Synthesis of polyimides.

the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for three days.

3. Results and discussion

3.1. Polymer synthesis

Two series of novel fluorinated polyimides (**5a–g** and **6a–g**) with an isomeric repeat unit were synthesized by a two-step procedure in which poly(amic acid)s (PAAs) were first prepared by ring-opening polyaddition of bis(ether anhydride)s **3a** and **3b**, respectively, with various CF_3-bearing bis(ether amine)s **4a–g** in DMAc, followed by the thermal and chemical imidization of PAA (Scheme 2). No difficulty was encountered in obtaining high molecular weight PAAs from the reactions of **4a–g** with **3a** or **3b**. Despite the amino groups in these bis(ether amine)s were less basic than a normal dramatic amine because of the inductive deactivation of the $-CF_3$ group, these CF_3-substituted bis(ether amine)s were still sufficiently reactive to give high molecular weight poly(amic acid)s when they were allowed to polymerize for an extended period of time (ca. 10 h). The maintained reactivity of these bis(ether amine)s is most likely based on the *meta* substitution to the amino group. Tough and flexible polyimide films were obtained by casting the PAA solution on glass substrate followed by thermal curing process up to 250 °C. All the chemically treated polyimides exhibited good solubility in organic solvents; therefore, the characterization of solution viscosity was carried out without any difficulty. As shown in Table 1, the inherent viscosities of these polyimides were in the range of 0.43–0.79 dL/g that corresponded to weight-average and number-average molecular weights of 22,000–44,000 and 17,000–25,000, respectively, relative to the polystyrene standards.

The complete imidization of polymers was confirmed by FTIR and NMR spectra. All of the polyimides showed characteristic imide absorption bands around 1780 cm^{-1} and 1730 cm^{-1} (imide carbonyl asymmetrical and symmetrical stretchings), 1380 cm^{-1} (C–N stretching), and 1050 and 750 cm^{-1} (imide ring deformation), together with the C–O and C–F multiple stretching absorptions in the region of 1100–1300 cm^{-1}. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the poly(amic acid) precursor into polyimide. A typical set of ^1H NMR and ^{13}C NMR spectra of the representative polyimide **5a** are illustrated in Fig. 4. Assignments of each carbon and proton assisted by 2D-NMR spectra (Fig. 5) are also given in the figures, and these spectra are in complete agreement with the

Table 1
Inherent viscosity, elemental analysis, and GPC data of polyimides

Polymer[a]		Formula (molecular weight)	Elemental analysis (%)				GPC data[c]		
Code	η_{inh} (dL/g)[b]			C	H	N	$\overline{Mn}\times 10^4$	$\overline{Mw}\times 10^4$	$\overline{Mw}/\overline{Mn}$
5a	0.63	$(C_{42}H_{20}O_8N_2F_6)_n$	Calcd	63.48	2.54	3.53	–	–	–
		$(794.62)_n$	Found	62.09	2.71	3.59			
5b	0.62	$(C_{46}H_{28}O_8N_2F_6)_n$	Calcd	64.95	3.32	3.29	1.8	2.8	1.6
		$(850.73)_n$	Found	63.37	3.30	3.26			
5c	0.59	$(C_{50}H_{36}O_8N_2F_6)_n$	Calcd	66.22	4.00	3.09	–	–	–
		$(906.83)_n$	Found	64.03	3.88	3.17			
5d	0.69	$(C_{48}H_{24}O_8N_2F_6)_n$	Calcd	66.21	2.78	3.22	–	–	–
		$(870.72)_n$	Found	65.54	2.92	3.32			
5e	0.79	$(C_{52}H_{32}O_8N_2F_6)_n$	Calcd	67.39	3.48	3.02	2.1	3.3	1.6
		$(926.83)_n$	Found	66.04	3.38	2.96			
5f	0.73	$(C_{51}H_{30}O_8N_2F_6)_n$	Calcd	65.49	2.69	3.12	1.9	2.9	1.6
		$(912.80)_n$	Found	64.67	2.80	3.15			
5g	0.43	$(C_{51}H_{24}O_8N_2F_{12})_n$	Calcd	60.01	2.37	2.74	1.5	2.2	1.7
		$(1020.74)_n$	Found	58.93	2.17	2.58			
6a	0.70	$(C_{42}H_{20}O_8N_2F_6)_n$	Calcd	63.48	2.54	3.53	1.9	3.2	1.7
		$(794.62)_n$	Found	63.11	2.51	3.38			
6b	0.48	$(C_{46}H_{28}O_8N_2F_6)_n$	Calcd	64.95	3.32	3.29	1.7	2.9	1.7
		$(850.73)_n$	Found	64.42	3.30	3.24			
6c	0.56	$(C_{50}H_{36}O_8N_2F_6)_n$	Calcd	66.22	4.00	3.09	1.9	3.4	1.8
		$(906.83)_n$	Found	66.00	4.20	2.85			
6d	0.54	$(C_{48}H_{24}O_8N_2F_6)_n$	Calcd	66.21	2.78	3.22	2.2	3.4	1.6
		$(870.72)_n$	Found	65.67	2.65	3.03			
6e	0.63	$(C_{52}H_{32}O_8N_2F_6)_n$	Calcd	67.39	3.48	3.02	2.5	4.4	1.8
		$(926.83)_n$	Found	66.91	3.59	2.72			
6f	0.48	$(C_{51}H_{30}O_8N_2F_6)_n$	Calcd	67.11	3.31	3.07	2.0	3.4	1.7
		$(912.80)_n$	Found	66.92	3.72	2.99			
6g	0.46	$(C_{51}H_{24}O_8N_2F_{12})_n$	Calcd	60.01	2.37	2.74	1.7	2.8	1.6
		$(1020.74)_n$	Found	59.86	2.20	2.44			

