

New Poly(amide imide imide)s Based on Tetraimide Dicarboxylic Acid Condensed from 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride, *m*-Aminobenzoic Acid, and 4,4''-Oxydianiline and Various Aromatic Diamines

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ABSTRACT: A series of new, organosoluble, and light-colored poly(amide imide imide)s were synthesized from tetraimide dicarboxylic acid (**I**) and various aromatic diamines by direct polycondensation with triphenyl phosphite and pyridine as condensing agents. **I** was prepared by the azeotropic condensation of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, *m*-aminobenzoic acid, and 4,4'-oxydianiline at a 2/2/1 molar ratio in *N*-methyl-2-pyrrolidone (NMP)/toluene. The thin films cast from *N,N*-dimethylacetamide (DMAc) had cutoff wavelengths shorter than 400 nm (365–394 nm) and color coordinate *b** values between 13.10 and 36.07; these polymers were lighter in color than the analogous poly(amide imide)s and isomeric polymers. All of

the polymers were readily soluble in a variety of organic solvents, including NMP, DMAc, *N,N*-dimethylformamide, dimethyl sulfoxide, and even less polar dioxane and tetrahydrofuran. The cast films exhibited tensile strengths of 90–104 MPa, elongations at break of 7–22%, and initial moduli of 1.9–2.4 GPa. The glass-transition temperatures of the polymers were recorded at 274–319°C. They had 10% weight losses at temperatures beyond 520°C and left more than a 50% residue even at 800°C in nitrogen. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 669–679, 2003

Key words: polyamides; polyimides; films

INTRODUCTION

Aromatic polyimides are well known as polymer materials of high performance because of their excellent thermal stabilities and balanced tensile and electric properties.^{1–7} They are mainly used in the aerospace and electronics industries in the forms of films and moldings. The optical transparency of polyimide films is especially important in some applications.^{8–11} However, wholly aromatic polyimides strongly absorb in the visible region of the ultraviolet–visible (UV–vis) spectrum and are pale yellow or deep reddish-yellow; besides, they are difficult to process because of high softening temperatures and limited solubility in commercially available solvents. To increase the optical applications of polyimides, a number of very lightly colored to colorless, transparent polyimide films have been synthesized and characterized. Rogers¹² first reported that optically transparent and colorless poly-

imides could be synthesized from a dianhydride and a diamine with hexafluoroisopropylidene [$-\text{C}(\text{CF}_3)_2-$] groups. Some publications have shown the formation of a charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.^{13–15}

For improved polyimide processability, various copolymers have been developed and reported, including poly(amide imide)s, the amide groups of which can improve the solubility.^{16,17} Furthermore, poly(amide imide)s are lighter in color than corresponding polyimides. Our laboratory has developed a convenient method for poly(amide imide) synthesis, and many alternating poly(amide imide)s have been prepared systematically by direct polycondensation.^{18–26} However, in this technique, the amounts of the condensing agents increase with increasing amounts of the monomers; this leads to a high synthetic cost, which hinders the industrialization of direct polycondensation. If alternating poly(amide imide)s can be synthesized from large molecular weight monomers, reducing the synthetic cost and industrializing direct polycondensation should be possible. Therefore, we designed and synthesized novel poly(amide imide imide)s based on large molecular weight tetraimide dicarboxylic acid (**I**) as a continuation of our system-

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atic study on dealing with the effects of new structures on basic characterization, especially coloration.

Unlike previous poly(amide imide)s with an amide/imide ratio of 1/1,^{18–26} in this study, novel alternating poly(amide imide imide)s with an amide/imide ratio of 1/2 were synthesized. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), *m*-aminobenzoic acid (*m*-ABA), and 4,4'-oxydianiline (4,4'-ODA or **III_c**) were used to prepare a new form of **I** that was reacted with various aromatic diamines to form poly(amide imide imide)s by direct polycondensation. Various properties of the resultant poly(amide imide imide)s, such as their solubility, coloration, tensile properties, and thermal stability, were investigated.

EXPERIMENTAL

Materials

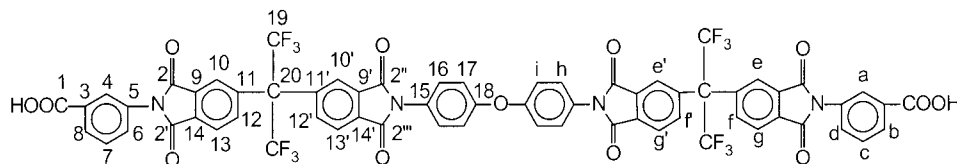
p-Phenylenediamine (**III_a**; Wako) and benzidine (**III_b**; TCI) were vacuum-distilled before use. All other diamines, including **III_c** (Wakayama), 4,4'-diaminobenzanilide (**III_d**; TCI), 1,4-bis(4-aminophenoxy)benzene (**III_e**; TCI), and 4,4'-bis(4-aminophenoxy)biphenyl (**III_h**; TCI), were used as received. The diamines 1,3-bis(4-aminophenoxy)benzene (**III_f**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**III_i**), 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (**III_j**), 2,2-bis[4-(3-aminophenoxy)phenyl]sulfone (**III_k**), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**III_l**) were obtained from Chriskev Corp. and were used without previous purification. 1,2-Bis(4-aminophenoxy)benzene (**III_g**) was prepared according to the method reported in a previous article.²⁷ *m*-ABA (TCI) and triphenyl phosphite (TPP; TCI) were used as received. 6FDA (Hoechst) was recrystallized from acetic anhydride before use. Commercially available calcium chloride (CaCl₂) was dried *in vacuo* at 150°C for 6 h. *N*-Methyl-2-pyrrolidone (NMP; Fluka), *N,N*-dimethylacetamide (DMAc; Fluka), *N,N*-dimethyl-

formamide (DMF; Fluka), and pyridine (Py; Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of I

