

Synthesis and Properties of Novel Poly(urethane-imide) Dispersions Based on 2,2-Bis[N-(3-hydroxyphenyl)phthalimidyl]hexafluoropropane

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ABSTRACT: Imide units are incorporated into thermoplastic and solvent-based polyurethane (PU) chains to improve the thermal stability of PU. However, these poly(urethane-imide) (PUI) materials have poor processability and suffer from solvent emission. To prepare easily processable and environmentally friendly PUI products, some waterborne PUIs are synthesized using a prepolymer process. A series of PUI dispersions with 25 wt % solid content, viscosities of 7.5–11.5 cps, and particle sizes of 63–207 nm was prepared. The composition–property relationship of PUIs, including the solubility behavior of PUI cast films, and their thermal and mechanical properties were estab-

lished. The solvent resistance and tensile strength of PUI film increased with the number of imide groups. All PUIs exhibited improved thermal stability but not char yield as the temperature increased. The inclusion of a little imide increased the decomposition temperature of PUI while maintaining the elasticity of the polymer, revealing successful translation of PUI into the water-based form. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 517–524, 2009

Key words: 2,2-bis[N-(3-hydroxyphenyl)phthalimidyl]hexafluoropropane; poly(urethane-imide); dispersion; prepolymer process

INTRODUCTION

Linear, segmented polyurethanes (PUs) that comprise alternating soft and hard segments provide unique possibilities for forming tailor-made polymers via the variation of block length and composition. They are all formed by diisocyanate polyaddition to form block copolymers. The double-phase separation of PU causes this material to particular special features, including elasticity, smoothness to touch, electrical insulation, and others.^{1,2} With respect to the solvent vapor-related problems of toxicity and pollution, waterborne PU dispersions have been increasing in importance in a wide range of applications to reduce solvent emissions into the atmosphere. However, PUs have shortcomings such as poor thermal stability; for example, satisfactory mechanical properties (strength, moduli, etc.) disappear above 80–90°C and thermal degradation occurs at temperatures of over 200°C.³

Various attempts to improve the thermal stability of PU have been made over a long period. One accepted approach involves the chemical modification of its structure by blending or copolymerizing

with more thermally stable polymers such as poly(urethane-urea),^{4,5} poly(urethane-epoxy),^{6–8} and polyurethane-diacetylene.⁹ Recently, more attention has been paid for the modification by adding highly thermally stable heterocyclic groups. Polyimide (PI) is an important class of heterocyclic polymers with remarkable heat-resistance properties and superior mechanical and electrical characteristics and durability.^{10–12} Various attempts have been made to incorporate PI or oligoimide units into PU. The reaction of isocyanate-terminated PU prepolymer with acid anhydride is the most commonly employed method for introducing the imide functional group into the PU backbone.^{13–15} A modified approach involves the reaction of acrylate end-capped PU prepolymer with maleimide end-capped PI to prepare crosslinked PU that contains imide groups in its linkage chains.¹⁶ The reaction of diol with isocyanate-terminated imide monomer has also been adopted.¹⁷ Poly(urethane-imide)s (PUIs) can be prepared by reacting 4,4'-(bismaleimidodiphenyl) methane with various bisfuranylmethylcarbamates through a Diels-Alder reaction.¹⁸

As stated earlier, all published investigations of PUI focus on its mechanical properties or thermal behaviors. However, specialized studies of the syntheses of waterborne PUI dispersions are unavailable. Preparing PUI dispersions is one of the

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economical and environmentally friendly methods for preparing easily processable PUIs. This study explores the possibility of introducing the imide function into the PU backbone by a reaction of imide that contains bisphenol with the diisocyanate monomer, and a series of PUI dispersions is prepared by varying the imide content. In the experiment, the anionic PUI dispersion is synthesized using toluene diisocyanate (TDI) and 2,2-bis[*N*-(3-hydroxyphenyl)phthalimidyl]hexafluoropropane (**I**) as the hard segment, 2,2-bis(hydroxymethyl)butyric acid (DMBA) as the ionic center, and poly(tetramethylene oxide) (PTMO) as the soft segment. The synthesis and characterization of the prepared diimide-bisphenol and PUI dispersions, as well as the physical and thermal properties of the polymers, are discussed. The effect of imide content on the solubility behavior, mechanical properties, and thermal properties is also examined.

