Soluble and Light-Colored Polyimides from 2,3,2′,3′-Oxydiphthalic Anhydride and Aromatic Diamines

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ABSTRACT: A series of polyimides were prepared from 2,3,2′,3′-oxydiphthalic anhydride (3,3′-ODPA) with various aromatic diamines via three different synthetic procedures. The one-step and two-step methods with the thermal imidization of poly(amic acids) (PAAs) yielded polyimides with a relatively low inherent viscosity; these produced brittle films. The polyimides prepared by the two-step method via the chemical imidization of PAA precursors exhibited a higher inherent viscosity and afforded tough and creaseable films. All the 3,3′-ODPA based polyimides had a significantly higher solubility than the corresponding poly-imides from 3,4,3′,4′-oxydiphthalic anhydride. The films cast from 3,3′-ODPA polyimides also showed high optical transparencies and less color, with an ultraviolet–visible absorption edge of 370–397 nm and low yellowness index values of 11.3–29.8. These polyimides exhibited glass-transition temperatures in the range 211–289°C and showed no significant decomposition below 500°C under nitrogen or air atmospheres. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1352–1360, 2005

Key words: polyimides; thermal properties; light color

INTRODUCTION

Aromatic polyimides are well accepted as high-performance polymeric materials because of their excellent thermal and mechanical properties at elevated temperatures.[1,2] They are widely used as dielectric interlayers for semiconductor devices and flexible printed circuits. However, solubility and processability are generally major concerns when working with polyimides. Considerable effort has been made to improve the solubility and melting processability of polyimides without loss of their other positive properties.[3–10]

The optical transparency of polyimide films is of special importance for some applications on space components, such as antennae, solar cells, and thermal control coating systems, and on optoelectronic devices, such as optical waveguides for communication interconnects and optical half-waveplates for planar lightwave circuits. However, most conventional polyimide films show considerable coloration, from pale yellow to deep brown, mainly due to charge-transfer complexing between alternating electron-donor (diamine) and electron-acceptor (dianhydride) segments.[11–13] One strategy for obtaining lightly colored or colorless polyimides is to use the lower electron acceptability of dianhydrides and the lower electron donatability of diamines as monomers to decrease both intramolecular and intermolecular charge-transfer interactions. St. Clair and coworkers[14,15] investigated the structure–coloration relationship systematically. The incorporation of bulky electron-withdrawing groups in the diamine portion of the polymer structure served to reduce the formation of interchain and intrachain charge-transfer complexes (CTCs). The incorporation of separator atoms into either the diamine or dianhydride monomers served to reduce the amount of conjugation and interchain and intrachain electronic interactions and, thereby, to lessen CTC formation. The use of metacatenated aromatic diamines also resulted in improved transparency.

In our recent studies[16–19] on polyimides based on trifluoromethylated bis(ether amines) and aromatic dianhydrides, we demonstrated that the use of hexafluoroisopropylidene-2,2-diphthalic anhydride (6FDA) and 3,4,3′,4′-oxydiphthalic anhydride (4,4′-ODPA) usually produced essentially colorless polyimide films. Although 4,4′-ODPA dianhydride has been used to produce less colored films than is conventional, its derived polyimides were usually insoluble in organic solvents. Recently, one attractive method for improving solubility and processability is to vary the catenation patterns of the dianhydrides in the polyimide backbone.[20–23] In this article, we report the synthesis of highly soluble and light-colored polyimides on the basis of 2,3,2′,3′-oxydiphthalic anhydride (3,3′-ODPA). As first reported by Gerber et al.[24] and

then by Ding et al.,[21] the cured films of 3,3′-ODPA polyimides from their poly(amic acid) (PAA) solutions were generally brittle; this was probably attributable to the formation of cyclic oligomers during thermal imidization. Gerber et al.[24] demonstrated that the polyimides synthesized from 3,3′-ODPA and diamines with an increased chain length could afford flexible films. Ding et al.[21] also reported that flexible films of 3,3′-ODPA polyimides could be cast from N,N-dimethylacetamide (DMAc) solutions of their samples prepared by chemical imidization. However, the properties of 3,3′-ODPA polyimides were not well understood. Herein, we report the successful preparation of flexible films from several 3,3′-ODPA polyimides and the basic properties of these polyimides.