A mixture of 4.11 g (30 mmol) of *m*-ABA and 3.00 g (15 mmol) of 4,4'-ODA was first dissolved in 45 mL of NMP. After the mixture was completely dissolved, 13.32 g (30 mmol) of 6FDA was added in one portion. The mixture was stirred at room temperature for 2 h. About 20 mL of toluene was then added, and the mixture was heated at the reflux temperature for about 3 h until about 1.2 mL of water was distilled off azeotropically via a Dean–Stark trap. After the complete removal of the water, the residual toluene was distilled off under reduced pressure. After cooling, the obtained solution was trickled into methanol, and the precipitated product was collected by filtration, purified by recrystallization from DMF–methanol solution, and dried *in vacuo* to give 18.38 g of a white powder of **I** (yield = 95%; mp > 400°C).

IR (KBr): 2500–3500 (acid —OH), 1784 (imide, symmetric C=O stretching), 1725 (acid C=O stretching and asymmetric imide C=O stretching), 1244 (ether C—O—C), 1375, 1111, 721 cm⁻¹ (imide, imide ring vibration, axial, transverse, and out of plane). ¹H-NMR [400 MHz, dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), δ]: 8.22, 8.21 (H_g + H_{g'}), 8.07 (H_a), 8.04, 8.02 (H_d), 8.00, 7.98 (H_f + H_{f'}), 7.78 (H_e + H_{e'}), 7.74, 7.72 (H_b), 7.71, 7.69, 7.67 (H_c), 7.53, 7.51 (H_h), 7.27, 7.25 (H_i). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ): 168.63 (C¹), 168.26, 168.14, 168.07, 167.93 (C², C^{2'}, C^{2''}, C^{2'''}), 158.01 (C¹⁸), 139.03 (C¹¹, C^{11'}), 137.51 (C⁵), 134.67 (C⁹, C^{9'}), 134.27 (C¹², C^{12'}), 133.61 (C¹⁴, C^{14'}), 133.30, 133.26 (C⁷, C¹³, C^{13'}), 130.92 (C⁶, C¹⁶), 130.61 (C⁴), 129.76 (C⁸), 128.70 (C¹⁵), 125.97, 125.91 (C¹⁰, C^{10'}), 125.16 (C³), 120.57 (C¹⁷), 124.87 (C¹⁹, quartet, ¹J_{C–F} = 290 Hz), 65.37 (C²⁰, multiplet, ²J_{C–F} = 26 Hz).

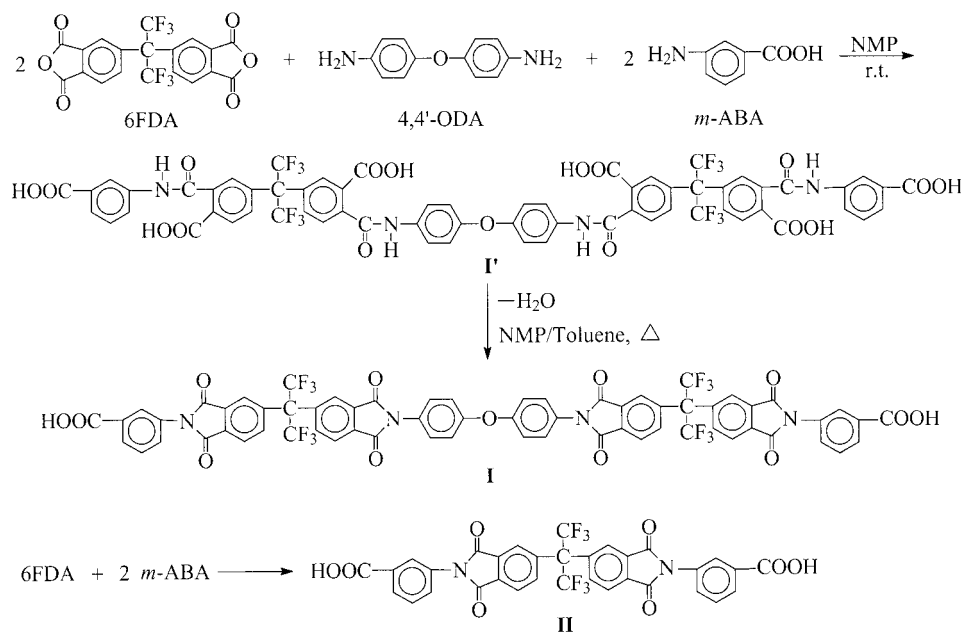


ELEM. ANAL. Calcd for C₆₄H₃₀N₄O₁₃F₁₂ (1290.94): C, 59.55%; H, 2.34%; N, 4.34%. Found: C, 59.44%; H, 2.40%; N, 4.40%.

