

# New Self-Curable, Aqueous-Based Polyurethane System by an Isophorone Diisocyanate/Uretedione Aziridinyl Derivative Process

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**ABSTRACT:** Uretedione aziridinyl derivative (UAD) was prepared through the dimerization of isophorone diisocyanate and the addition reaction of aziridine to its isocyanate (NCO) end groups. An NCO-terminated polyurethane (PU) prepolymer was prepared from the addition of isophorone diisocyanate, poly(propylene glycol)s, and dimethylolpropanic acid. A mixture of UAD with the PU prepolymer and its NCO terminal groups were hydrolyzed to form primary amino groups during a water dispersion process. Meanwhile, the uretedione group of UAD reacted with these

primary amino groups in the aqueous phase. Then, these aziridine end groups of UAD became part of an aqueous-based PU and served as latent internal curing agents. The self-curable, aqueous-based PU system obtained with this new UAD process is a convenient alternative for improving the performance of aqueous-based PUs. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 845–859, 2004

**Key words:** polyurethanes; uretedione; aziridine

## INTRODUCTION

The applications and production processes of solvent-based polyurethanes (PUs) are well developed. However, because of environmental, economic, and safety problems, solvent-based PUs are being gradually replaced by aqueous-based PUs.

Aqueous-based PUs are being applied widely throughout the world, being environmental friendly products without solvents. There has been great demand for aqueous-based PU resins, but their physical and mechanical properties are still insufficient in comparison with those of solvent-based PUs. Difficulties have been encountered in current technologies for producing aqueous-based PUs with enhanced molecular weights and crosslinking densities.

A conventional self-emulsified PU dispersion containing carboxyl groups can be prepared through the reaction of isophorone diisocyanate (IPDI) with poly(propylene glycol) (PPG) in the presence of 2,2-dimethylolpropanic acid (DMPA). The isocyanate (NCO) terminal groups of the PU prepolymer are hydrolyzed into amino groups by a water dispersion.<sup>1,2</sup> These amino groups

may react partially with the remaining NCO groups for self-chain extension, forming urea bonding, or they may be present in the water phase without a further reaction. Both carboxyl groups and amino groups of this aqueous-based PU can stabilize the PU dispersion and also result in high hydrophilicity of the polymer.

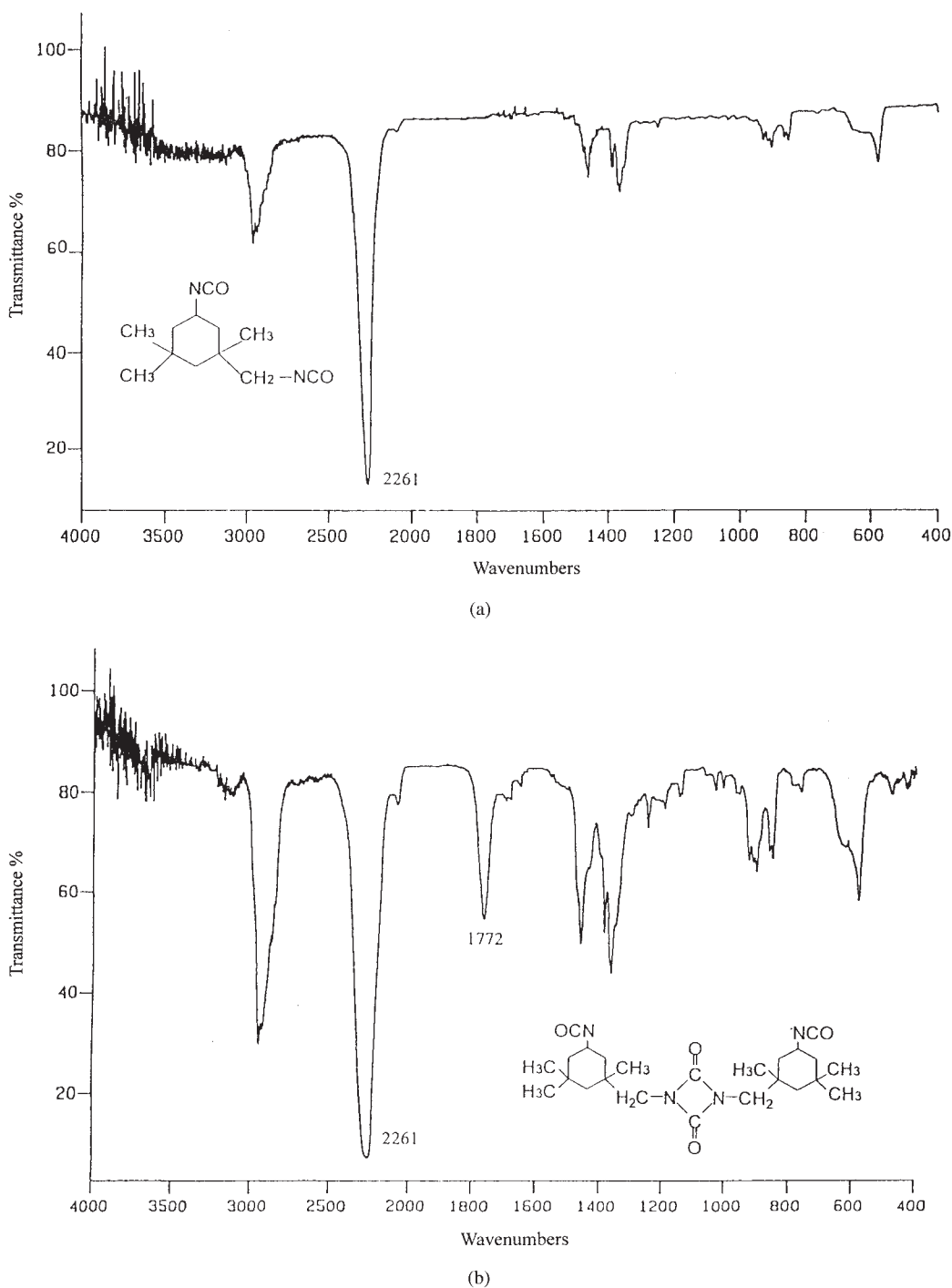
The carboxyl groups contained within aqueous-based PUs provide surface charges to the surfaces of PU micelles (particles), thereby causing repulsion between PU particles and resulting in uniform PU particle size distribution in the water phase. Because of the hydrophilic properties of the carboxyl group, these PUs become self-emulsified (or water-reducible) in the water phase. Such conventional aqueous-based PUs have a disadvantage similar to that of a polymer surfactant, in that after drying into films, they exhibit high hydrophilicity.

The improvements in aqueous-based PUs<sup>1,2</sup> are normally achieved with postcuring reactions<sup>3–11</sup> or polymer hybridization,<sup>12–14</sup> which enhances the molecular weight, crosslinking density, and performance properties of PUs, thereby broadening their applications.

A convenient postcuring reaction of aqueous-based PUs is mainly based on the carboxyl groups reacting with an aziridinyl curing agent when the pH drops below 6.0 or upon air drying.<sup>2,3</sup> Amino groups can react with the epoxide groups in the polymers and form hybridized polymers. The resulting aqueous-based PUs have properties that are improved according to the curing dosage. These postcured and hybrid-

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**Figure 1** FT-IR spectrum of (a) IPDI, (b) FT-IR spectrum of IPDI-uretedione.

ized polymers are obtained from the mixing of two or more components, which become single components before the final applications.

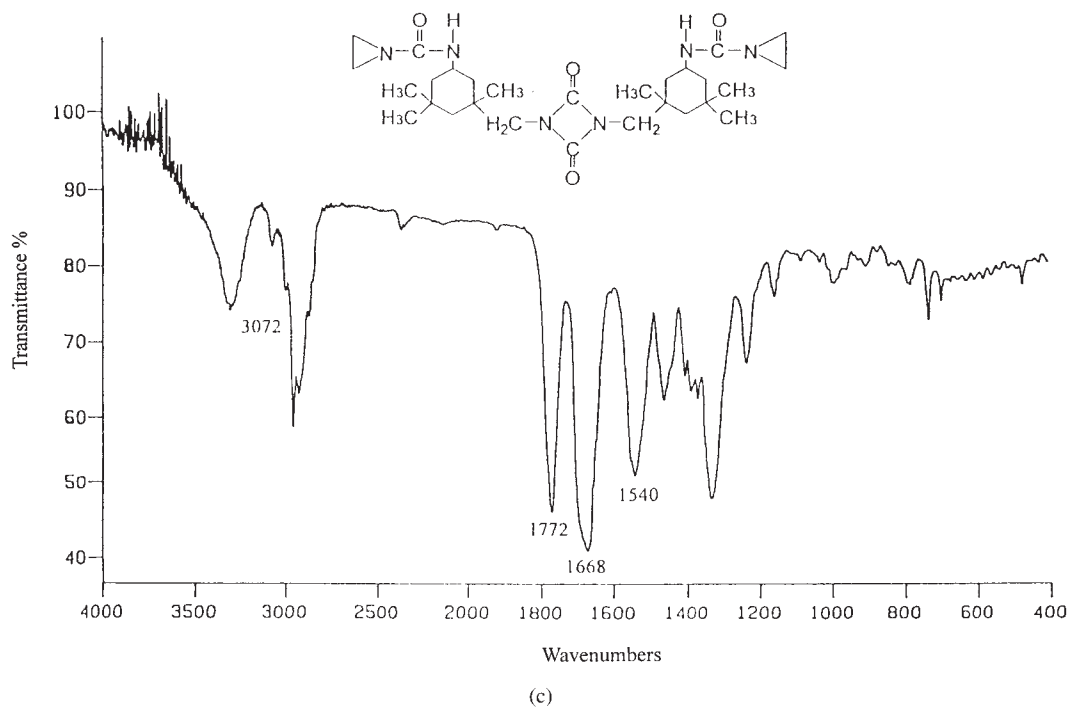
A new curing agent can be prepared through the dimerization of IPDI, which forms an uretedione moiety containing an IPDI dimer, and its NCO terminal groups react further with aziridine (AZ), leading to IPDI/uretedione aziridinyll derivative (UAD). When UAD is mixed with an NCO-terminated PU prepolymer during a water dispersion process, it becomes