EXPERIMENTAL

Materials

3,3′-ODPA was kindly supplied by Manac, Inc. (Fukuyama, Japan), and was used without further purification. 4,4′-Oxydianiline (ODA; I_a; Tokyo Chemical Industrial (TCI), Tokyo, Japan), 3,4′-oxydianiline (I_b; Chriskev Co., Leawood, KS), 4,4′-(1,4-phenylenedioxy)dianiline (I_c; TCI), 4,4′-(1,3-phenylenedioxy)dianiline (I_d; TCI), 4,4′-bis(4-aminophenoxy)biphenyl (I_g; Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (I_k; Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (I_l; Chriskev) were used as received. 1,4-Bis(4-aminophenoxy)-2-tert-butylbenzene (I_e; mp = 129–130°C), 1,4-bis(4-aminophenoxy)-2,5-di-tert-butylbenzene (I_f; mp = 241–242°C), 4,4′-bis(4-aminophenoxy)-3,3′,5,5′-tetramethylbiphenyl (I_h; mp = 225–226°C), bis[4-(4-aminophenoxy)phenyl] ether (I_i; mp = 109–110°C), and bis[4-(4-aminophenoxy)phenyl] sulfide (I_j; mp = 121–122°C) were synthesized according to well-established procedures reported in the literature.[25–28] 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA; Chriskev) and 6FDA (Hoechst Celanese Co., Coventry, RI) were used as received. Pyromellitic dianhydride (PMDA; Lancaster, Morecambe, UK), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; Acros, Geel, Belgium), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA; New Japan Chemical Co., Osaka, Japan), and 4,4′-ODPA (Manac) were recrystallized from acetic anhydride before use. N-Methyl-2-pyrrolidone (NMP; Fluka, Buchs, Switzerland), DMAc (Fluka), N,N-dimethylformamide (DMF; Fluka), and pyridine (Py; Wako, Osaka, Japan) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of polyimides

Method 1: thermal imidization

Diamine I_h (0.424 g, 1 mmol) was dissolved in 4.4 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 3,3′-ODPA (0.310 g, 1 mmol) was added to the diamine solution in one portion. The mixture was stirred for 1 h and then diluted with 1.3 mL of DMAc to give a solution with a concentration of 12% (w/v) solids. The inherent viscosity (η_{inh}) of the resulting PAA was 1.1 dL/g, as measured at a concentration of 0.5 g/dL in DMAc at 30°C. The PAA solution was then poured into a glass culture dish, which was placed in a 100°C oven overnight for the removal of the casting solvent. The semidried PAA film was further dried and imidized by sequential heating 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. The thermally cured film of polyimide III_h (see Table I for formulas of the series III polyimides) was highly brittle, and its η_{inh} was 0.29 dL/g in DMAc.

Method 2: polyimide preparation in m-cresol

A mixture of I_h (1 mmol) and 3,3′-ODPA (1 mmol) in 4.4 mL of m-cresol was stirred at 50°C for 1 h, and then, the reaction was heated to 200°C and stirred at 200°C for 3 h. The cooled polyimide solution was poured into methanol to precipitate a white powder. The η_{inh} of this polyimide sample was 0.32 dL/g in DMAc. The film cast from DMAc was brittle.

Method 3: chemical imidization

A PAA solution was prepared as described for method 1, and then 0.7 mL of acetic anhydride and 0.3 mL of Py were added to the 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 a 100°C oven for 1 h to evaporate the solvent and to form a thin solid film. The polyimide film was sequentially heated to 200°C and held at that temperature for 2 h to remove the residual solvent. The resultant polyimide film was flexible and creaseable, with an η_{inh} of 0.59 dL/g in DMAc. This polyimide sample exhibited number-average molecular weight (M_n) and weight-average molecular weight (M_w) values of 18,000 and 28,000, respectively:

IR (film): 1780 (asymmetric C=O stretching); 1724 (symmetric imide C=O stretching); 1587–1506 (aromatic C=C stretching); 1383 (C—N stretch); 1244 (C—O); 1109, 746 cm^{-1} (imide ring deformation). ^{1}H-NMR (500 MHz, CDCl$_3$, δ, ppm): 7.77–7.76 (d, 2H, H$_a$), 7.76–7.73 (t, 2H, H$_b$), 7.32 (s, 4H, H$_f$), 7.29 (d, 4H, H$_d$, J = 8.8 Hz), 7.28 (d, 2H, H$_c$), 6.89 (d, 4H, H$_e$, J = 8.8 Hz), 2.17 (—CH$_3$). ^{13}C-NMR (125 MHz, CDCl$_3$, δ, ppm): 166.6, 164.7 (C$^{15′,15}$), 157.4 (C^{14}), 152.7 (C^4), 150.2 (C^5), 137.7 (C^{10}), 136.4 (C^{12}), 134.2 (C^1), 131.6 (C^7), 128.0 (C^6), 127.7 (C^2), 124.9 (C^9), 124.6 (C^8), 120.0 (C^{11}), 119.7 (C^{13}), 115.1 (C^3), 16.5 (C^{16}).
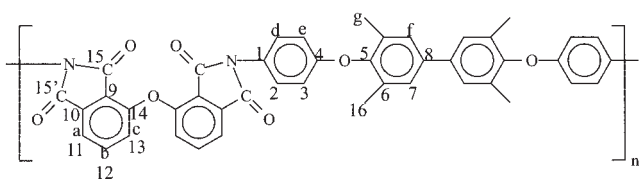
TABLE I
η_{inh} and Elemental Analysis of the Polyimides

