Synthesis and Characterization of Block Copoly(urethane–imide)

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SYNOPSIS

A newly synthetic method has been developed for the preparation of block copoly(urethane–imide) (PUI). The copolymer was yielded from the direct reaction of the prepolyurethane terminated with isocyanate and the prepolyimide terminated with anhydride. The latter is prepared by reacting an excess amount of pyromellic dianhydride (PMDA) with bis[4-(3-aminophenoxy)phenyl] sulfone (BAPS) in one-step polymerization. The structure was confirmed by infrared (IR) spectra. Other characterizations were evaluated. Among them were solubility, viscosity, mechanical properties, and thermal properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyimide derivatives have been one of the high-performance polymers because of their outstanding thermal and high-temperature mechanical properties.[1-4] But they have poor solubility in organic solvents and difficult processability. Therefore, soluble polyimide derivatives are highly desirable to facilitate processing. As an approach to improve the polymer soluble characteristics, polyimides have been modified by incorporating various functional moieties into the polymer backbone.[5,6]

Many authors have investigated the methods for preparation of the polyimide derivatives from anhydride and diisocyanate instead of diamine reagents[7,8] and have also studied the structure property relation to polyimide from anhydride and isocyanate.[9,10] The isocyanate group reacts readily with various organic compounds, and isocyanates may react with themselves.[11-13] The reaction takes place by addition across the $C{=}N$ double bond. The electronic structure of the isocyanate group indicates that it has the following resonance hybrids[11-14]:

$$R-N^--C^+{=}O \rightleftharpoons R-N{=}C{=}O \rightleftharpoons$$
$$R-N{=}C^+-O^-$$
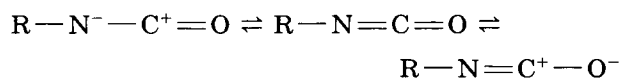
Among the important and well-studied isocyanate reactions, a related reaction is the preparation of imide from carboxylic anhydride and isocyanate, as follows[14]:
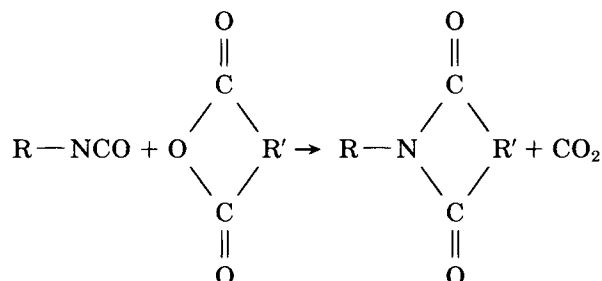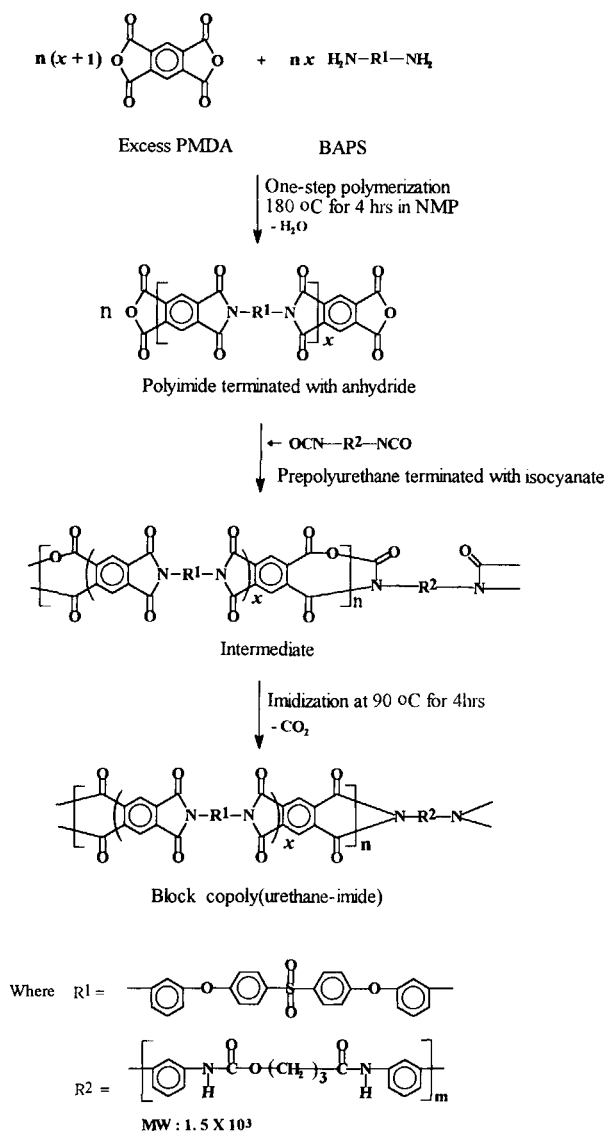