Synthesis of the poly(amide imide imide)s

A typical example of polycondensation was as follows. A mixture of 1.291 g (1.0 mmol) of **I**, 0.292 g (1.0 mmol) of diamine **III_e**, 0.15 g of CaCl₂, 1.2 mL of Py,

0.6 mL of TPP, and 5.0 mL of NMP was heated with stirring at 100°C for 3 h. The viscosity of the reaction solution increased after 1 h, and an additional 3.0 mL of NMP was added to the reaction mixture. At the end of the reaction, the obtained polymer solution was trickled into 400 mL of stirred methanol. The stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under reduced pressure. The inherent viscosity (η_{inh})



Scheme 1 Synthesis of I and II.

of the polymer in DMAc at a 0.5 g dL^{-1} concentration at 30°C was 0.74 dL g^{-1} . All other poly(amide imide imide)s were synthesized in a similar manner.

Preparation of the poly(amide imide imide) films

An approximately 10% polymer solution was made by the dissolution of poly(amide imide imide) in DMAc. The solution was poured into a glass culture dish 9 cm in diameter that was placed in a 90°C oven overnight for the removal of the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried *in vacuo* at 160°C for 6 h. The obtained films were about 0.05 mm thick.

Measurements

^1H - and ^{13}C -NMR spectra were determined on a JEOL EX-400 FT-NMR spectrometer. IR spectra were recorded on a Horiba 720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were carried out with a PerkinElmer model 2400 CHN analyzer. The η_{inh} values of all the polymers were determined with a Cannon-Fenske viscometer. The coloration of the polymers was evaluated with a Macbeth Color-Eye colorimeter. Measurements were performed with films at an observational angle of 10° with a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. UV-vis spectra of the polymer films were recorded with a Shimadzu UV-1601 UV-vis recording spectrophotometer at room temperature in air. Differential scanning calorimetry (DSC) traces were measured on a TA Instruments DSC 2010 at the rate of $15^\circ\text{C min}^{-1}$ in

flowing nitrogen ($40 \text{ cm}^3 \text{ min}^{-1}$). A thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on samples ($10 \pm 2 \text{ mg}$) heated in flowing nitrogen or air ($100 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $20^\circ\text{C min}^{-1}$. An Instron 1130 universal tester with a load cell of 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens 0.5 cm wide, 6 cm long, and about 0.05 mm thick, and an average of at least five individual determinations was reported.

RESULTS AND DISCUSSION

Monomer synthesis

I was synthesized with the ring-opening addition of 4,4'-ODA, 6FDA, and *m*-ABA in a 1/2/2 molar ratio at room temperature in an amide-type solvent (e.g., NMP or DMAc) followed by the intramolecular cyclodehydration of the intermediate tetraamide hexacarboxylic acid (I'; Scheme 1). For the synthesis of I, the addition of 4,4'-ODA, 6FDA, and *m*-ABA might not have formed the structure of the intermediate I' completely in the initial period, and some other diacids were produced. However, the exchange reaction of amic acid was carried out during a long period of stirring,²⁸ and the product with the lowest free energy was prepared. From the molar ratio of the monomers, I' was a more stable structure among the intermediates. Therefore, a higher purity of I was obtained after the cyclodehydration of I'. The structure of monomer I was confirmed by elemental analysis and IR, ^1H -NMR, and ^{13}C -NMR spectroscopy.

The ^1H - and ^{13}C -NMR spectra of **I** are shown in Figures 1 and 2. The ^1H -NMR spectrum of **I** shows five main signals due to the different environments of the protons. The relative shifts of **I** are similar to those of the diimide diacid model compound (**II**). The corresponding protons of two diacids appear in similar shift ranges. The signals of $\text{H}_{\text{a-g}}$ of **I** appear at 7.67–8.22 ppm and are also exhibited in the spectrum of **II**. $\text{H}_{\text{h,i}}$ appears at a higher field than the rest of the protons, and H_{i} adjacent to the imide ring resonates at a lower field than H_{i} . From the integrals of the protons, it is shown that the proposed structures of **I** formed with high purity. The ^{13}C -NMR spectrum of **I** shows five signals of the carbonyl of the acid group and imide ring. With their different environments, the carbonyls of the imide ring ($\text{C}^{2,2',2'',2''}$) display four different signals (168.26, 168.14, 168.07, and 167.93 ppm). There are 22 signals for the carbon of benzene according to the structure of **I**, but only 16 signals for the carbon of benzene can be found in the spectrum because of the close or overlapped shifts of C^{9-14} and $\text{C}^{9'-14'}$. A comparison of monomer **I** and model compound **II** shows that the relative shift positions in **I** are very similar to those in **II**. Furthermore, the splitting of the ^{13}C signals caused by couplings between carbon and fluorine also can be observed in these spectra. The magnitudes of the one-bond and two-bond carbon–fluorine couplings, $^1J_{\text{C-F}}$ and $^2J_{\text{C-F}}$, are 290 and 26 Hz, respectively.

Polymer synthesis

A series of poly(amide imide imide)s (**IV_{a-d}**) were synthesized from **I** and various diamines by means of direct polycondensation with TPP/Py as the condensing agent in NMP in the presence of CaCl_2 (Scheme 2). Polymerization also can proceed directly with the resultant solution of diacid synthesis. The results of the preparation of the poly(amide imide imide)s are summarized in Table I. All the reactions went smoothly in homogeneous solutions under the conditions listed in Table I. Higher molecular weights of these polymers could be obtained with a higher initial reactant concentration and the addition of a proper amount of supplemental NMP to the viscous reaction medium before the formation of a swollen gel. Besides, an advantage of poly(amide imide imide) synthesis from large molecular weight **I** is that a lot of product can be obtained with a small amount of TPP. In other words, when the same amount of TPP was used, the same number of moles of a polymer in this study and in other reports was formed, but the weight of the polymer in this study was larger. Therefore, new types of poly(amide imide imide)s could significantly reduce the cost of synthesis and, therefore, help in industrializing direct polycondensation.

