

Polymer Hybrids from Self-Emulsified PU Anionomer and Water-Reducible Acrylate Copolymer via a Postcuring Reaction

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ABSTRACT: Water-reducible acrylate copolymer is obtained from a free-radical copolymerization of *n*-butyl acrylate, acrylic acid, and methacrylic acid. Self-emulsified aqueous-based polyurethane (PU) anionomer is prepared by the conventional method. The latent curing agents (di- and triaziridinyl compounds, HDDA-AZ and TMPTA-AZ) are synthesized from the reaction of aziridine with hexandiol diacrylate and trimethylolpropane triacrylate, respectively. These two polymers and the latent curing agent are miscible in each other and become a single component and self-curable polymer dispersion. The carboxyl ions of polymers

not only stabilize the aqueous polymer dispersions but also serve the curing site toward latent curing agent in the drying process. These two polymers blend with a curing agent, which results in new polymer hybrid formation. These polymer hybrids have the improvements on performance properties and the cost/performance benefits. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3578–3587, 2003

Key words: PU anionomer; water-reducible acrylate copolymer; aziridinyl curing agent; polymer hybrids

INTRODUCTION

The widespread applications of aqueous-based polyurethane (PU) are gradually becoming the world market trend because of the increasing importance of economical and safety requirements as well as environmental regulations. However, the current aqueous-based PU does not readily dominate the traditional PU application market because of its inferior performance and high cost.

The self-emulsified PU anionomer is prepared from the conventional process.^{1,2} The performance properties of aqueous-based PU resin can be modified by an aziridinyl postcuring agent,^{3–9} an internal curing agent of uretedione derivative,¹⁰ or a hybridization process with epoxy resin.^{11–13}

A postcuring reaction of aqueous-based PU anionomer is mainly based on its carboxyl group reacting with an aziridinyl curing agent when its pH value drops below 6.0 or on air drying.^{2,3} The resulting self-cured aqueous-based PU has the properties improved according to its curing dosage.

One of the PU hybrids is obtained from a reactive blending of aqueous-based PU dispersion with glycidyl methacrylate (GMA) copolymer emulsion.⁷ The reaction takes place between the terminal amino group and epoxide side group of PU and GMA copolymer, respectively, and results in a toughened PU hybrid film.

