Synthesis and Characterization of Soluble Random Copolyimides

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ABSTRACT: Random copolyimides with different proportions of a diamine component were prepared by polymerizing different compositions of diamines with various dianhydrides and imidized thermally to 260°C. The imidization percent of poly(amic acid) was characterized at various temperatures by infrared spectroscopy. The homopolyimide based on bis[4-(3-aminophenoxy)phenyl]sulfone and pyromellitic dianhydride was the only one soluble. By changing the compositions of bis[4-(3-aminophenoxy)phenyl]-sulfone and other diamines with pyromellitic dianhydride in *N*-methyl-2-pyrrolidone, soluble random copolyimides could be prepared. By random copolymerization, the thermal properties and viscosities of homopolyimide could be controlled. All the soluble polyimides prepared in this work were amorphous because of the lack of stereoregularity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 272–277, 1999

Key words: soluble polyimide; imidization; bis[4-(3-aminophenoxy)phenyl]sulfone; copolymerization

INTRODUCTION

Linear aromatic polyimides are used as films and coatings where durability at temperatures in the range of 200–300°C is required. Aromatic polyimides are particularly attractive for applications because of their inherent toughness, flexibility, low density, and thermal stability.[1–4] However, major drawbacks of aromatic polyimides are that they have a very high melting point and are difficult, if not impossible, to dissolve in the usual organic solvents, which causes difficulties in processing; their glass transition temperatures, being very high, practically in the same range with their decomposition, make their processing possible only from poly(amic acid) intermediates. The widely utilized two-stage process for the manufacture of polyimides from poly(amic acid)s still has some disadvantages connected with the limited storage stability of the intermediate poly(amic acid)s and with the evolution of low molecular weight volatile products during the heterocycle imidization. These problems can be circumvented through incorporation of amide, ester, ether, or other flexibilizing groups and bulky units in the polymer backbone.[5–8] Although the use of flexible groups does make the polymer more tractable, mechanical properties usually suffer. In general, random copolyimides are synthesized through copolymerization from a single dianhydride and two or more kinds of diamines, or from a single diamine and two or more kinds of dianhydrides, in order to enhance a polymer's properties and solubility.[9,10]

In this work, we synthesized and characterized various soluble random copolyimides based on pyromellic dianhydride and bis[4-(3-aminophenoxy)-phenyl]sulfone with various diamine compositions (Table I). This report describes how diamine

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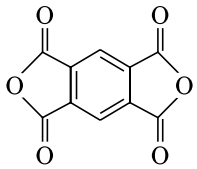
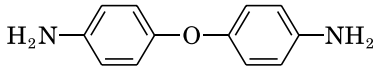
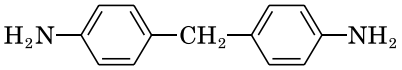
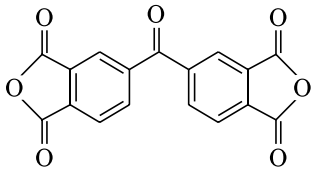
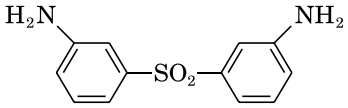
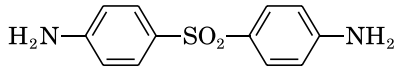
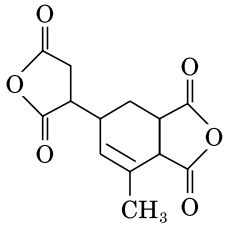
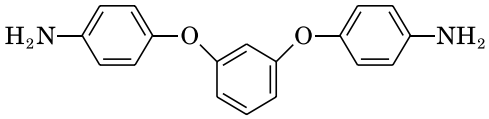
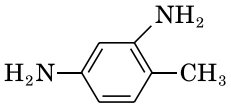
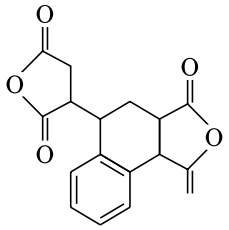
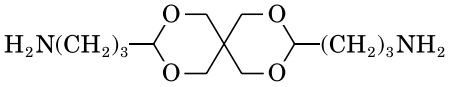
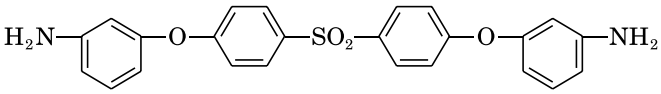
Table I Structures of Dianhydrides and Diamines Used in Polymer Syntheses

Code	Structures of Dianhydrides	Code	Structures of Diamines
PMDA		ODA	
		MDA	
BTDA		3,3′-DDS	
		4,4′-DDS	
DMCA		TPE-R	
		TODA	
DTDA		BAOTSU	
		BAPS-m	

structures affect the polyimide solubility and thermal properties.