The η_{inh} values of the **IV** series polymers were 0.59–0.99 dL g^{-1} . All of the poly(amide imide imide)s could be solution-cast into transparent and tough films, and this indicated medium to high molecular weights. The compositions and structures of these poly(amide imide imide)s were characterized by their IR spectra and elemental analyses. A typical IR spectrum is depicted in Figure 3. The FTIR spectrum of polymer **IV_e** exhibited characteristic absorption bands for the imide ring at 1784, 1724 (asymmetrical and symmetrical $\text{C}=\text{O}$ stretching vibrations), 1375 ($\text{C}-\text{N}$ stretching vibration), 1111, and 721 cm^{-1} (imide-ring deformation). The absorptions of amide groups appeared at 3367 ($\text{N}-\text{H}$ stretch) and 1649 cm^{-1} ($\text{C}=\text{O}$ stretch). The results of the elemental analyses of all the poly(amide imide imide)s are listed in Table I. The uptakes of water were 0.80–2.82%, which were calculated from the weight changes of the vacuum-dried polymer samples after they were exposed to air at room temperature for 1 h. When the found values were corrected by the elimination of the amount of absorbed water, the corrected values agreed with the calculated ones.

Properties of the polymers

The solubilities of the poly(amide imide imide)s are summarized in Table II. The concentration for the solubility tests was 0.1 g mL^{-1} , and the samples used were the stringy product of poly(amide imide imide) synthesis. In the **IV** series, the diamines were relatively rigid (e.g., **III_{a-e,h}**), but the formed polymers had good solubilities in organic solvents. All the **IV** series polymers had excellent solubilities in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO, and they were also soluble in less polar solvents such as *m*-cresol, Py, dioxane, and tetrahydrofuran (THF). **IV_b** was insoluble in dioxane because its diamine moieties were stiff, and this led to a lower percentage of flexible groups in the main chain. **IV_d** was also insoluble in Py, and this was attributed to the higher percentage of amide groups in its backbone, which formed more intermolecular hydrogen bonds. These polymers had better solubilities than typical poly(amide imide)s derived from trimellitic anhydride,^{18–25} and they were all readily soluble in NMP and DMAc without LiCl. Compared with the available commercial polyimide **VI**, the series **IV** polymers exhibited better solubility in less polar solvents such as dioxane and THF. This might be due to the presence of the hindered hexafluoroisopropylidene linkage and meta-oriented phenylene units in **I** that reduced polymer interchain and intrachain interactions and disturbed the coplanarity of aromatic units, thereby reducing the packing efficiency and crystallinity.

The coloration of the polymers was elucidated from the yellowness or redness indices observed with a

