

# Preparation of Soluble Copolyurethaneimide Containing Oxyethylene and Oxypropylene Units

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**ABSTRACT:** Soluble copolyurethaneimides were synthesized by the isocyanate method in a solution of *N*-methyl-2-pyrrolidone (NMP). The isocyanate-terminated prepolyurethane prepared from low molecular weight poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) and methylene diisocyanate was reacted with pyromellitic dianhydride at high temperature. The resulting copolyurethaneimides were soluble in polar solvents like *N*-methyl-2-pyrrolidone and *N,N'*-dimethylformamide. The film-forming

properties were investigated by changing the molecular weights of PEG and PPG. With PPG, the film-forming property was enhanced. The inherent viscosity, solubility, thermal property, molecular weight distribution, and mechanical property were compared with the aromatic polyimide. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3502–3507, 2002

**Key words:** copolyurethaneimide; prepolyurethane; isocyanate method

## INTRODUCTION

Aromatic polyimides have various advantages, such as good mechanical properties, excellent solvent resistance, and thermal stability, and have been used where durability at high temperature and various solvents is required.<sup>1–5</sup> However, they have application limits because of processing difficulties and their too high glass transition temperatures. The solubility of polyimides can be enhanced by introducing polar groups (amide, ester, ether, or other flexibilizing groups) or bulky substituents along the polymer backbone<sup>6–8</sup> and incorporation of ortho- or meta-oriented phenylene rings.<sup>9,10</sup>

By introducing flexible urethane group in the polyimide main chain, the solubility of the polyimide can be enhanced. In particular, with gas separation membranes, although the selectivity is slightly lower than other polymeric membrane, polyurethane has shown good gas permeability.<sup>11,12</sup> By incorporating a rigid imide group, the selectivity can be better.

In this work, we synthesized and characterized soluble copolyurethaneimides containing polyethylene oxide and polypropylene oxide units by the isocyanate method.<sup>13</sup> The thermal properties of the copolyurethaneimides were compared with those of aromatic polyimides.<sup>14–17</sup>

## EXPERIMENTAL

### Materials

Reagent grade *N*-methyl-2-pyrrolidone (NMP, Aldrich, Milwaukee, WI) was dried by refluxing over calcium hydride. All other solvents were used as received. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m, Tokyo Kasei, Tokyo, Japan) was purified by recrystallization in ethanol. Pyromellitic dianhydride (PMDA) was obtained from Tokyo Kasei Chemicals and purified by recrystallization in hot acetic anhydride. Poly(ethylene glycol)s (PEG 200, 600, and 1000) and poly(propylene glycol)s (PPG 600, 1000, 2000, and 3000) were obtained from Aldrich and used as received. Methylene diisocyanate (MDI) was obtained from Tokyo Kasei Chemicals and used as received.

### Polymer synthesis and characterization

Polyimide was synthesized by a two-step method. BAPS-m was dissolved in NMP at room temperature. A stoichiometric amount of PMDA was added in three portions within 30 min and vigorously mixed for 6 h to yield a homogenous and viscous poly(amic acid) intermediate solution with constant viscosity. The solid content of the resulting solution was 20% by weight. Poly(amic acid) film prepared by evaporating NMP at 80 °C for 12 h was then thermally imidized in a dry oven. The imidization conditions are as follows: 2 h at 180 °C, 2 h at 230 °C, and 2 h at 270 °C.

Copolyurethaneimides were prepared with PEG, PPG, MDI, and PMDA in a 250-mL three-necked