Polymer code[a]	η_{inh} (dL/g)[b]	Formula (formular weight)		Elemental analysis (%)		
				C	H	N
III$_a$	0.52	$(C_{28}H_{14}O_6N_2)_n$	Calcd	70.89	2.97	5.90
		$(474.43)_n$	Found	69.53	3.34	5.66
III$_b$	0.41	$(C_{28}H_{14}O_6N_2)_n$	Calcd	70.89	2.97	5.90
		$(474.43)_n$	Found	69.55	3.34	5.98
III$_c$	0.54	$(C_{34}H_{18}O_7N_2)_n$	Calcd	72.08	3.20	4.94
		$(566.53)_n$	Found	70.82	3.47	4.73
III$_d$	0.62	$(C_{34}H_{18}O_7N_2)_n$	Calcd	72.08	3.20	4.94
		$(566.53)_n$	Found	70.62	3.42	4.97
III$_e$	0.60[c]	$(C_{38}H_{26}O_7N_2)_n$	Calcd	73.30	4.21	4.50
		$(622.63)_n$	Found	71.90	4.24	4.32
III$_f$	0.52	$(C_{42}H_{34}O_7N_2)_n$	Calcd	74.32	5.05	4.13
		$(678.74)_n$	Found	73.24	5.33	4.33
III$_g$	0.43	$(C_{40}H_{22}O_7N_2)_n$	Calcd	74.76	3.45	4.36
		$(642.62)_n$	Found	73.60	3.71	4.25
III$_h$	0.59[c]	$(C_{44}H_{26}O_7N_2)_n$	Calcd	76.07	3.77	4.03
		$(694.70)_n$	Found	73.96	4.01	4.13
III$_i$	0.54	$(C_{40}H_{22}O_8N_2)_n$	Calcd	72.95	3.37	4.25
		$(658.62)_n$	Found	71.78	3.63	4.22
III$_j$	0.55	$(C_{40}H_{22}O_7N_2S_1)_n$	Calcd	71.21	3.29	4.15
		$(674.68)_n$	Found	70.34	3.53	4.07
III$_k$	0.60	$(C_{43}H_{28}O_7N_2)_n$	Calcd	75.43	4.12	4.09
		$(684.70)_n$	Found	73.90	4.33	4.15
III$_l$	0.52[c]	$(C_{43}H_{22}O_7N_2F_6)_n$	Calcd	74.32	5.05	4.13
		$(678.74)_n$	Found	73.54	5.28	4.22

[a] The polyimide samples were obtained by the chemical imidization method.
[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.
[c] GPC data: **III$_e$** ($M_n = 2.4 \times 10^4$, $M_w = 4.3 \times 10^4$, $M_w/M_n = 1.76$); **III$_h$** ($M_n = 1.8 \times 10^4$, $M_w = 2.8 \times 10^4$, $M_w/M_n = 1.60$); and **III$_l$** ($M_n = 2.2 \times 10^4$, $M_w = 3.6 \times 10^4$, $M_w/M_n = 1.60$).

The other 3,3'-ODPA polyimides were synthesized by a procedure analogous to method 3. The η_{inh} values and elemental analysis results of all of the series **III** polyimides are summarized in Table I.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer (Kyoto, Japan). Elemental analyses were run in a HERAEUS VarioEL-III CHN analyzer. M_w's and M_n's were obtained by gel permeation chromatography (GPC) on the basis of polystyrene calibration with a Waters 2410 apparatus with tetrahydrofuran (THF) as the eluent. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AV-500 Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer. The η_{inh} values were determined at a concentration of 0.5 g/dL with an Ubbelohde viscometer at 30°C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments

TGA 2050 (New Castle, DE). Measurements were carried out on 9–11-mg film samples heated in flowing nitrogen or air (40 cm^3/min) at a heating rate of 20°C/min. Differential scanning calorimetry (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 with a universal tester (LLOYD LRX) with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–60 μm thick, 0.5 cm wide, and 6 cm long. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth color-eye colorimeter. Measurements were taken with films 30–60 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 films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer (Columbia, MD).