EXPERIMENTAL

Materials

The dianhydrides, pyromellitic dianhydride (PMDA, Aldrich, Milwaukee, WI), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Aldrich), 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl)-3-cyclohexene-1,2-dicarboxylic anhydride (DMCA, Tokyo Kasei, Tokyo, Japan), and 4-(2,5-dioxotetrahydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride (DTDA, Tokyo Kasei, Tokyo, Japan), were recrystallized from acetic anhydride followed by vacuum drying at 140°C for 4 h before use. The diamines, bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m, Wakayama Seika Kogyo, Japan), 1,3-bis(4-aminophenoxy)benzene (TPE-R, Tokyo Kasei, Tokyo, Japan), 4,4′-methylene dianiline (MDA, Aldrich), 4,4′-oxydianiline (ODA, Aldrich), *m*-toluylene diamine (TODA, Tokyo Kasei), 3,3′-diaminodiphenyl sulfone (3,3′-DDS, Tokyo Kasei), 4,4′-diaminodiphenyl sulfone (4,4′-DDS, Tokyo Kasei), and 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (BAOTSU, Tokyo Kasei) were recrystallized three times from ethanol. *N*-Methyl-2-pyrrolidone (NMP, Aldrich) was distilled twice over calcium hydride and then stored in sealed, dark flasks over molecular sieves.

Polymer Synthesis by Thermal, Two-step Method

BAPS-m (4.325 g, 10 mmol) was dissolved in 42.1 mL of NMP, and the temperature of the resulting

solution was kept at room temperature. A stoichiometric amount of PMDA (2.181 g, 10 mmol) was added to the solution in three portions within 30 min, and the mixture was stirred for 6 h to yield a homogeneous, viscous solution. The solid content of the resulting solution was 20% by weight. In a similar manner, the poly(amic acid) solutions were prepared using other diamines and dianhydrides in the same solvent. Each of the poly(amic acid) solutions was coated onto a glass plate using a doctor knife to a thickness of 250 μm. After 12 h of drying at 80°C, the transparent poly(amic acid) films were peeled from the glass plate. The resulting pale yellow partially dried films were clamped to a stainless frame. Then, the film was gradually heated in an oven up to 260°C (180°C, 2 h; 230°C, 2 h; 260°C 2 h). All the other polyimides were prepared by the same procedures as above.

Polymer Characterization

Inherent viscosities were measured on 0.5 g/dL NMP solutions at 30°C in an Ubbelohde viscometer. Infrared (IR) spectra of polyimide and poly(amic acid)s were made using a MIDAC Model M2000, over 400–4000 cm^{-1}. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with TA Instruments Model DSC 2910 and DuPont Model 951, respectively. The DSC was conducted under nitrogen at a heating rate of 20°C/min. All DSCs were run twice and the second run taken for the data. TGA experiments were run under nitrogen at a heating rate of 20°C/min. Second-run curves of TGA were considered after a first run up to 250°C to eliminate absorbed water and small residuals of solvent. Wide-angle X-ray diffraction (WAXD) patterns were taken for each polymer using a ROTA FLEX RU-200 diffractometer (Rigaku, Tokyo) with Ni-filtered Cr radiation at 30 kV, 100 mA, and wide-angle diffraction 2θ from 10° to 40°. The tests of solubility were performed in various solvents for 7 days at room temperature.

RESULTS AND DISCUSSION

Polyimide Synthesis and Characterization

The homopolyimide and copolyimides were prepared by the traditional two-step method in a solution of NMP. Although homopolyimide prepared from PMDA and BAPS-m is soluble only in polar solvents, soluble random copolyimides were synthesized in order to increase the thermal properties. BAPS-m and other kinds of diamines were dissolved in NMP except BAOTSU and a stoichiometric amount of PMDA was added in three portions within 30 min. Although BAOTSU was insoluble in NMP, it was soluble in the poly(amic acid) solution prepared from PMDA and BAPS-m. This fact will be very useful for synthesizing polyimide from diamine monomers like 4,4′-diaminostilbene-2,2′-disulfonic acid that are not soluble in polar solvents. By means of this addition process, the viscosity of poly(amic acid) was found to be increased effectively.[5,12] Then, imidization of the poly(amic acid) film was conducted at various temperatures for 2 h. The inherent viscosities of various soluble polyimides are shown in Table II. We could increase the viscosity compared to the homopolyimide through random copolymerization using reactive diamines such as MDA, TPE-R, and ODA having an electron-donating flexible group. By using diamines having electron-withdrawing flexible groups and bulky substituents like 3,3′-DDS, 4,4′-DDS, and TODA, the viscosity decreased.[10] By changing the compositions of BAPS-m and other diamines, we conducted solubility experiments of the resulting copolyimides.

