Synthesis and Characterization of Soluble Alternating Aromatic Copolyimides

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ABSTRACT: Aromatic alternating copolyimides have been synthesized by the reaction of various precursors for imido diamine with 6FDA. The alternating copolyimides appeared to have enhanced solubility in organic solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) when compared with the corresponding random isomers. Various NMR experiments including 2-D COSY spectra have been performed for the characterization of the alternating copolyimides. On the basis of the NMR results, the synthetic pathway of the aromatic copolyimide through the reaction of a precursor for imido diamine with a dianhydride leads to a copolymer with a complete alternating sequence without randomization during the cyclization reaction. The glass transition temperatures of the alternating copolyimides obtained by DSC measurements showed values similar to those of the corresponding random ones. The decomposition behavior obtained by TGA exhibited close degradation temperatures of the alternating copolyimides regardless of the monomers used.

Introduction

Aromatic polyimides have received considerable interest for high technology applications due to their outstanding thermal stability and mechanical properties.[1,2] However, applications of aromatic polyimides are restricted because of their poor solubility in organic solvents that cause difficulty in fabrication. Therefore, several approaches such as incorporation of flexible bridging units,[3–5] bulky aromatic pendant groups,[6–8] or asymmetric catenation[9] into rigid polymer backbones have improved their processability. One successful approach that has improved the solubility of polyimides is the introduction of flexible hexafluoroisopropylidene groups between the rigid phenyl rings in the polymer backbone.[10,11] However, chain flexibility of the propylidene group can be attributed to decreasing thermal stability, although it may contribute to solubility increase.

In order to achieve a combination of desired properties such as solubility, thermal stability, and mechanical properties, it is necessary to merge the properties of each polyimide into one system. Such modification of properties is generally achieved through copolymerization or polymer blending. Copolymerization is particularly attractive since tailoring the properties of the resulting polymers is possible even on molecular levels which cannot be achieved through a blending approach.

Copolymerization, using either a diamine and two different dianhydrides or a dianhydride and two different diamines, leads to a random copolyimide with disordered chemical sequences.[12–16] This chemical disorder could affect chain dynamics by controlling the degree of interchain associations and entanglements. Therefore, physical properties of copolymers could be affected by chemical disorder.

It is in this context that we have proceeded to synthesize the alternating copolyimides containing a diamine and two different dianhydride units. Previously, we have described the synthesis of alternating copolyimides using a precursor for an aromatic imido diamine and a dianhydride.[17,18] This synthetic pathway has provided a successful methodology to yield alternating copolyimides.

We describe herein the synthesis and chemical characterization of the alternating copolyimides obtained from a phenylenediamine and 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) as one of the two different dianhydride units. We also describe solubility differences between the alternating copolyimides and their constitutional random isomers.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) (from Aldrich) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) (from TCI) were used as received. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 1,4-phenylenediamine (*p*-PDA) were purchased from Aldrich and purified by sublimation under reduced pressure. 1,3-Phenylenediamine (*m*-PDA) (from Aldrich) was fractionally distilled under reduced pressure. Triethylamine, *N*-methylpyrrolidinone (NMP), and *N,N*-dimethylacetamide (DMAc) were distilled over CaH_2. Ethyl chloroformate was used after fractional distillation. Tetrahydrofuran was distilled over $LiAlH_4$.

Techniques. All NMR spectra were measured at 30 °C on a JEOL GXS-500 spectrometer operating at 500-MHz proton frequency or a Bruker-300 spectrometer. DMSO was used as a solvent unless specified, and its chemical shifts were used as reference. In order to elucidate the proton–proton connectivity, a 2D ^{1}H–^{1}H COSY-45 spectrum was recorded using a 45° mixing pulse. To confirm the cross peak patterns of the 2D ^{1}H spectrum, a 2D spectrum was simulated by use of a FT-NMR from Hare Research Inc. For the assignment of the ^{13}C NMR spectra, a 2D ^{1}H–^{13}C COSY spectrum was measured using a normal heteronuclear shift correlation pulse sequence.