[a] Polyimide samples prepared by the chemical imidization method.

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

[c] Relative to polystyrene standards with THF as the eluent.

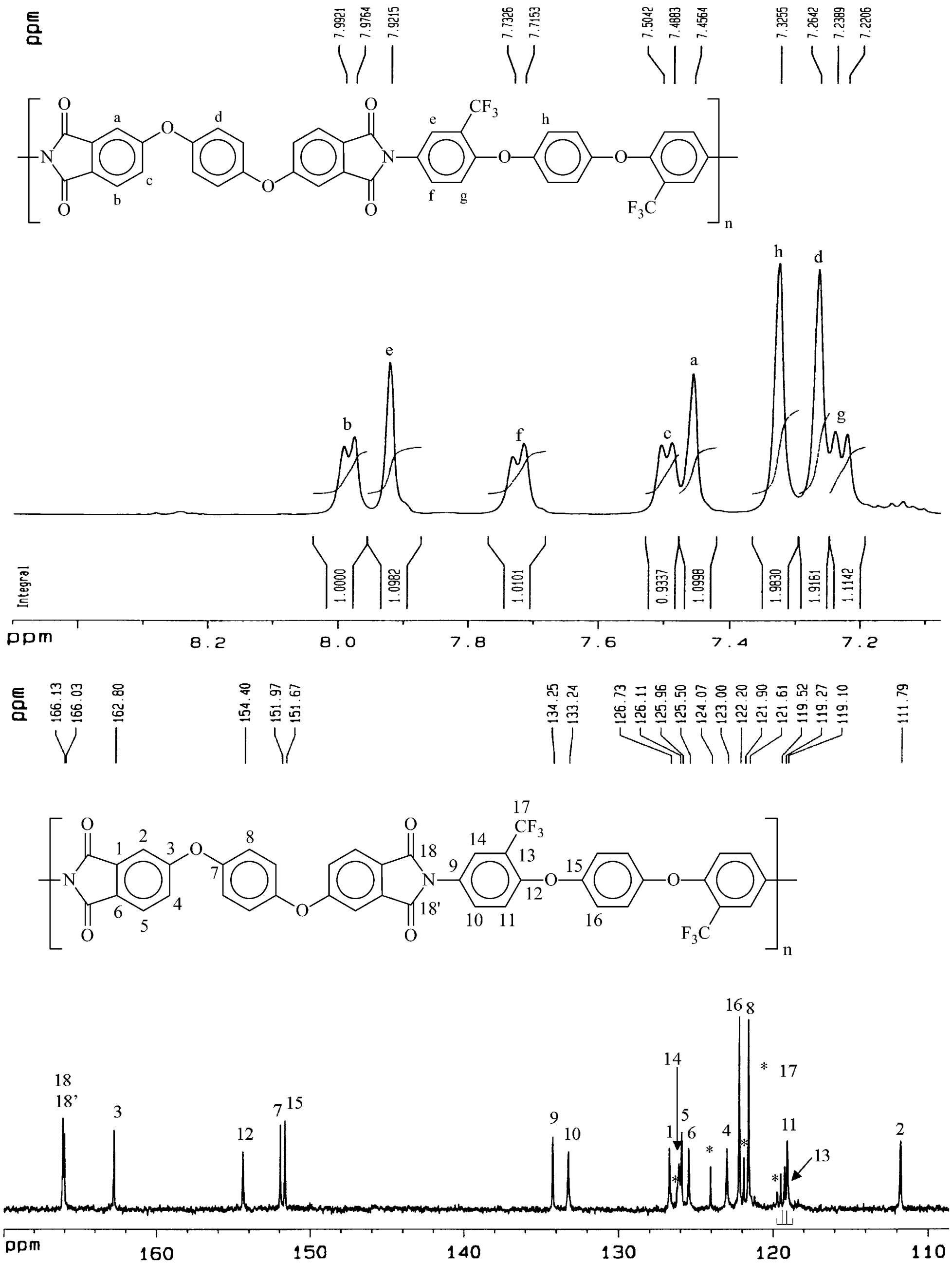


Fig. 4. ^{1}H NMR and ^{13}C NMR spectra of polyimide **5a** in DMSO-d_6.

proposed polymer structure. In addition to IR and NMR spectra, the elemental analysis results of these polyimides shown in Table 1 also generally agree with the calculated values for the proposed structures.

3.2. Polymer solubility

The solubility of these polyimide films was tested in various organic solvents, and the results are listed in Table 2. All the **5** and **6** series polymers obtained via either thermal (H) or chemical (C) imidization were readily soluble in amide-type solvents, such as NMP, DMAc and DMF, and