RESULTS AND DISCUSSION

Polymer synthesis

The most commonly used procedures for the preparation of polyimides are two-stage processes that in-
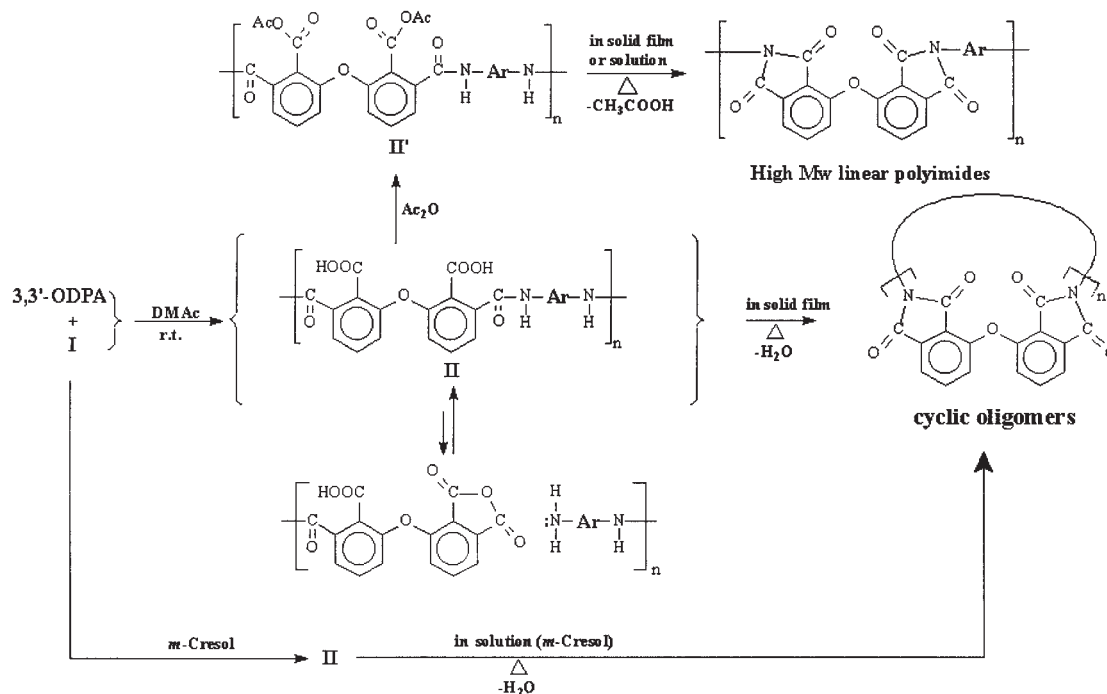
Scheme 1 Mechanism of the thermal imidization of PAAs (series **II**) and poly(*o*-anhydride amides) (series **II'**) of the 3,3'-ODPA system.

volve the preparation of a PAA precursor by the addition of a tetracarboxylic acid dianhydride to a solution of diamine in a polar aprotic solvent, such as NMP or DMAc, at ambient temperature, followed by cyclodehydration, or imidization. The imidization step can be thermally induced or treated by chemical dehydrating agents. Because the polyimide is often insoluble and infusible, the polymer is usually processed in the form of PAA, which is thermally imidized in place. There are many factors involved in the successful synthesis of polyimides with these two-stage procedures. A detailed description of two-stage methods and the reaction mechanisms involved is provided in a compendium by Wilson, Stenzenberger, and Hergenrother.[1] Polyimides that are soluble in organic solvents can be prepared by one-pot methods. In these procedures, the dianhydride and diamine are stirred in a high-boiling organic solvent, such as *m*-cresol, at a high temperature (ca. 180–220°C). Under these conditions, chain growth and imidization essentially occur spontaneously.

Although 3,3'-ODPA has a highly bent configuration, highly viscous PAA solutions were obtained by the reaction of 3,3'-ODPA with conventional aromatic diamines in DMAc at room temperature within 3 h. The η_{inh} values of the obtained PAA solutions were generally higher than 1.0 dL/g, indicative of the formation of high-molecular-weight polymers. However, the thermally cured polyimide films from their PAA solutions were highly brittle. The η_{inh} values of these thermally