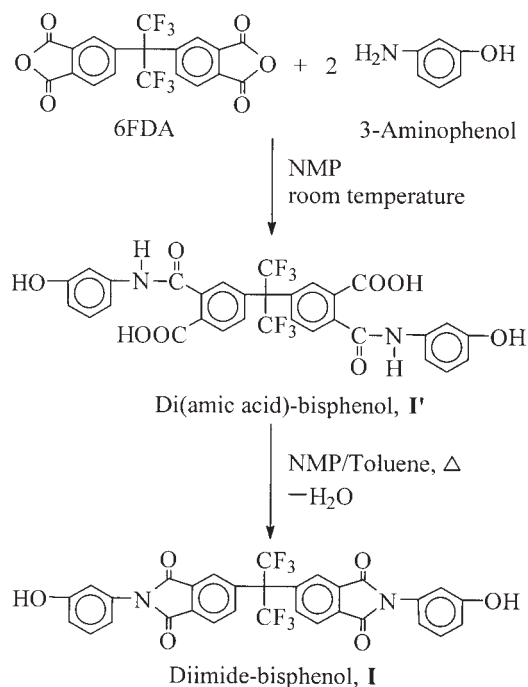
EXPERIMENTAL

Materials

The following reagents were used without further purification: poly(tetramethylene oxide) (PTMO, $M_n \sim 2000$, reagent grade; Aldrich, Milwaukee, WI), toluene diisocyanate (TDI; Bayer, Leverkusen, Germany), 2,2-bis(hydroxymethyl)butyric acid (DMBA, reagent grade; Aldrich), and 3-aminophenol (reagent grade; TCI, Tokyo, Japan). 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA; Hoechst, Charlotte, NC) was recrystallized from acetic anhydride before use. Triethylamine (TEA, reagent grade; Aldrich), ethylene diamine (EDA, reagent grade; Delamine, Amerfoort, Netherlands), and *N*-methyl-2-pyrrolidone (NMP, reagent grade; Acros, Morris Plains, NJ) were immersed in 4-Å molecular sieves for more than 1 week before being used.

Synthesis of diimide-bisphenol

3-Aminophenol (10.9 g, 0.1 mol) was dissolved in 50 mL dried NMP in a 150-mL flask. After 3-aminophenol had dissolved completely, 22.2 g (0.05 mol) 6FDA was added to it in one portion. The mixture was stirred at room temperature for 1 h. Toluene (10 mL) was then added, and the mixture was heated at reflux for ~ 3 h, until around 1.8 mL water had distilled off azeotropically in a Dean-Stark trap. Heating was continued to distill off the residual toluene. After cooling, distilled deionized water was added, and the precipitated product was isolated by filtration, purified by recrystallization from acetone–distilled deionized water solution, and dried in vacuum to yield 26.6 g diimide-bisphenol **I** (beige powder; 85% yield).



Scheme 1 Synthesis of diimide-bisphenol.

Diimide-bisphenol **I** (Scheme 1): mp 246°C. FTIR (KBr): 3200–3500 (phenol, —OH), 1781 (imide, symmetric C=O stretching), 1722 (imide, asymmetric C=O stretching), 1385, 1106, 721 cm^{-1} (imide ring vibration, axial, transverse, and out of plane) (Fig. 1).

$^1\text{H-NMR}$ (400 MHz, acetone- d_6 , δ): 8.88 (2H, H_a), 8.14, 8.12 (2H, H_c), 8.06 (2H, H_b), 7.90 (2H, H_d), 7.37, 7.35, 7.33 (2H, H_e), 7.02–6.97 (2H, H_f), 6.95–6.92 ppm (2H, H_g) [Fig. 2(a)]. $^{13}\text{C-NMR}$ (100 MHz, acetone- d_6 , δ): 166.865, 166.766 (C^1 , C^1), 158.521 (C^8), 139.073 (C^4), 136.920 (C^{10}), 133.973, 133.872, 133.566 (C^2 , C^5), 130.425 (C^{12}), 129.672 (C^7), 128.953, 126.025, 123.128, 120.224 (C^{14}), 125.145, 124.817 (C^3 , C^6), 118.964 (C^{11}), 116.054 (C^{13}), 115.074 (C^9), 66.021 ppm (C^{15}) [Fig. 2(b)].