Table II Properties of Homopolyimide and Copolyimides Synthesized

Polymer Code	Viscosity (dL/g)[a]	T_g (°C)[b]	T_{10} (°C)[c]	T_m (°C)[d]
PI-a	0.47	250	580	650
PI-b	0.51	255	590	675
PI-c	0.48	262	605	680
PI-d	0.44	280	590	670
PI-e	0.41	295	510	610
PI-f	0.54	205	590	680
PI-g	0.39	273	650	710
PI-h	0.44	252	520	630

[a] Measured at the concentration of 0.5 g/dL polymer in NMP at 30°C.
[b] Observed by DSC at a heating rate of 20°C/min.
[c] 10% weight-loss temperature measured by TGA at a heating rate of 10°C/min.
[d] Maximum weight-loss temperature measured by TGA at a heating rate of 10°C/min.

The degree of imidization of poly(amic acid) to polyimide was analyzed by the band-ratio method. The absorbance of the asymmetric carbonyl stretch at 1780 cm^{-1} was ratioed with a reference aromatic stretch at 1500 cm^{-1}. Through IR spectra analysis, the percentages of imidization of polyimides were calculated by using the following equation[11]:

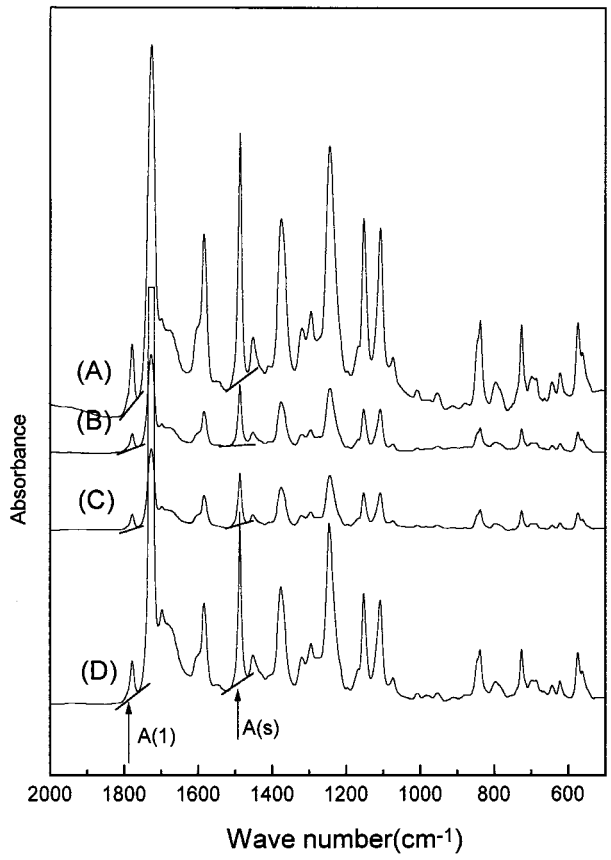


Figure 1 IR spectra of polyimide at different curing conditions: (A) 80°C 12 h, 180°C 2 h, 230°C 2 h, and 260°C 2 h; (B) 80°C 12 h, 180°C 2 h, and 230°C 2 h; (C) 80°C 12 h and 260°C 2 h; (D) 80°C 12 h and 180°C 2 h.

$$\text{Percent imidization} = \frac{[A(1)/A(s)]_t - [A(1)/A(s)]_{t=0}}{[A(1)/A(s)]_{t=\infty} - [A(1)/(A(s)]_{t=0}}$$

where $A(1)$ is the absorbance of the imide peak at 1780 cm^{-1}, $A(s)$ is the absorbance of the standard reference at 1500 cm^{-1}, and $t = \infty$ was taken as the time beyond which no further changes in the imide peak were observed.

The poly(amic acid) film was cured at temperatures of 180, 230, and 260°C for 2 h at each temperature. The IR spectrum was recorded at each curing stage and evaluated by the above equation. Figures 1 and 2 show the resulting spectra obtained during cure. Poly(amic acid) was completely cyclized to imide rings within 100 min at 260°C. However, at a cure below 230°C, poly(amic acid) film could not be completely converted into polyimide. When the sample was heated at 180 and 230°C, the imide peaks grew to approximately 63 and 85% within 100 min, respectively. Although the heating time was longer, the degree of imidization was not increased. According to our results, complete imidization was achieved at above 260°C.