Thermal analyses were performed on a DuPont 910 differential scanning calorimeter and a 915 thermogravimetric analyzer fitted with a 9900 computer thermal analyzer. In all cases, heating rates were 10 °C/min. Gel permeation chromatography (GPC) was carried out with a Spectra-Physics SP 8810 liquid chromatograph fitted with a SP 8450 variable UV detector and a Doyosoda TSK gel column. A solution of 0.3 M LiBr/0.3 M H_3PO_4/1% vol THF in *N,N*-dimethylformamide was used as a mobile phase. A calibration plot constructed with polystyrene standards was used to determine the molecular weights.

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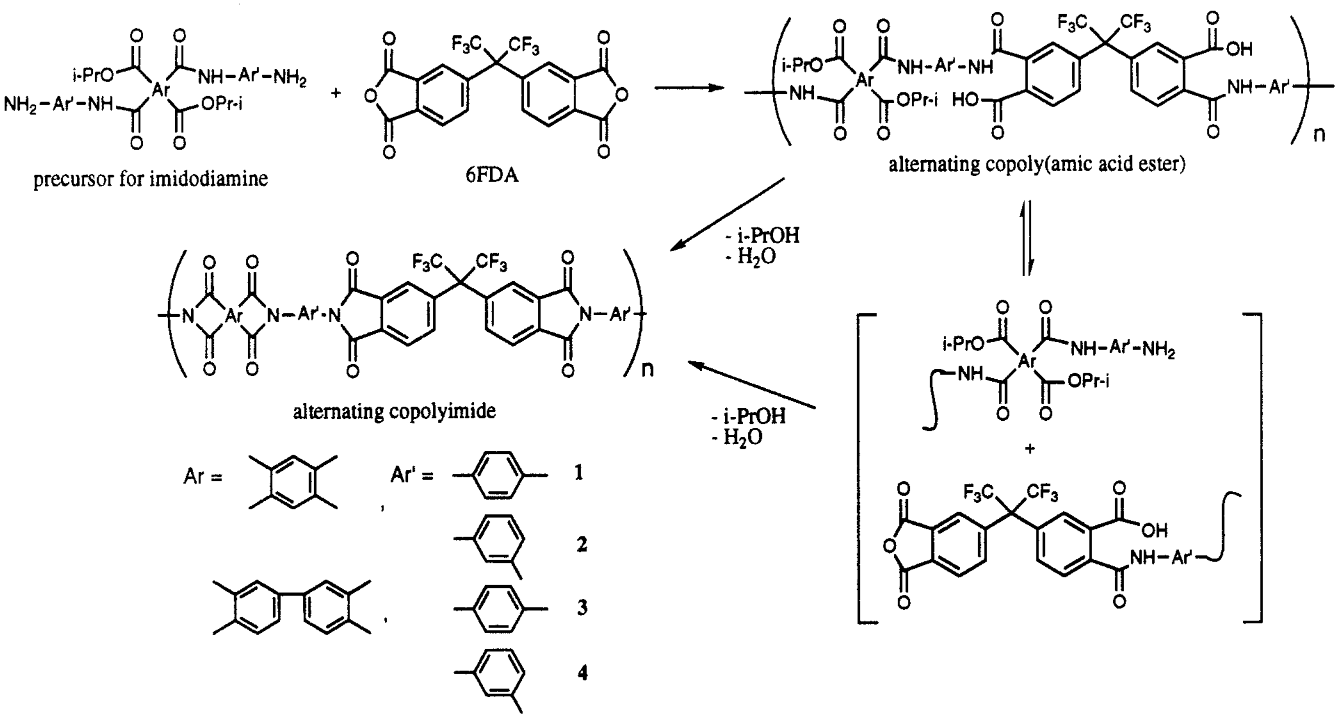
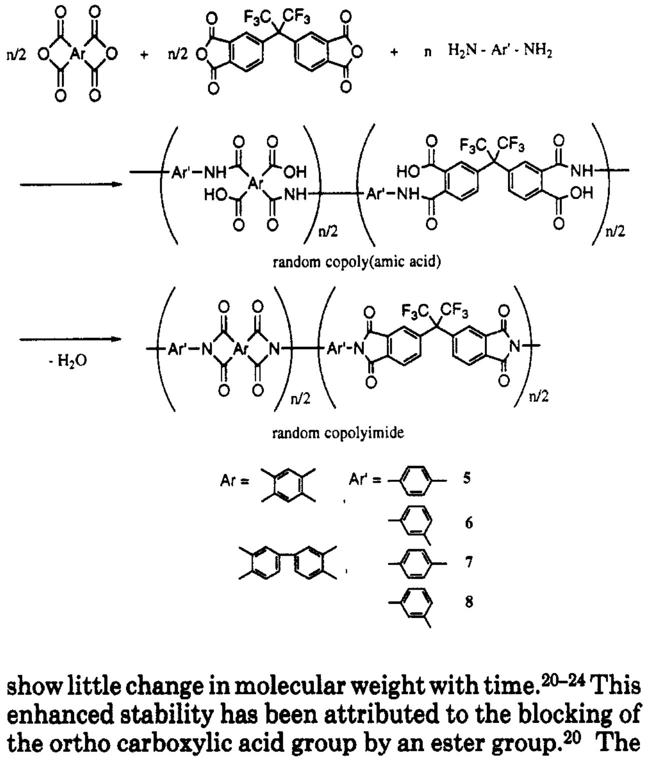
Scheme 1. Alternating Copolymerization of Precursor for Imido Diamine with 6FDA