in chlorinated hydrocarbons like dichloromethane and chloroform. Most of the chemically imidized **5**(C) and **6**(C) polyimides showed a better solubility in 1,4-dioxane, tetrahydrofuran (THF), *m*-cresol, pyridine (Py), and DMSO than those prepared by the thermal imidization method. The solubility of the fluorinated **5** and **6** series polyimides was obviously higher than their analogs without the pendent CF_3 groups. This can be attributed to the effect of the bulky trifluoromethyl groups, which inhibited close packing and reduced the chain–chain interactions leading to an enhanced solubility. Thus, all the **5** and **6** series polyimides could be easily processed from solutions.

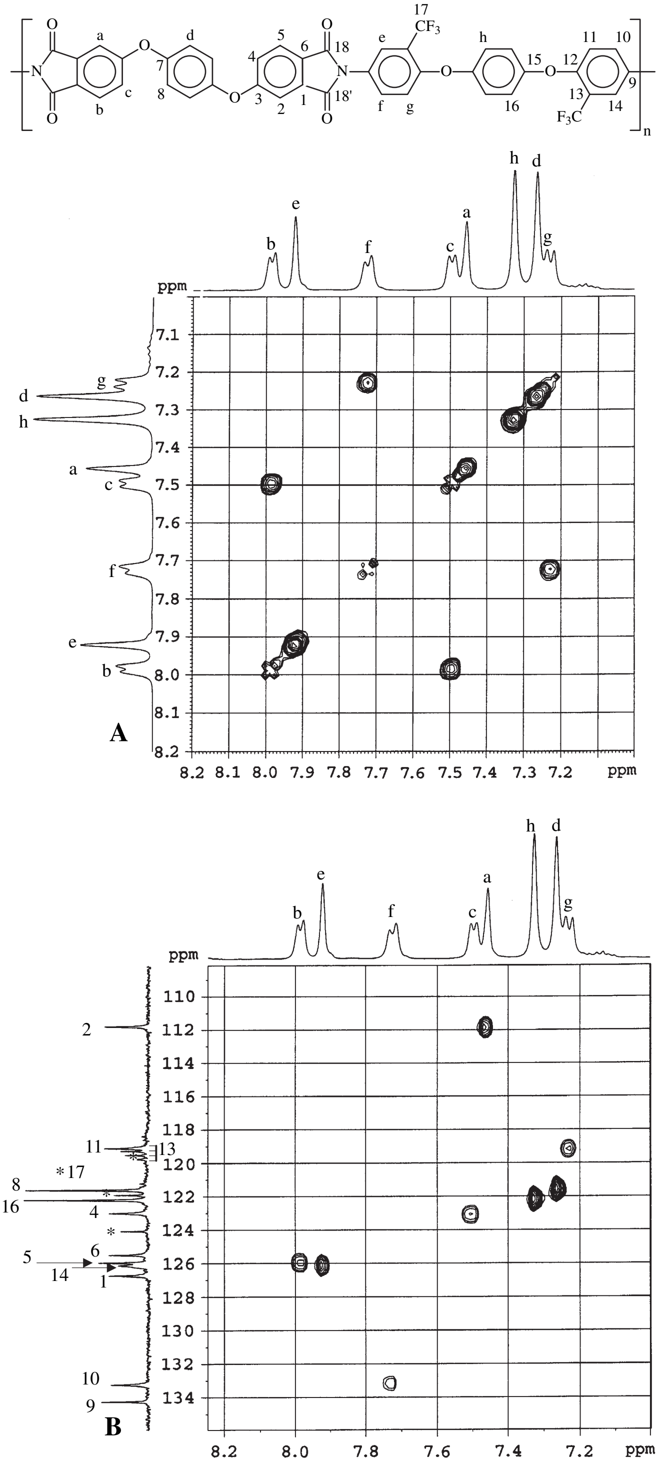


Fig. 5. (A) COSY spectrum and (B) HETCOR spectrum of polyimide **5a** in DMSO-d_6.

