Synthesis and Characterization of Soluble Polyimides and Its Ultrafiltration Membrane Performances

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ABSTRACT: Soluble polyimides were synthesized and characterized from two diamines and four dianhydrides by the two- and the one-step method. Most of the polyimides could be soluble by one-step method except α,α'-bis(4-aminophenyl)-1,4-diisopropyl benzene/3,3',4,4'-benzophenonetetracarboxylic dianhydride system in limited organic solvents. Glass transition temperatures ranged from 186 to 233°C and crystalline melt temperatures were not observed. All the soluble polyimides showed good thermal, mechanical, and electrical properties. The polyimides did not have crystalline structure and limited solubilities. The effective solvent had a medium dispersion component associated with weak polar and hydrogen components. The polymer from one-step polymerization had a narrower molecular weight distribution than the two-step method. Polyimide synthesized with 4,4'-oxydiphthalic anhydride and bis[4-(3-amino-phenoxy)phenyl]sulfone by two-step method could only be prepared by the typical phase inversion method. Other membranes except this polyimide membrane could not be prepared by the typical phase-inversion method because of poor solubility about polar solvents. The flux of this ultrafiltration membrane was very high, and this membrane could especially retain polymer having a molecular weight 20,000 to above 90%. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 907–918, 1999

Key words: soluble polyimides; ultrafiltration membrane

INTRODUCTION

During the late 1950s and early 1960s, requirements for thermally stable materials produced a rapid growth in new polymers.[1–3] Lists of such polymers included polybenzimidazoles, polytriazines, and polyimides. Especially, fully aromatic polyimides due to their aromatic and heterocyclic structure were long known for their outstanding electrical, thermal, and high-temperature mechanical properties and are widely used, especially in aerospace and electrical applications.[4–5] Polyimide is stable at above 300°C for a long period of time. However, unless carefully de-signed, polyimides have high softening temperatures and are often insoluble in most organic solvents in their fully imidized form, making them extremely difficult to fabricate. Therefore, several approaches, such as incorporation of flexible bridging units,[6–7] bulky pendant groups,[8–9] or asymmetric meta catenation[10] into the rigid polymer backbone, were made to obtain processable or soluble polyimides. In recent years, soluble polyimides have become very important and needed as solar cells and thermal control systems.[11]

Polyimides usually are manufactured by the two-step method. Poly(amic acid) is synthesized between dianhydride and diamine in a suitable solvent. This poly(amic acid) solution is then fabricated into a film by casting and removing the solvent. The resulting poly(amic acid) film is then thermally converted into the polyimide by the

Figure 1 Structure of the diamine and dianhydride monomers used.

Figure 3 Percent imidization change of poly(amic acid) I-a versus various temperatures.

removal of water. There is another method called the one-step method. In this method, soluble polyimides are successfully synthesized in boiling organic solvents such as nitrobenzene, *m*-cresol, and phenol containing isoquinoline, by heating at 100–200°C from the dianhydride and diamine.[12–13] The water generated by imidization is removed by using azeotroping cosolvents such as toluene or *N*-cyclohexylpyrrolidone. Under these conditions, chain growth and imidization essentially occur spontaneously. Another interesting feature of the one-step method is that it can yield a higher degree of crys-

Figure 2 IR spectra of (A) poly(amic acid) I-a and (B) the corresponding polyimide.

Figure 4 ^{1}H-NMR spectra of (A) poly(amic acid) I-a and (B) corresponding polyimide.

tallinity than can be obtained from the two-step method.[14]

Ultrafiltration is typically used to retain macromolecules and colloids from a solution, the lower limit being solutes with molecular weights of a few thousand Daltons. The number of membrane applications increase as they become more resistant to higher temperatures (>100°C), to a wide range of pH (1–14), and to organic solvents. Polyimide membrane is especially important for these purposes.

In this article, we wish to report the preparation and characterization of soluble polyimides by using the one- and two-step method from a combination of various diamines and dianhydrides. We used the one-step method to simplify the polymerization process and also to improve their solvent solubility.