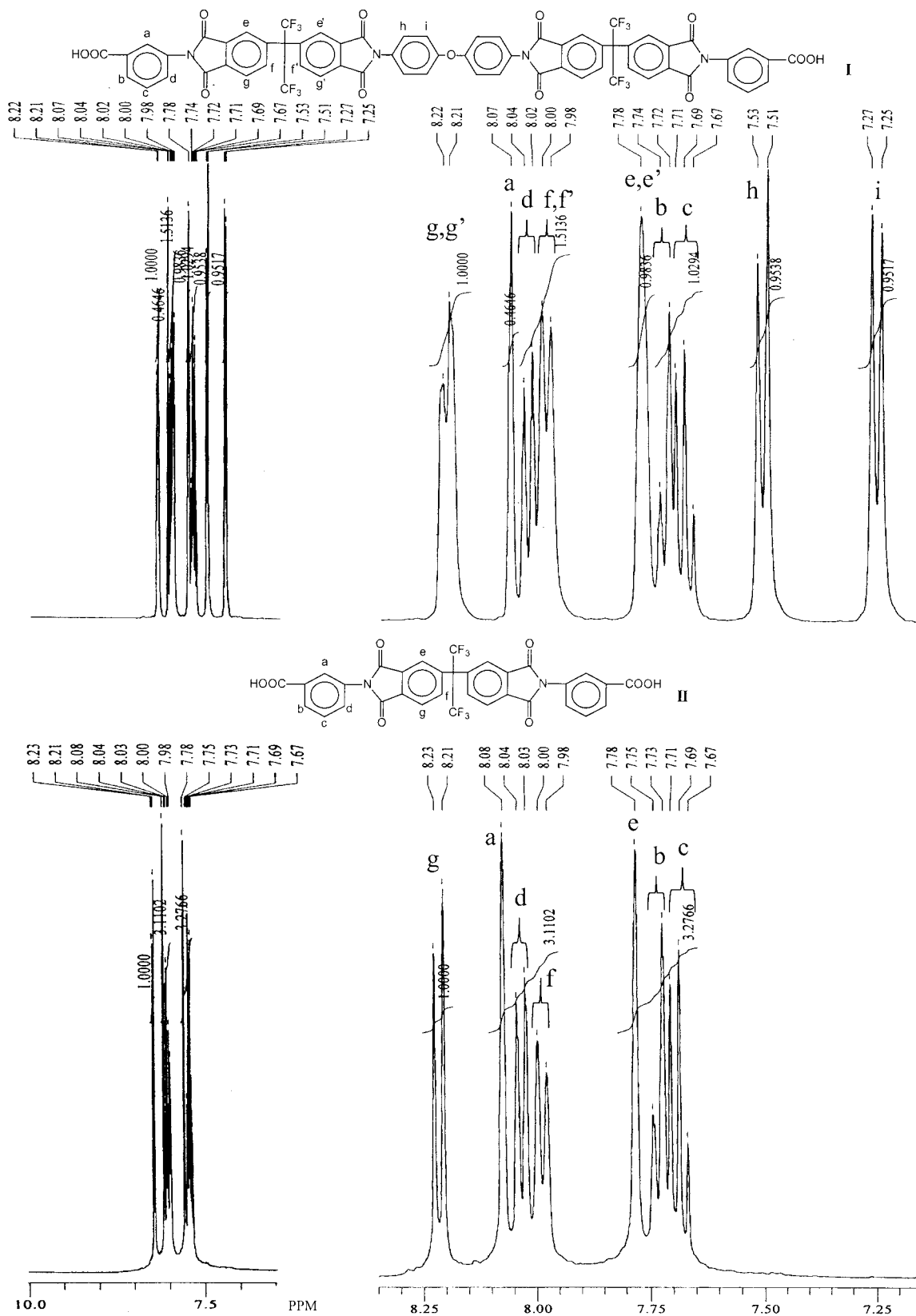


Figure 1 $^1\text{H-NMR}$ spectra of I and II in $\text{DMSO-}d_6$.

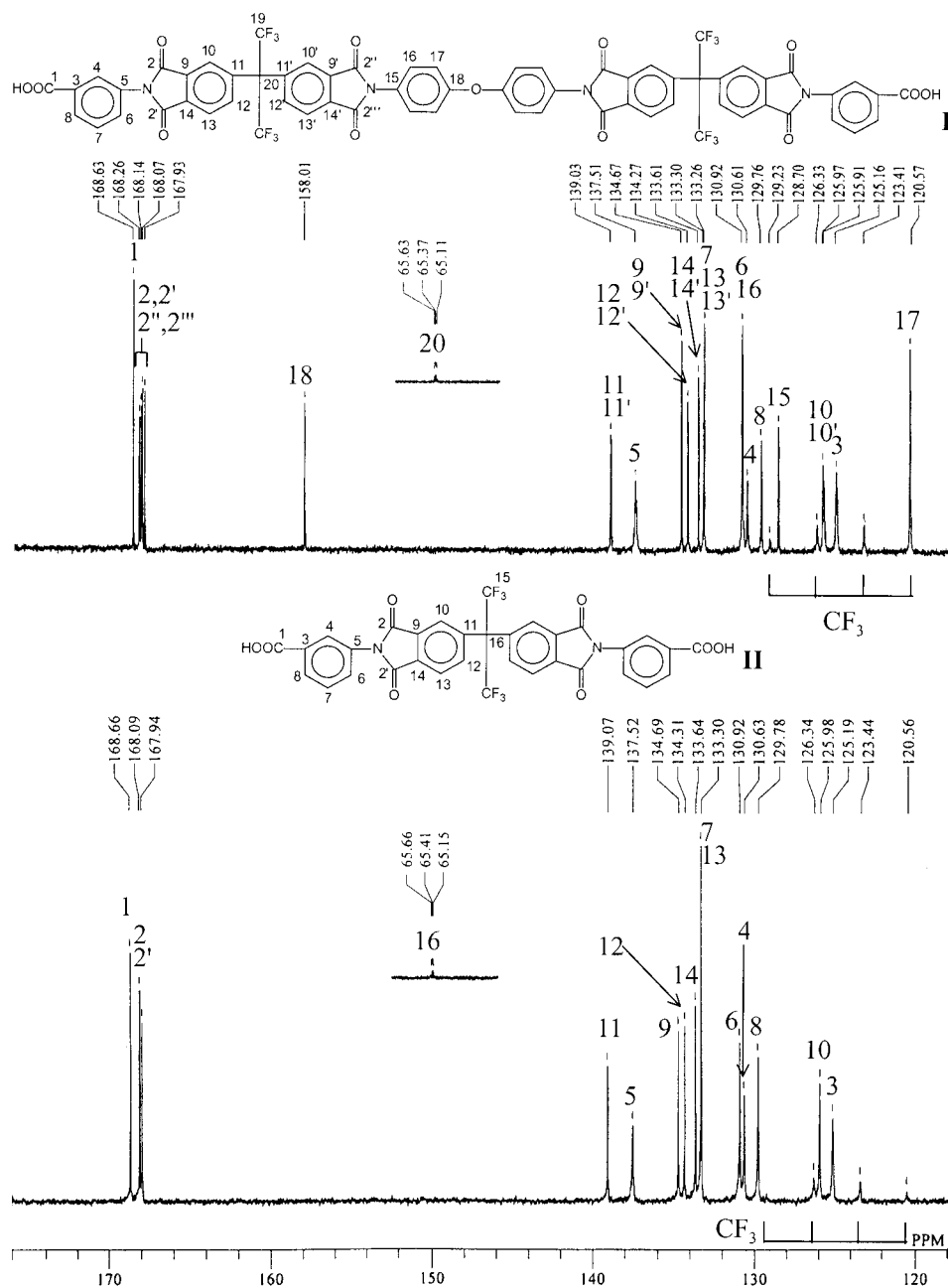


Figure 2 ^{13}C -NMR spectra of I and II in $\text{DMSO}-d_6$.