Synthesis of the Precursor for Imido Diamine. *N,N'*-Bis(4-aminophenyl)-2,5-bis[(isopropyloxy)carbonyl]benzene-1,4-dicarboxamide (PDPM), *N,N'*-bis(3-aminophenyl)-2,5-bis[(isopropyloxy)carbonyl]benzene-1,4-dicarboxamide (MDPM), *N,N'*-bis(4-aminophenyl)-4,4'(4,3' or 3,3')-bis[(isopropyloxy)carbonyl]-biphenyl-3,3'(3,4' or 4,4')-dicarboxamide (PDBP), and *N,N'*-bis-(3-aminophenyl)-4,4'(4,3' or 3,3')-bis[(isopropyloxy)carbonyl]-biphenyl-3,3'(3,4' or 4,4')-dicarboxamide (MDBP) were synthesized as described previously.[17,18] Their detailed characterization was also described in the previous publications.

Polymerization. All polymerizations were carried out in DMAc under nitrogen using equimolar amounts of diamine and dianhydride. A typical procedure for the preparation of an alternating copolyimide or a homopolyimide is as follows: To a solution of PDPM (2.000 g, 3.86 mmol) in DMAc (24 mL) was added 6FDA (1.713 g, 3.86 mmol) at room temperature. After stirring for 3 h, the solution was cast on a glass plate. The plate was heated for 0.5 h each at 80, 150, 250, and 350 °C with a heating rate of 3 °C/min under a flow of nitrogen. The film was removed from the plate, washed with water and methanol, and dried in 1–2 mmHg at 100 °C for 10 h. Random copolyimides were prepared as follows: Two different dianhydrides (1:1 mole ratio) and a stoichiometric amount of a diamine were dissolved in DMAc at 0 °C. After stirring for 3 h at room temperature, the solution was cast on a glass plate. The cyclization reaction was carried out in a manner similar to that described for the alternating copolyimide.

Scheme 2. Random Copolymerization of Diamine with Two Different Dianhydrides



Results and Discussion

Synthesis. The precursors for imido diamines containing isopropyl esters were synthesized and purified as reported previously.[17,18] Scheme 1 outlines the polymerization of the precursors for imido diamines with 6FDA and the cyclization reaction to yield alternating copolyimides. For comparison, the corresponding random copolyimides containing 6FDA were also prepared using a conventional method, as outlined in Scheme 2. The copolymerization of PMDA or BPDA and 6FDA as two dianhydride units with a diamine will lead to sequentially random polymer chains.

The lack of stability of poly(amic acid) solutions toward depolymerization has been attributed to a catalytic effect caused by the presence of an ortho carboxylic acid group.[19] Alkyl esters of poly(amic acid)s are much more stable in solution than the parent poly(amic acid)s and consequently show little change in molecular weight with time.[20-24] This enhanced stability has been attributed to the blocking of the ortho carboxylic acid group by an ester group.[20] The polymerization of the precursors for imido diamine with 6FDA yielded poly(amic acid ester)s where half of the carboxylic acid groups were blocked by isopropyl groups. Our previous results showed that a molecular weight decrease of the poly(amic acid ester) was suppressed considerably when compared with that of the corresponding poly(amic acid),[18] indicating that the poly(amic acid ester) was stabilized effectively by amide ester units in spite of the presence of amide acid units in its structure.