The objectives of this article are the synthesis and characterization of a block of copoly(urethane–imide)s (PUIs), which were yielded from the direct reaction of an isocyanate-terminated polyurethane and the anhydride-terminated polyimide. The latter could be prepared by one-step polymerization.

EXPERIMENTAL

Reagents

Pyromellic dianhydride (PMDA, Aldrich Chemical Co.) was recrystallized from 4-methyl-2-pentanone followed by vacuum drying and stored in a desiccator

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n (x + 1)   Excess PMDA   +   n x   H₂N—R¹—NH₂   BAPS

One-step polymerization
180 oC for 4 hrs in NMP
- H₂O

n   N—R¹—N

Polyimide terminated with anhydride

← OCN—R²—NCO
Prepolyurethane terminated with isocyanate

N—R¹—N ... N—R²—N

Intermediate

Imidization at 90 oC for 4hrs
- CO₂

N—R¹—N ... N—R²—N

Block copoly(urethane-imide)

Where R¹ =

R² =

MW : 1.5 X 10³

Scheme 1

over $CaCl_2$ and silicagel. Bis[4-(3-aminophenoxy)phenyl] sulfone (BAPS, Wakayama Seika Kogyo Co.) was purified by recrystallization in ethanol followed by vacuum drying at 60°C for 4 h and stored in a drying oven. Polyurethane (PU) oligomer terminated with isocyanate, a commercially available prepolymer (SKP-6000, molecular weight [MW] about 1500, Sunkyoung Industries, Korea), was dried under reduced pressure at 40°C and then stored in a drying chamber. The prepolymer was used without further purification. 1-Methyl-2-pyrrolidone (NMP) was dehydrated with CaH_2 and then distilled before being stored in 4-Å molecular sieves. Other laboratory-grade reagents were used without further purification.

Measurements

The viscosity of polymer solution was measured with a Ubbelohde viscometer at the concentration of 0.5 g/dL in NMP at 30°C. The molecular weight distribution was evaluated from gel permeation chromatography (GPC, water 150°C). The infrared (IR) spectrum was recorded in film using a Hartman & Braun model BOMEM DA 8.16. The thermal properties were measured by using thermogravimetric analysis (TGA, Perkin-Elmer TGA7) and differential scanning calorimetry (DSC, Dupont 1090). The tensile strength and elongation were measured at room temperature using an Instron testing machine model TT-C. This test used the film with 150 μm thickness, 10 mm width, and 50 mm length. To determine solubility, polymer samples were immersed in the various solvents and allowed to shake for 7 days. If the sample was only partially dissolved or swelled, it was heated at 70°C for 24 h.

Preparation of Block PUIs

A four-necked flask was equipped with a sealed teflon stirrer, a nitrogen inlet tube, a thermometer, and a reflux condenser with distilling receiver and was charged with BAPS and NMP at 20°C. Under flow of nitrogen, excess molar PMDA was added into the flask to prepare polyamic acid (PAA), and the reaction mixture was kept at this condition for 4 h. When the reaction was completed, the azeotroping agent, p-xylene, was added to the reaction mixture. Next, the temperature was raised rapidly to 180°C in about 30 min, and continued for 4 h under flow of nitrogen to obtain polyimide (PI) terminated with anhydride. The viscose solution was allowed to cool at 20°C. Subsequently, PU was added to the solution and the reaction was continued until the viscosity increased no more. If the reaction was completed, the contents of the flask were warmed rapidly up to 70–140°C, and that temperature was maintained for 4 h to the cyclization with liberated carbon dioxide as the byproduct. On completion of this reaction, the viscous solution was cooled and poured into a large quantity of methanol, in which the PUI deposited. The precipitate was filtered off, washed free of NMP by repeated use of methanol, and dried in vacuo at 70°C (Scheme 1).