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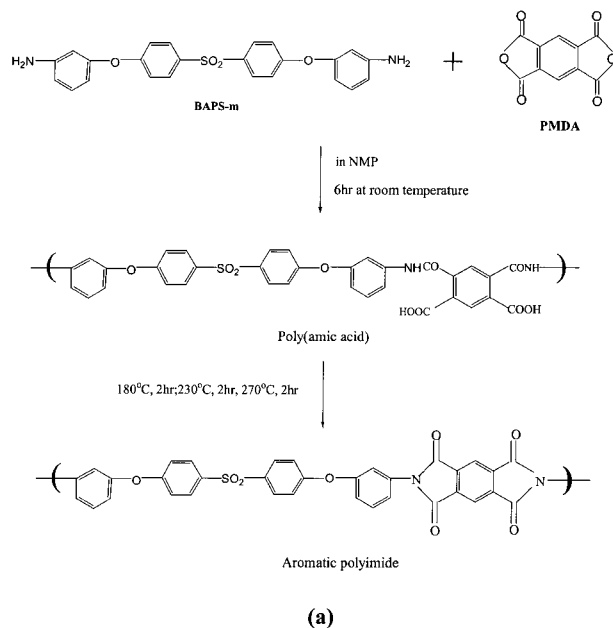
round-bottomed flask equipped with a thermometer, nitrogen gas inlet, and a mechanical stirrer. First, 0.009 mol of PEG or PPG was dissolved in NMP and 0.01 mol of MDI was added slowly to obtain 15 wt % isocyanate-terminated prepolyurethane prepolymer solution at room temperature. The color of the solution was yellowish red. Then, a stoichiometric amount of PMDA was added at one time. The temperature was increased to 70 °C. The reaction was carried out at 70 °C for 1 h and at 120–130 °C for 24 h. The carbon dioxide gas was allowed to escape and the viscous solution turned deep red. The molecular weights of PEG and PPG were changed to prepare copolyurethaneimides with good film-forming properties.

The inherent viscosity of the polymer solution (0.5 g/dL) was measured in NMP at 30 °C with an Ubbelohde viscometer. Fourier-transform infrared (FT-IR) spectra of various polyimides were made with a MIDAC model M2000 over the range 4000–400  $\text{cm}^{-1}$ . Characteristic major absorption bands at 1650, 1530, and 1720, assigned to amide I, amide II, and acid carbonyl of poly(amic acid), respectively, completely disappeared. In their places, the absorption bands of the imide ring appeared at 1780 (asymmetric carbonyl group of imide ring), 1720 (asymmetric carbonyl group of imide ring), and 1370 (C—N band of imide ring).

Thermal stability was determined by thermogravimetric analysis (TGA, Dupont Model 951) at a heating rate of 20 °C/min in nitrogen. Molecular weights (number average and weight average molecular weight) and molecular weight distribution (polydispersity index) were obtained by high-temperature gel permeation chromatography (GPC, Waters 150CV) with a  $\mu$ -Styragel 10 column (solvent, 80 °C DMF and LiBr 0.05 M; standard, polystyrene; flow rate, 1.0 mL/min). Mechanical properties (tensile strength, elongation, and modulus) were measured with a Mini-map. The tests of solubility were performed in the various solvents for 7 days at room temperature.

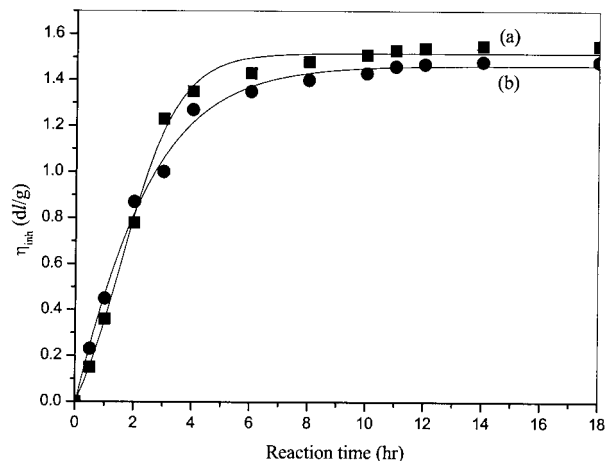
## RESULTS AND DISCUSSION

Aromatic polyimide and copolyurethaneimide were synthesized by a thermal two-step method and isocyanate method, respectively. The reaction routes of aromatic polyimide, PUI-1, and PUI-2 are shown in Scheme 1. Isocyanate-terminated prepolyurethane was prepared by reacting PEG or PPG with excess MDI in NMP at room temperature. The color of the solution was slightly yellowish red at first. As the reaction progressed, the solution gradually turned brown. Because the solution was too viscous, more NMP was added to lower the viscosity of the solution. The concentration of the resulting polymer solution was 5 wt %. Then, PMDA was added at one time. The temperature was increased to 70 °C. The reaction was