cured polyimide samples decreased to a lower level between 0.2 and 0.3 dL/g. If the polyimides were prepared via the chemical imidization of their PAA solutions by means of acetic anhydride and Py, they had a relatively higher η_{inh} value (generally > 0.5 dL/g) and could be cast into flexible and tough films. The relatively lower η_{inh} values of the thermally cured polyimides may have been due to the reversion process of PAA during thermal imidization. As shown in Scheme 1, during thermal imidization of PAA, a small percentage of the *o*-carboxycarboamide group may have reverted to amines and anhydrides. Although the process of reversion exists in all PAA films, the anhydride and amine end group could have recombined during thermal imidization for the system involving 4,4'-ODPA. For 3,3'-ODPA, the generated cyclic oligomers were probably more stable than the linear oligomers; therefore, the end groups could no longer recombine to form high-molecular-weight polymers. In contrast, the reversion process did not occur during thermal imidization of poly(*o*-anhydride amide) (**II'**), a possible intermediate from the reaction of PAA with acetic anhydride. Thus, the synthesis of polyimides via PAA and subsequent chemical imidization led to high-molecular-weight polymers; there was no reason to think that there was a major redistribution of species on chemical imidization. Under these conditions, the polymerizations are normally under kinetic control. When the reaction is carried out under vigorous, high-temperature conditions (in refluxing *m*-cresol), the reversion process occurs, and an equilibrium
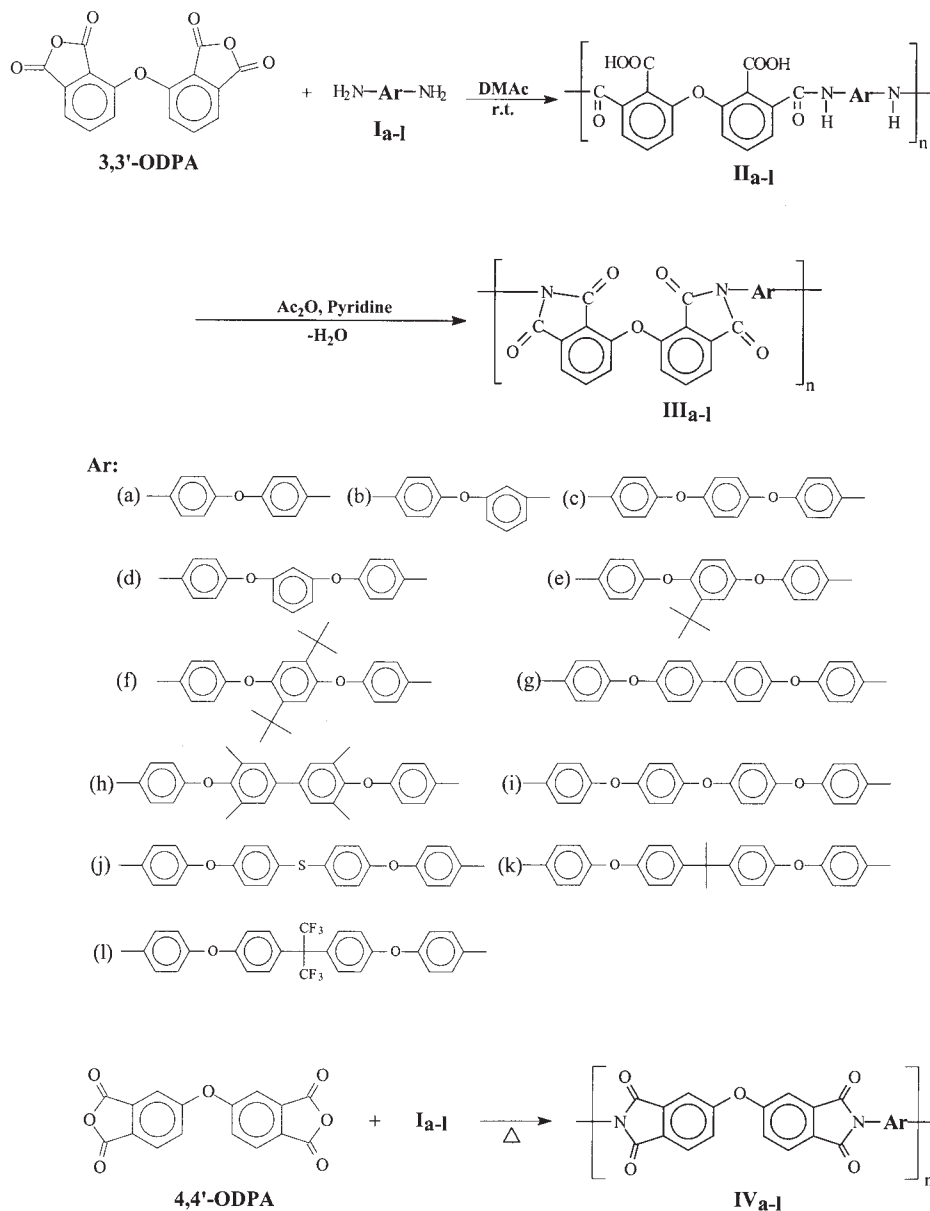
Scheme 2 Synthesis of the 3,3′-ODPA and 4,4′-ODPA polyimides.

is reached. The cyclic oligomers are the thermodynamic products because they are more stable.

Thus, a series of high-molecular-weight, film-formable polyimides (III_a–III_l) were prepared from 3,3′-ODPA and various aromatic diamines (I_a–III_l) via PAA and subsequent chemical imidization (Scheme 2). As shown in Table I, polyimides III_a–III_l thus obtained had η_{inh} values ranging from 0.41 to 0.62 dL/g in DMAc at 30°C. The molecular weights of all of the polyimides were high enough to permit the casting of flexible and tough films. The M_w and M_n values of three THF-soluble polyimides, III_e, III_h, and III_l, were recorded in the range 28,000–43,000 and 18,000–24,000, respectively, relative to polystyrene standards.