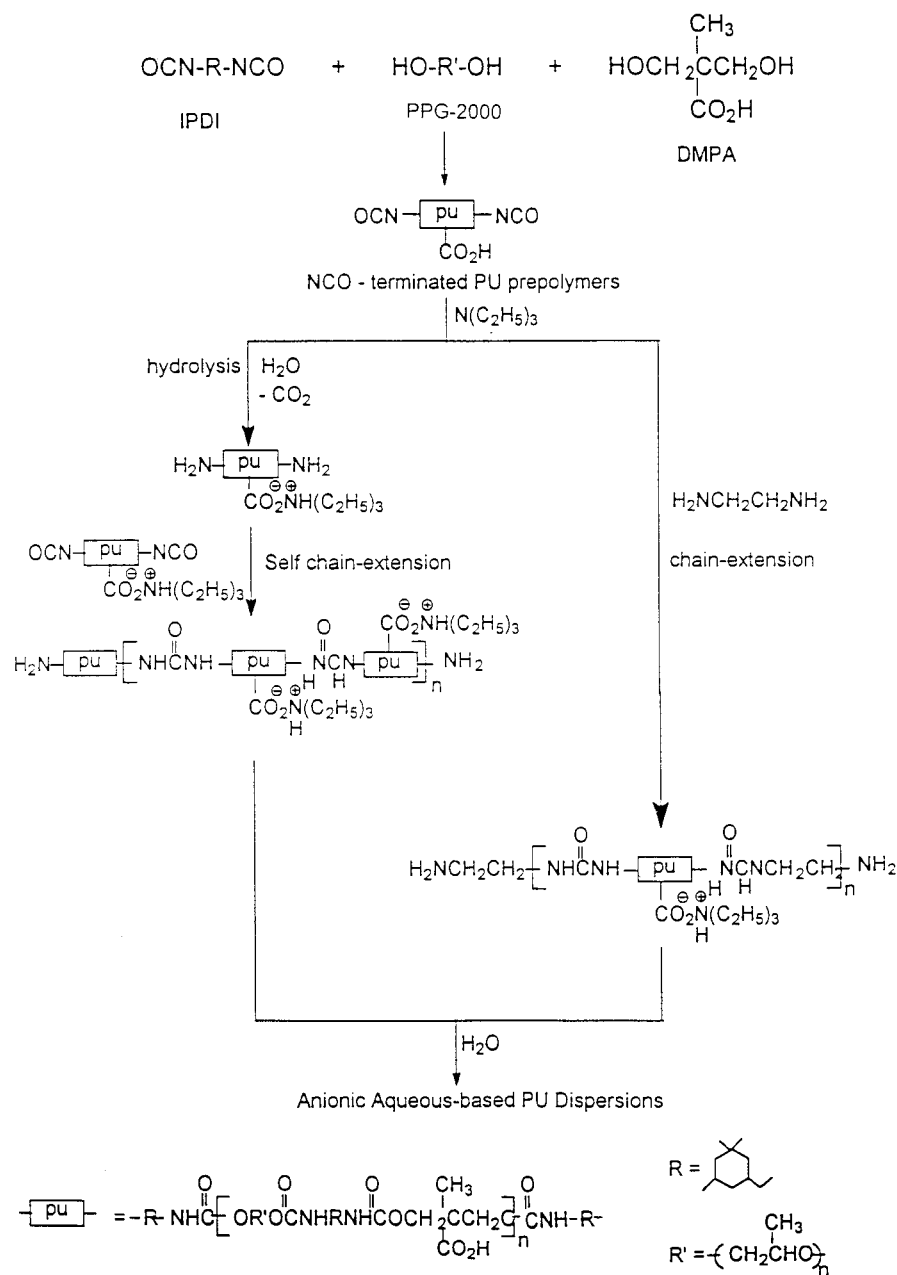
Properties of acrylate copolymers can be tailor-made according to the compositions of acrylate monomers. Most importantly, these acrylate copolymers can be modified from less expensive acrylate monomers with an easy free-radical copolymerization process. A water-reducible acrylate copolymer emulsion is prepared from copolymerization of butyl acrylate, acrylic acid, and methacrylic acid and then neutralized with triethylamine and followed by water dispersion.

Latent curing agents (HDDA-AZ and TMPTA-AZ) are synthesized from the reaction of aziridine with hexandiol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA), respectively. Both are water soluble and stable at high pH (>8.0) environment.

Both water-reducible acrylate copolymer emulsion and self-emulsified aqueous-based PU dispersions consist of the internal ionic center, carboxyl groups. No critical micelle concentration (CMC) existed and can be blended in any ratio without disturbing the stability of aqueous polymer dispersion. Equal weights of these polymers are blended, respectively, with various dosages of latent curing agent (HDDA-AZ or TMPTA-AZ), and become single-component

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Scheme 1 Preparation of aqueous-based PU anionomers.

self-curable polymer dispersion. The carboxyl groups of these blended polymers are reactive toward the curing agent on drying and result in new polymer hybrid formations. The investigation of these polymer hybrids will be discussed in this article.