**Scheme 1** The reaction scheme of aromatic polyimide and copolyurethaneimides.

carried out at 70 °C for 1 h and at 120 °C for 3 h. The color of the viscous solution turned deep red. The change of inherent viscosity with increasing the reaction time is shown in Figure 1. The results show that a reaction time of 6 h is enough for PUI-1 and PUI-2. No precipitation took place during imidization by the isocyanate method, indicating that the copolyurethaneimide could be soluble in NMP. In the case of PEG, when the molecular weight of the PEG was <600, the film-forming properties were good. In contrast, when high molecular weight PEG (>600) was used, the film-forming properties of the resulting copolyurethaneimide were bad because of the increased hydrophilicity of the resulting polymer. In the case of PPG, the film-



**Figure 1** Progress of polyaddition for isocyanate-terminated prepolyurethane synthesis: (a) PEG 600, (b) PPG 2000 in NMP.



TABLE I  
Inherent Viscosities and Solubilities of Various Polyimides

Code	$\eta_{inh}$ (dL/g)	Solvent <sup>a</sup>						
		NMP	DMF	DMAc	DMSO	THF	DCM	DCE
PI	0.47	++	++	++	+	—	—	—
PUI-1	1.31	++	++	++	+	—	—	—
PUI-2	1.25	++	++	++	+	—	—	—

<sup>a</sup> Key: ++, soluble at room temperature; +, soluble on heating; —, insoluble.

Abbreviation: NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; DCM, 1,1-dichloromethane; DCE, 1,1-dichloroethane.

forming properties were good with low molecular weight PPG (PPG 2000), but not with high molecular weight PPG (>PPG 2000). Because there is more PPG in the resulting polymer, the polymer with a PPG unit is more hydrophilic than one with a PEG unit. In other words, a more hydrophilic copolyurethaneimide can be prepared by using PPG instead of PEG. The inherent viscosities and solubilities of the resulting copolyurethaneimides are shown in Table I. The inherent viscosity of this polyurethaneimide was much higher than that of aromatic homopolyimide prepared from PMDA and BAPS-m because of the chain-enlarging PEG or PPG unit and highly reactive isocyanate group. Moreover, this polymer was solvent resistant except for polar solvents like NMP, DMAc, DMF, and DMSO. This resistance means that copolyurethaneimide can be used in the area of non-aqueous systems.

The structure of the copolyurethaneimide was confirmed by FT-IR and proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy. As shown in the FT-IR spectrum in Figure 2, the copolyurethaneimide con-

tains prominent characteristic bands of the imide and the urethane linkages. The peaks at around 3700–2700  $\text{cm}^{-1}$  are characteristic absorptions of the urethane linkages. The absorption peak at 1240  $\text{cm}^{-1}$  also appears to be due to a C—O—C linkage of the urethane. The peaks at 1650 and 1530  $\text{cm}^{-1}$  that appeared after imidization were assigned to amide I and amide II, respectively. These peaks could not be detected in the fully imidized polyimides. Imide ring absorptions at 1782 (imide I), 1370 (imide II), 1120 (imide III), and 720 (imide IV)  $\text{cm}^{-1}$  were attributed to the axial, transverse, and out-of-plane vibrations of carbonyl group and C—N band of the cyclic imide structure, respectively. These results indicate that imidization was successfully conducted. As shown in the <sup>1</sup>H NMR spectra in Figure 3, ethylene oxide and propylene oxide protons were detected. In the case of PUI-1 containing an ethylene oxide unit, ethylene oxide protons of PEG and the methylene linkage of MDI (3.8 ppm) were detected at 4–2 ppm. In the case of PUI-2 containing a propylene oxide unit, propylene oxide protons of PPG