Synthesis of PUI dispersions

A 500-mL four-necked round flask equipped with a half-moon stirrer, a thermometer, and a nitrogen gas inlet was used. Reaction temperature was controlled using a thermostat propylene glycol bath. DMBA and diimide-bisphenol **I** were dissolved in dried NMP in the flask. After the two monomers had dissolved completely, PTMO was added to it in one portion. The mixture was stirred at 70°C for 20 min. Then, a water bath was used to control the temperature below 50°C. The TDI was then added to the flask, and the temperature was raised to 80°C for 4 h. The reaction proceeded until the theoretical isocyanate (NCO) reached the end point, and NCO-terminated prepolymer was obtained. The NCO

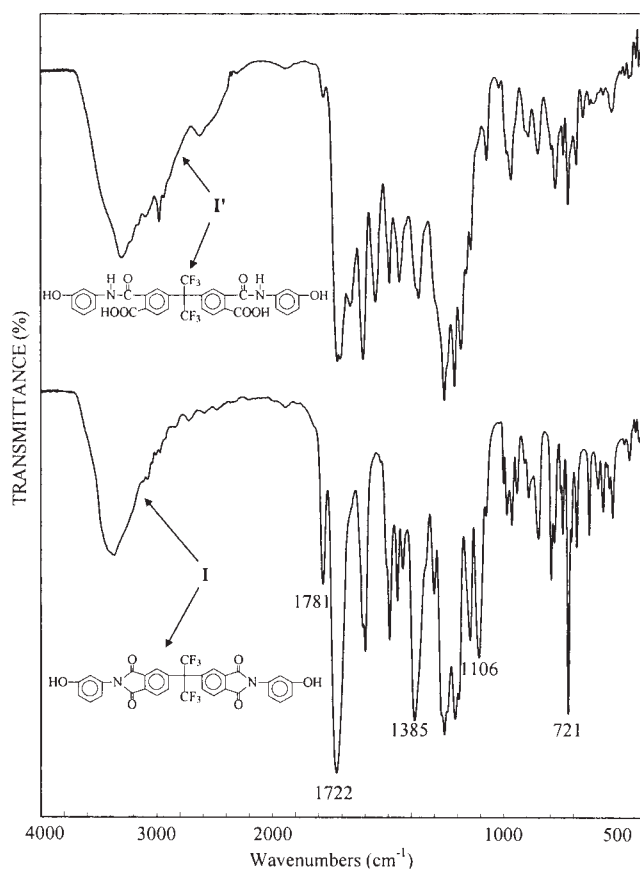


Figure 1 FTIR spectra of diimide-bisphenol **I** and its di(amic acid)-bisphenol precursor **I'**.

content of the prepolymer was measured by the standard dibutylamine back-titration method (ASTM D 1638). TEA was added to neutralize the COOH groups at 50°C, and PUI anionomers were thus obtained. The PUI anionomer was then dispersed in distilled deionized water, and the chain extension reaction proceeded by adding EDA. The final amino-terminated PUI dispersions had about 25% solid content and were of pH 7–8.

Table I presents the recipe for preparing PUI dispersions. All PUI dispersions were synthesized by an analogous procedure as described.

Measurements

Melting points were measured in capillaries using a Fargo melting point apparatus (model MP-2D) without correction. FTIR spectra were recorded using a Jasco FT/IR-460 Plus Fourier transform IR spectrometer. ¹H- and ¹³C-NMR spectra were determined using a Jeol EX-400 FT-NMR spectrometer. The viscosity was determined at room temperature using a Brookfield Viscometer (LVT). The average particle size of the PUI dispersions was measured by dynamic light scattering (HORIBA Ltd., LB-500). The PUI films were prepared by pouring dispersions

into a glass culture dish, followed by drying at 50°C for 72 h (PUI film thickness was about 0.6 mm). Then the films were removed and placed in a desiccator ready for testing. The solvent resistances of all polymers were determined at a concentration of 1% (w/w) in NMP, DMF, DMSO, MEK, acetone, ethanol, *n*-hexane, and THF at 25°C. Tensile properties were carried out with an Instron model 4467 Universal Tester with a load cell of 50 kg. A gauge length of 2.54 cm and a crosshead speed of 50 cm/min were used for this study. Reported data are the average values of at least six replica tests. Differential scanning calorimetry (DSC) traces were measured using TA Instruments DSC Q10 at a rate of 10°C/min in flowing nitrogen (40 cm³/min). Thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2950. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (60 cm³/min) at a heating rate of 15°C/min.