It is known that a depolymerization reaction at the amide acid units and recombination of the resulting end groups occur during the thermal imidization process of poly(amic acid)s.[25-27] The two competing reactions give rise to a continuous change of repeating unit sequence until all amide acid units cyclize to form imide rings. The reactions

Table 1. Solubility of Alternating and the Corresponding Random Copolyimides[a]

alternating copolyimide				random copolyimide			
polymer[b]	NMP	DMSO	DMAc	polymer[b]	NMP	DMSO	DMAc
1	ps	ps	ps	5	i	i	i
2	s	s	s	6	ps	ps	i
3	ps	ps	ps	7	i	i	i
4	s	s	s	8	s	ps	i

[a] All polyimide samples were prepared by imidization up to 350 °C and immersed in boiling solvents for 20 min: s = soluble; ps = partly soluble; i = insoluble. [b] Inherent viscosities (dL/g) of the corresponding precursor polymers have the following ranges: 1 and 5, 0.95–1.01; 2 and 6, 0.50–0.55; 3 and 7, 0.75–0.83; 4 and 8, 0.47–0.53.

might, therefore, occur at amide acid units of the poly(amic acid ester)s during the thermal process (Scheme 1). Amide ester units, however, would not be depolymerized due to the effective blocking of the acid catalyzed equilibration by isopropyl esters, and thus the resulting copolyimides maintained their structures of alternating sequences.

Solution Properties. The solubility behavior of copolyimides derived from alternating copoly(amic acid ester) and its corresponding random copoly(amic acid) of which the inherent viscosities are similar is summarized in Table 1. The copolyimides containing a meta linkage of the diamine unit show better solubility in NMP and DMSO than those of para isomers irrespective of copolymer sequences. This difference in solubility between para and meta isomers of polyimides is characteristic of many other types of polymers and is probably due to the fact that meta geometry tends to hinder packing of polymer molecules to decrease interchain interactions.[28]

An intriguing observation in this study is the drastic difference in solubility between the alternating copolyimides and the corresponding random isomers. The alternating copolyimides exhibited much enhanced solubility in NMP, DMSO, and most importantly DMAC, while the corresponding random isomers were insoluble or partially soluble in NMP and DMSO and insoluble in DMAC.

From viscosity and GPC measurements of polymers 2 and 4 in Table 2, it is expected that the molecular weight of polyimides does not change significantly from that of the corresponding precursor after the imidization process. Considering the similarity of polymerization chemistry involved, the difference in solubility cannot be accounted for only by the difference in molecular weights. The drastic improvement in solubility of the alternating copolyimides may be due to the lack of interchain interactions between rigid homopolymer segments, while the interactions cannot be avoided in the case of random copolyimides. It is known that the homopolymerization of PMDA or BPDA with phenylenediamine gives rise to insoluble polymer due to strong interchain interactions.[28-30]

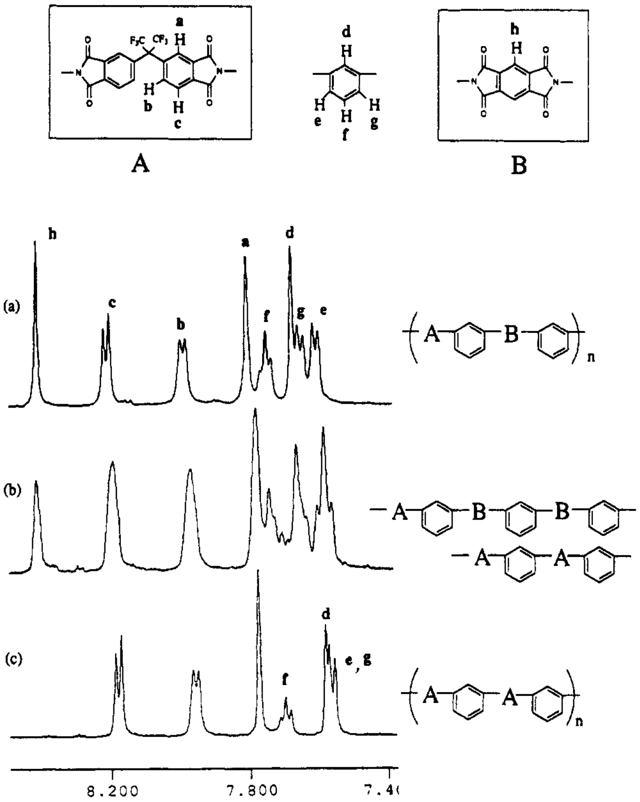
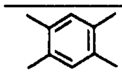
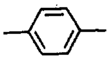
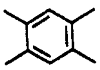
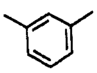
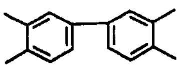
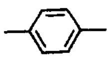
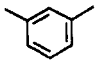