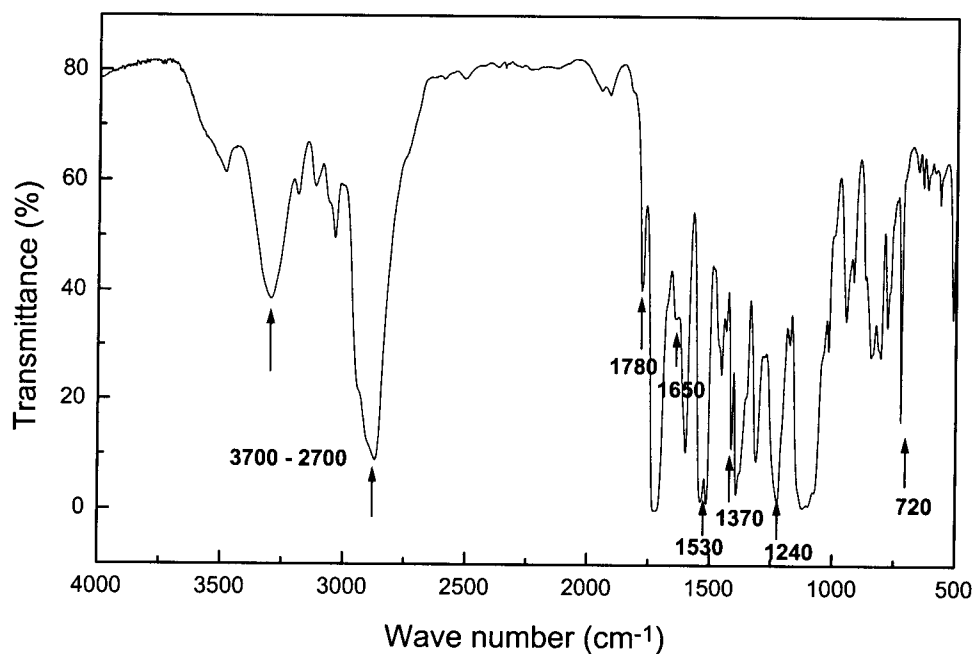


Figure 2 FT-IR spectrum of PUI-1.

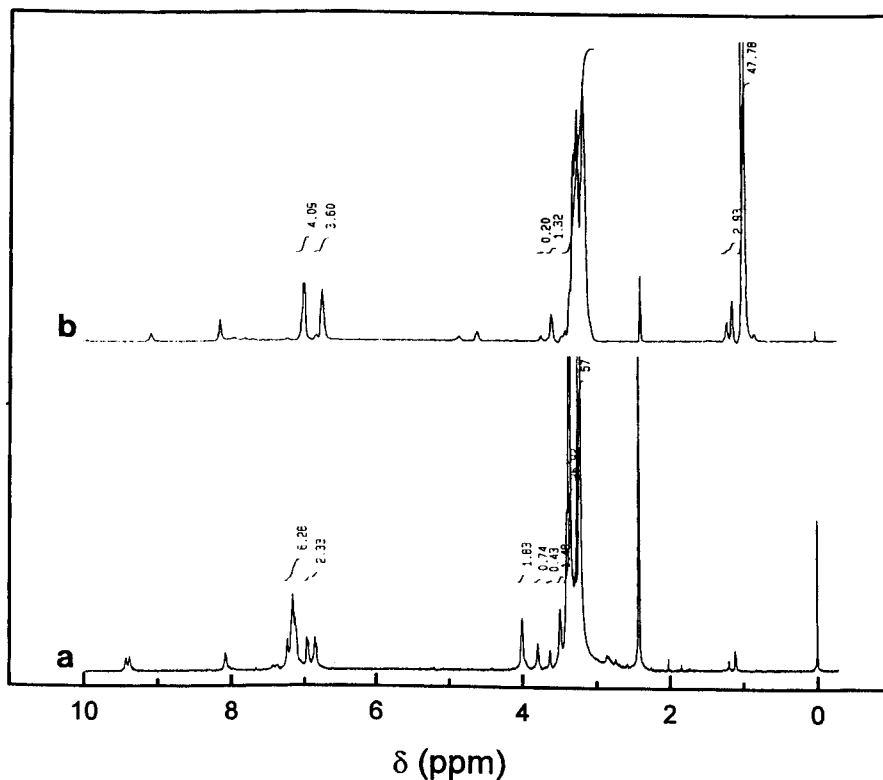


Figure 3  $^1\text{H}$  NMR spectra of (a) PUI-1 and (b) PUI-2.

and the methylene linkage of MDI (3.8 ppm) were detected at 4–0.5 ppm. In addition, the protons of the aromatic rings appeared at  $\sim 7.0$  ppm. The additional low field peaks of 9.5 ppm came from the urethane NH groups.