RESULTS AND DISCUSSION

Monomer synthesis

PUI dispersions **II**_{0–15} were synthesized in two steps. 3-Aminophenol and 6FDA were used to prepare diimide-bisphenol **I**, which was then reacted with diols and diisocyanate by the prepolymer process to yield PUI dispersions. 2,2-Bis[*N*-(3-hydroxyphenyl)phthalimidy]hexafluoropropane (**I**), the new polymer-forming diimide-bisphenol with preformed imide rings, was synthesized via a two-stage procedure that included the ring-opening addition of 6FDA with two equivalent amounts of 3-aminophenol at room temperature in polar solvent to yield the amide-amide intermediate. Then, thermal cyclodehydration *in situ* bisphenol **I** at the reflux temperature by toluene–water azeotropic distillation, as shown in Scheme 1. The crude **I** was purified by recrystallization from acetone–distilled deionized water. The structure of monomer **I** was confirmed by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopy. FTIR spectroscopy is used to monitor the formation of an imide ring during ring dehydration. Figure 1 presents the corresponding FTIR spectra. As the di(amic acid)-bisphenol **I'** was converted into the diimide-bisphenol **I**, the characteristic absorption bands of the imide ring were observed near 1780, 1720 (asymmetrical and symmetrical C=O stretching vibration), 1390 (C–N stretching vibration), 1100 and 720 cm⁻¹ (imide ring deformation) and those of the amide and carboxyl groups near 2980, 2630, 1670, and 1560 cm⁻¹ disappeared, indicating the virtually total conversion of the amic acid precursor into imide group.

Figure 2 presents the ¹H and ¹³C-NMR spectra of diimide-bisphenol **I**. The ¹H-NMR spectrum

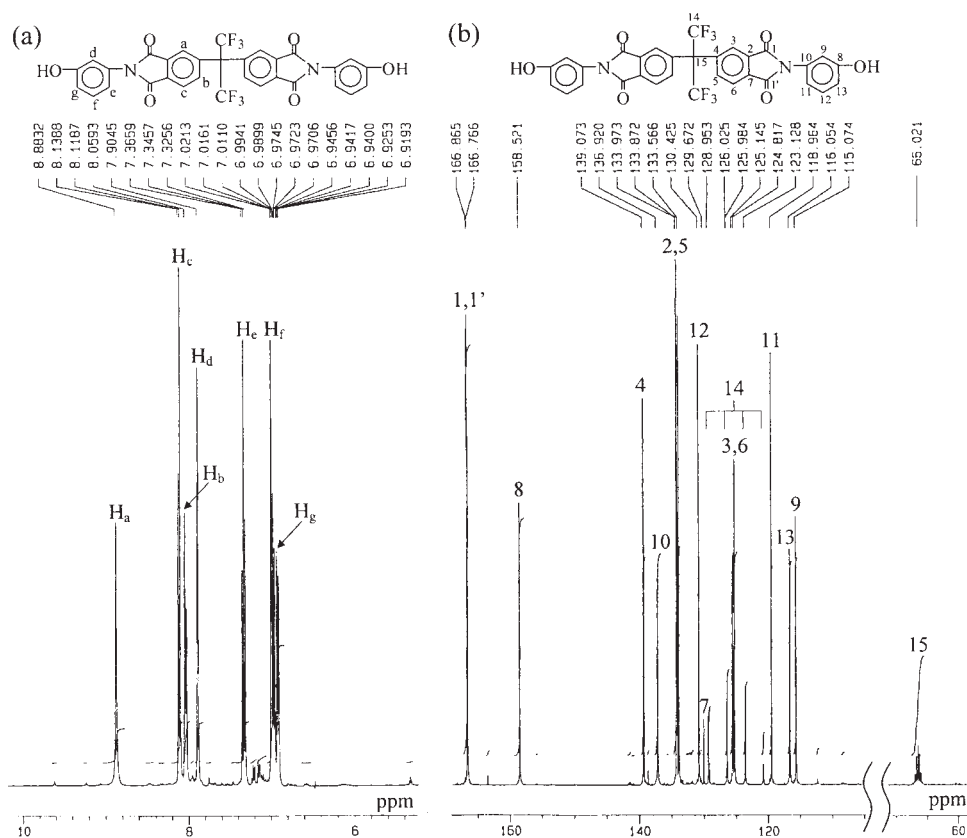


Figure 2 ^1H -NMR and ^{13}C -NMR spectra of diimide-bisphenol I (acetone- d_6).