Properties of Polymers

It was found that by controlling the compositions of BAPS-m and other diamines various soluble copolyimides could be prepared. The copolyimides obtained were dissolved in various solvents for 24 h at 80°C. Table III shows BAPS-m and other diamine compositions to obtain soluble copolyimides. The solubilities of diamines increased as follows: ODA ≈ MDA < BAOTSU < TPE-R < 4,4′-DDS < TODA < 3,3′-DDS < BAPS-m. In general, introducing asymmetric flexibilizing and bulky units into the polymer backbone increases the solubility of polyimide.[5–8] According to Table III, the —SO_2— unit among flexibilizing groups exhibited higher solubility than did other flexible groups like ether and methylene. 3,3′-DDS and TODA are especially soluble compared to other diamines because of asymmetric —SO_2— flexibilizing groups and asymmetric bulky substituents, respectively.

It was possible to change the thermal properties through copolymerization. Figure 3 and Table

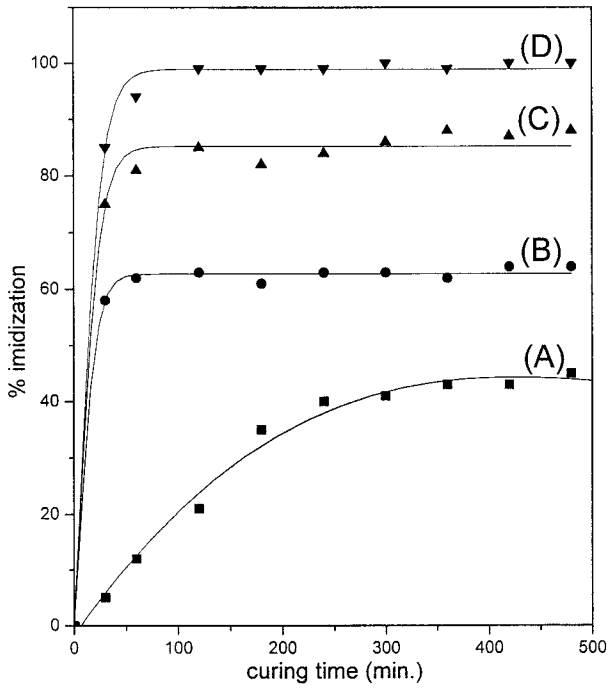
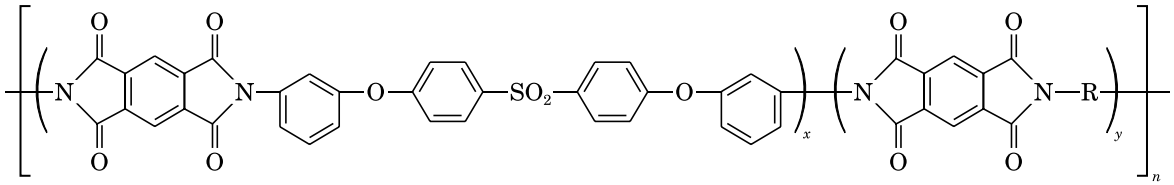
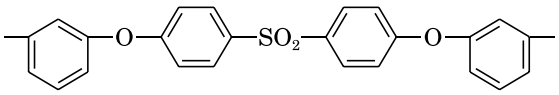
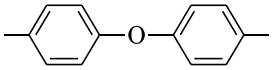
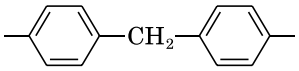
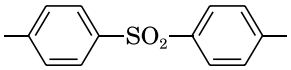
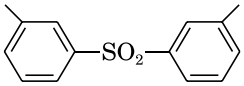
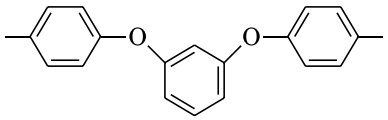
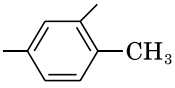


Figure 2 Percent imidization change versus various temperatures: (A) 80°C; (B) 180°C; (C) 230°C; (D) 260°C.