3.3. Optical properties

Transmission UV–vis spectra were measured for the thin films of all polyimides. Typical UV–vis spectra of some representative polyimide films are illustrated in Fig. 6. All fluorinated polyimide films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and colorless. As shown in Table 3, the **5**(C) and **6**(C) polyimides showed a very low yellowness index (b^*) of 6.2–9.4. The slightly higher yellowness index of the thermally imidized PEI films might be a result of thermal oxidation of chain-end amino groups. All the polyimides containing the CF_3 group revealed slightly lower cut-off wavelengths and lower b^* values than their respective CF_3-free counterparts. The bulky and electron-withdrawing CF_3 group in the diamine moieties was presumably effective in decreasing CT complexes between polymer chains through steric hindrance and inductive effect (by decreasing the electron-donating property of diamine moieties). The electron-donating ether groups in the dianhydride moiety also contribute somewhat toward decreasing the overall electron affinity of the phthalimide units, and subsequently lower the intermolecular CT interaction. Thus, almost all the **5** and **6** series polyimides could be cast into optically transparent and colorless films. For comparison, the color co-ordinates and cut-off wavelengths of Ultem 1000 and some common polyimides synthesized from commercially available aromatic dianhydrides with a non-fluorinated bis(ether amine) **4′a** are also given in Table 3. The films of common polyimides PMDA/**4′a** and BTDA/**4′a** appeared with a deep yellow color and revealed a relatively high b^* value above 80. The ODPA/**4′a** polyimide was pale yellow in color and showed a lowered b^* value of 30.4. In contrast to these conventional polyimides, the film of **6′a**(H) showed a very low b^* value of 18.3 comparable to that of Ultem film. Thus, it seems to be that the dianhydride structure is more influential in determining the color intensity of polyimides than the diamine structure.

3.4. Mechanical properties

The tensile properties of the polyimide films are reported in Table 4. These polymer films showed similar type of behavior with respect to the elastic deformation range at small strains. The **5** and **6** series polyimides showed tensile strengths at break of 80–103 MPa, elongations at break of 6–17%, and initial moduli of 1.8–2.3 GPa. The tensile properties of the **5** series polyimides are comparable with those of the **5′** series analogs. These results indicate that the incorporation of the CF_3 group into the structure of polyimides not only improves solubility but also retains the good mechanical properties. All these polymer films possess good tensile properties indicating that they are strong materials.

3.5. Thermal properties

The thermal behavior data of the polyimides, collected from DSC and TGA curves, are summarized in Table 5. The T_g values of the **5** and **6** series polyimides are in the range of 206–288 °C and 186–266 °C, respectively. The increasing order of T_g generally correlated with that of the chain rigidity. In each series, the polyimides derived from bis(ether amine) **4f** showed the lowest T_g values due to the increase in flexibility of polymer chain determined by the isopropylidene bridges, whereas the polyimides obtained from bis(ether amine) **4e** had the highest T_gs because of the rigid tetramethylbiphenyl