EXPERIMENTAL

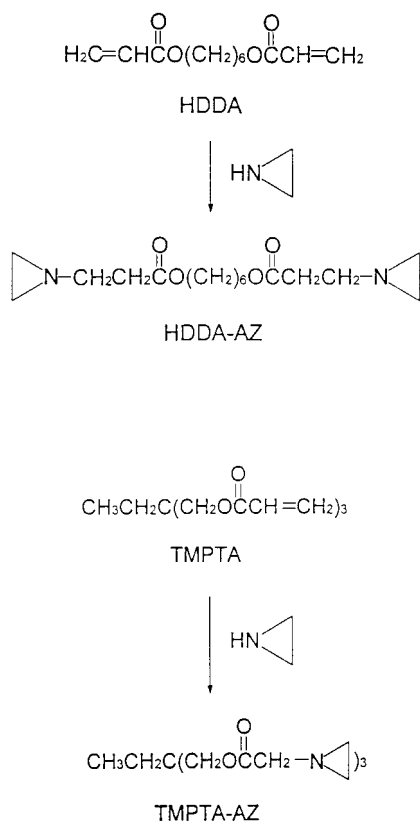
Materials

Triethylamine (TEA), ethylenediamine (EDA), and 2,2-dimethylolpropanoic acid (DMPA) were supplied by Aldrich Chemical Co., Inc. Acetone, methanol, and other

solvents were dried and distilled over anhydrous calcium chloride before use. Isophorone diisocyanate (IPDI) was supplied by Hul Chemical Co. Polypropylene glycol-1000 (PPG-1000) was supplied by Arco Chemical Co. Acrylic acid, methacrylic acid, *n*-butyl acrylate, TMPTA, and 1,6-hexandiol diacrylate (HDDA) were obtained from Rohm and Haas Co. All the materials were used as received without further purification.

Instruments

Dynamic mechanical thermal behavior of polymer film was performed with a dynamic mechanical ther-



Scheme 2 Preparation of aziridinyl curing agents.

mal analyzer (MK-II, Polymer Laboratories). Thermogravimetric data were measured by a Hi-Resolution TGA 2950 thermogravimetric analyzer (TA). Stress and strain curves of PU films were taken with Shimadzu Autograph S-100-C. NMR spectra were measured by a Bruker 300 MHz.

Preparation of latent aziridinyl curing agents

Ethyleneimine (or aziridine) was prepared from ethanolamine according to the published method.¹⁴ Aziridine (1.2 mol) was added dropwise to HDDA (1.0 mol) or TMPTA (1.0 mol) through an additional funnel. The reaction mixture was kept at 50°C for another hour until the acrylate stretching vibration frequency at 1634 cm^{-1} disappeared in IR spectrum. The excess amount of aziridine was removed under vacuum (Scheme I).

Preparation of anionic aqueous-based PU dispersion³

PPG-2000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before being mixed with IPDI (0.3 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 CaCl_2

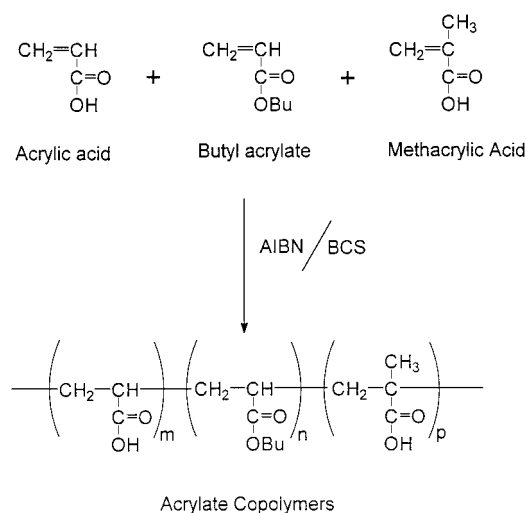
drying tube. The reaction mixture was kept at 110°C for about 4 h, until the NCO percentage drops below 3.0 (ASTM D-1638 NCO determination method) and remained constant for another half-hour. Then, freshly dried acetone (230 mL) was added into the reaction flask (when it is cooled down below 50°C) to adjust the viscosity of PU prepolymer. Aqueous-based PU dispersion was obtained from a high shear rate mixing of PU prepolymer with 450 mL aqueous solution of ethylenediamine (0.08 mol) and triethylamine (0.10 mol). Anionic PU dispersion contains 30% solid contents with a pH value at 8.5 after acetone is removed under vacuum (Scheme II).