[Fig. 2(a)] of I included seven main signals because the protons have different environments. The H_a and H_b ortho-oriented to the hexafluoroisopropylidene group shifted to the downfield region because of the shielding effect. Signals associated with H_c and H_d close to the imide ring and phenolic hydroxyl group (ortho-oriented protons) appeared in the upfield region of the spectrum in Figure 2(a),

because of resonance and the electron-donating effect. H_e was located at the ortho position of the imide ring, and so the signal associated with H_e appeared at a lower field than those of H_f and H_g because of the resonance. The H_g signal appeared at a higher upfield region than the H_f signal, because the strong electron-donating effect of the phenolic hydroxyl group affected H_g . The ^{13}C -NMR spectrum

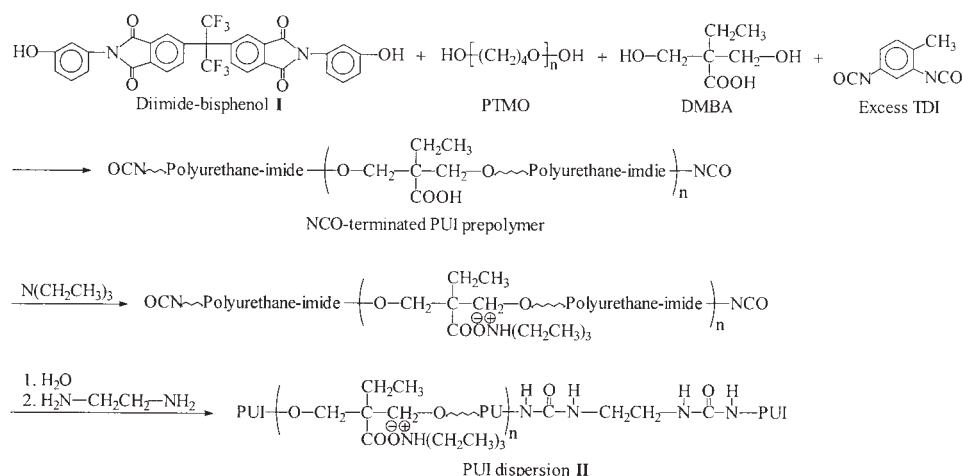
TABLE I
Basic Recipe for the Synthesis of PUI Dispersions

Components	Amount ^a (g)			
	II ₀ ^b	II ₅	II ₁₀	II ₁₅
PTMO	74.1	94.3	77.2	74.6
DMBA	5.2	6.7	5.7	5.7
Diimide-bisphenol I	0	6.9	12.2	19.5
TDI	20.7	29.0	27.1	29.7
NMP	8.7	14.4	27.5	27.5
TEA	3.5	4.6	3.9	3.9
EDA	1.1	1.5	1.4	1.5
Distilled deionized water	287.8	391.6	335.2	337.4
Hard segment content ^c (wt %)	25	32	38	43

^a Molar ratio of NCO/OH = 1.6; degree of chain extension = 40%; solid contents = 25%.

^b Subscript number means weight % of diimide-bisphenol I based on PUI weight [(I/PUI) × 100%].

^c Hard segment content weight ratio in copolymerization is calculated with [(DMBA + diimide-bisphenol I + TDI + EDA)/PUI] × 100%.



Scheme 2 Preparation of water-based poly(urethane-imide) dispersions.

[Fig. 2(b)] included 20 signals, which were consistent with the predicted structure of I. Signals for carbons C^1 and $C^{1'}$ of the carbonyl groups were evidenced in the downfield region at 166.865 and 166.766 ppm, and the difference between the shifts of C^1 and $C^{1'}$ was caused by the difference between the distances to the $-\text{C}(\text{CF}_3)_2-$ group. The C^8 signal also appeared in the downfield region at 158.521 ppm, because the hydroxyl group is inductively electron withdrawing. The fluorine atoms of $-\text{CF}_3$ split the C^{14} signal, yielding a quartet (128.953, 126.025, 123.128, and 120.224 ppm, coupling constant $J = 290$ Hz).