Table 2
Solubility behavior of polyimides

Polymer code[a]	Solvents[b]									
	NMP	DMAc	DMF	DMSO	*m*-Cresol	Py	Dioxane	THF	CH_2Cl_2	$CHCl_3$
5a(C)	+++	+++	+++	(S)	(S)	+	+	(S)	+++	+++
5b(C)	+++	+++	+++	++	+++	+++	+++	+++	+++	+++
5c(C)	+++	+++	+++	(S)	(S)	+++	+	(S)	+++	+++
5d(C)	+++	+++	+++	+	+++	+++	+	(S)	+++	+++
5e(C)	+++	+++	+++	(S)	+++	+++	+++	+++	+++	+++
5f(C)	+++	+++	+++	+	+++	+++	+++	+++	+++	+++
5g(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
5a(H)	+++	+++	+++	+++	(S)	(S)	(S)	(S)	(S)	(S)
5d(H)	+++	+++	+++	(S)	+++	(S)	(S)	−	(S)	−
5g(H)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
5′a(H)	−	(S)	(S)	−	(S)	−	−	−	(S)	−
5′b(H)	+++	+++	+++	(S)	++	++	++	−	(S)	+
5′c(H)	(S)	(S)	−	−	(S)	−	−	−	(S)	(S)
5′d(H)	−	−	−	−	(S)	−	−	−	−	−
5′e(H)	−	(S)	−	−	−	(S)	−	−	(S)	(S)
5′f(H)	+++	+++	+++	(S)	+++	+++	+++	+	+++	+++
5′g(H)	+++	+++	+++	(S)	+++	+++	+++	+	+++	+++
6a(C)	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
6b(C)	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
6c(C)	+++	+++	+++	(S)	+++	+++	+++	+++	+++	+++
6d(C)	+++	+++	+++	++	+++	+++	+++	+++	+++	+++
6e(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
6f(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
6g(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
6a(H)	+++	+++	+++	+	+	+++	++	+++	+++	+++
6b(H)	+++	+++	+++	+	++	+++	++	+++	+++	+++
6e(H)	+++	+++	+++	++	+	+++	++	+++	+++	+++
6g(H)	+++	+++	+++	++	++	+++	+++	+++	+++	+++
6′a(H)	−	−	−	−	(S)	−	−	−	−	(S)
6′b(H)	++	+++	+++	−	++	+++	++	+++	+++	+++
6′c(H)	(S)	(S)	(S)	−	−	(S)	(S)	(S)	+++	+++
6′d(H)	−	−	−	−	−	−	−	−	−	−
6′e(H)	−	−	−	−	−	−	−	−	+++	+++
6′f(H)	+++	+++	(S)	−	+++	+++	+++	+++	+++	+++
6′g(H)	+++	+++	+++	+	+++	+++	+++	+++	+++	+++

[a] (H): polyimide samples obtained by the thermal imidization method; (C): polyimide samples obtained by the chemical imidization method.
[b] +++, 100 mg sample dissolved in 1 mL solvent (10%); ++, soluble at 5%; +, soluble at 1%; −, insoluble; S, swelling.

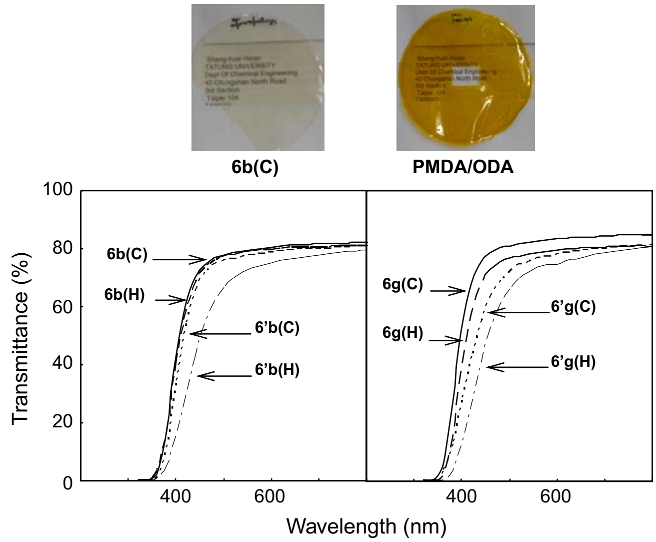


Fig. 6. UV−vis spectra of some polyimide films. Photographs show physical appearance of **6b**(C) film and of a standard PMDA/ODA polyimide film.

segment. The T_g order of **5c** (**6c**) > **5b** (**6b**) > **5a** (**6a**) indicates that the introduction of *tert*-butyl group increases the stiffness of the polymer backbone. It is reasonable that the **5** series polyimides showed a higher T_g than the respective isomeric **6** series polyimides which contain *m*-phenylene ring in the dianhydride segment. In comparison with the analogs **5′** and **6′** series, the **5** and **6** series exhibited lower T_g values due to the reduced interchain CT interaction and packing efficiency produced by the pendent $-CF_3$ groups.

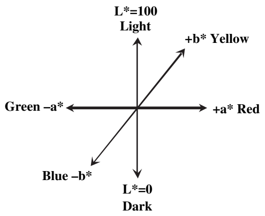
The thermal stability of the polyimides was studied by thermogravimetic analysis (TGA). Typical TGA thermograms of polymers **6b** and **6′b** are shown in Fig. 7. The temperatures at a 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA curves. The T_{10} values of the **5** series in nitrogen and air stayed within 487−559 °C and 492−545 °C, and for the **6** series within 487−553 °C and 485−544 °C. Most of them left more than 50% char yield at 800 °C in nitrogen. It is quite reasonable that the methyl-substituted polyimides like **5e** and **6e** began to decompose at lower temperatures compared with the unsubstituted **5d** and