The formation of the polyimides was confirmed with IR, NMR, and elemental analysis. The results of elemental analysis for all of the polyimides are listed in Table I. The elemental analysis values generally agreed with the calculated values of the proposed structures, excepting only the values found for the C percentages, which were always lower than the theoretical ones. That certainly could be attributed to the aromatic nature of these polymers, which commonly leave a small coal residue in the standard conditions of microanalysis. All of the polyimides exhibited characteristic imide group absorptions around 1780 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretching), 1380 cm^{-1} (C—N stretching), and 1100 and 730 cm^{-1} (imide ring deformation). The disappearance of the amide and carboxyl bands indicated a virtually complete conversion of the PAA precursors into polyimides. Figure 1 shows a typical set of
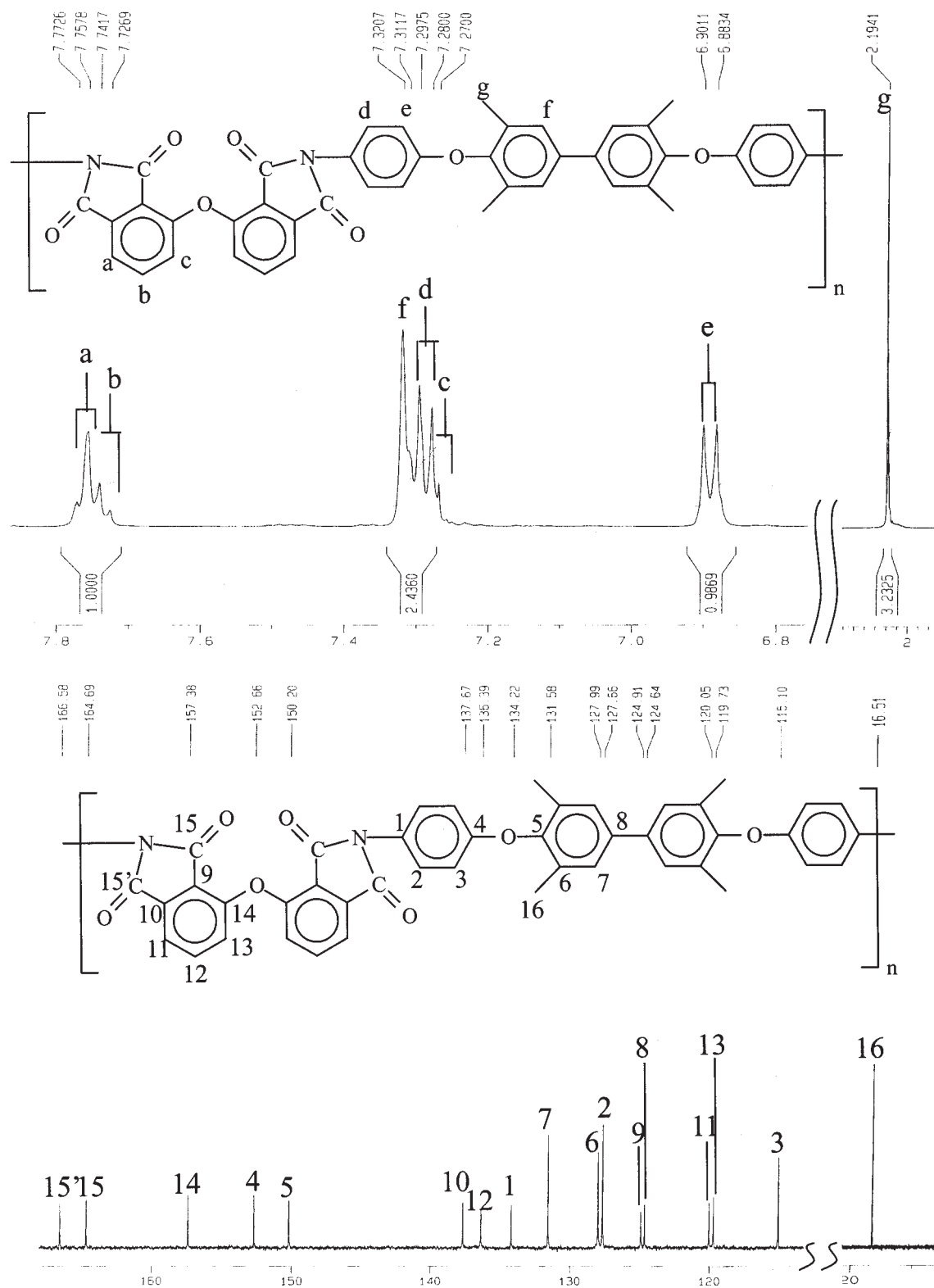
Figure 1 ¹H-NMR and ¹³C-NMR spectra of polyimide **III_h** in CDCl₃.

¹H-NMR and ¹³C-NMR spectra for polyimide **III_h** in CDCl₃, where all of the peaks were readily assigned to the hydrogen and carbon atoms of the repeating structure.

Properties of polymers

The solubility properties of **III_a–III_l** are reported in Table II. For comparison, the solubility behavior of the

TABLE II
Solubility Properties of the Polyimides in Various Solvents

Polymer code[a]	NMP	DMAc	DMF	DMSO	m-Cresol	Py	Dioxane	THF	CH$_2$Cl$_2$	CHCl$_3$
III$_a$	++	++	+	+	+++	+++	−	−	−	−
III$_b$	++	+++	+	+++	+++	+++	−	−	++	+
III$_c$	++	+++	+	+	+++	+++	+	−	+	+
III$_d$	++	+++	+	+	+++	+++	−	−	++	++
III$_e$	++	+++	++	+	+++	+++	++	++	++	++
III$_f$	++	++	+	−	++	++	+	−	+	+
III$_g$	++	+++	++	−	++	++	−	−	++	++
III$_h$	++	+++	++	+	+++	+++	−	++	++	++
III$_i$	++	+++	++	+	+++	+++	+++	−	++	++
III$_j$	++	+++	+	+	++	+++	++	−	+++	++
III$_k$	++	+++	++	+	++	+++	+++	−	+++	++
III$_l$	++	+++	++	++	+++	+++	+++	++	+++	++
IV$_a$	−	−	−	−	−	−	−	−	−	−
IV$_b$	−	−	−	−	−	−	−	−	−	−
IV$_c$	−	−	−	−	−	−	−	−	−	−
IV$_d$	−	−	−	−	−	−	−	−	−	−
IV$_e$	−	−	−	−	−	−	−	−	−	−
IV$_f$	−	−	−	−	−	−	−	−	−	−
IV$_g$	−	−	−	−	−	−	−	−	−	−
IV$_h$	+	S	S	S	+	+	−	−	−	−
IV$_l$	++	++	++	+	+	++	+	++	++	++