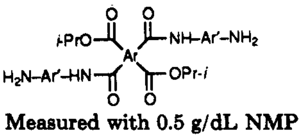
Figure 1. 500-MHz ^{1}H NMR spectra of (a) the alternating copolyimide (polymer 2), (b) the corresponding random copolyimide (polymer 6, soluble part), (c) the homopolyimide derived from *m*-PDA and 6FDA.

Characterization. We have performed NMR experiments on the alternating copolyimide, the corresponding random isomer, and the homopolyimide containing only 6FDA as a dianhydride unit. ^{1}H NMR spectra of polymer 2, the soluble part of polymer 6, and the homopolyimide are compared in Figure 1a–c, respectively. The ^{1}H NMR spectra of the alternating copolyimide and the homopolyimide exhibit distinctive splitting patterns, while the random copolyimide shows broad signals at the range 7.5–7.8 ppm which are indicative of a mixture of different repeating unit sequences or chemical disorder.

Table 2. Inherent Viscosity and Molecular Weight of Poly(amic acid ester)s and the Corresponding Copolyimides

precursor for imido diamine[a]		poly(amic acid ester)		polyimide		
Ar	Ar′	η_{inh} (dL/g)[b]	$10^{-4}M_w$ (GPC)	polymer	η_{inh} (dL/g)[c]	$10^{-4}M_w$ (GPC)
		1.20	17.0	1		
		0.51	6.0	2	0.83	8.7
		0.82	11.7	3		
		0.47	5.5	4	0.53	6.9

[a] Ar and Ar′ in the structure of diamine,



$$i\text{-PrO}-\overset{O}{\overset{\|}{C}}\quad\overset{O}{\overset{\|}{C}}-\text{NH}-\text{Ar}'-\text{NH}_2 \quad \text{Ar} \quad \text{H}_2\text{N}-\text{Ar}'-\text{HN}-\underset{O}{\underset{\|}{C}}\quad\underset{O}{\underset{\|}{C}}-\text{OPr-}i$$

[b] Measured with 0.5 g/dL DMAc solutions at 30 °C. [c] Measured with 0.5 g/dL NMP solutions at 30 °C.

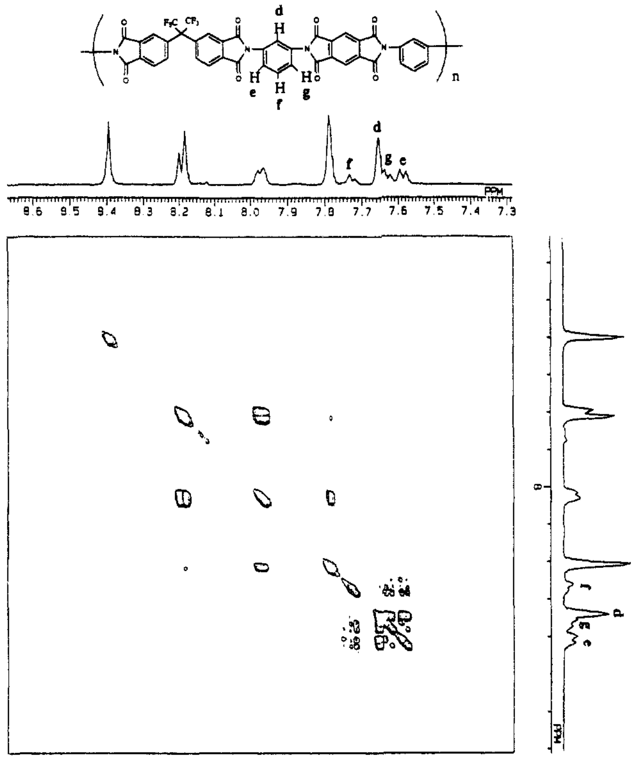


Figure 2. 2D ^{1}H NMR (COSY) spectrum of the alternating copolyimide (polymer 2).