Table 3
Color co-ordinates and cut-off wavelengths (λ_0) from UV–vis spectra of polyimide films

Polymer code[a]	Film thickness (μm)		Color co-ordinates[b]						λ_0 (nm)	
			b^*		a^*		L^*			
Blank			1.0		−0.4		96.2			
Imidization method	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)
5a	55	53	6.4	11.1	−1.9	−2.8	90.3	89.2	382	377
5b	59		8.7		−2.2		90.9		378	
5c	62		8.5		−2.6		91.9		377	
5d	66	49	6.3	10.9	−2.2	−2.9	91.7	89.1	376	377
5e	58		8.4		−2.9		92.6		373	
5f	67		6.8		−2.0		91.6		376	
5g	81	55	9.4	15.5	−1.6	−1.8	89.9	88.2	385	380
5′a		55		18.0		−4.1		89.2		375
5′b		59		19.4		−4.0		87.1		378
5′c		62		18.1		−4.9		88.5		375
5′d		66		16.5		−3.5		87.1		374
5′e		58		20.6		−5.4		89.0		378
5′f	53	67	16.5	18.3	−3.1	−3.2	88.5	87.4	389	375
5′g	49	54	15.0	17.0	−3.0	−2.4	86.6	88.2	383	372
6a	46	45	6.2	6.7	−1.7	−1.7	95.3	94.4	366	368
6b	61	67	9.0	10.3	−2.1	−2.7	94.2	94.7	375	372
6c	68		8.4		−2.3		94.7		374	
6d	61		7.7		−2.0		94.7		373	
6e	56	51	8.2	12.3	−2.5	−3.2	95.2	94.7	373	369
6f	53		7.0		−1.8		94.9		372	
6g	72	69	7.0	9.5	−1.2	−2.2	94.4	94.3	372	368
6′a		44		18.3		−3.7		92.3		374
6′b	56	48	11.3	21.6	−3.4	−4.2	92.2	91.5	373	378
6′c		47		17.3		−4.8		93.9		372
6′d		39		14.5		−3.4		93.3		373
6′e		47		19.9		−5.0		93.3		374
6′f	53	38	13.5	14.4	−2.9	−3.7	91.8	93.6	373	370
6′g	55	63	12.7	15.1	−3.7	−2.5	91.9	83.0	373	377
PMDA/**4′a**		39		80.5		3.7		84.8		440
BTDA/**4′a**		37		87.8		2.3		86.5		446
ODPA/**4′a**		50		30.4		−7.4		81.8		387
Ultem 1000		42		18.9		−3.1		90.2		385

[a] PMDA: pyromellitic dianhydride; BTDA: 3,4,3′,4′-benzophenonetetracarboxylic dianhydride; ODPA: 4,4′-oxydiphthalic anhydride.

[b] The CIE $L^*a^*b^*$ scale.



6d. The TGA data indicated that these fluorinated polyimides had fairly high thermal stability regardless of the introduction of the CF_3 groups.

3.6. Dielectric constants and water uptakes

The dielectric constants and water uptakes of all the polyimides are reported in Table 6. For comparison, the data of a standard polyimide film from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) are also included in Table 6. The **5** and **6** series polyimides exhibited the dielectric constants at 1 MHz in the range of 3.05–3.49 and 2.79–3.20, respectively, which are lower than the corresponding non-fluorinated polyimides and the standard PMDA/ODA polyimide. The decreased dielectric constants could be explained by the attribution of the bulky $-CF_3$ substituents in the polymer backbone, which has low polarizability and increase the free volume of the polymer chain. Polyimides **5g** and **6g** exhibited

Table 4
Tensile properties of polyimide films

Polymer[a]	Strength at yield (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
5a	–	97	11	2.1
5b	99	93	17	1.9
5c	–	89	10	2.0
5d	–	100	14	2.3
5e	–	87	11	2.2
5f	96	91	13	2.0
5g	–	83	8	1.8
5′a	–	98	11	1.9
5′b	–	103	12	2.0
5′c	–	101	9	2.3
5′d	–	85	8	1.9
5′e	–	87	10	1.8
5′f	–	91	13	1.8
5′g	–	80	11	1.7
6a	–	103	13	2.1
6b	85	81	9	1.9
6c	100	97	16	2.0
6d	103	95	14	2.0
6e	106	99	16	2.3
6f	84	80	13	1.8
6g	–	83	6	2.2

Whereas the **5′** series were prepared via the thermal imidization process.