The properties of the one-step method were compared with those from the two-step method. In addition, we prepared and characterized ultrafiltration membrane with this synthesized polyimide.

EXPERIMENTAL

Materials

The chemical structures of the diamine and dianhydride monomers used for this study were given in Figure 1. Solvents and reagents were commercially available and were used as received unless otherwise indicated. *N,N'*-dimethylacetamide (DMAc; Aldrich), *N*-methyl-2-pyrrolidone (NMP; Aldrich), benzonitrile (Aldrich), and nitrobenzene (Yakuri,

Table I   Effect of Reaction Solvents on Polyimide Synthesis for 4 h at 15 wt % Monomer Concentration

	Solvent				
	NMP	*m*-Cresol	Nitrobenzene	Benzonitrile	Phenol
Inherent viscosity (dL g^{-1})	0.27	0.35	0.51	0.47	0.34

Japan) were distilled twice over calcium hydride. All solvents were then stored in sealed, dark flasks over molecular sieves. 4,4'-Oxydiphthalic anhydride (ODPA), 4-(2,5-dioxotetrahydrofuran-3-yl) tetralin-1,2-dicarboxylic anhydride (DTDA), 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DMCA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were from Tokyo Kasei and 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) and α,α'-bis(4-aminophenyl)-1,4-diisopropyl benzene (BAPDB; Tokyo Kasei) were recrystallized three times from ethanol.

Polymer Synthesis by Thermal Two-Step Method

BAPS-*m* (4.325 g, 10 mmol) was dissolved in 42.1 mL of DMAc, and the temperature of the resulting solution was kept at room temperature. A stoichiometric amount of ODPA (3.1022 g, 10 mmol) was added to the solution in three portions, and the mixture was stirred for 6 h to yield a homogeneous, viscous solution. The solid content of the resulting solution was varied from 5 to 25% by weight. In a similar manner, the poly(amic acid) solutions were prepared using other diamines and dianhydrides in the same or different solvents. Each of the poly(amic acid) solutions was coated on a glass plate using a doctor's knife to a thickness of 250 μm. After 12 h of drying at 80°C, the formed films were peeled from the glass plate to yield transparent poly(amic acid) films. The resulting pale yellow partially dried films were clamped to a stainless steel frame. Then, the film was gradually heated in an oven up to 250°C over a period of 1–2 h.

Polymer Synthesis by One-Step Method

In a 250-mL four-necked flask, stoichiometric amounts of dianhydride and diamine were dissolved in dry nitrobenzene. The concentrations of monomers ranged from 5 to 25% by weight. Then, the temperature of the mixture was gradually increased to 185–200°C, while being stirred in a stream of nitrogen, and then was maintained at a given temperature for a given period of time in an atmosphere of nitrogen. On completion of the reaction, the viscous polymer solution was cooled in a stream of nitrogen, diluted with nitrobenzene, and the polymer separated by precipitation in methanol.

Measurements

Inherent viscosities were measured on 0.5 g dL^{-1} DMAc solutions at 30.0 ± 0.1°C in a Ubbelohde viscometer. Infrared (IR) spectra of polyimide and poly(amic acid) were examined using Digilab model FTS-60, over 400–4000 cm^{-1}. ^{1}H-NMR spectra were recorded on a Varian Unity 300 spectrometer, using deuterated dimethylformamide (DMF) as solvent and tetramethylsilane as a reference at 20°C. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) studies were performed with Dupont model 1090 and 951, re-

Table II   Effect of Reaction Temperature on Poly(amic acid) Synthesis in DMAc for 3 h at 15 wt % Monomer Concentration

	Temperature (°C)				
	40	50	60	70	80
Inherent viscosity (dL g^{-1})	0.19	0.23	0.27	0.27	0.25

Figure 5 Effect of reaction time on poly(amic acid) synthesis in DMAc at 15 wt % monomers concentration and reaction temperature 60°C.