Another interesting result is that in the spectrum of the random copolyimide (Figure 1b) the intensity ratio of proton signal h (due to PMDA unit) to a (due to 6FDA unit) is much lower than that in the spectrum of the alternating isomer (Figure 1a). This result tells us that fewer homopolymer sequences of PMDA and phenylenediamine units than of 6FDA and phenylenediamine units exist in the soluble parts of the random copolyimide, indicating that insolubility of the random copolymers can be attributed to homopolymer sequences consisting of the PMDA or BPDA unit, as described earlier.

In order to elucidate the NMR splitting patterns, a 2D ^{1}H–^{1}H COSY-45 NMR experiment was performed for polymer 2, as shown in Figure 2. On the basis of the splitting patterns and the positions of the chemical shifts, proton resonances corresponding to protons d–g can be readily assigned. The proton resonances d–g in the range 7.57–7.76 ppm apparently arise from a proposed structure where the substituents A and B represent 6FDA and PMDA units, respectively (see Figure 1). As a result, proton resonances e and g are expected to show different chemical shifts. Proton signal g can be assigned to appear at a lower field than proton signal e due to more inductive deshielding effects by the carbonyl groups of the PMDA unit than by the hexafluoroisopropylidene group of 6FDA.

In order to confirm the cross peak patterns for proton signals d–g, the COSY spectrum was simulated using FT-NMR. J_{ef} and J_{fg} were measured at 7.5 and 8.0 Hz, respectively, from the ^{1}H NMR spectrum. All other coupling constants were assumed to a small value of 0.5 Hz because they were too small to be measured. The 90°-t_1-45°-t_2 pulse sequence was applied, and the magnitude spectrum was obtained. The simulation result shown in Figure 3 is in good agreement with the experimental spectrum, although the latter suffers some signal degrading, notably in the cross peaks involving proton resonance f.

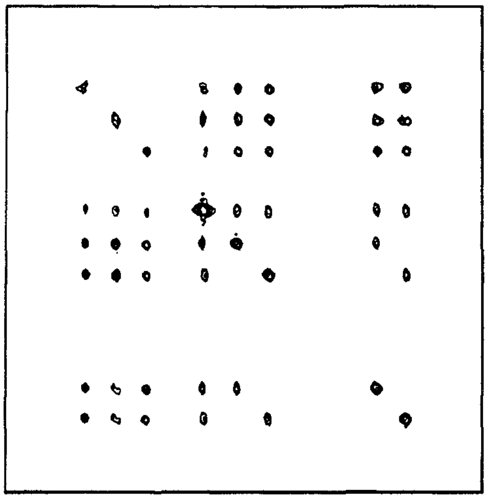


Figure 3. Simulated result of 2D ^{1}H NMR (COSY) spectrum of the polymer 2 in the range 7.57–7.76 ppm.

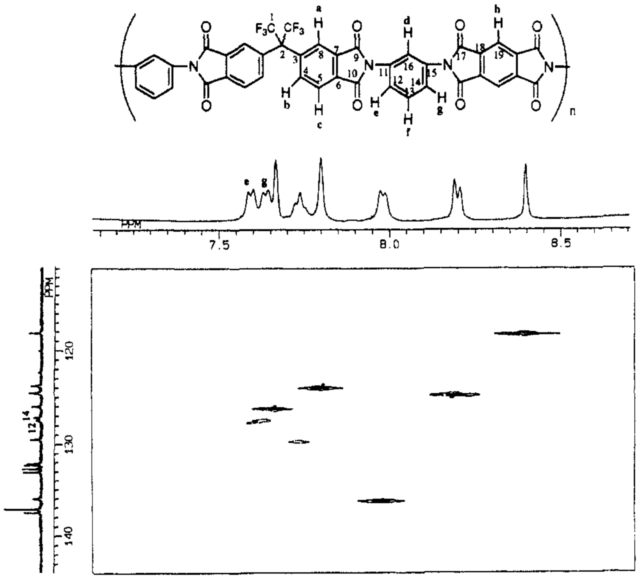


Figure 4. 2D ^{1}H–^{13}C NMR (COSY) spectrum of the alternating copolyimide (polymer 2).