Table III Molecular Structures and Diamine Compositions of the Soluble Homopolyimide and Copolyimides:



Code	R	x	y
PI-a		—	—
PI-b		0.923	0.077
PI-c		0.929	0.071
PI-d		0.8	0.2
PI-e		0.25	0.75
PI-f		0.833	0.167
PI-g		0.33	0.67
PI-h		0.85	0.15

II show the thermal properties of homopolyimide PI-a and copolyimides PI-b to PI-h. By adding other diamines in polyimide based on BAPS-m and PMDA, the glass transition temperature and thermal stability could be controlled. Figure 3 shows the glass transition temperatures of PI-a to PI-h. The polymers PI-a to PI-h have glass transition temperatures of 205–295°C by DSC. The T_g's tend to decrease in the order PI-e > PI-d > PI-g > PI-c > PI-b > PI-h ≈ PI-a > PI-f. The T_g of the basic homopolyimide PI-a was decreased or increased by random copolymerization in the range of 30–50°C. By introducing the sulfone unit and the bulky substitution group (—CH_3) in polyimide, the T_g was increased. Introducing other asymmetric flexible units like TPE-R resulted in a lower T_g. Table II shows the thermal stabilities of polyimides PI-a to PI-h. All the polyimides showed good thermal stabilities characterized by no weight loss below 480°C in nitrogen. The temperatures at which 10% weight loss was observed for these polyimides were in the range of 510–650°C in nitrogen and the maximum weight loss temperatures were in the range of 610–710°C in nitrogen. Polyimides consisting of symmetric diamines PI-b, PI-c, and PI-d showed enhanced thermal stabilities. The degradation temperature of PI-g having a methyl-substituted *p*-phenylenediamine group was the highest. The thermal stability of copolyimide PI-h having an aliphatic group was lower than that of homopolyimide PI-a. By introducing symmetric aromatic diamine

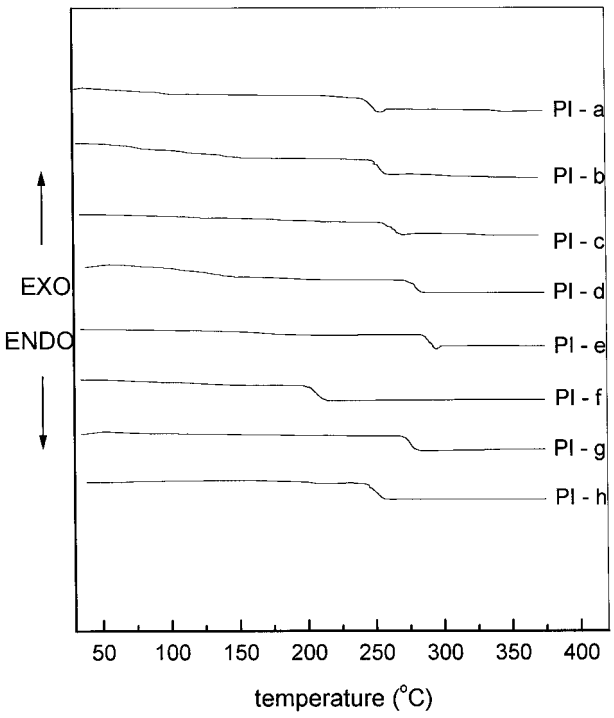


Figure 3 DSC thermograms of the various soluble polyimides.

groups, the thermal stabilities of the soluble copolyimides were increased.

The crystallinity of the various polyimides was characterized by WAXD with 2θ from 10°–40°. The scattering patterns of all the polyimides were interpreted as amorphous. This is attributed to the asymmetric structure of BAPS-m, resulting in the lack of stereoregularity. Although PI-b, PI-c, PI-d, and PI-h were prepared from a symmetric diamine monomer, BAPS-m, having an asymmetric structure, is the main component in these copolyimide as shown in Table III. In general, polyimides containing symmetric, bulky substituents appear to pack efficiently while polyimides containing asymmetric, bulky substituents pack quite loosely.[13]

CONCLUSIONS

Soluble random copolyimides based on PMDA and BAPS-m were synthesized through a typical thermal two-step method by changing the molar ratio of BAPA-m and other diamines. Random copoly(amic acid) was imidized by cyclizing at different temperatures. At below 230°C, poly(amic acid) film could not be completely converted into polyimide. Complete imidization was achieved at above 260°C. Using diamines with electron-donating flexible groups increased the viscosities of polymers and vice versa. The solubilities of diamines increased as follows: ODA ≈ MDA < BAOTSU < TPE-R < 4,4′-DDS < TODA < 3,3′-DDS < BAPS-m. The thermal properties of homopolyimide could be controlled by changing the molar ratio of BAPS-m and other diamines. All the polyimides had excellent thermal stabilities. The T_g's were in the range of 205–295°C. By introducing the sulfone linkage and bulky substituent, the T_g's were increased. The flexible ether linkage made the T_g lower. The thermal stabilities of the random copolyimides were good. Scattering patterns of all the polyimides prepared were interpreted as being amorphous because of less stereoregularity.

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