Figure 7 Effect of reaction concentration (A) on poly-(amic acid) I-a synthesis in DMAc at reaction temperature 60°C for 3 h and (B) on one-step polyimide I-a in nitrobenzene at reaction temperature 200°C for 4 h.

Figure 6 Effect of reaction time on one-step polyimide synthesis in nitrobenzene at 15 wt % monomers concentration and reaction temperature 200°C.

spectively. The DSC sample was tested under nitrogen at a heating rate of 10°C min^{-1}. TGA and DTG samples were tested under air and nitrogen at a heating rate of 20°C min^{-1}. 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 5° to 40°. For the measurements of mechanical properties, strips of 15×50 mm were cut from polymer films and measured on an Instron model TT-C at room temperature. The surface resistivity and volume resistivity were determined using a Hewlett Packard model 4329A. The tests of solubility were performed in the various solvents for seven days. A triangular solubility chart is constructed with the Hansen's fractional values of dispersive (δ_d), polar (δ_p), and hydrogen (δ_h) solubility parameter.

Membrane Preparation and Investigations

Polyimide was dissolved in NMP for 24 h at 60°C. The casting solution was cast onto polypropylene

Figure 8 (A) TGA and (B) DTG thermogram of polyimide I-a at a heating rate 20°C min^{-1} under air and nitrogen.

nonwoven fabric with a doctor knife gap of 200 μm. The membrane was precipitated by immersion into deionized ice water just after casting in an environment of 65 ± 5% relative humidity, 25 ± 1°C, and evaporation for 0.5 min. After 1 h, the remaining solvent was completely exchanged from coagulated membrane by keeping it in deionized water.

Cross sections of the membranes were observed by using scanning electron microscopy (SEM, JSM-5410LV). Air-dried membrane samples were fractured under cryogenic conditions using liquid nitrogen. The fractured membranes were coated with gold before SEM photographs were taken.

All membranes were initially subjected to 2 kg cm^{-2} of deionized water until they reached steady state. Operating conditions were 25 ± 1°C and 1 kg cm^{-2}. Poly(ethylene glycol) (PEG; M_W: 6000, 10,000, and 20,000) were used as solutes (1000

mg L^{-1}) in the feed solution. The solute concentrations in the feed and the permeate were determined by high-performance liquid chromatography (Waters 410) measurements. The solute rejection R is defined as

$$R(\%) = (1 - C_p/C_f) \times 100$$

where C_p and C_f are the PEG concentrations in the permeate and the feed, respectively.

RESULTS AND DISCUSSION

Polymer Synthesis and Identification

Polyimides were prepared by the conventional two-step procedure and one-step method. In the two-step method, to obtain high molecular weight poly(amic acids), the process of monomer addition

Figure 9 DSC thermograms of polyimide I-a (A) first, (B) second, and (C) third trial at a scan rate of 10°C min^{-1}.

in a polar solvent plays an important role.[15–16] Diamine was first dissolved in DMAc at room temperature, and then stoichiometric amounts of

Table III   Characteristics of Polyimides Prepared from Various Monomers

Polymer Code[a]	T_g (°C)[b]	10% Weight Loss Temperature (°C)[c]
I-b	232.5	560
I-c	186.2	450
I-d	188.2	450
II-b[d]	—	—
II-c	190.0	470
II-d	188.5	450

[a] Reaction by one-step method was carried out as follows: monomer concentrations 20% by mass in nitrobenzene at 200°C for 9 h.

[b] Glass transition temperature (T_g) was measured by DSC at a heating rate of 10°C min^{-1}.

[c] Temperature at 10% mass loss was recorded by TGA at a heating rate of 20°C min^{-1}.