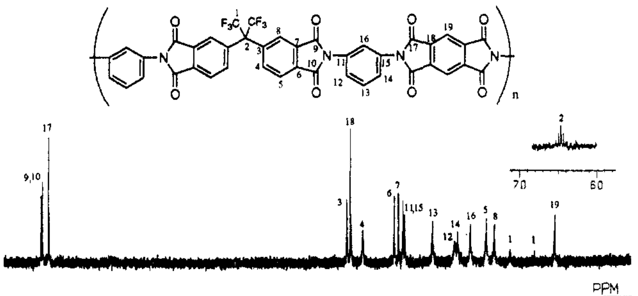


Figure 5. 125-MHz ^{13}C NMR spectrum of the alternating copolyimide (polymer 2).

The 2D ^{1}H–^{13}C COSY spectrum of polymer 2 is shown in Figure 4. With the aid of the proton spectrum assignments, protonated carbons were readily assigned. The carbon resonances at 127.1 and 127.4 ppm are found to be correlated with the proton doublet centered at 7.60 and 7.64 ppm, respectively. These results provide clear evidence that the alternating copolyimides prepared in this study are consistent with the proposed structure.

Figure 5 shows the ^{13}C NMR spectrum of polymer 2 along with complete assignments. With the aid of the ^{1}H–^{13}C COSY spectrum of polymer 2, protonated carbons were easily assigned. All other nonprotonated carbons could be assigned by comparing with the ^{13}C spectra of the corresponding random isomer and homopolymer. On the basis of these NMR results, we can safely conclude that the synthetic pathway of the aromatic copolyimide

Table 3. Glass Transition Temperatures of Alternating and Random Copolyimides and the Corresponding Homopolyimides

copolyimide				homopolyimide			
alternating copolyimide		random copolyimide					
polymer	T_g (°C)	polymer	T_g (°C)	polymer	T_g (°C)	polymer	T_g (°C)
1	*a*	5	*a*	*p*-PDA/PMDA	>500	*p*-PDA/6FDA	326
2	338	6	335	*m*-PDA/PMDA	430	*m*-PDA/6FDA	297
3	342	7	356	*p*-PDA/BPDA	>500	*p*-PDA/6FDA	326
4	308	8	310	*m*-PDA/BPDA	329	*m*-PDA/6FDA	297

[a] No transition was observed below 450 °C by DSC.

Table 4. Thermal Decomposition Temperatures of Alternating Copolyimides

polymer	T_{di} (°C)[a]	T_{d5} (°C)[b]	weight % of residue at 800 °C
1	456	545	56.5
2	440	515	53.9
3	450	545	58.2
4	430	535	57.8

[a] T_{di}: initial degradation temperature. [b] T_{d5}: 5% weight loss temperature.

via the reaction of a precursor for imido diamine and a dianhydride leads to the copolymer with a complete alternating sequence without randomization during the thermal cyclization.

Thermal Properties. The thermal behavior of the polymers was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Table 3 summarizes the glass transition temperatures of the alternating copolyimides in comparison with random copolyimides and homopolyimides. The glass transition temperatures of the copolyimides tend to be lower than the average values of their corresponding homopolyimides, but those of the copolyimides 1 and 5 could not be compared because their T_gs were not observed in DSC. The alternating copolyimides have glass transition temperatures above 308 °C which are similar to those of the random ones. The glass transition temperatures of the copolyimides tend to decrease with decreasing stiffness of the polymer backbone.

The decomposition temperatures obtained by TGA measurements corresponding to the alternating copolyimides are summarized in Table 4. All of the alternating copolyimides show similar decomposition behaviors characterized by no weight loss below 430 °C under nitrogen. The temperature at which 5% weight loss is observed for these copolyimides is in the range 515–545 °C depending on the precursors for the imido diamine used. All the alternating copolyimides show a carbonized residue of more than 50% at 800 °C in nitrogen atmosphere. The alternating copolyimides have the highest char yield of up to 58%. These results indicate that the alternating copolyimides have good thermal stabilities, even through they appear to have an enhanced solubility of the polymer in organic solvents.

Conclusions

We have been able to synthesize the alternating aromatic copolyimides containing 6FDA which exhibit a distinct difference in solubility compared with the corresponding random isomers. The postulated chemical structure with the alternating sequences was verified by various NMR techniques. Complete assignments for all the protons and carbons in the alternating copolyimide have been made by the combination of 1D and 2D NMR experiments. We have also demonstrated that the synthetic pathway for alternating copolyimide provides a successful approach to increasing solubility and processability of polyimides without sacrificing their thermal stability.