part of the PU, serving as an internal latent curing agent.<sup>15</sup> The UAD process for this new self-curable PU system is evaluated in this report.

## EXPERIMENTAL

### Materials

Triethylamine, ethylenediamine (EDA), and DMPA were supplied by the Aldrich Chemical Co., Inc, USA. IPDI was supplied by Hul Chemical Co, Germany.



**Figure 1** (c) FT-IR spectrum of IPDI-UAD.

PPG-1000 was supplied by Arco Chemical Co, USA. All the materials were used as received without further purification. Acetone, ethanol, tetrahydrofuran (THF), and other solvents were dried and distilled over anhydrous calcium chloride before use.

### Instruments

The dynamic mechanical thermal behavior of the polymer films was determined with an MK-II dynamic mechanical thermal analyzer from Polymer Laboratories, England. The thermogravimetric data were measured with a Hi-Resolution TGA 2950 thermogravimetric analyzer (TA), USA. Stress-strain curves of the PU films were taken with a Shimadzu Autograph S-100-C, Japan. NMR spectra were measured with a Bruker 300-MHz instrument, Germany.

### Preparation of IPDI-UAD

The dimerization of IPDI was performed according to published methods.<sup>2</sup> IPDI (20 g) was mixed with 0.1 g of tributyl phosphine as a catalyst. The reaction mixture was kept at 85°C under a nitrogen atmosphere for 1.5 h. The IPDI-dimer/uretidione derivative was identified with Fourier transform infrared (FTIR) and Fourier transform nuclear magnetic resonance.

Ethyleneimine (or AZ) was prepared from ethanolamine according to a published method.<sup>16</sup> A toluene solution (5 mL) of AZ (2.5 g) was added to a toluene solution (15 mL) of the previously formed IPDI/ure-

tidione derivative (10 g) through an addition funnel. The reaction mixture was kept at 50°C for 2 h more after the addition was completed. The reaction was completed when the NCO number of the reaction mixture dropped to zero (the absorption peak of NCO was not observed at 2261 cm<sup>-1</sup> in an FTIR spectrum).

### Preparation of the new self-curable, aqueous-based PU system<sup>15</sup>

PPG-2000 (0.2 mol) and DMPA (0.1 mol) were dried at 110°C overnight before being mixed with IPDI (0.4 mol) in a 500-mL, four-necked resin flask. The resin flask was equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a CaCl<sub>2</sub> drying tube. The reaction mixture was kept at 110°C for about 4 h under nitrogen until the NCO percentage dropped below 3.5 (ASTM D 1638 NCO determination method) and remained constant for another half-hour. The thus formed NCO-terminated PU prepolymer was then cooled to room temperature.

Previously prepared PU prepolymer (40 g each) samples were mixed with 0.75, 1.12, or 2.23 g of the UAD curing agent after neutralization with triethyl amine with constant agitation. Each mixture was diluted with dry acetone to obtain a workable viscosity (e.g., 1000 cps). Then, a self-curable, aqueous-based PU dispersion was obtained through high-shear-rate mixing with deionized water. The anionic, self-curable, aqueous-based PU dispersion had a pH value of

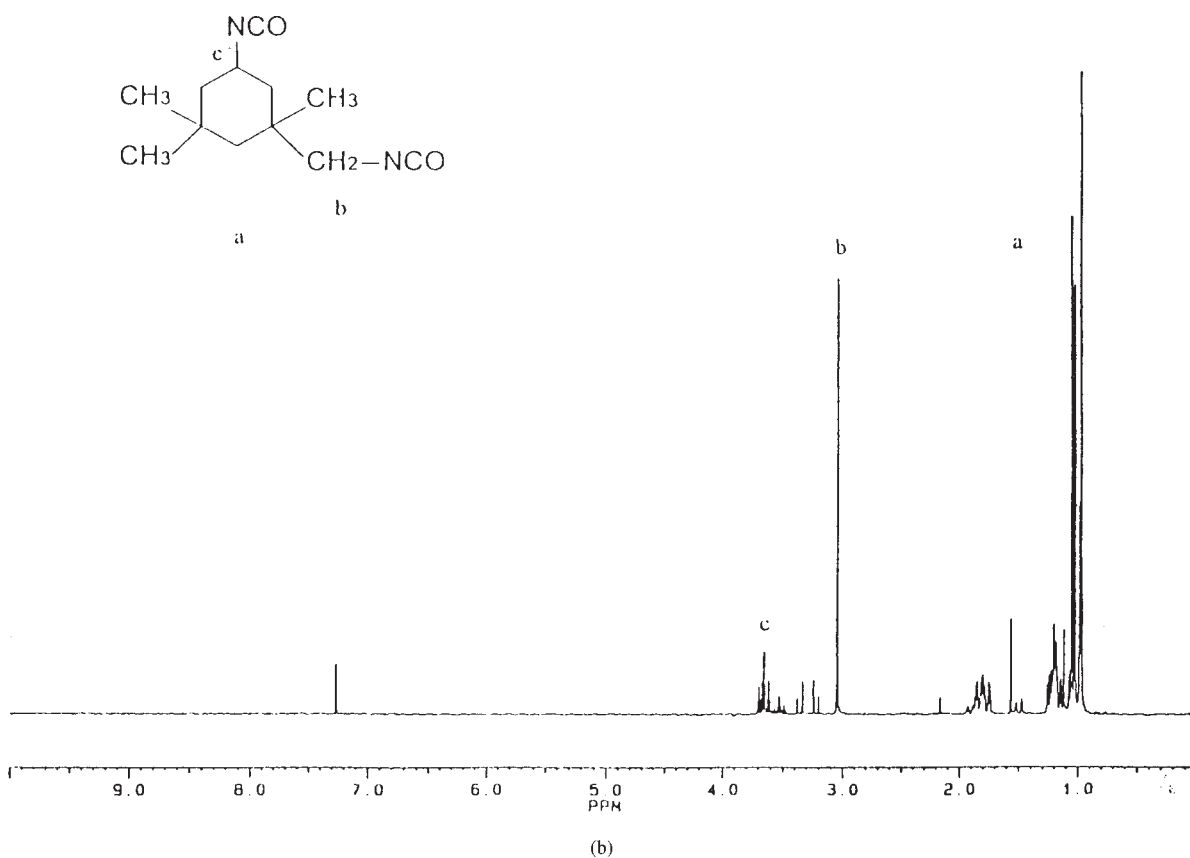
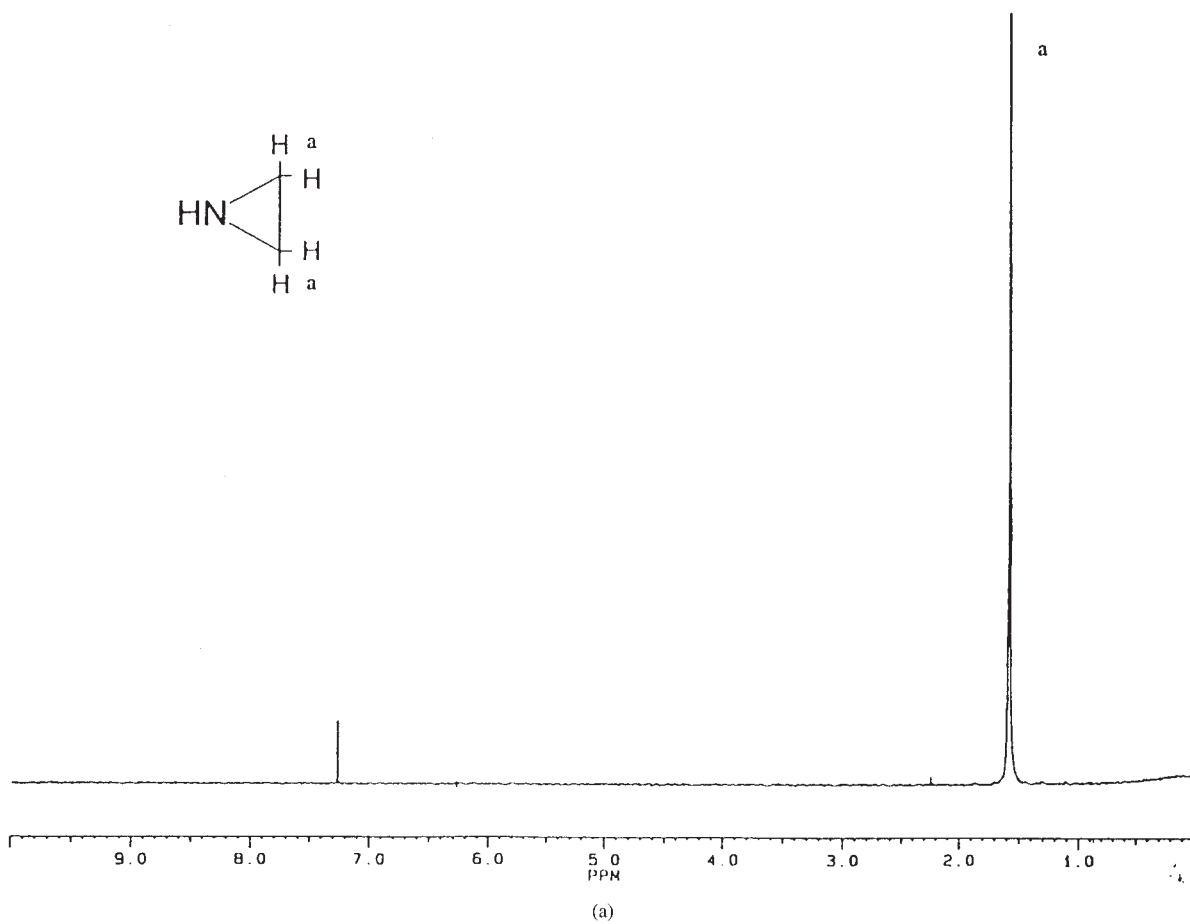