[d] Polymer was precipitated during reaction.

dianhydride were added in three portions within 30 min. The viscosity of poly(amic acid) was found to increase effectively. The flexible polyimide films could be obtained by the thermal cyclodehydration. Figure 2 shows the IR spectra of poly(amic acid) and the corresponding polyimide I-a. The IR spectrum of poly(amic acid) I-a [Fig. 2(A)] revealed characteristic major absorptions at 1650, 1530, and 1720 cm^{-1}. These bands are assigned to amide I, amide II, and acid carbonyl group (C═O), respectively.[17] The characteristic absorptions around 3280 cm^{-1} is the representative N—H and O—H group. These bands disappeared entirely after cyclodehydration, and the absorptions of the imide ring, appearing at 1782 and 1720 cm^{-1}, were attributed to the asymmetric and symmetric stretches of the carbonyl group of imide. The C—N band at 1370 cm^{-1} verified the formation of the imide structure. The thermal conversion of poly(amic acid) to polyimide was monitored by IR spectroscopy. The degree of imidization was analyzed by the band ratio method.[18]

Table IV   Mechanical and Electrical Properties of Polyimide I-a

	Property			
Sample	Tensile Strength (kg mm^{-2})	Elongation (%)	Surface Resistivity (Ω)	Volume Resistivity (Ω cm)
Vespel	8.75	7.5	—	$1.0 \times 10^{12-13}$
One-step	9.67	4.2	1.0×10^{13}	1.72×10^{10}
Two-step	9.73	4.0	1.0×10^{13}	1.72×10^{10}

The percent imidization of poly(amic acid) was calculated by using the following equation[18]:

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 at 250°C.

The percent imidization of polyimide I-a versus time at various temperatures are shown in Figure 3. When the poly(amic acid) I-a was heated at 180°C for 100 min, the imidization was approximately 70% and leveled off, indicating that the imidization reaction could not be completed by curing at 180°C. When the sample was then cured at 215°C for 100 min, the imide peak grew to 90%. This shows that the curing temperature should be over 200°C. The polymer's structure was also confirmed by ^{1}H-NMR spectroscopy. The spectra of poly(amic acid) I-a and polyimide were shown in Figure 4. As expected, the aromatic protons were detected around 7.2–8.2 ppm, depending on the position in the aromatic ring. The aromatic carboxylic acid proton peak was shown at approximately 10.5 ppm. At about 6.8 ppm, the aromatic amide proton peak was observed. When poly(amic acid) was cyclodehydrated to polyimide, the aromatic carboxylic acid proton and aromatic amide proton peak completely disappeared. This means that the poly(amic acid) was completely converted into polyimide.

Effect of Reaction Conditions

The results in Table I show that the inherent viscosity of polyimide synthesized in nitrobenzene was higher than that of other reaction solvents. These results were due to the basicity differences of the various solvents. Because of the solvent's basicity, the equilibrium shifts to the left or right. This fact affects the product's molecular weight. It also follows from Table II that the polyimides were very stable at elevated temperatures in nitrobenzene. The considerable instability of polyimides in NMP may be explained by alkaline hydrolysis of the polymer in this medium. The marked degradation of the polyimide at elevated temperatures in solvent types of amide may be caused by acceleration of the hydrolysis of the polymer.[19] Taking these data into account, nitrobenzene was the most stable solvent and was used for all experiments in this study. Table II also shows the effect of reaction temperature during poly(amic acid) synthesis. The optimum condition of I-a polyimide for a reaction temperature is said to be 60°C. Below 60°C, the activation energy for I-a poly(amic acid) is not enough, whereas depolymerization may occur with propagation above 70°C. Generally, the poly(amic acid) is known to be polymerized in the temperature range of 15–75°C[20]; above 75°C, a decrease in the molecular weight of the poly(amic acid) becomes marked. Because of the electron-withdrawing sul-

Figure 10   X-ray patterns of polyimide I-a for one and two-step method, respectively.