RESULTS AND DISCUSSION

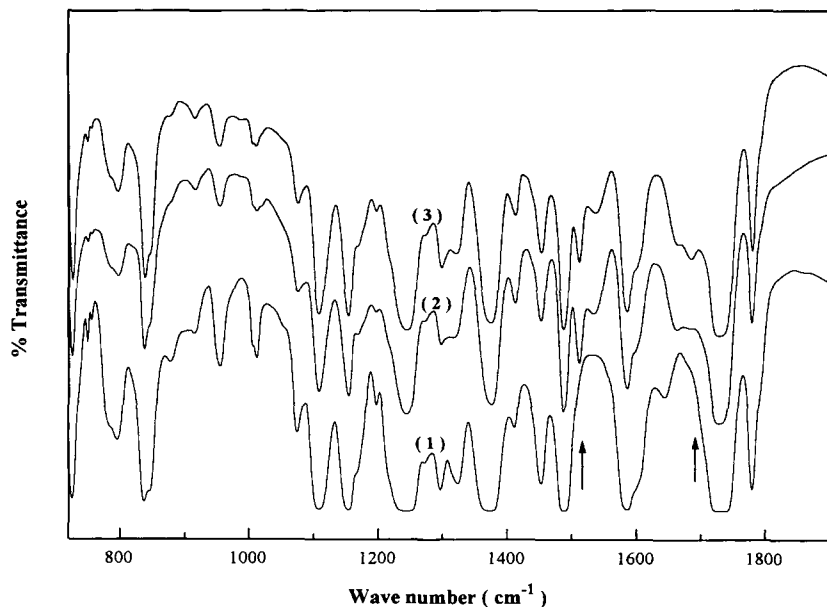Figure 1 represents the IR spectra of PUI, which was prepared from PMDA/BAPS (1.0/0.9 mol ra-

Figure 1   IR spectra of (1) PMDA/BAPS polyimide, (2) PUI-12, and (3) PUI-16.

tio), PI, and PU terminated with isocyanate. PMDA/BAPS homopolyimide was characterized by the absorption peaks of imide groups at about 1780, 1300, and 720 cm^{-1}. The band at 1780 cm^{-1} was

related to the stretching vibration of $C=O$ linkages of the imide ring and the bands at 1300 and 720 cm^{-1} assigned to the $C-N$ stretching vibration of cyclic imide groups. The spectra of PUI exhibited the new absorption bands near 1700–1720 cm^{-1} and
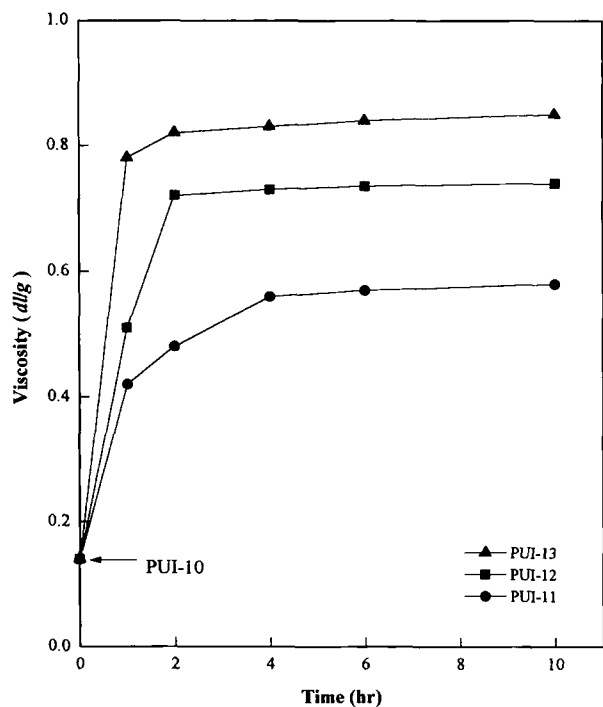