Figure 2 (a) <sup>1</sup>H-NMR spectrum of Aziridine, (b) <sup>1</sup>H-NMR spectrum of IPDI.

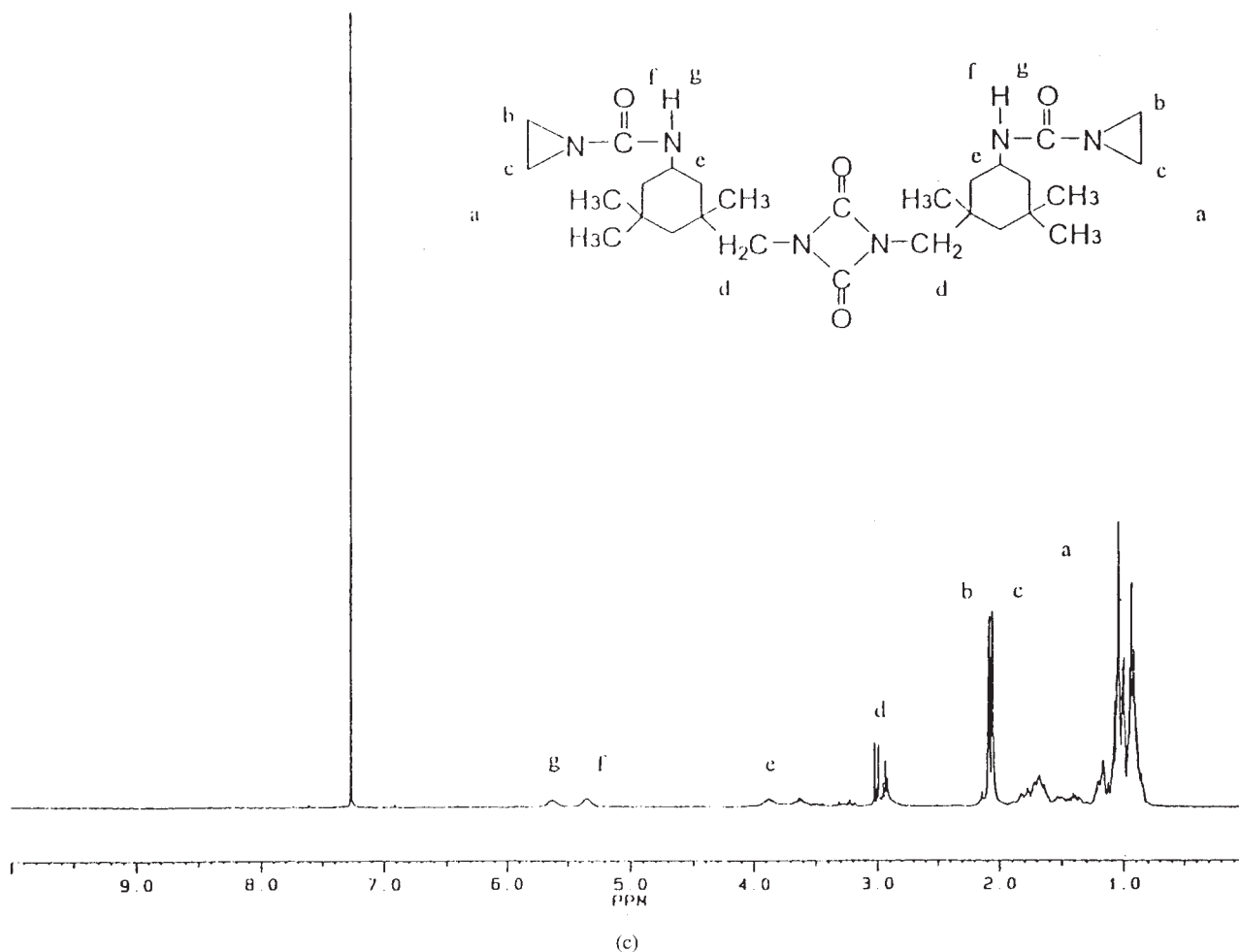


Figure 2 (c)  $^1\text{H-NMR}$  spectrum of IPDI.

8.5 after acetone was removed *in vacuo* (as shown later in Scheme 2).

#### Properties of the single-component, self-cured, aqueous-based PU resin

##### Tensile strength and elongation

The films cast from these self-curable, aqueous-based PU dispersions were air-dried at room temperature and then at  $50^\circ\text{C}$  for 24 h. They were conditioned in a 75% relative humidity chamber at  $25^\circ\text{C}$  for 72 h before the measurements. Each specimen was cut into a dumbbell shape  $1.2 \pm 0.1$  mm thick. The gauge length was 40 mm, and the measurement was performed at a crosshead speed of 40 mm/min. Six specimens for each sample were taken, and the three measurements that showed the medium value of the tensile strength were selected for calculating the mean value.

##### Gel content

A known weight of an oven-dried film was placed in a Soxhlet extractor for continuous extraction with THF

for 24 h. The polymer gel remaining after extraction was dried and calculated according to the test results. Three tests were carried out and averaged for each sample.

##### Ethanol uptake

A known weight ( $W_0$ ) of a dried polymer film (60 mm  $\times$  60 mm  $\times$  1 mm) was immersed in a distilled water bath for 8 days for water uptake. It was also immersed in an ethanol (95%) bath for 48 h for ethanol absorption. The towel-dried sample weight ( $W_1$ ) and the oven-dried film weight ( $W_2$ ) were obtained. Three measurements were averaged for each sample. The percentage of the water uptake, the ethanol absorption, and the weight losses of the polymer films in water and ethanol were calculated according to the following equations:

$$W_A\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

$$W_x\% = \frac{W_0 - W_2}{W_0} \times 100\%$$

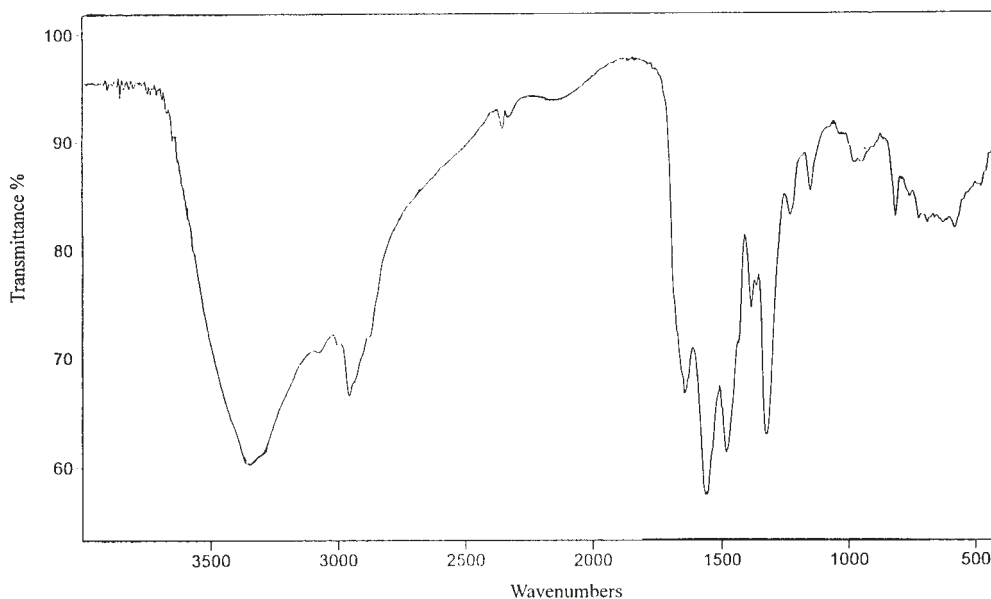


Figure 3 FTIR spectrum of an adduct of IPDI-UAD with EDA.