Synthesis and characterization of PUI dispersions

Diimide-bisphenol I with a variable weight ratio of hard segment to PUI was formulated with PTMO, DMBA, and TDI and reacted in NMP to yield isocyanate-terminated prepolymers. Then, dispersion and chain extension yielded PUI dispersions, as presented in Scheme 2. The physical properties of the PUI films depend on their molecular structure. They also depend on the functional group content and on the molar ratio of NCO/OH. The isocyanate used herein was TDI, which was an 80 : 20 mixture of the 2.4 and 2.6 isomers. TDI is not generally corrosive toward metals or other materials at room tempera-

ture. DMBA, a carboxylic group that contains diol, was used to produce a water-dispersible urethane prepolymer without any significant reaction between the carboxylic group and the isocyanate group, because the hydroxyl group is much more reactive than the isocyanate.

Samples were prepared by varying the diimide-bisphenol I content, as listed in Table I. No difficulty was encountered in obtaining imide-modified prepolymers from the reactions of I with the other reagents. Although the phenol is less reactive with NCO than with the alcohols, I was still sufficiently reactive to give the theoretical NCO end-point prepolymers when they were allowed to polymerize for a sufficiently long period. All of the products are considered to be good dispersions with a subtranslucent to sallow appearance, as the particle sizes increased with the I content in the PUI dispersions and the incidental sedimentation was always negligible, as shown in Table II. In fact, the polymer dispersions were all stable for more than 6 months. All of the PUI dispersions exhibited similar properties, and they had pH values of 7–8, average particle sizes of 60–210 nm, and viscosities of 8–12 cps. When diimide-bisphenol I was applied up to 20 wt % content, the resulted dispersion was unstable. Therefore, the discussion of PUI with diimide-bisphenol I above 15 wt % content was not included in this study.

TABLE II
Properties of PUI Dispersions

Code	II ₀	II ₅	II ₁₀	II ₁₅
Dispersion appearance ^a	Translucent with blue light	Light yellow	Pale yellow	Sallow
Dispersion pH value	7.4	7.7	7.7	7.9
Average particle size (nm)	63	81	132	207
Brookfield viscosity (cps)	11.5	8.5	7.5	10
Storage stability (months)	>6	>6	>6	>6

^a PUI dispersions were prepared with diimide-bisphenol I random distribution.

TABLE III
Solvent Resistance of PUI Films in Various Solvents

Code	Solvents ^a [solubility parameter (cal/cm ³) ^{0.5}]							
	NMP [11.3]	DMF [12.14]	DMSO [11.98]	MEK [9.3]	Acetone [9.9]	Ethanol [12.7]	<i>n</i> -Hexane [7.3]	THF [9.04]
II ₀	+	+	+h	+h	SW	+h	–	+h
II ₅	+	+	±	+h	SW	+h	–	+h
II ₁₀	+	+	±	SW	SW	+h	–	+h
II ₁₅	+	+	SW	–	–	–	–	–
Cured II ₁₀ ^b	SW	SW	–	–	–	–	–	–

^a Immersed in solvent for 1 day: +, soluble at room temperature; +h, soluble after heating; SW, swelling; ±, partially soluble; –, no change.

^b II₁₀ mixed with 5% crosslinker (solid/solid); the crosslinker has epoxy value of 5.6 mequiv./g.

Solvent resistance

Table III presents the qualitative solvent resistance of the PUI films. The samples were immersed in various solvents—NMP, DMF, DMSO, MEK, acetone, ethanol, *n*-hexane, and THF—for a day. As indicated in Table III, no sample changed in *n*-hexane, but swelled in acetone. In the case of II_{0,5,10}, small amounts of the samples dissolved in DMSO, and most dissolved after heating in MEK, ethanol, and THF. The solubility is thought to be associated with the deficiency of the imide group, because it becomes insoluble for II₁₅ with a diimide-bisphenol I content of up to 15 wt %. However, all of the PUI films were soluble in aprotic polar solvents, such as NMP and DMF. Copolymer PUI had a better solvent resistance than pure PU II₀, while the imide content sufficed in the backbone, as in II₁₅. The absence of a crosslinking structure in the polymer is responsible for the poor solvent resistance of PUIs II.¹⁹ When II₁₀ is mixed with a little epoxy crosslinker, the prepared PUI film has a network structure and improved solvent resistance. The solvent resistance results are related to the solubility parameter theory. According to the theorem of Hildebrand, an aggressive solvent is one that has a solubility parameter that is within plus or minus one of the solubility parameter of the material when measured in (cal/cm³)^{0.5}. As indicated in Table III, these PUI IIs, dissolved in NMP and DMF, may have a solubility parameter between 11.3 and 12.1 (cal/cm³)^{0.5}. Therefore, they exhibited better solvent resistance in MEK, acetone, ethanol, *n*-hexane, and THF. Although etha-

nol has a solubility parameter of 12.7, it is still a poor solvent for PUIs, since it is too volatile and tends to absorb water vapor.