+++ = soluble at a concentration of 10% (100-mg sample in 1 mL of the solvent); ++ = soluble at 5%; + = soluble at 1%; − = insoluble; S = swelling.
[a] Polyimides III$_{a–l}$ were prepared via chemical imidization, and polyimides IV$_{a–l}$ were prepared via thermal imidization.

series **IV** polyimides based on 4,4′-ODPA are also included in Table II. All polyimides of the **III** series could be dissolved at 5–10% concentration in the amide-type solvents, such as NMP and DMAc, and also in the phenolic solvent m-cresol and the basic solvent Py. Most of the series **III** polyimides were also soluble in chlorinated solvents such as dichloromethane and chloroform at a concentration of 5–10% but were less soluble in dimethyl sulfoxide (DMSO), l,4-dioxane, and THF. The polyimides of 4,4′-ODPA had poor solubility because of a strong chain–chain interaction and dense chain packing, which resulted from their more extended chain, whereas the ortho-substituted phthalimide units in the 3,3′-ODPA polyimides caused a twisty chain, which interrupted the close chain packing and chain–chain interactions and thus enhanced solubility in organic solvents.

The thin film tensile properties for the series **III** polyimides are shown in Table III. They had strengths at break of 73–106 MPa, elongations at break of 7–13%, and initial moduli of 1.5–1.9 GPa, indicating that they were strong, tough films.

The color intensities of the polyimides were elucidated from the yellowness index (b*), redness index (a*), and lightness index (L*) observed with a Macbeth color-eye colorimeter. As shown in Table IV, all of the **III** series polyimides exhibited low b* values, ranging from 11.3 to 29.8. The color coordinates of five referenced polyimides derived from common dianhydrides with ODA (**I$_a$**) are also shown in Table IV. The films of the PMDA/ODA

and BTDA/ODA polyimides were a deeper yellow and showed relatively higher b* values of 80.3 and 78.9, respectively. The films of the BPDA/ODA and DSDA/ODA polyimides were pale yellow in color and revealed slightly reduced b* values of 59.4 and 55.6, respectively. The b* of 4,4′-ODPA/ODA (**IV$_a$**) polyimide was very close to that of **III$_a$** (3,3′-ODPA/ODA). Moreover, the color intensities of the **III** series could also be elucidated from the cutoff wavelength (λ_0) observed in UV–vis absorption spectra. The λ_0 values of the **III** series poly-

TABLE III
Tensile Properties of the Polyimide Films

Polymer code[a]	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
III$_a$	95	9	1.6
III$_b$	78	7	1.9
III$_c$	106	11	1.7
III$_d$	76	9	1.5
III$_e$	81	9	1.5
III$_f$	81	8	1.7
III$_g$	77	7	1.9
III$_h$	73	8	1.6
III$_i$	96	11	1.7
III$_j$	80	8	1.6
III$_k$	87	10	1.5
III$_l$	97	13	1.6

[a] These polyimides were obtained by the chemical imidization method.

TABLE IV
Color Coordinates and λ_0 Values from UV–vis Spectra of the Polyimide Films

Polymer code	Film thickness (μm)	Color coordinates[a]			λ_0 (nm)
		b^*	a^*	L^*	
Blank	—	1.0	−0.4	96.2	—
III_a	54	20.0	−7.2	94.1	379.5
III_b	52	11.9	−4.2	95.0	371.5
III_c	60	18.4	−6.7	95.1	381.5
III_d	68	18.3	−5.8	93.6	380.0
III_e	75	20.9	−7.0	94.4	383.5
III_f	67	28.5	−8.2	93.7	396.5
III_g	48	29.8	−9.7	92.3	397.0
III_h	70	28.0	−10.1	94.9	393.0
III_i	64	20.5	−4.6	93.0	382.0
III_j	47	21.0	−4.3	90.4	380.0
III_k	60	17.0	−6.3	95.2	376.0
III_l	60	11.3	−4.0	95.2	370.0
PMDA/ODA	37	80.3	8.4	83.0	449.0
BTDA/ODA	29	78.9	−5.2	89.0	429.0
BPDA/ODA	47	59.4	−11.0	90.0	426.0
DSDA/ODA	37	55.6	−10.4	90.0	410.0
4,4'-ODPA/ODA	41	23.2	−8.4	95.0	384.0

Samples of the series **III** polyimides were prepared by the chemical imidization method, whereas the referenced polyimides were prepared by the thermal imidization method.