$$W_E \% = \frac{W_1 - W_2}{W_2} \times 100\%$$

$$W_y \% = \frac{W_0 - W_2}{W_0} \times 100\%$$

where  $W_A$  and  $W_x$  are the amount of water uptake by the polymer film and the amount of the polymer dissolved into water, respectively, and  $W_E$  and  $W_y$  are the amount of ethanol absorption by the polymer film and the amount of the polymer dissolved into ethanol, respectively.

#### Dynamic mechanical analysis (DMA)

The conditioned PU films for dynamic mechanical analyses were carried out in the bending mode at a heating rate of 3°C/min from -80 to 150°C at a 1.0 Hz frequency for each sample.

#### Thermogravimetric analysis (TGA)

The conditioned samples were measured with a thermogravimetric analyzer at a heating rate of 10°C/min from the ambient temperature to 500°C. This was performed under a nitrogen or air atmosphere for the measurements of the polymer thermal and thermooxidative stabilities, respectively.

## RESULTS AND DISCUSSION

The posttreatments of aqueous-based PUs are effective for improving PU properties. One example is the postcuring reaction of aqueous-based PU carboxyl

groups with an aziridiny curing agent.<sup>1-5</sup> The phosphorus-containing aziridiny curing agents also serve as a reactive flame retardant.<sup>10,11</sup> PU properties are modified further by the polymer hybridization of glycidyl methacrylate copolymer emulsions<sup>12</sup> and aqueous-based epoxy resins,<sup>13</sup> respectively. This polymer hybridization process provides an alternative for modifying aqueous-based performance properties.

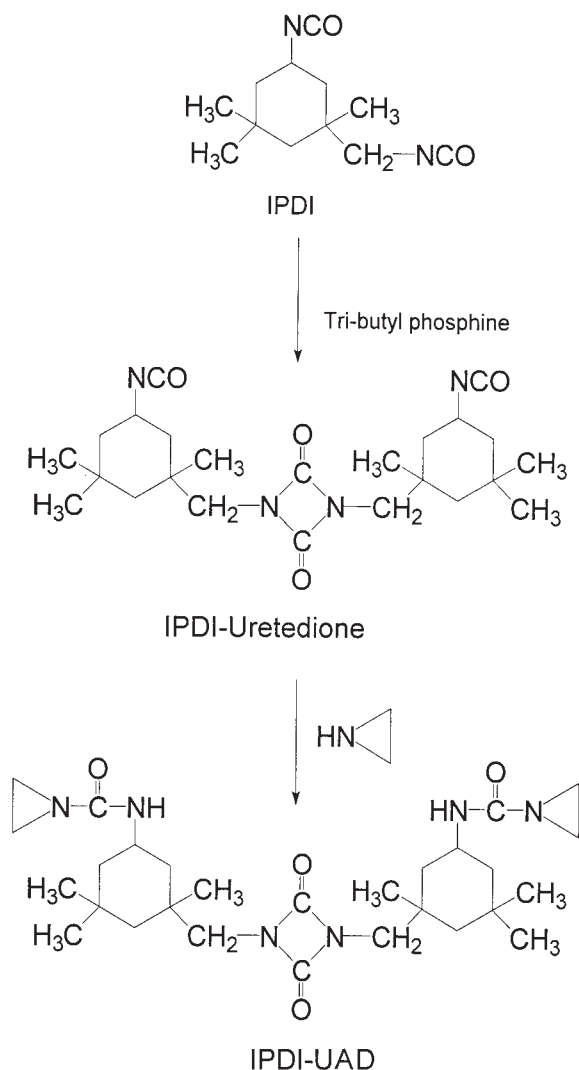
Aqueous-based PUs with carboxyl groups can be prepared with a conventional PU prepolymer process.<sup>1,2</sup> The PU carboxyl group is the ionic center and the curing site and is derived from DMPA.

A new curing agent, IPDI-dimer/UAD, has been synthesized through the AZ addition of IPDI-dimer. This curing agent has uretedione and aziridiny functional groups.<sup>15</sup>

The primary amino groups are obtained from the hydrolysis of PU NCO terminal groups during water addition. Its primary amino group only reacts with the uretedione moiety of the curing agent, and the aziridiny groups become part of the PU molecule. The resultant PU dispersion, consisting of aziridiny groups, is a new self-curable, aqueous-based PU system. The resulting aqueous-based PU dispersion consists of carboxyl and aziridiny groups, and its curing reaction takes place automatically between them upon drying. This UAD is a key compound of this process for making new self-curable, aqueous-based PU systems.

#### IPDI-UAD

IR spectra of IPDI and IPDI-dimer show an NCO absorption peak at 2261 cm<sup>-1</sup> [Fig. 1(a)], and the IPDI-



**Scheme 1** Preparation of the IPDI-UAD internal curing agent.

dimer shows a new peak at  $1772\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  of the uretdione moiety [Fig. 1(b)]. As for the adduct from an AZ addition reaction of the IPDI-dimer, the original NCO absorption peak disappears, and two new absorption peaks appear at  $1668$  and  $1540\text{ cm}^{-1}$  (for amide I and II bands, respectively) and  $3072\text{ cm}^{-1}$  for the asymmetric stretching frequency of  $\text{CH}_2$  from the AZ moiety [Fig. 1(c)]. The chemical shifts of aziridine methylene at  $1.65\text{ ppm}$  [Fig. 2(a)] are shifted to  $2.05$  and  $2.08\text{ ppm}$  in the  $^1\text{H-NMR}$  spectra; there are two urea ( $-\text{CONH}-$ ) chemical shifts at  $5.35$  and  $5.62\text{ ppm}$  after AZ addition to the NCO group and the formation of the UAD adduct [Fig. 2(b)]. These are evidence of UAD adduct formation (Scheme 1).

#### Model reaction of UAD with EDA

In the IR spectrum of the solid product from the reaction of UAD and EDA at the ambient temperature,

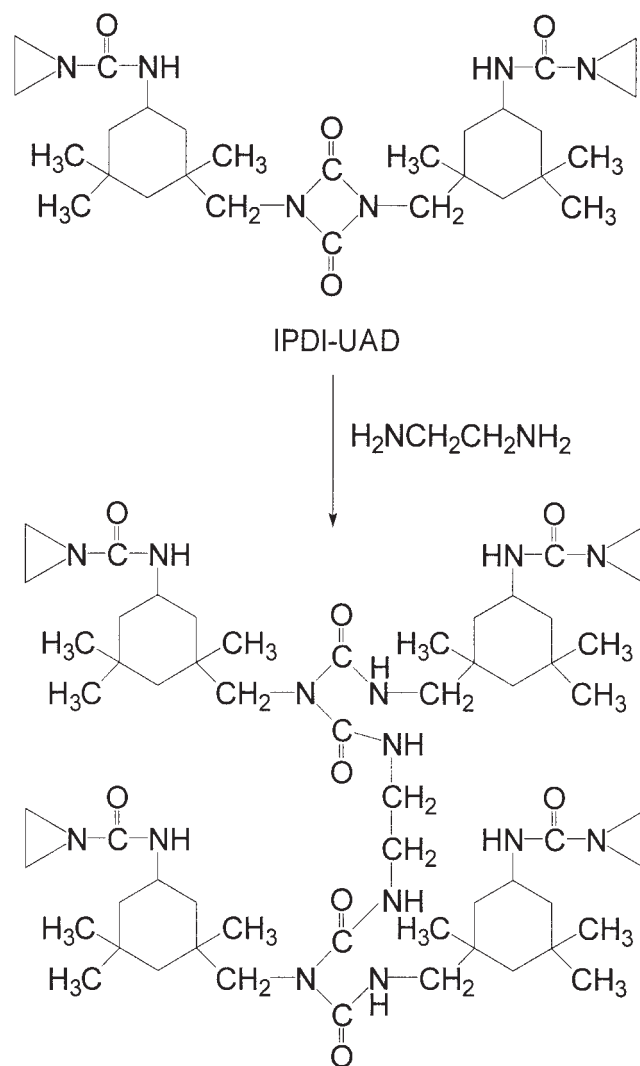
the original  $\text{C}=\text{O}$  stretching frequency of uretdione at  $1772\text{ cm}^{-1}$  is disappearing. This is the result of urea formation from a ring-opening reaction of uretdione by the primary amine of EDA (Scheme 2).