Tensile properties

The tensile properties of all of the PUI were obtained in the form of the film cast at 50°C. These films were subjected to a tensile test using an Instron machine, and Table IV summarizes the results. For PU elastomers, the better phase separation and a more developed reinforcing hard domain structure increase the stiffness of the material and improve the tensile strength.²⁰ The tensile strength and modulus of II_{0,5,10} increased with the I content of PUIs, because of the larger phase separation. The tensile strength of these samples was very good (over 300 kg/cm²). The PUI films had a larger tensile strength and modulus than pure PU when the amount of I segments in the structure of the polymer was under 10 wt %. The good tensile properties of the PUIs may be associated with the cumulative effect of the formation of more number of hydrogen bonds,¹³ since two carbonyl groups per imide groups are available and the imide rings present in hard segments exhibit a dipole–dipole interaction. The elongation decreased as the imide structure (hard segment) content increased, while the tensile strength increased in inverse proportion to the proportional imide content. Yeganeh and Shamekhi¹⁴ made similar observations of the effect of imide content on the tensile properties of PUIs, on which they

TABLE IV
Tensile Properties of PUI Films

Code	Hard segment content (%)	Tensile strength (kg/cm ²)	Modulus at 100% elongation (kg/cm ²)	Elongation at break (%)
II ₀	25	310	25	720
II ₅	32	420	28	710
II ₁₀	38	440	34	690
II ₁₅	43	35	23	410

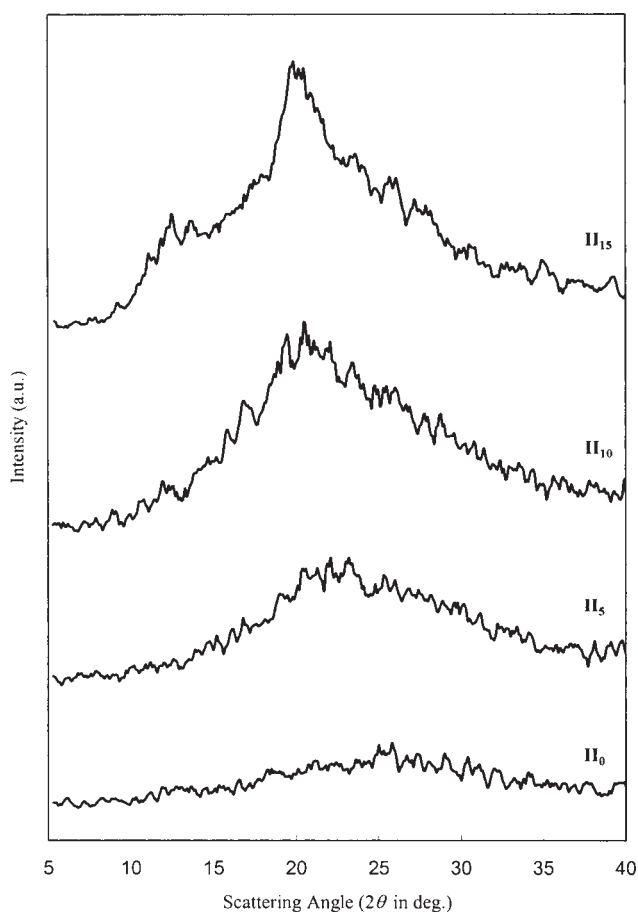


Figure 3 X-ray diffraction patterns of PUI films.

made wide-angle X-ray diffraction measurements by film sampling using nickel-filtered Cu K α radiation to confirm the crystalline characteristics of these polymers. As presented in Figure 3, PUI II₁₅ had a more crystalline nature than other polymers II and had better solvent resistance, as stated in Table III. This result agrees with the general rule that solubility decreases as crystallinity increases. However, the strength and elongation of film II₁₅ was significantly lower because visible crystal domains were found in

the film, because the hard segment content was 43%. Furthermore, when diimide-bisphenol I was applied up to 20 wt % content of PUI components, the casting film cracked easily, because of high crystallinity and too many hard segment content.