Macbeth Color-Eye colorimeter, and the CIE LAB color system was applied. The color coordinates of the IV series poly(amide imide imide)s and corresponding polymers V–VII are given in Table III. The cutoff wavelengths of the polymers were also recorded from the transmission UV–vis spectra. The item “Paper” listed in Table III was the result of the white paper used as a standard. When the polymer films were tested, a white piece of paper was placed behind the films as a ground. For the colorless films in this study, therefore, the values of a^* and b^* were close to 0, and the value of L^* was about 92. The IV series polymers showed L^* values ranging between 86.39 and 90.62,

indicating good transparency. The coloration of the polymers was compared with respect to b^* values, and all of the poly(amide imide imide)s showed light colors in the range of 13–36, which depended on the structure of the diamine component. The cutoff wavelengths also indicated that these polymers were lightly colored. Polymer IV_b with III_b as a diamine monomer had the largest b^* value (the longest cutoff wavelength) in this series, and this indicated that polymers containing biphenyl moieties in the main chain would have stronger color intensity. This was also found for IV_{h-1} with a tetraphenylene diether diamine, so IV_h showed a larger b^* value and a longer cutoff wave-

TABLE I
Synthesis and Elemental Analysis of Poly(amide imide imides)

Polymer	Additional NMP (mL)	η_{inh}^b (dL/g)	Formula and weight	Average molecular weight	Elemental analysis (%) ^c			Moisture uptake (%) ^d
					C	H	N	
IV _a	3	0.72	(C ₇₀ H ₃₄ N ₆ O ₁₁ F ₁₂) _n (1363.05) _n	Calcd.	61.68	2.51	6.17	2.66
				Found	60.04	2.40	5.97	
				Corrected	61.64	2.34	6.13	
IV _b	3	0.94	(C ₇₆ H ₃₈ N ₆ O ₁₁ F ₁₂) _n (1439.15) _n	Calcd.	63.43	2.66	5.84	1.37
				Found	61.65	2.58	5.76	
				Corrected	62.50	2.55	5.84	
IV _c	3.5	0.76	(C ₇₆ H ₃₈ N ₆ O ₁₂ F ₁₂) _n (1455.15) _n	Calcd.	62.40	2.65	6.62	2.00
				Found	61.15	2.45	5.65	
				Corrected	62.37	2.40	5.76	
IV _d	5	0.99	(C ₇₇ H ₃₉ N ₇ O ₁₂ F ₁₂) _n (1482.18) _n	Calcd.	62.40	2.65	6.62	2.82
				Found	60.64	2.49	6.43	
				Corrected	62.35	2.42	6.61	
IV _e	3	0.74	(C ₈₂ H ₄₂ N ₆ O ₁₃ F ₁₂) _n (1547.25) _n	Calcd.	63.66	2.74	5.43	2.37
				Found	62.15	2.34	5.14	
				Corrected	63.62	2.29	5.26	
IV _f	3	0.81	(C ₈₂ H ₄₂ N ₆ O ₁₃ F ₁₂) _n (1547.25) _n	Calcd.	63.66	2.74	5.43	2.43
				Found	62.11	2.20	5.12	
				Corrected	63.62	2.15	5.24	
IV _g	0	0.76	(C ₈₂ H ₄₂ N ₆ O ₁₃ F ₁₂) _n (1547.25) _n	Calcd.	63.66	2.74	5.43	2.43
				Found	62.11	2.21	5.03	
				Corrected	63.62	2.16	5.15	
IV _h	1	0.72	(C ₈₈ H ₄₆ N ₆ O ₁₃ F ₁₂) _n (1623.35) _n	Calcd.	65.11	2.86	5.18	2.60
				Found	63.42	2.40	4.79	
				Corrected	65.07	2.34	4.92	
IV _i	2	0.65	(C ₉₁ H ₅₂ N ₆ O ₁₃ F ₁₂) _n (1665.43) _n	Calcd.	65.63	3.15	5.05	2.04
				Found	64.29	2.64	4.72	
				Corrected	65.60	2.59	4.82	
IV _j	3.5	0.59	(C ₈₈ H ₄₆ N ₆ O ₁₅ F ₁₂ S) _n (1687.41) _n	Calcd.	62.64	2.75	4.98	0.80
				Found	61.76	2.75	4.94	
				Corrected	62.25	2.73	4.98	
IV _k	3	0.78	(C ₈₈ H ₄₆ N ₆ O ₁₅ F ₁₂ S) _n (1687.41) _n	Calcd.	62.64	2.75	4.98	1.40
				Found	61.61	2.77	4.91	
				Corrected	62.47	2.73	4.98	
IV _l	6	0.81	(C ₉₁ H ₄₆ N ₆ O ₁₃ F ₁₈) _n (1773.37) _n	Calcd.	61.63	2.61	4.74	2.00
				Found	60.40	2.11	4.36	
				Corrected	61.61	2.07	4.45	

^a Polymerization was carried out with 1 mmol of each monomer in 5 mL of NMP, 1.2–1.4 mL of Py, 0.14–0.25 g of CaCl₂, and 2 mmol (0.6 mL) of TPP at 100°C for 3 h.