#### Self-curable, aqueous-based PU system with UAD process

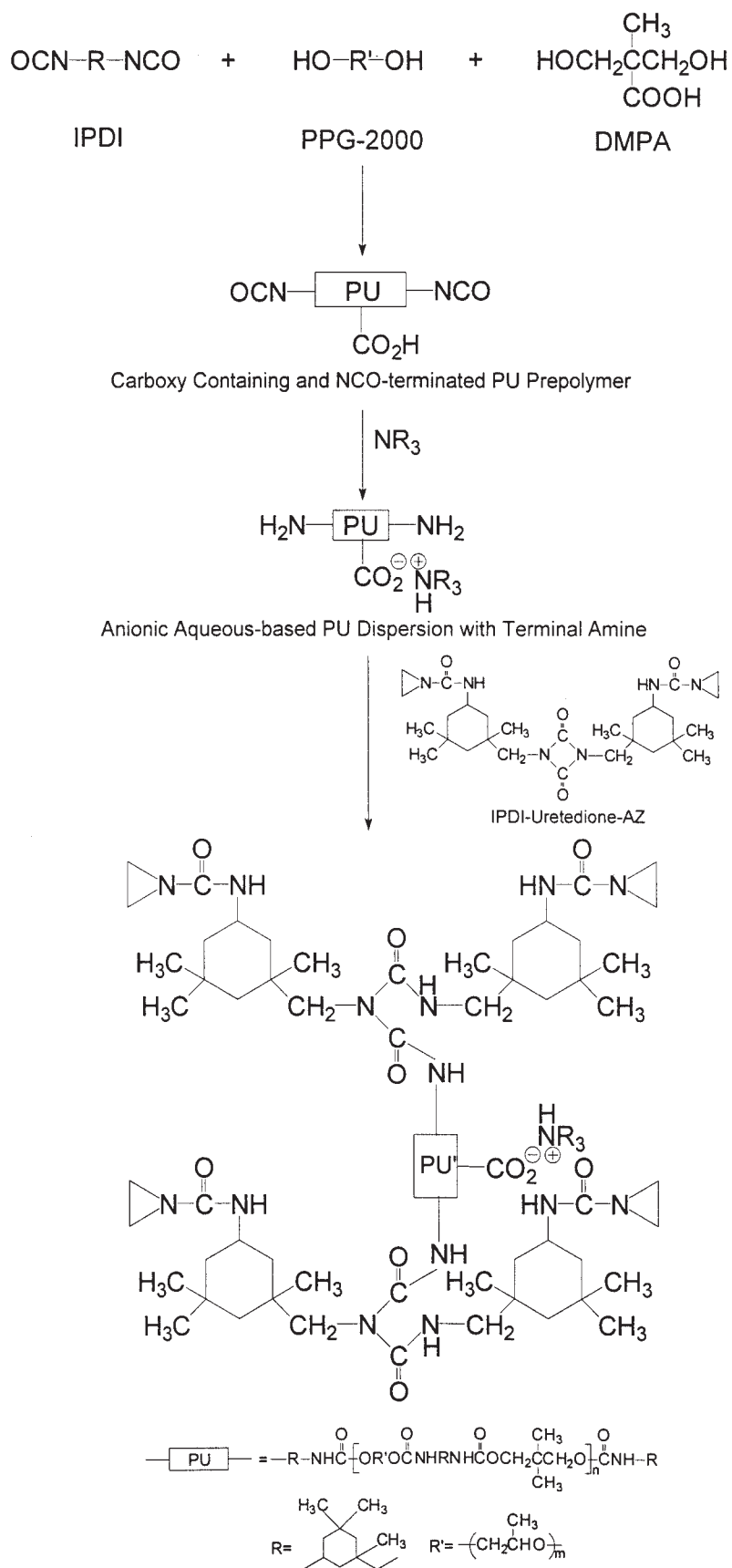
A PU film from an NCO-terminated PU prepolymer without UAD had a gel content of zero, which indicated that PU was a linear thermoplastic. Mixtures of an NCO-terminated PU prepolymer with 3.7, 5.6, and 11.2 phr UAD were prepared. Each mixture was added to water with agitation, and this resulted in the formation of self-curable, aqueous-based PU dispersions.

#### Gel content

PU films were obtained from these PU dispersions with gel contents of 94.7, 97.1, and 97.5%, respectively.

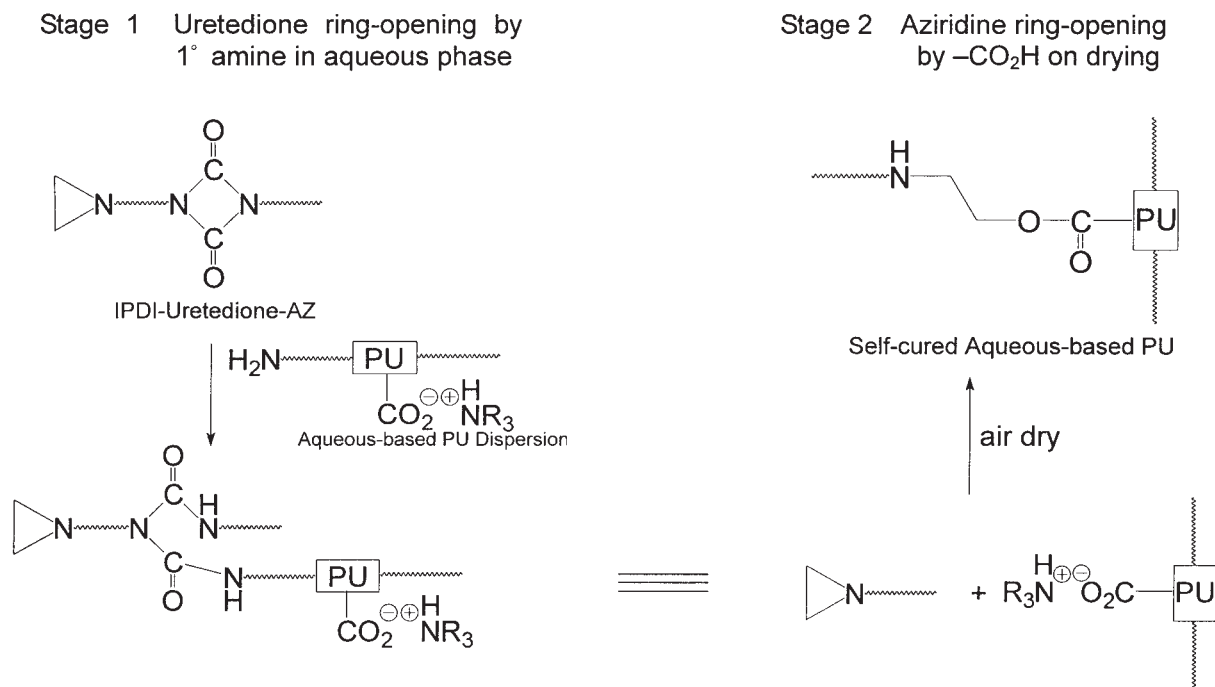


**Scheme 2** Model reaction of IPDI-UAD with EDA.



**Scheme 3** Self-curing, aqueous-based PU system with the IPDI-UAD process.





## Aziridine and Carboxyl moiety Containing Aqueous-based PU Dispersion

Scheme 4 Aqueous-based PU curing mechanism with IPDI-UAD.