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References and Notes

(1) Mittal, K. L. *Polyimides: Synthesis, Characterization and Application*; Plenum Press: New York, 1984.

(2) Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* **1976**, *11*, 161.

(3) St. Clair, A. K.; St. Clair, T. L.; Smith, E. N. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1976**, *17*, 359.

(4) Bell, V. L.; Stump, B. L.; Gager, H. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2275.

(5) Critchley, J. P.; White, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1809.

(6) Imai, Y.; Malder, M. M.; Kakimito, M. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *22*, 2189.

(7) Oishi, Y.; Ishida, M.; Imai, J. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 10.

(8) Yang, C. P.; Chen, W. T. *Macromolecules* **1993**, *26*, 4865.

(9) Gerber, M. K.; Pratt, J. R.; St. Clair, T. L. *Proc. Int. Conf. Polyimides, 3rd* 1988, 101.

(10) Brode, G. L.; Kwiatkowski, G. T.; Hawakami, J. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15* (1), 761.

(11) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001.

(12) Oishi, Y.; Itoyo, K.; Kakimoto, M.; Iami, Y. *Polym. J.* **1989**, *21*, 771.

(13) Lee, D. S.; Quin, G. *Polym. J.* **1989**, *21*, 751.

(14) Leung, L.; Williams, D. J.; Karasz, F. E.; MacKnight, W. *J. Polym. Bull.* **1980**, *16*, 457.

(15) Hedrick, J. L.; Labadie, J. W.; Palmer, T. D.; Russell, T. P. *In Polyimides: Materials, Chemistry and Characterization*; Ferger, C., Khojastech, M., McGrath, J. E., Eds.; Elsevier; Amsterdam, 1989; p 61.

(16) Kawai, H.; Akahori, R.; Nagano, K. Jpn. Kokai Tokyo Koho JP 01 16, 834, 1989.

(17) Rhee, S. B.; Park, J. W.; Moon, B. S.; Chang, J. Y. *Macromolecules* **1993**, *26*, 404.

(18) Rhee, S. B.; Park, J. W.; Moon, B. S.; Lee, M. H.; Chang, J. Y. *Makromol. Chem.*, submitted for publication.

(19) Frost, L. W.; Kesse, I. *J. Appl. Polym. Sci.* **1964**, *8*, 1039.

(20) Kharkov, S. N.; Vinogradova, S. V.; Vygodskii, Y. S.; Gerashchenko, Z. V. *Vysokomol. Soyedin.* **1971**, *A13*, 1190.

(21) Kharkov, S. N.; Krasnov, Ye P.; Lavrova, Z. N.; Baranova, S. A.; Aksevova, V. P.; Chegola, A. S. *Vysokomol. Soyedin.* **1971**, *A13*, 833.

(22) Molodtsvova, Y. D.; Timofeyeva, G. I.; Pavlova, S. S. A.; Vygodski, Y. S.; Vinogradova, S. V.; Korshak, V. V. *Vysokomol. Soyedin.* **1977**, *A19*, 346.

(23) Nishizaki, S.; Moriwaki, T. *Ind. Chem. Mag.* **1968**, *71*, 1559.

(24) Kudryavtsev, V. V.; Koton, M. M.; Meleshko, T. K.; Sklizkova, V. P. *Vysokomol. Soyedin.* **1975**, *A17*, 1764.

(25) Ree, M.; Yoon, D. Y.; Volksen, W. *J. Polym. Sci., Part B: Polym Phys. Ed.* **1991**, *29*, 1203.

(26) Ree, M.; Yoon, D. Y.; Volksen, W. *Polym. Mater. Sci. Eng.* **1989**, *60*, 179.

(27) Hasegawa, M.; Shindo, Y.; Sugimura, T.; Horie, K.; Yokota, R.; Mita, I. *J. Polym. Sci. Part A: Polym. Chem. Ed.* **1991**, *29*, 1515.

(28) Houlihan, F. M.; Bachman, B. J.; Wilkins, C. W.; Pryde, C. A. *Macromolecules* **1989**, *22*, 4477.

(29) Dine-Hart, R. A. *Makromol. Chem.* **1971**, *143*, 189.

(30) Critchley, J. P.; Gratten, P. A.; White, M.-A.; Pippett, J. S. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1789.