Figure 2   Viscosity of PUI derivatives as a function of reaction time. Reaction was carried out with 15% reagents concentration in NMP at 20°C under flow of nitrogen.
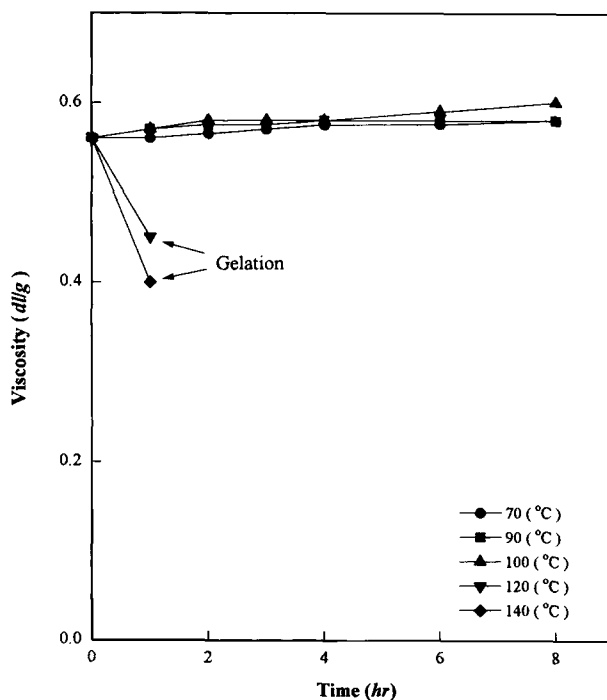

Figure 3   Influences of curing temperature and time on the viscosity of PUI-11 in the cyclization with liberated CO_2.

Table I   Variation of PU Content on Viscosity and Solubility of PUI

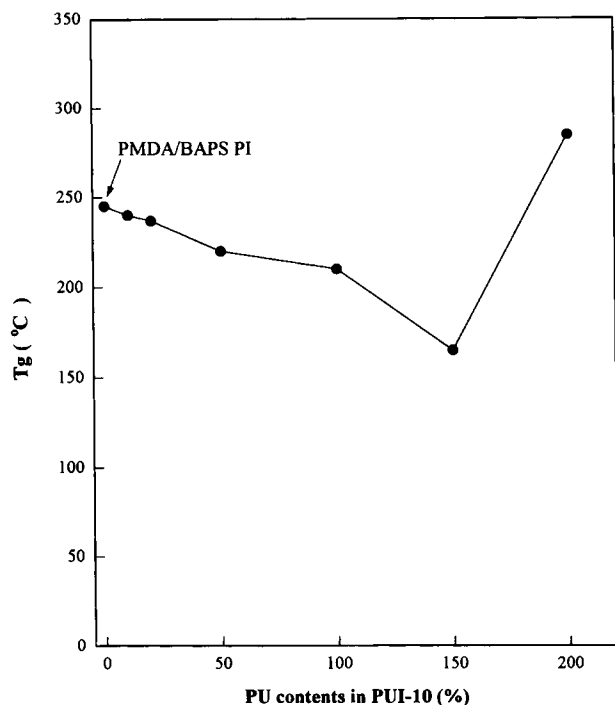| No.	PMDA/BAPS (mol ratio)	PU Contents[a] (wt %)	Viscosity[b] (dL/g)	Remarks[c]
PUI-10	1.0/0.9	0	0.14	S
PUI-11		10	0.56	S
PUI-12		20	0.73	S
PUI-13		40	0.83	S
PUI-14		50	0.94	S
PUI-15		80	1.20	S
PUI-16		100	1.00	S
PUI-17		150	0.42	PG
PUI-18		200	—	G
PUI-20	1.0/0.8	0	0.09	S
PUI-21		10	0.32	S
PUI-22		20	0.54	S
PUI-23		40	0.88	S
PUI-24		80	0.50	S
PUI-25		100	0.50	S
PUI-26		150	—	G
PUI-27		200	—	G
PUI-30	1.0/0.7	0	0.08	S
PUI-31		20	0.36	S
PUI-32		40	0.42	S
PUI-33		100	—	G
PUI-40	1.0/0.5	0	0.05	S
PUI-41		20	0.48	S
PUI-42		40	0.51	S
PUI-43		100	0.67	S