These data provided evidence of crosslinking reactions taking place with UAD. This was caused by a series reaction of a ring opening of UAD with the primary amine, which came from the hydrolysis of

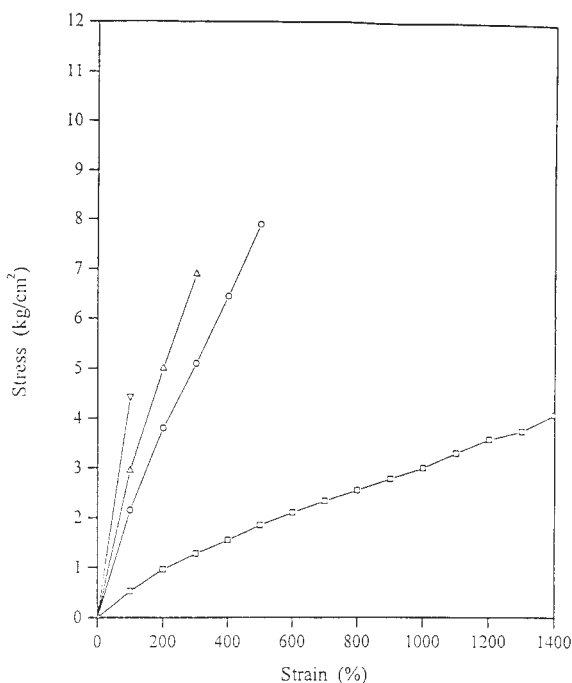
terminal NCO groups of the PU prepolymer during the water addition process. Then, the AZ moieties containing the curing agent became part of the aqueous-based PU, and self-curable, aqueous-based PU

TABLE I  
Properties of Self-Cured, Aqueous-Based PU with IPDI-UAD

Properties	PU <sup>a</sup>	IPDI-UAD (phr)		
		2.7	5.6	11.2
		Tensile Stress (kg/cm <sup>2</sup> )		
Elongation (%)				
100	0.5	2.2	3.0	4.4
200	1.0	3.8	5.0	—
300	1.3	5.1	6.9	—
400	1.6	6.5	—	—
500	1.9	7.9	—	—
600	2.1	—	—	—
700	2.3	—	—	—
800	2.6	—	—	—
900	2.8	—	—	—
1000	3.0	—	—	—
Tensile strength at break (kg cm <sup>-2</sup> /%)	—	8.3/520	5.1/357.5	6.8/173.8
Gel content (%)	—	94.7	97.1	97.5
Ethanol uptake (%)	—	377.5	279.8	218.1
Polymer weight dissolved in ethanol (%)	—	4.5	2.9	2.0
Hardness <sup>b</sup>	64.5	72.4	75.0	81.1

<sup>a</sup> Original aqueous-based PU (elongation > 1000%). PU dissolved in THF and ethanol (95%) for the measurements of the gel content and ethanol uptake, respectively.

<sup>b</sup> Measured Shore A durometer.



**Figure 4** Stress-strain curves of self-cured PU with various dosages of IPDI-UAD: (□) original PU, (○) PU with 3.7% IPDI-UAD, (△) PU with 5.6% IPDI-UAD, and (▽) PU with 11.2% IPDI-UAD.

dispersions formed with this internal curing agent. The final self-cured PU films were obtained from these aqueous-based PU dispersions with various dosages of the internal curing agent upon drying (Scheme 4).

#### Ethanol uptake and hardness

The original PU film dissolved in ethanol completely. However, the ethanol uptakes of self-cured PU films

were 377.5, 279.8, and 218.1% for UAD dosages of 3.7, 5.6, and 11.2 phr, respectively. The hardness of the PU films also increased from 64.5 for the original PU to 74.4, 75.0, and 81.1 with the same curing dosages. This was due to higher molecular network formation with a higher PU crosslinking density, which was caused by the increasing internal curing dosage (Table I).

#### Mechanical properties

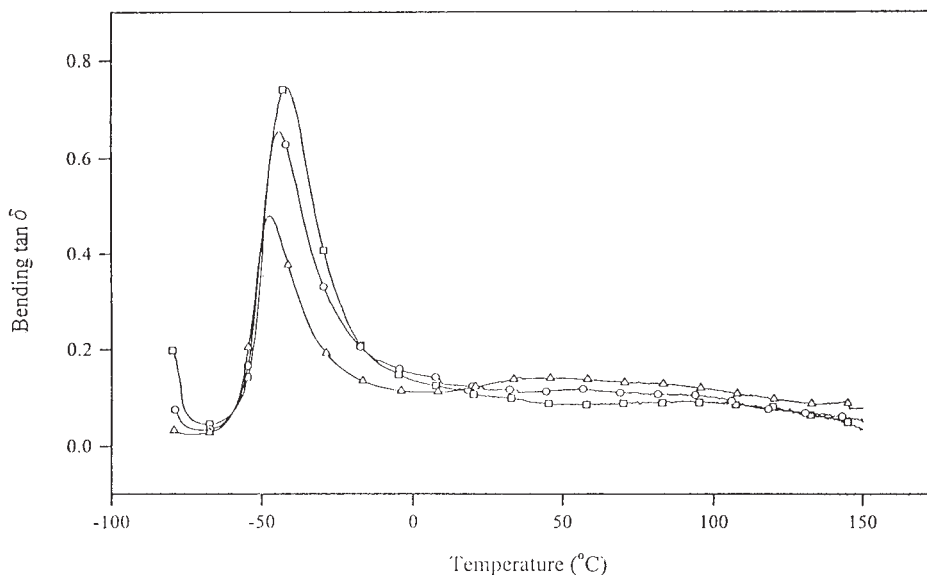
The original PU film had an elongation greater than 1400%; its tensile stress was 1.85 kg/cm<sup>2</sup> at 500% elongation. However, for a PU film with an internal curing agent concentration of 3.7 phr, its tensile stress increased to 7.9 kg/cm<sup>2</sup> at the same elongation, and the tensile strength was 8.3 kg/cm<sup>2</sup> at 520% elongation. The PU films had tensile strengths of 9.1 kg/cm<sup>2</sup> at 358% elongation and 6.8 kg/cm<sup>2</sup> at 174% elongation with 5.6 and 11.2 phr curing dosages, respectively (Fig. 4). These mechanical properties of the self-cured PU films also indicated the higher crosslinking density created by the higher curing dosage.

#### DMA

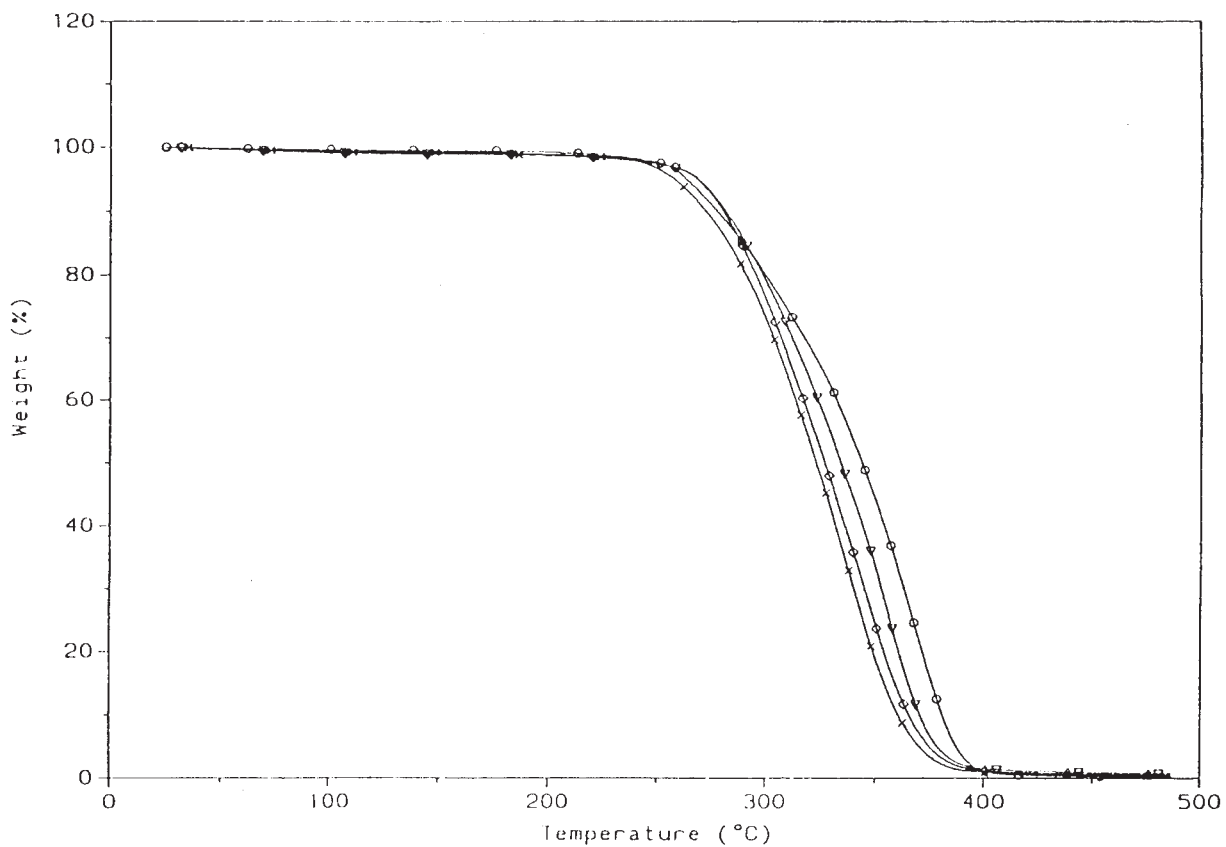
The damping curves indicate that PU films with a higher UAD curing dosage had a higher storage modulus (Fig. 5). The low-temperature damping peak intensity decreased with increasing curing dosage. These self-cured PUs had higher PU crosslinking density, which caused a smaller free volume.