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

^c For C and N: Corrected value = Found value × (100% + Moisture uptake %). For H: Corrected value = Found value × (100% – Moisture uptake %).

^d Moisture uptake (%) = (W – W₀)/W₀ × 100%, where W = weight of the polymer sample after standing at room temperature and W₀ = weight of the polymer sample after being dried in vacuum at 100°C for 10 h.

cessability of novel poly(amide imide imide)s without sacrificing tensile properties.

The thermal properties of all the poly(amide imide imide)s were evaluated by thermogravimetry (TG) and DSC. The thermal behavior data of all the polymers are listed in Table V. Because the residual water or solvent and the history of thermal annealing may sometimes influence the first run of DSC, samples were at first heated to 400°C and then quenched to room temperature, and glass-transition temperatures (T_g 's) were determined on the subsequent DSC heating trace. The T_g values of the IV series polymers were 274–319°C, depending on the structure of the diamine

component and following the increasing stiffness of the polymer backbones. The insertion of the flexible ether group increased the overall flexibility of the polymer chain and resulted generally in a decrease in T_g , as evidenced by the T_g order shown in Table V: **IV_{a,b}** > **IV_c** > **IV_{e,f,g}**. **IV_a** showed the highest T_g value because of the higher percentage of amide groups in the backbone, which would form more intermolecular hydrogen bonds. As for isomers, **IV_e**, with its completely para-oriented diamine structure, showed a higher T_g value than **IV_{f,g}**, which was derived from meta- or ortho-oriented diamines. The reason is that the meta- or ortho-position substituent increased the

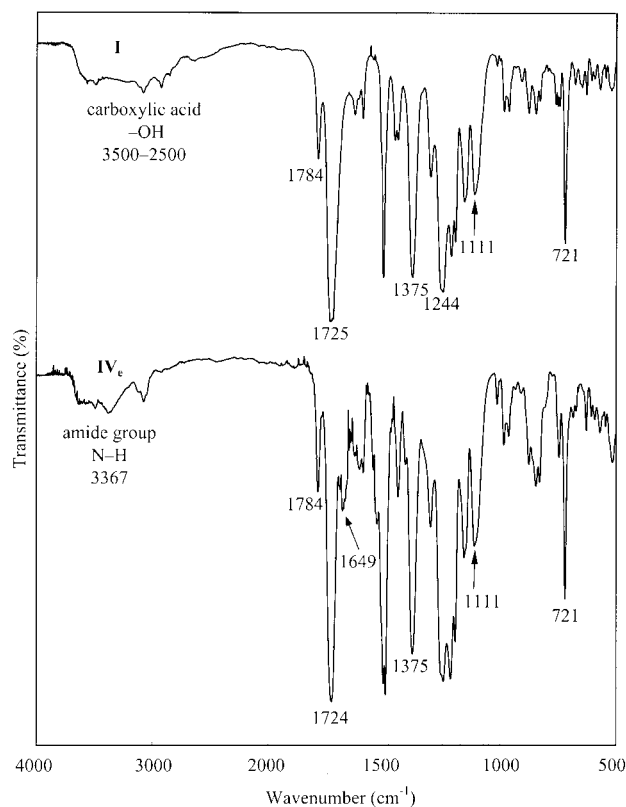


Figure 3 FTIR spectra of I and IV_e.

intermolecular free volumes so that the polymer chains were easy to rotate. This was also found between polymers IV_{j,k'}, so IV_j showed a larger T_g value than IV_k did. Diamine III_i had a structure analogous to that of III_l, but the substituent magnitude of $-\text{CH}_3$ was much smaller than that of $-\text{CF}_3$. Therefore, IV_l, based on III_l, had increased steric hindrance, and their polymer chains consequently rotated at a higher temperature.

The thermal stability of these poly(amide imide imide)s was characterized by TG analysis conducted at a heating rate of $20^\circ\text{C min}^{-1}$. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original thermograms and are also tabulated in Table V. The T_{10} values of these polymers stayed within $523\text{--}550^\circ\text{C}$ in nitrogen and within $534\text{--}545^\circ\text{C}$ in air. The TG traces indicated that the IV series polymers possessed good thermal stability with no significant weight loss up to approximately 450°C . The anaerobic char yield of all the polymers at 800°C was above 50%, showing a high intrinsic fire resistance. The excellent thermal stability of the series IV polymers was due to the higher proportion of the thermostable imide group in the main chain. Furthermore, the thermal properties of the IV series poly(amide imide imide)s were compared with those of polyimide VI, and polymers IV and VI displayed no significant differences; therefore, the thermal properties of IV were not affected by the diamine component and copolymerization.