Figure 11   Triangular solubility chart of polyimide I-a at 20°C in the Hansen region: (○) soluble, (△) swelling, and (×) insoluble in (1) NMP, (2) DMAc, (3) DMF, (4) m-cresol, (5) chloroform, (6) dioxane, (7) formamide, (8) chlorobenzene, (9) dichloroethane, (10) acetone, (11) phenol, (12) methanol, (13) n-hexane, (14) benzene, and (15) THF.

fone group in BAPS-m and electron-donating ether group in ODPA, the reactivity is decreased. BAPS-m and ODPA have low pKa values and can lower the equilibrium constant. In basic aprotic solvent, decreasing the reaction temperature results in a shift of equilibrium to the right and an increase in the molecular weight and vice versa. Some exceptions to the above generalizations are found with unreactive monomers such as BAPS-m and ODPA. In these cases, the molecular weight of the poly(amic acid) increases as the temperature is increased. However, molecular weight of the poly(amic acid) decreases above 75°C. Therefore, enough activation energy is needed for high molecular weight poly(amic acid). Below 60°C, the activation energy for poly(amic

acid) is not enough, whereas depolymerization occurs above 70°C. Above 100°C, a cyclization to imide is caused to precipitated the resulting polyimide as well as lower the molecular weight of the poly(amic acid). Above 150°C, the cyclization is so rapid that polyimide is sometimes precipitated during the reaction. The poly(amic acid) synthesis is an addition reaction, that is, molecular weight increases rapidly with time. Figure 5 shows that the viscosities increase rapidly until 3 h. So, in this study, the reaction time for high molecular weight was above 3 h in polar aprotic solvent. Figure 6 represents the viscosity change with reaction time during the one-step polymerization process. The viscosity increased gradually with time but did not change after 9 h. So, for one-step

polymerization, the reaction proceeded above 9 h. As shown in Figure 7, the inherent viscosity by two- and one-step method was gradually increased with reaction concentrations up to 20 wt %. However, above this limiting concentration, the viscosity started to decrease. This is due to the greatly increased viscosity of the reaction medium at high conversions. A high viscosity in the high conversion region may lead to a decrease in reactivity of a functional group. Furthermore, in the case of the one-step method, the large increase of viscosity causes the decrease in the efficiency of water removal and may lead to a decrease in the reaction rate with increasing conversion.

Thermal Analysis

The thermal behavior of the polyimides was evaluated by DTG, TGA, and DSC. The thermo-oxidative stability of polyimide I-a was shown under air and nitrogen in Figure 8. These polyimides had excellent thermo-oxidative stability. The TGA curves indicate that the film undergoes no essential weight loss below 500°C. They exhibit a 50% weight loss at a temperature of approximately 670°C and a complete degradation at about 750°C. The DTG curves also indicate that the first degradation temperature is 500°C. Therefore, it is strongly suggested that the usable temperature range is below 500°C. Figure 9 shows the DSC thermogram of polyimide I-a. The glass transition temperature appeared around 213°C. However, the crystalline melting temperature of polyimide was absent on DSC curves. The results obtained for all the polyimides were summarized in Table III. The glass transition temperatures of polyimides were 186–233°C.

Mechanical and Electrical Properties

The mechanical and electrical properties were measured for polyimide I-a at room temperature and listed in Table IV. Polyimide sample I-a synthesized by one-step and two-step method showed good mechanical properties, a high tensile strength and a somewhat low elongation, compared with the commercial blend (Vespel). The electric resistivity of polyimide I-a was also much lower than Vespel. The differences in the mechanical and electrical properties, between the two samples prepared from the one-step and the two-step method, were negligible.

X-ray Diffraction of Polymers

Figure 10 shows X-ray diffraction intensity curves of polyimide I-a. Both polyimide samples

Table V   Solubility Properties[a] of Various Polyimides Synthesized by One- and Two-Step Method

Polymer Code	Polymerization Method	
	One-Step Method[b]	Two-Step Method[c]
I-a	+	+
I-b	+	−
I-c	+	−
I-d	+	−
II-a	+	−
II-b	−	−
II-c	+	−
II-d	+	−

[a] + and − stand for soluble and insoluble, respectively.
[b] Reaction was carried out as follows: monomer concentrations 20% by mass in nitrobenzene at 200°C for 9 h.
[c] Reaction was carried out as follows: monomer concentrations 20% by mass in DMAc at 60°C for 3 h.

synthesized by the one-step and two-step method showed broad peaks, indicating the absence of crystallinities in resulting polymers. There were no significant differences in crystallinities between the two methods. The possible reason is that the polymer has plenty of kinky structure inhibiting regular packing.