#### TGA

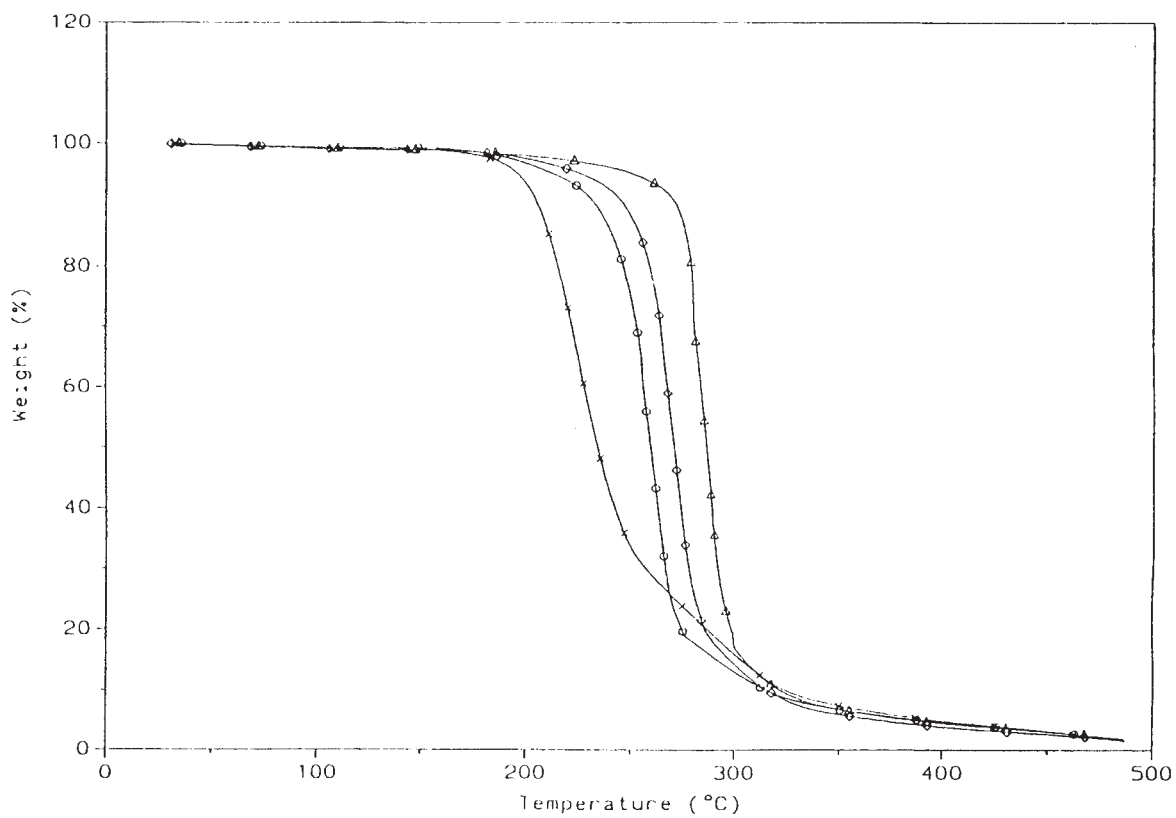
TGA measurements under a nitrogen atmosphere indicated the thermal stability of the PU samples. The



**Figure 5** Damping curves of self-cured PU with various dosages of IPDI-UAD: (□) original PU, (○) PU with 3.7% IPDI-UAD, and (△) PU with 5.6% IPDI-UAD.



(a)



(b)

**Figure 6** TGA of self-cured PU systems with various dosages of IPDI-UAD under (a) nitrogen [( $\times$ ) original PU, ( $\diamond$ ) PU with 3.7% IPDI-UAD, ( $\nabla$ ) PU with 5.6% IPDI-UAD, and ( $\circ$ ) PU with 11.2% IPDI-UAD] and (b) air [( $\times$ ) original PU, ( $\circ$ ) PU with 3.7% IPDI-UAD, ( $\diamond$ ) PU with 5.6% IPDI-UAD, and ( $\Delta$ ) PU with 11.2% IPDI-UAD].

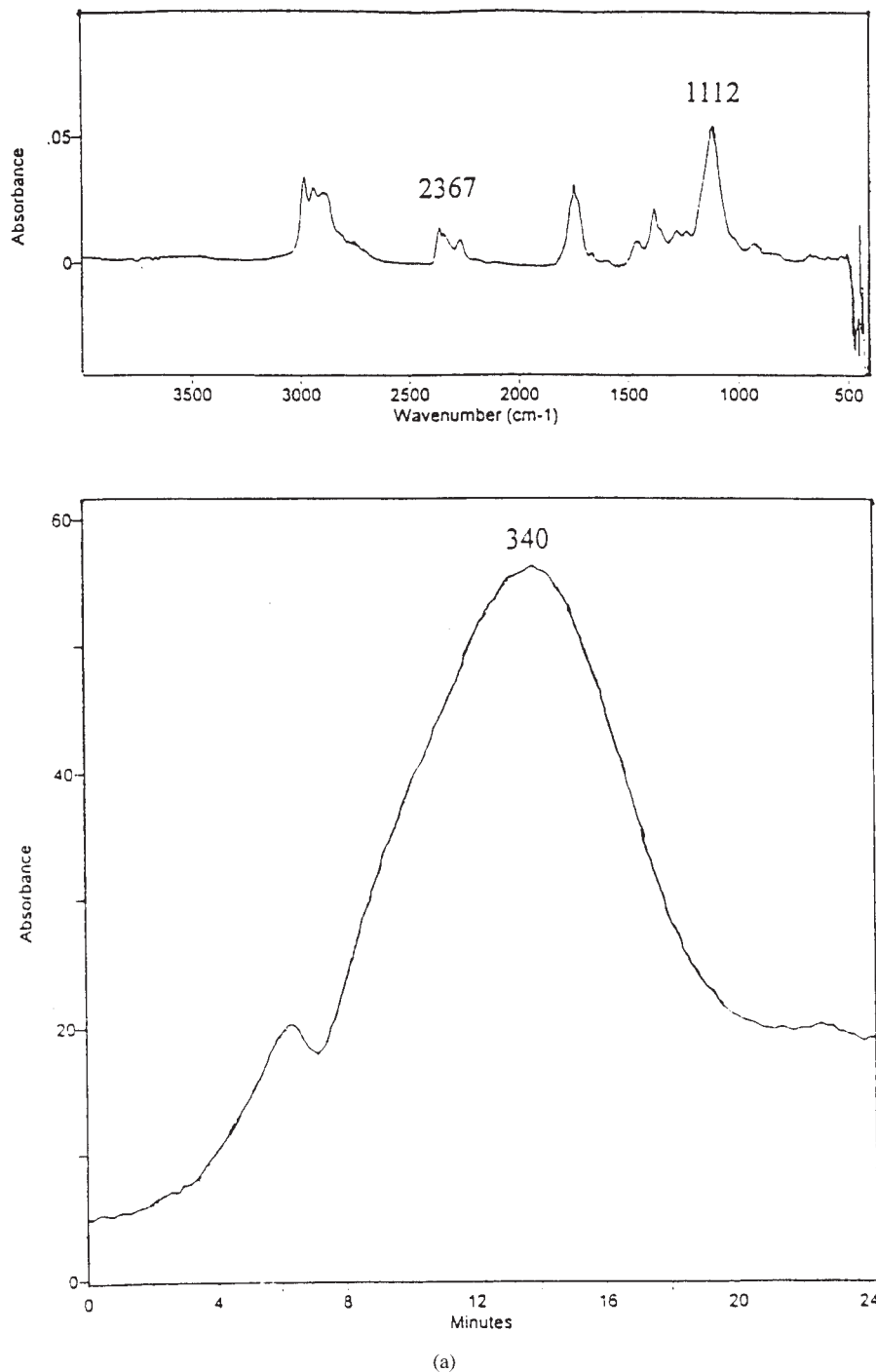
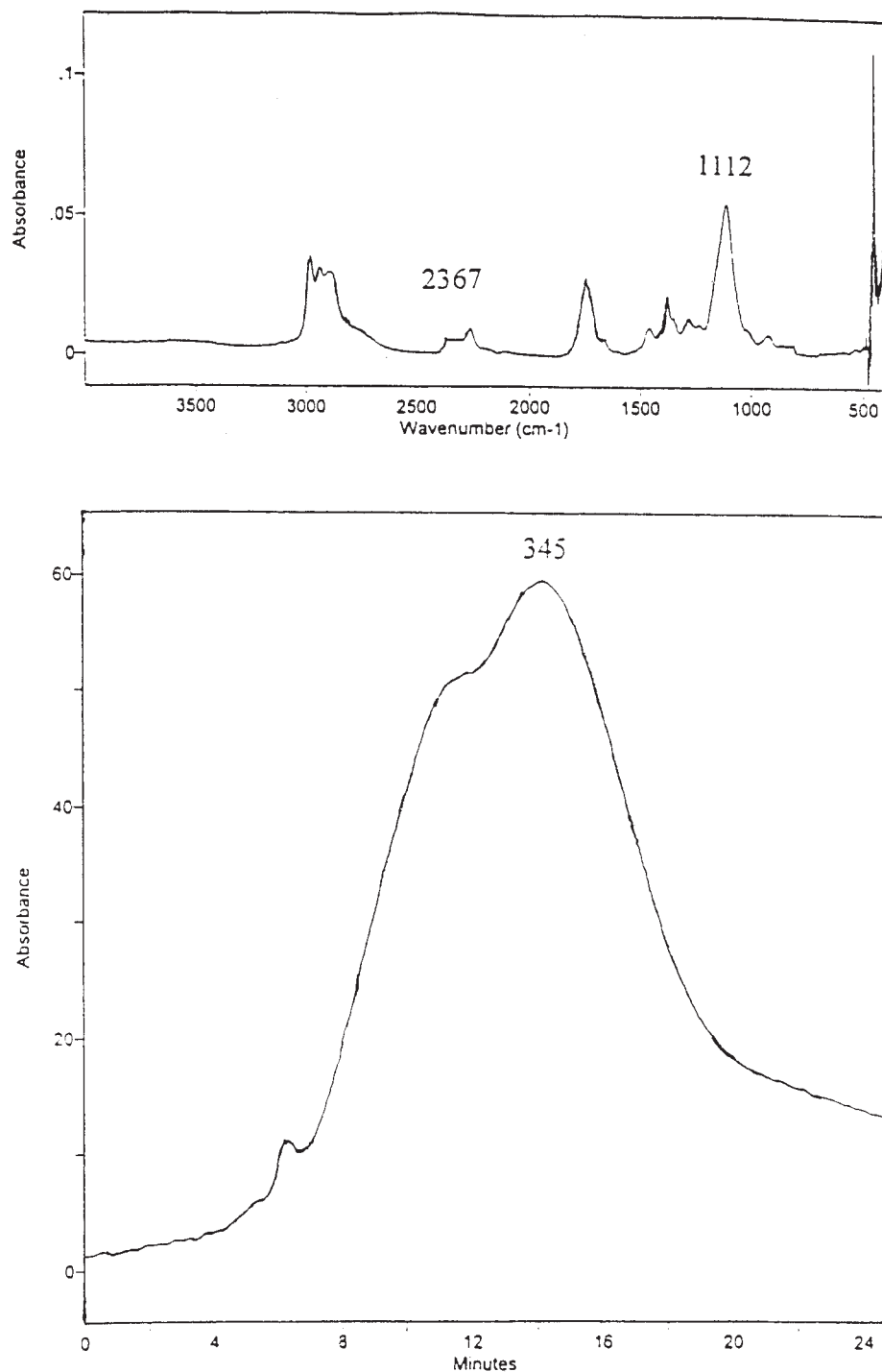