CONCLUSIONS

Most common polyimides and poly(amide imide)s have intense color and are insoluble in organic solvents. A series of novel poly(amide imide imide)s with light-colored and soluble characterizations were successfully synthesized on the basis of a new form of I. These poly(amide imide imide)s had good solubilities, and they especially exhibited better solubilities than common poly(amide imide)s in less polar solvents. They could be cast into transparent and tough films, which had good tensile properties. The films were light in color and highly transparent, and they were lighter in color than other similar polymers. Therefore, these polymers demonstrated a good combination of

TABLE II
Solubility of Poly(amide imide imides)

Polymer	Solvent							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF
IV _a	+	+	+	+	+	+	S	+
IV _b	+	+	+	+	+	+	–	+
IV _c	+	+	+	+	+	+	+	+
IV _d	+	+	+	+	+	–	S	+
IV _e	+	+	+	+	+	+	+	+
IV _f	+	+	+	+	+	+	+	+
IV _g	+	+	+	+	+	+	+	+
IV _h	+	+	+	+	+	+	+	+
IV _i	+	+	+	+	+	+	+	+
IV _j	+	+	+	+	+	+	+	+
IV _k	+	+	+	+	+	+	+	+
IV _l	+	+	+	+	+	+	+	+
VI	+	+	+	+	+	+	–	–

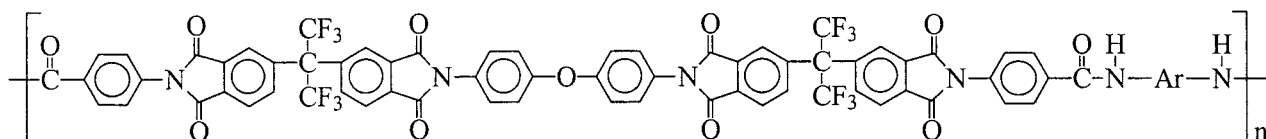
Solubility was measured at a polymer concentration of 0.1 g/mL: + = soluble on heating; S = swelling; – = insoluble.

TABLE III
Optical Properties of Polymer Films

Polymer	Color coordinates ^a			Cutoff wavelength (nm)	Film thickness (μm)
	L*	a*	b*		
Paper	92.51	0.66	-0.28		
IV _a	86.39	-5.23	34.47	391	60
IV _b	87.75	-7.70	36.07	394	50
IV _c	86.85	-4.28	28.63	380	55
IV _d	87.58	-6.44	32.81	386	51
IV _e	87.12	-3.74	26.35	379	53
IV _f	86.60	-3.85	26.03	377	55
IV _g	87.64	-4.66	22.64	371	58
IV _h	87.55	-5.50	26.46	380	55
IV _i	87.54	-3.08	24.37	378	60
IV _j	89.31	-4.71	21.08	376	60
IV _k	89.66	-3.55	15.09	365	63
IV _l	90.62	-3.52	13.10	371	61
V _b	83.18	-3.28	49.28	404	60
V _c	87.16	-4.33	30.56	381	72
V _d	88.39	-6.57	32.89	389	53
VI	94.17	-7.42	37.27	387	52
VII _b ^b	85.97	-4.74	42.19	401	50
VII _c	89.53	-6.55	28.29	384	63
VII _d	86.22	-3.99	39.91	392	59
VII _h	87.67	-5.64	27.97	380	47
VII _i	88.35	-3.28	24.21	380	59
VII _l	88.82	-4.37	24.69	376	61

^a L* is lightness; 100 means white, whereas 0 implies black. A positive a* means red, whereas a negative a* indicates green. A positive b* means yellow, whereas a negative b* implies blue.

^b Structures of polymers VII:



physical properties and optical transparency, and they may be considered new candidates for processable high-performance polymeric materials.

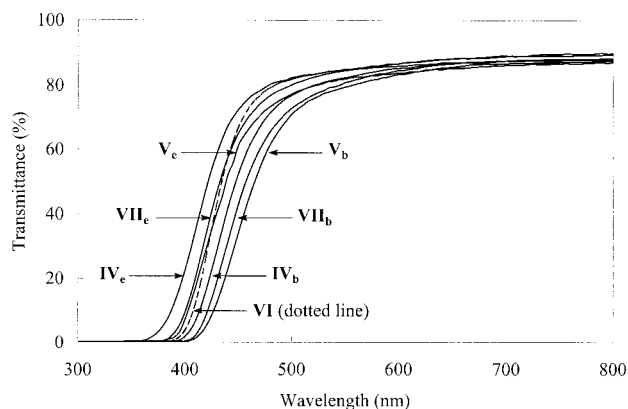


Figure 4 Transmission UV-vis absorption spectra of certain polymers.

TABLE IV
Tensile Properties of Poly(amide imide imide) Films

Polymer	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
IV _a	108	103	22	2.0
IV _b	—	100	7	2.4
IV _c	—	90	7	2.2
IV _d	—	98	8	2.4
IV _e	—	93	7	2.1
IV _f	98	93	12	1.9
IV _g	—	91	8	1.9
IV _h	—	99	10	2.1
IV _i	—	95	9	2.0
IV _j	—	94	10	2.0
IV _k	—	104	10	2.3
IV _l	101	93	17	2.1
VI	—	135	12	2.4

Films were cast by slow evaporation of polymer solutions in DMAc.

TABLE V
Thermal Behavior of Polymers

Polymer	TGA			Char yield (%) ^c
	DSC T_g (°C) ^a	Decomposition temperature (°C) ^b		
		In nitrogen	In air	
IV _a	315	550	540	50
IV _b	317	544	542	51
IV _c	296	539	541	51
IV _d	319	523	534	51
IV _e	286	543	542	53
IV _f	279	549	545	58
IV _g	277	543	541	58
IV _h	279	541	545	55
IV _i	277	538	537	56
IV _j	296	542	534	53
IV _k	274	544	540	52
IV _l	280	547	537	53
VI	303	538	553	56

^a Midpoint of the baseline shift in the second heating DSC trace with a heating rate of 15°C/min under a nitrogen atmosphere.

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

^c Residual weight percentage at 800°C under a nitrogen atmosphere.

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