[a] The color parameters were calculated according to a CIE LAB equation. An L^* of 100 is white, and 0 is black. A positive a^* of indicates red, and a negative a^* indicates green. A positive b^* indicates yellow, and a negative b^* indicates blue.

imides were recorded in the range 370–397 nm. Figure 2 shows the UV–vis spectra of some polyimide films. III_a showed a higher transmittance and lower λ_0 than the corresponding polyimides derived from common dianhydrides, such as PMDA/ODA, BPDA/ODA, and 4,4'-ODPA/ODA (IV_a). The lightest colored III_l showed the shortest λ_0 because the hexafluoroisopropylidene group
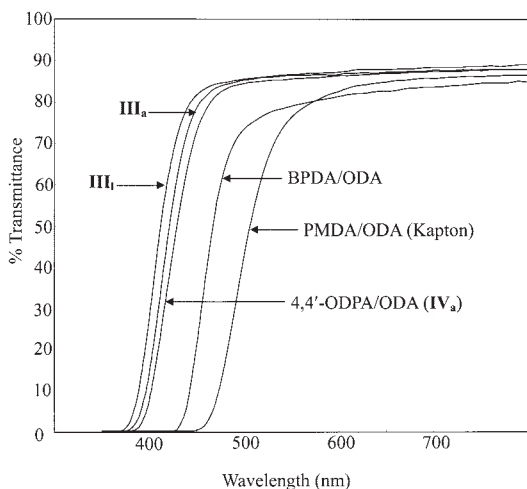
Figure 2 Thin-film UV–vis spectra of some of the polyimides.

in the diamine portion significantly prevented CTC formation. The light colors of the 3,3'-ODPA polyimides could be explained by decreased intermolecular interactions. The highly twisted structure and ether linkage in 3,3'-ODPA were effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-accepting properties of the dianhydride moieties). The decrease in intermolecular CTC formation was understandable also from the significant solubility of polyimides prepared from 3,3'-ODPA.

The thermal properties of polyimides III_a–III_l are shown in Table V. DSC experiments were conducted at a heating rate of 15°C/min in nitrogen. Quenching from 400°C to room temperature produced predominantly amorphous samples so that the glass-transition temperatures (T_g's) of all of the polyimides could be easily measured in subsequent heating DSC traces. The T_g values of these polyimides ranged from 211 to 289°C. The decreasing order of T_g generally correlated with that of chain flexibility. For example, polyimides III_i–III_k, synthesized from long-chain, flexible diamines, exhibited relatively lower T_g values. The introduction of a less symmetrical m-phenylene unit increased the overall flexibility of the polymer chain and, thus, resulted in a decrease in T_g, as shown by the T_g orders observed in Table V: III_a (267°C) > III_b (242°C) and III_c (239°C) > III_d (227°C). As expected, the $tert$-butyl- and methyl-substituted polyimides III_e (T_g = 250°C), III_f (T_g = 247°C), and III_h (T_g = 289°C) exhibited higher T_g values than the corresponding unsubstituted polyimides III_c (T_g = 239°C) and III_g (T_g = 257°C) due to the increased barrier of chain rotation and movement. The T_g values of polymers III_a and III_c were slightly lower than those reported in literature,[21] and these differences may have been due to different values for instrument sensitivity, heating story, and molecular weights of the polymers. The TGA data indicated that these polyimides had fairly high thermal stabilities. The temperatures for 10% weight loss (T_{10}'s) of these polyimides in nitrogen and air atmospheres stayed within 473–562°C and 499–569°C, respectively. Polymers III_e, III_f, and III_h revealed slightly lower stabilities because of the presence of alkyl substituents along their backbones.

CONCLUSIONS

A series of high-molecular-weight polyimides (III_a–III_l) were successfully synthesized from 3,3'-ODPA with various aromatic diamines I_a–I_l by a two-step method via the chemical imidization of PAA precursors. These polyimides displayed a dramatically enhanced solubility compared to their analogs derived from 4,4'-ODPA. Their cast films had good mechanical properties and were very light in color. They showed T_g's in the range 211–289°C and high thermal stabilities. The excellent

TABLE V
Thermal Properties of the Polyimides

Polymer	T_g (°C)[a]	T_5 (°C)[b]		T_{10} (°C)[b]		Char yield (%)[c]
		In N_2	In air	In N_2	In air	
III$_a$	267 (290)[d]	513	509 (500)[d]	540	536	50
III$_b$	242	524	523	546	543	55
III$_c$	239 (253)[d]	532	518 (493)[d]	550	541	52
III$_d$	227	533	519	551	545	53
III$_e$	250	492	513	513	513	33
III$_f$	247	495	484	505	499	21
III$_g$	257	545	544	562	569	56
III$_h$	289	461	476	473	512	46
III$_i$	211	540	526	557	549	50
III$_j$	214	541	530	556	551	51
III$_k$	218	512	513	523	530	44
III$_l$	234	523	516	542	536	50

T_5 = temperature at which a 5% weight loss was recorded.
[a] Baseline shift in the second heating DSC traces with a heating rate of 15°C/min.
[b] Recorded by TGA at a heating rate of 20°C/min.
[c] Residual weight (%) when heated to 800°C in nitrogen.
[d] Data from ref. 21.

properties associated with 3,3′-ODPA based polyimides demonstrate promising potential for future applications.

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