Thermal properties of copolyurethaneimides were evaluated by TGA. The TGA curves shown in Figure 4 indicate that the two copolyurethaneimides samples produced exhibited  $<10\%$  weight loss at  $\sim 200$   $^{\circ}\text{C}$ , probably corresponding to residual solvents and waters due to its hydrophilic properties, and decom-

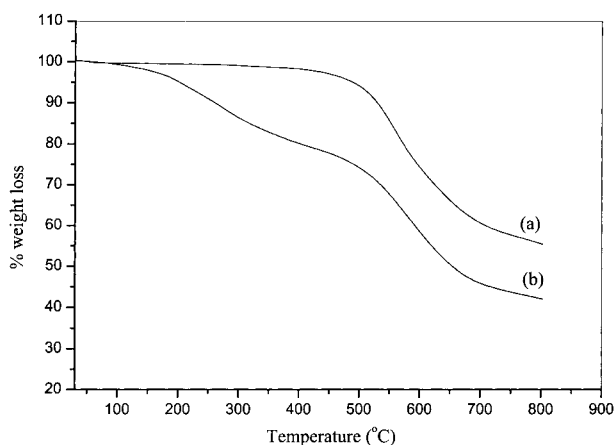


Figure 4 TGA thermograms of (a) homopolyimide and (b) PUI-1.

posed in two stages. The first stage, between 200 and 350  $^{\circ}\text{C}$ , depends on the nature of the copolyurethaneimide with  $\text{CO}_2$  group decomposition of the urethane linkage. The second stage of degradation of copolyurethaneimides occurs between 400 and 500  $^{\circ}\text{C}$ . These copolyurethaneimides are not more thermally stable than the homopolyimide. The thermal properties of all polymers are listed in Table II.

As shown in Table III, number-average molecular weight of copolyurethaneimide is lower than that of homopolyimide, however, the weight-average molecular weight of the copolyurethaneimide is much higher than that of homopolyimide. These differences are attributed to the same reason, the high viscosity of the copolyurethaneimide. The higher weight-average molecular weight than number-average molecular weight of the copolyurethaneimide rendered its polydispersity index much higher than that of the ho-

TABLE II  
Thermal Properties of Homopolyimide and Copolyurethaneimides

Code	Decomposition Temperature ( $^{\circ}\text{C}$ )		
	$T_1^a$	$T_{10}^b$	$T_{\max}^c$
PI	550	580	650
PUI-1	110	220	590
PUI-2	105	240	570

**TABLE III**  
Molecular Weight Distribution of Homopolyimide and Copolyurethaneimides

Code	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PDI ( $M_w/M_n$ )
PI	14.1	16.2	1.15
PUI-1	9.94	24.7	2.49
PUI-2	5.35	15.6	2.92

mopolyimide. The flexible urethane and aliphatic ether linkage can affect the mechanical properties. In other words, the tensile strength of copolyurethaneimide is lower than that of homopolyimide, whereas elongation is much higher than in the rigid homopolyimide. The rigid imide group of copolyurethaneimide can reduce elongation and increase the tensile strength compared with polyurethane. The results are shown in Table IV.

### CONCLUSIONS

Soluble copolyurethaneimides were synthesized by the isocyanate method. Isocyanate-terminated prepolyurethane was imidized by reaction with PMDA at high temperature. Prepolyurethane was prepared from PEG or PPG and MDI. By using low molecular weight PEG (below PEG 600) and PPG (below PPG 2000), copolyurethaneimides with good film-forming properties were synthesized. Their inherent viscosity was much higher than that of the homopolyimide because of the high molecular weight prepolyurethane. The copolyurethaneimides were stable in vari-

**TABLE IV**  
Mechanical Properties of Homopolyimide and Copolyurethaneimides

Code	Tensile Strength (psi)	Elongation (%)	Modulus (psi)
PI	11800	6	235000
PUI-1	6200	47	131000
PUI-2	7800	38	185000

ous solvents, except polar solvents like NMP, DMAc, and DMF. The thermal stability of the copolyurethaneimides was worse than that of the homopolyimide because of degradation of the urethane linkage at  $\sim 300$  °C. The tensile strength of the copolyurethaneimides was lower than that of the homopolyimide. Elongation of the copolyurethaneimides was higher than homopolyimide because of the soft segment.

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