Thermal properties

The thermal properties of all the PUIs were evaluated by TGA and DSC. Table V presents the thermal behavior data of all the polymers. Since the residual water or solvent and the history of thermal annealing may sometimes affect the first run of DSC, the samples were first heated to 200°C and then quenched to -100°C, and the glass transition temperature (T_g) was taken as the midpoint of the change in slope of the baseline in the subsequent DSC heating trace. The soft- and hard-segment T_g values of all PUIs are similar. PUI II exhibited a glass transition at approximately -68°C, which is characteristic of soft segments. Also, hard segments underwent a glass transition at ~ 180°C. However, Table V demonstrates that the T_{gh} values of the PUI series did not vary, as the aromatic imide content increased because of the interactions between the different phases. Since the hard segments, comprising imide groups and urethane groups, are regularly distributed, discontinuous hard segment domains are formed, distributed within a continuous soft segment domain. This distribution slightly affects the steric hindrance of the rotation of the PUI copolymers. Notably, the difference between T_{gh} values is only 1–3°C. PUI exhibited an exotherm that began around 220°C, which was assigned to thermal degradation. Comparing the T_{gh} values of polymers II_{5,10,15} with their analogous II₀ in Table V indicate that this result is attributable to the presence of imide rings in the PUIs, whose T_{gh} is a little higher than that of PU.

The thermal stability of these polymers was characterized by TGA at a heating rate of 15°C/min. The temperatures of 5, 10, and 50% weight loss (T_d) in

TABLE V
Thermal Behavior Data of PUIs

Code	DSC		TGA					
	T_{gs}^b (°C)	T_{gh}^c (°C)	T_d^a in air (°C)			T_d in nitrogen (°C)		
			5%	10%	50%	5%	10%	50%
II ₀	-67	178	256	279	367	255	278	368
II ₅	-68	182	245	273	365	241	273	396
II ₁₀	-68	181	244	270	382	243	268	396
II ₁₅	-67	184	246	272	390	252	280	405

^a Temperature was recorded by TGA at a heating rate of 15°C/min.

^b From the second heating traces of DSC measurements conducted with a heating rate of 10°C/min in nitrogen; T_{gs} , T_g of soft segment.

^c T_{gh} , T_g of hard segment.

atmospheres of nitrogen and air were determined from the original thermograms and presented in Table V. The initial decomposition temperatures (5% T_d) of the polymers are $\sim 240^\circ\text{C}$. As was the case in Hasmukh and Hemant's experimental investigation,²¹ the PUI films underwent two-step decomposition in nitrogen, while the polymer film without imide decomposed in a single step. Since the dipoles at the urethane groups are the weakest sites in terms of thermal stability, the first step in the range of $250\text{--}350^\circ\text{C}$ was caused by the rupture of thermally labile urethane bonds. In this temperature range, the breakdown of the urethane linkage into isocyanate and hydroxy occurred.³ The second step involved the decomposition of the imide component and the polymer skeleton.

The TGA data reveal that the films lose less than 3% of their initial weight below 200°C , because of the volatiles such as residual solvents and water. They underwent minor decomposition $\sim 200^\circ\text{C}$ and considerable decomposition at around 250°C . PUI exhibited major weight loss (10–85%) occurring in the range of $270\text{--}420^\circ\text{C}$. The decomposition temperatures of PUIs prepared by the developed method were improved to over 350°C unlike those of PU **II**₀, especially in an atmosphere of nitrogen, revealing the effectiveness of the approach. The 50% T_d shifted to higher temperature as the **I** content increased. These results may have followed from the fact that the more thermally stable imide moiety began to decompose after the urethane moiety was degraded. The residual weight of PUIs at 600°C in nitrogen stayed in the range of 5–10%, depending on the **I** content. A comparison with **II**₀ indicates that PUIs have a higher char residue because of the polymer chains containing imide groups.

CONCLUSIONS

New bisphenol **I** with preformed imide units was prepared and characterized. A series of PUI dispersions that contain diimide-bisphenol **I** was successfully synthesized. Low-viscosity and water-based dispersion supports good processability. The solvent

resistance, tensile strength, and thermal stability of the PUI film were improved when a suitable amount of imide group was introduced into the polymer backbone. The inclusion of only 10% **I** improved the 50% decomposition temperature of PUI by about $\sim 20^\circ\text{C}$, and the film was elastic. The goal to improve upon the poor processability and the solvent emission problem of PUI was met by preparing a series of environmentally friendly waterborne PUIs.

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