[a] The **5** and **6** series polyimides were prepared by the chemical imidization method.

the lowest dielectric constants in their own series because of the existence of hexafluoroisopropylidene group in the diamine moiety. As expected, the fluorinated poly(ether imide)s exhibited lower water absorptions (0.18–0.65%) compared to the corresponding non-fluorinated analogs (0.23–0.90%) due to the hydrophobic nature of the CF_3 group. The low water absorptions ensure that these polymers have stable dielectric performance.

Table 5
Thermal properties of polyimides

Polymer[a]	T_g (°C)[b]	T_{10} (°C)[c]		Char yield (%)[d]
		In N_2	In air	
5a	208	544	542	51
5b	226	515	514	47
5c	241	505	498	49
5d	226	559	545	59
5e	288	487	492	58
5f	208	529	521	54
5g	206	554	543	52
5′a	225	535	525	51
5′b	231	511	503	37
5′c	246	498	500	32
5′d	236	545	526	58
5′e	288	483	466	55
5′f	217	523	511	47
5′g	229	532	518	56
6a	191	546	538	51
6b	204	520	527	52
6c	217	513	518	48
6d	203	553	544	58
6e	266	487	485	61
6f	188	533	531	59
6g	186	547	535	52
6′a	199	528	524	58
6′b	212	503	508	52
6′c	222	495	495	47
6′d	215	539	530	64
6′e	259	477	458	66
6′f	192	479	476	52
6′g	202	497	478	58

[a] Samples 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 TGA at a heating rate of 20 °C/min.

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

4. Conclusions

Two series of fluorinated polyimides (**5** and **6**) were, respectively, synthesized from 1,4-bis(3,4-dicarboxyphenoxy)-benzene dianhydride (**3a**) and 1,3-bis(3,4-dicarboxyphenoxy)-benzene dianhydride (**3b**) with various CF_3-containing aromatic diamines (**4a–g**) via the thermal or chemical imidization technique. The combination of these dianhydride and diamine monomers was a successful process for reducing overall charge transfer complex formation due to either or both inter- and intramolecular electronic interactions. Thus, the prepared polyimides were highly soluble in organic solvents and could be processed into almost colorless films compared to the bright yellow color of conventional/commercial aromatic polyimide films. The increased optical transparency in these aromatic polyimides has been achieved at no sacrifice in thermal stability, flexibility, toughness, or mechanical properties. They also showed low dielectric constants and low water uptakes. Therefore, these polyimides demonstrate a good combination of useful properties and should be useful for the applications where high optical transparency and thermal stability are the needed requirements.

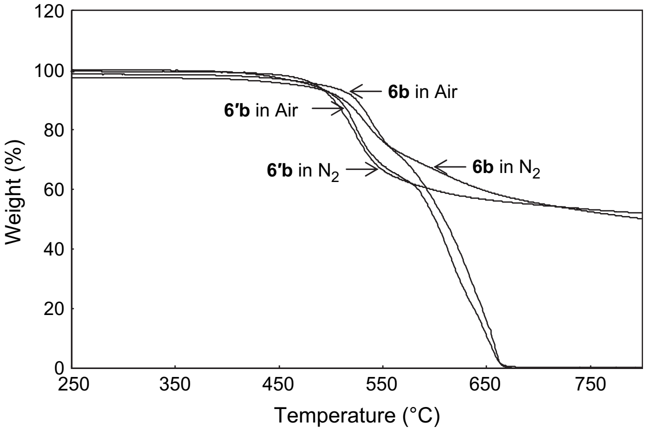


Fig. 7. Typical TGA curves of polyimides **6b** and **6′b** with a heating rate of 20 °C/min.

Table 6
Water uptakes and dielectric constants of polyimide films

Polymer[a]	Film thickness (μm)	Water uptake (%)	Dielectric constant (dry)			
			1 kHz	10 kHz	1 MHz	40 MHz
5a	87	0.31	3.52	3.47	3.36	3.37
5b	85	0.24	3.63	3.56	3.49	3.54
5c	63	0.25	3.45	3.37	3.33	3.30
5d	70	0.29	3.32	3.31	3.21	3.26
5e	62	0.28	3.26	3.24	3.17	3.20
5f	52	0.33	3.26	3.20	3.16	3.23
5g	73	0.19	3.15	3.10	3.05	3.14
5′a	43	0.41	4.05	3.99	3.80	3.85
5′b	52	0.30	4.01	3.98	3.89	3.96
5′c	48	0.32	3.64	3.61	3.52	3.57
5′d	32	0.31	3.94	3.90	3.84	3.82
5′e	42	0.31	3.91	3.83	3.72	3.76
5′f	43	0.42	4.06	4.03	3.93	4.01
5′g	43	0.23	4.00	3.96	3.57	3.55
6a	113	0.65	3.13	3.10	3.01	3.05
6b	63	0.25	3.17	3.10	3.07	3.17
6c	96	0.37	3.03	3.01	2.96	3.00
6d	82	0.41	3.29	3.26	3.20	3.19
6e	64	0.44	3.20	3.18	3.13	3.12
6f	72	0.29	2.98	2.96	2.90	2.91
6g	101	0.18	2.90	2.86	2.79	2.80
6′a	42	0.90	3.90	3.88	3.81	3.84
6′b	54	0.73	3.91	3.87	3.81	3.87
6′c	30	0.77	3.96	3.95	3.89	3.96
6′d	31	0.69	3.88	3.85	3.74	3.71
6′e	38	0.75	3.84	3.78	3.72	3.78
6′f	30	0.74	4.06	4.00	3.90	3.98
6′g	72	0.64	3.51	3.42	3.34	3.38
PMDA/ODA	40	0.52	3.90	3.86	3.84	3.83