[a] Contents of PU against PI total weight.
[b] Measured at concentration 0.5 g/dL in NMP at 30°C.
[c] S, soluble; PG, partial gelation; G, gelation in reaction medium.
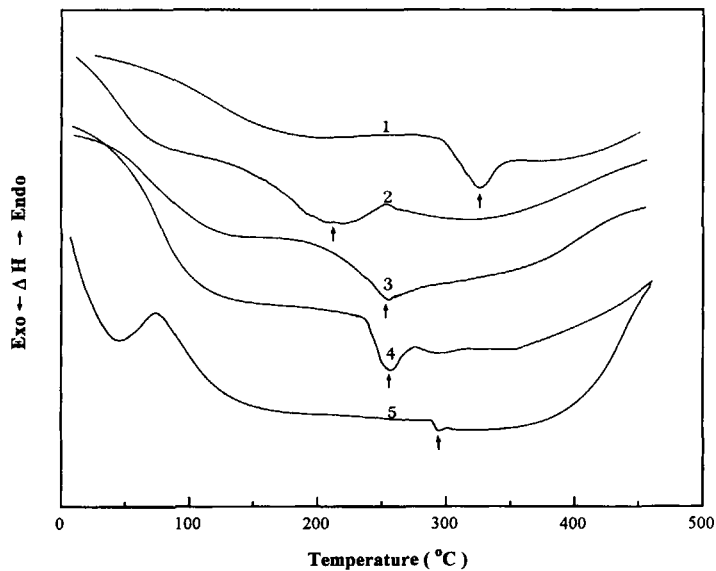
Figure 4   DSC traces for (1) PUI-27, (2) PUI-17, (3) PUI-11, (4) PMDA/BAPS polyimide, and (5) PUI-18. Heating rate is 10°C/min under flowing air.
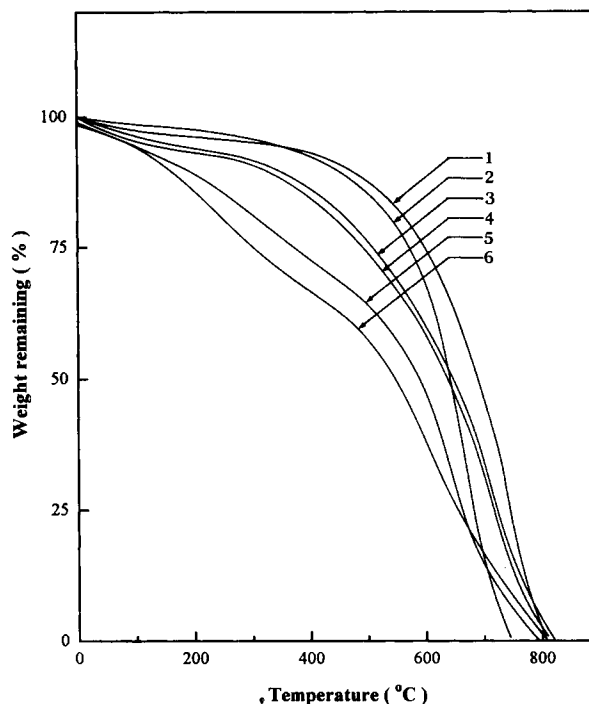
Figure 5   Evolution of the T_g of PUI derivatives versus PU contents in PUI-10.

Figure 6   TGA thermograms of (1) PUI-27, (2) PMDA/BAPS polyimide, (3) PUI-11, (4) PUI-12, (5) PUI-14, and (6) PUI-16. Heating rate is 20°C/min under flowing air.

1530–1540 cm^{-1}, which was related to the stretch vibration of $C = O$ linkages of urethane groups. The presence of newly detectable bands suggested that the polymer prepared should confirm the PUI.