Figure 7 TGA/FTIR of (a) original aqueous-based PU under nitrogen.

major decomposition temperature of the original PU was 335°C, and it was 366°C with 3.7 phr UAD. However, for PU films with internal curing agent concentrations of 5.6 and 11.2 phr, the major decomposition temperature decreased to 354 and 341°C, respectively [Fig. 6(a)]. The TGA measurements under air demonstrated phenomena similar to those under a nitrogen atmosphere [Fig. 6(b)]. These TGA data indicated that UAD dosages increased polymeric networks among

PU molecules. However, when the curing dosage increased to 5.6 or 11.2 phr UAD, COOH/AZ (the equivalent ratio of COOH and AZ groups) was 1.0 and 1.5, respectively. The thermal stability decreased with increasing curing dosage. Because of its dosage, although COOH/AZ was 1.0, its curing reaction took place in the solid state.

The thermal decomposition products of PU were analyzed with TGA and FTIR. IR spectra of the major



(b)

Figure 7 TGA/FTIR of (b) self-cured PU with IPDI-UAD under nitrogen.

decomposition products and the gas flow (under nitrogen) of the original PU and self-cured PU are similar [Fig. 7(a,b)] because of the same PU ingredients and compositions. However, among the thermooxidative decomposition products under air, the  $\text{CO}_2$  peak is larger and the decomposed gas flow is faster than for those under a nitrogen atmosphere [Fig. 7(c)].

## CONCLUSIONS

A new internal curing agent, IPDI-UAD, was synthesized and applied to the preparation of aqueous-based PU dispersions via an NCO-terminated PU prepolymer process. PU primary amino groups were hydrolyzed from the NCO terminal groups in the aqueous phase.

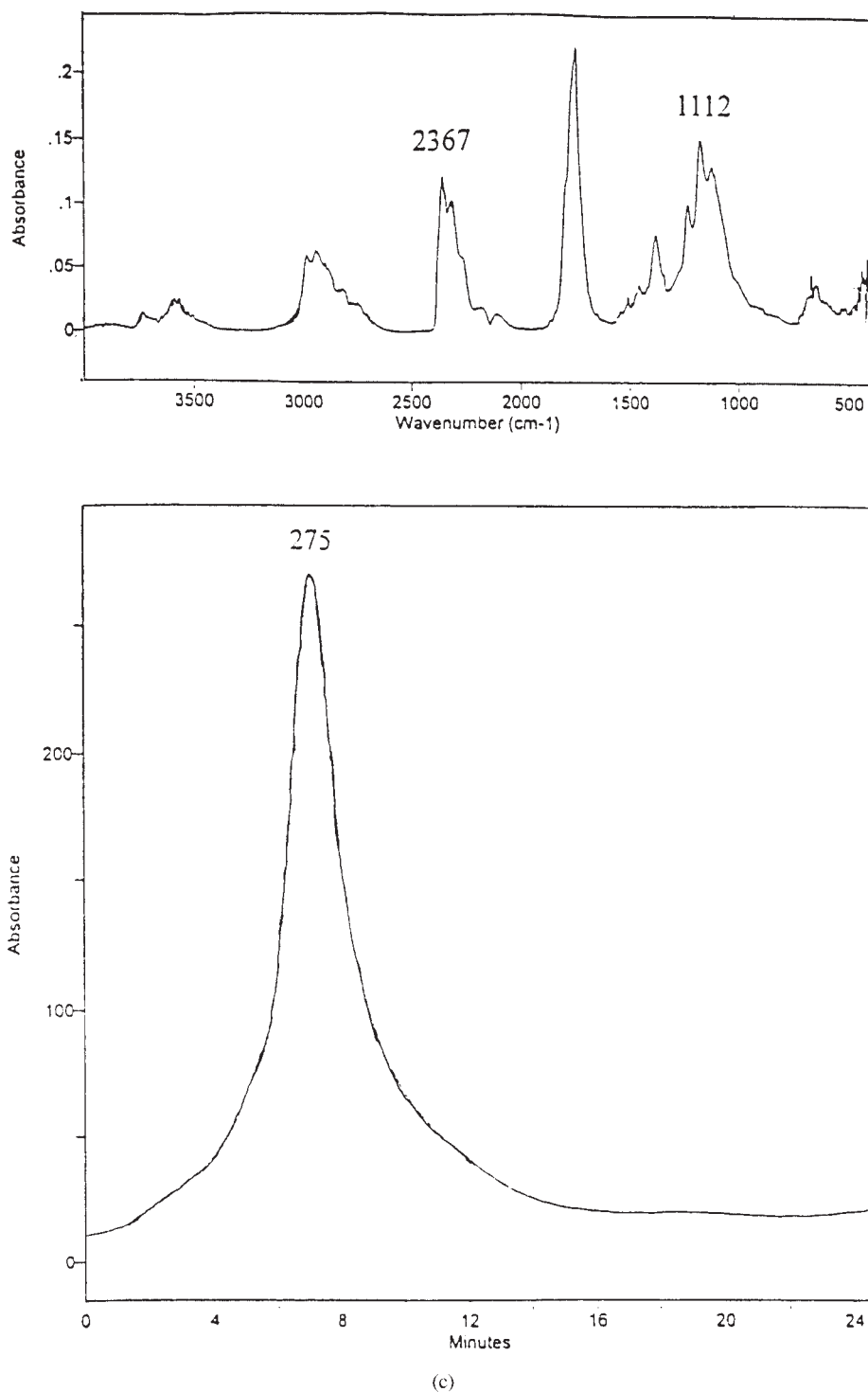


Figure 7 (c) TGA/FTIR of self-cured PU with IPDI-UAD under air.

The uretidione moiety only reacted with the PU primary amine in this aqueous system and left AZ moieties, which became part of the PU molecule during the water dispersion process. Self-cured, aqueous-based PU films with improved properties resulted from this new self-curing, aqueous-based PU system with UAD as an internal curing agent. It provides a convenient alternative for improving PU performance.

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