[a] These polyimide films were obtained by the thermal imidization method.

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 94-2216-E-036-014).

References

[1] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. Glasgow and London: Blackie; 1990.
[2] Ghosh MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996.
[3] St Clair AK, St Clair TL. US Pat 4,595,548; 1986.
[4] St Clair AK, St Clair TL. US Pat 4,603,061; 1986.
[5] Matsuura T, Hasuda Y, Nishi S, Yamada N. Macromolecules 1991;24:5001.
[6] Chun BW. Polymer 1994;35:4203.
[7] Matsumoto T, Kurosaki T. Macromolecules 1997;30:993.
[8] Matsumoto T, Kurosaki T. Macromolecules 1999;32:4933.
[9] Kato J, Seo A, Shiraishi S. Macromolecules 1999;32:6400.
[10] Dine-Hart RA, Wright WW. Makromol Chem 1971;143:189.
[11] Yang CP, Hsiao SH, Yang HW. Macromol Chem Phys 2000;201:409.
[12] Huang W, Yan DY, Lu QH, Tao P. J Polym Sci Part A Polym Chem 2002;40:229.
[13] Banerjee S, Madhra MK, Salunke AK, Jaiswal DK. Polymer 2003;44:613.
[14] Yang CP, Hsiao SH, Wu KL. Polymer 2003;44:7067.
[15] Myung BY, Ahn CJ, Yoon TH. Polymer 2004;45:3185.
[16] Yang CP, Su YY, Hsiao FZ. Polymer 2004;45:7529.
[17] Liu BJ, Hu W, Matsumoto T, Jiang ZH, Ando S. J Polym Sci Part A Polym Chem 2005;43:3018.
[18] Yang CP, Su YY. Polymer 2005;46:5778.
[19] Yang CP, Su YY. Polymer 2005;46:5797.
[20] Li HS, Liu JG, Rui JM, Fan L, Yang SY. J Polym Sci Part A Polym Chem 2006;44:2665.
[21] Li HS, Liu JG, Wang K, Fan L, Yang SY. Polymer 2006;47:1443.
[22] Liaw DJ, Huang CC, Chen WH. Polymer 2006;47:2337.
[23] White DM, Takekoshi T, Williams FJ, Relles HM, Donahue PF, Mathews RO, et al. J Polym Sci Polym Chem Ed 1981;19:1635.
[24] Takekoshi T, Kochanowski JE, Manello JS, Webber MJ. J Polym Sci Polym Chem Ed 1985;23:1759.
[25] Takekoshi T, Kochanowski JE, Manello JS, Webber MJ. J Polym Sci Polym Symp 1986;74:93.
[26] Eastmond GC, Paprotny J. Macromolecules 1995;28:2140.
[27] Heath DR, Takekoshi T. US Pat 3,879,428; 1975.
[28] Hsiao SH, Dai LR. J Polym Sci Part A Polym Chem 1999;37:665.
[29] Xie K, Zhang SY, Liu JG, He MH, Yang SY. J Polym Sci Part A Polym Chem 2001;39:2581.
[30] Yang CP, Su YY, Wu KL. J Polym Sci Part A Polym Chem 2004;42:5424.
[31] Yang CP, Hsiao FZ. J Polym Sci Part A Polym Chem 2004;42:2272.
[32] Yang CP, Hsiao SH, Hsu MF. J Polym Sci Part A Polym Chem 2002;40:524.
[33] Yang CP, Hsiao SH, Chen KH. Polymer 2002;43:5095.
[34] Yang CP, Chen RS, Chen KH. J Appl Polym Sci 2005;95:922.
[35] Yang CP, Chen RS, Chen KH. J Polym Sci Part A Polym Chem 2003;41:922.