Figure 2 shows the value of viscosity as a function of the reaction time. A seven-membered heterocycle intermediate was formed by the reaction of isocyanate and anhydride. The viscosity of the intermediate increased with time up to the nearly maximum value, but after that value, the value of viscosity was nearly unchanged. The optimum reaction time for preparation of high-molecular-weight intermediate could be defined as 4 h.

It was necessary to investigate optimum thermal conditions in order to complete deliberation of carbon dioxide without conformation of crosslinkages and decomposition of the intermediate.[11,12] Figure 3 shows the viscosity and appearance of polymers treated under different cure temperatures and times. The polymer treated above 100°C was precipitated from the reaction mixture in the first hour; on the other hand, below 100°C, the value of viscosity slightly increased in the first hour and the polymer was not deposited in the reaction mixture during cyclization reaction. Those behaviors could be explained by the reactivity of functional groups and the formation of crosslinks.[11–13] The isocyanate groups reacted with active hydrogen compounds and

themselves. In this reaction, the crosslinks might be occurring by the reactions between the isocyanate group and the active hydrogen, including the residual carboxylic acid and secondary amine in PI moiety and the secondary amine in PU moiety, and by the reaction of themselves. Therefore, the polymers became insoluble in the reaction mixture and separated as a precipitate. On the basis of the results, all the PUI prepared for further synthesis in this study were treated at 90°C for 4 h under flow of nitrogen.

PIs terminated with anhydride groups were prepared from the various molar ratios of PMDA/BAPS, and PU content in PUI was varied in order

Table II   Mechanical Properties of PUI

No.	Tensile Strength (kg/mm^2)	Elongation (%)
PMDA/BAPS PI	7.20	7.7
PUI-11	8.90	9.0
PUI-12	7.40	10.0
PUI-14	5.10	11.3
PUI-16	5.10	15.6
PUI-43	3.60	7.0

Properties measured at room temperature.

to determine content effects on the PUI properties. Contents of 10, 20, 30, 50, 80, 100, 150, and 200% (w/w) PU in PI were prepared and PUI properties evaluated. Table I represents the viscosity of PUI as a function of PU contents. The viscosity increased with increasing the contents of PU. Particularly, the polymer containing above 150% (w/w) PU in PI was somewhat anomalous in exhibiting precipitation or gelation. This anomaly clearly appeared to increase with PU contents. It could be explained from those results that (1) the chain-growth polymerization occurred by the reaction of PI and PU, exactly, because both polymers served as extenders for each other; (2) the potentiality of crosslinks increased with increasing the contents of PU moiety; and (3) the self-reaction of isocyanate groups as well as the strong hydrogen bond in urethane probably led to gelation.[11-13]

Figure 4 represents typical DSC curves of PUI. DSC measurements were of particular interest in that (1) glass transition temperature (T_g) was apparently unaffected by the contents of 10 or 20% (w/w) PU in PI, and (2) T_g was depressed by the introduction of PU and decreased continuously with increasing the contents of that. No doubt, the more thermally sensitive urethane was contributing to a lower T_g. Compared with PI, the contribution was not great in the range below 100%; the decreased temperature of the PUI with 100% PU was near 50°C. But above 100%, decreased temperature was dramatic, near 100°C. The T_g of the PUI containing above 150% PU rapidly increased, which probably

Retention volume
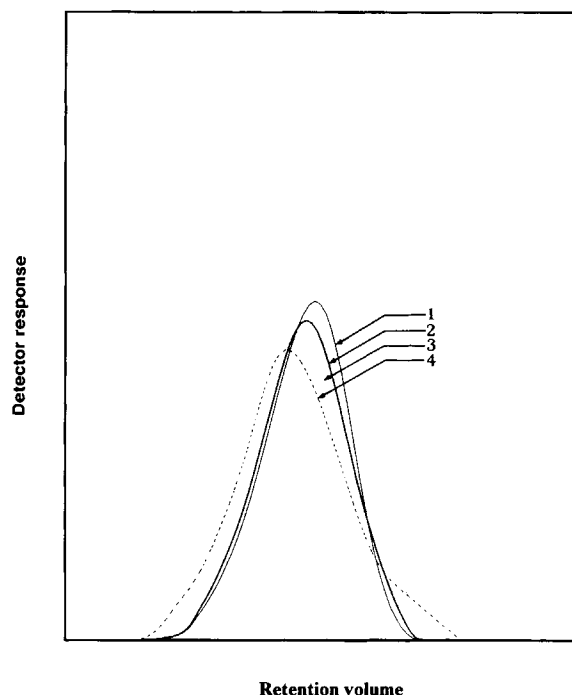
Figure 7   GPC of (1) PUI-11, (2) PUI-12, (3) PUI-13, and (4) PUI-17.