Solubility Properties

The location of various types of solvents and the solubility of polyimide I-a in the chart were presented in Figure 11. This diagram shows that solvents dissolving polyimides I-a have medium dispersion components associated with somewhat weak polar and hydrogen components. These good solubilities can have advantages for processing. Table V shows the solubility properties of various polyimides synthesized by the one- and two-step method. In the one-step method, all the polyimides except the BAPDB/BTDA system were soluble in limited solvents. However, in the two-step method, only the ODPA/BAPS-*m* system was soluble.

Membrane Preparation and Investigations

Membranes were prepared by the traditional phase-inversion method. Polyimide I-a casting solution synthesized by the one- and two-step method dissolved in NMP was cast onto polypropylene nonwoven fabric, and then immersed into a nonsolvent, ice-water bath. Only I-a polyimides showed good solubilities in polar solvents, imply-

(A)

(B)

(C)

(D)

Figure 12   SEM photographs of polyimide I-a synthesized from one- and two-step method. (A) Cross section of polyimide I-a synthesized from one-step method; (B) sublayer of polyimide I-a synthesized from one-step method; (C) cross section of polyimide I-a synthesized from two-step method; (D) sublayer of polyimide I-a synthesized from two-step method.

ing that it is possible to prepare membranes by the typical phase-inversion method.

Figure 12 shows the cross sections of polyimide membranes. The membrane synthesized by two-step method had straightforward fingerlike voids in the sublayer and hyperthin top skin layer in contrast to membranes synthesized by the two-step method. Table VI shows polyimide I-a ultra-filtration membrane performances. The flux of polyimide I-a by two-step method was higher than that of polyimide I-a by one-step method. The rejection was the opposite, meaning that the

one-step polyimide membrane's transport resistance is lower.

CONCLUSIONS

A series of soluble polyimides from two diamines and four dianhydrides by one and two-step method except for the BAPDB/BTDA system was successfully synthesized. The optimum reaction conditions of polyimide I-a for the two-step

Table VI Polyimide I-a Ultrafiltration Membrane Performances

	PWF $(L\ m^{-2}\ h^{-1})$[a]	PEG Solute Rejection (%)[b]			
		6000	10,000	20,000	35,000
Polyimide I-a[c]	80	85	91	97	99
Polyimide I-a[d]	265	48	72	90	99

[a] PWF (pure water flux) was measured at following conditions: pressure was 1 Kg cm^{-2} and fluid velocity was 2.5 L min^{-1}.
[b] Solute rejection of polyethylene glycol (PEG) was measured at concentration 1000 ppm in water.
[c] This polymer was synthesized from one-step method.
[d] This polymer was synthesized from two-step method.

method were as follows: reaction solvent: DMAc; reaction temperature: 60°C; reaction time: 3 h; reaction concentration: 20 wt %. The effective reaction conditions for the one-step method were as follows: reaction solvent: nitrobenzene; reaction temperature: 200°C; reaction time: 9 h; reaction concentration: 20 wt %. The inherent viscosities of soluble polyimides were between 0.42 and 0.66 dL g^{-1} for the one-step method. All the soluble polyimides were amorphous and did not have crystalline structure. Glass transition temperatures ranged from 186 to 233°C. Soluble polyimides underwent essential weight loss below 500°C. We could prepare the ultrafiltration membrane by the phase-inversion method with polyimide I-a, of which solubility is the best. Membrane prepared by polyimide I-a synthesized from one-step method showed low pure water flux and high solute rejection as an ultrafiltration membrane. On the other hand, membrane prepared by polyimide I-a synthesized from the two-step method showed very pure water flux and high solute rejection.

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