was related to the crosslinks. Figure 5 shows the evaluation of the T_g versus the contents of PU. The melting temperature (T_m) of PUI did not exist on the DSC curves.

TGA profiles of the polymers are shown in Figure 6. Apparently, PUI samples were degraded in some

Table III   Solubility of PUI Containing 10 wt % PU

No.	Solvent	δ_d	δ_p	δ_h	δ_t	Remarks[a]
1	Acetic acid	7.1	3.9	6.6	10.5	SW
2	Acetone	7.6	5.1	3.4	9.8	IS
3	Chlorobenzene	9.3	2.1	1.0	9.6	IS
4	Chloroform	8.7	1.5	2.8	9.3	IS
5	m-Cresol	8.8	2.5	6.3	11.1	S
6	N,N-Dimethylacetamide	8.2	5.6	5.0	11.1	S
7	N,N-Dimethylformamide	8.5	6.7	5.5	12.1	S
8	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	S
9	1,4-Dioxane	9.3	0.9	3.6	10.0	IS
10	Foramide	8.4	12.8	9.3	17.9	SW
11	Formic acid	7.0	5.8	8.1	12.2	SW
12	Glycerol	8.5	5.9	14.3	17.6	IS
13	N-Methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	S
14	Nitrobenzene	9.8	4.2	2.0	10.9	S
15	Pyridine	9.3	4.3	2.9	10.7	SW
16	Tetrahydrofuran	8.2	2.8	3.9	9.5	IS

Samples heated continuously at 25°C for 7 days or, with samples partially soluble in solvent, at 70°C for 24 h.
[a] S, soluble; SW, swell; IS, insoluble in solvent.

different pattern compared with PI. In the TGA traces of copolymers, the onset of thermal degradation gradually shifted to lower temperature with increasing PU contents. The reason for these results could be that the more thermally sensitive PU moiety began to decompose before PI moiety was degraded. These experiments indicated that the initial thermal degradation was due to a decomposed urethane chain. The imide moiety was decomposed at the higher temperature.

Mechanical properties of the polymers with various contents of PU are shown in Table II. The elongation gradually increased with increasing the contents of PU, while the tensile strength was inversely proportional to the contents of the urethane portion.

The solubility of PUI with various contents of PU in organic solvents is summarized in Table III. Most copolymers showed good solubility in some organic solvents, but the polymer containing above 150% PU dramatically decreased the solubility in those solvents. No doubt that the excess amount of PU terminated with isocyanate was contributing to the enhanced crosslinking reaction. This could be explained in the same manner as the effect of PU contents previously. However, the solubility might be increased by the protection of the free functional groups. The residual isocyanate groups were generally protected by the active hydrogen compounds (methanol). The good solubility was advantageous in the processability of polymer and expands the practical application.

Figure 7 shows GPC chromatogram of PUI. The molecular weight distribution (MWD) of the polymers gradually broadened with increasing PU portion. The retention volume was slightly shifted to the high molecular weight. The polydisperse indexes (PDIs) are in the range 1.5–3.5.

CONCLUSION

PUIs could have been synthesized via chemical incorporation of PU terminated with isocyanate into PI terminated with anhydride. The optimum curing condition was found to be at 90°C for 4 h. Increasing PU contents up to 150% (w/w) in PI, the solubility and elongation were increased but thermal stability was decreased. Above 150% (w/w) PU contents, anomalous solubility and thermal behavior occurred. The solubility was significantly decreased; on the other hand, thermal stability was increased. The anomalous behavior could be prevented partially by the protection of the residually free functional groups.

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