Preparation of water-reducible acrylate copolymer emulsion

A free-radical solution copolymerization of *n*-butyl acrylate, methylmethacrylic acid, and acrylic acid (molar ratios: 4.0/0.7/0.7) was carried out in butyl cellulose (BCS, 400 mL) with a free-radical initiator, AIBN (1.2 g). The copolymerization was kept at around 80°C for 3 h. The acid fraction of acrylate copolymer was neutralized with aqueous triethylamine solution and resulted in the formation of water-reducible acrylate copolymer emulsion. It comprised 30% (w/w) solid content (Scheme III).

Polymer hybrids from PU anionomer and acrylate copolymer

An equal weight of water-reducible acrylate copolymer emulsion and self-emulsified aqueous-based PU dispersion was blended. The polymer blend was treated further with various dosages of latent curing agent (HDDA-AZ or TMPTA-AZ) at room temperature and resulted in the formation of a stable single



Scheme 3 Preparation of acrylate copolymers.

TABLE I
Properties of Polymer Hybrids with Aziridinyl Curing Agent

	Polymer hybrids									
	PU	PU/Acrylate ^b	TMPTA-AZ (phr) ^a				HDDA-AZ (phr)			
			7.7	9.2	11.5	15.3	8.4	10.0	12.7	16.9
AZ/COOH ^c			0.7	0.9	1.1	1.5	0.8	1.0	1.2	1.6
Elongation (%)			Tensile stress (kg/cm ²)							
100	4.0	5.5	6.4	7.2	9.4	11.4	6.0	7.5	8.5	—
200	6.2	7.8	10.1	—	—	—	10.1	—	—	—
300	8.7	11.4	—	—	—	—	—	—	—	—
400	11.9	15.9	—	—	—	—	—	—	—	—
500	16.3	21.5	—	—	—	—	—	—	—	—
Elongation at break (kg/cm ² /%)	20.0/559	22.5/515	10.3/206	11.4/196	12.2/152	11.9/108	10.3/206	9.5/138	9.6/114	8.0/91
Gel content (%)	85.4	80.1	90.6	90.8	91.2	91.7	92.8	94.0	94.3	95.8
Ethanol uptake (%)	2705	2269	412	366	299	250	332	287	280	211
Weight loss in ethanol	8.6	8.3	8.2	7.5	6.6	5.8	6.6	5.5	5.5	4.6

^a Curing dosage based on 100 phr solid aqueous-based polymers.

^b Blend of PU and acrylate copolymer without curing; the total COOH content is 7.2×10^{-2} equivalents per 100 g solid polymer blend.

^c The equivalent ratio of aziridinyl group and carboxyl group in polymer hybrid curing system.

component and self-curable polymer dispersion at a higher pH (>8.0) condition. Polymer hybrids were obtained from this polymer dispersion after film casting and air drying.

Properties of the polymer hybrids

Tensile strength and elongation

The cast films were air dried at room temperature and then at 50°C for 24 h. They were conditioned in a 75% relative humidity chamber at 25°C for 72 h before the measurements. Each specimen was cut in a dumbbell shape of 1.2 ± 0.1 mm thickness. The gauge length was 40 mm and the measurement was performed at a cross-head speed of 40 mm/min. Six specimens for each sample were taken, and the three measurements that showed the highest tensile strength were selected for calculating the mean value.

Gel content

A known weight of oven-dried film was put into a Soxhlet extractor for continuous extraction with tetrahydrofuran (THF) for 24 h. 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 and ethanol absorption

A known weight (W_0) of $60 \times 60 \times 1$ mm dried polymer film 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 water uptake (W_A), ethanol absorption (W_E), and weight losses (W_x , W_y) of the polymer films in water and in ethanol were calculated according to the following equations, respectively:

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

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

where W_A and W_x are the amount of water uptake by the polymer film and the amount of polymer dissolved into water, respectively, and

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

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

where W_E and W_y are the amount of ethanol absorption by the polymer film and the amount of polymer dissolved into ethanol, respectively.

Dynamic mechanical thermal analysis (DMTA)

Air-dried PU films were dried further in a 50°C oven for 24 h and then conditioned in a 75% relative humidity chamber at 25°C for 72 h before testing. Dy-

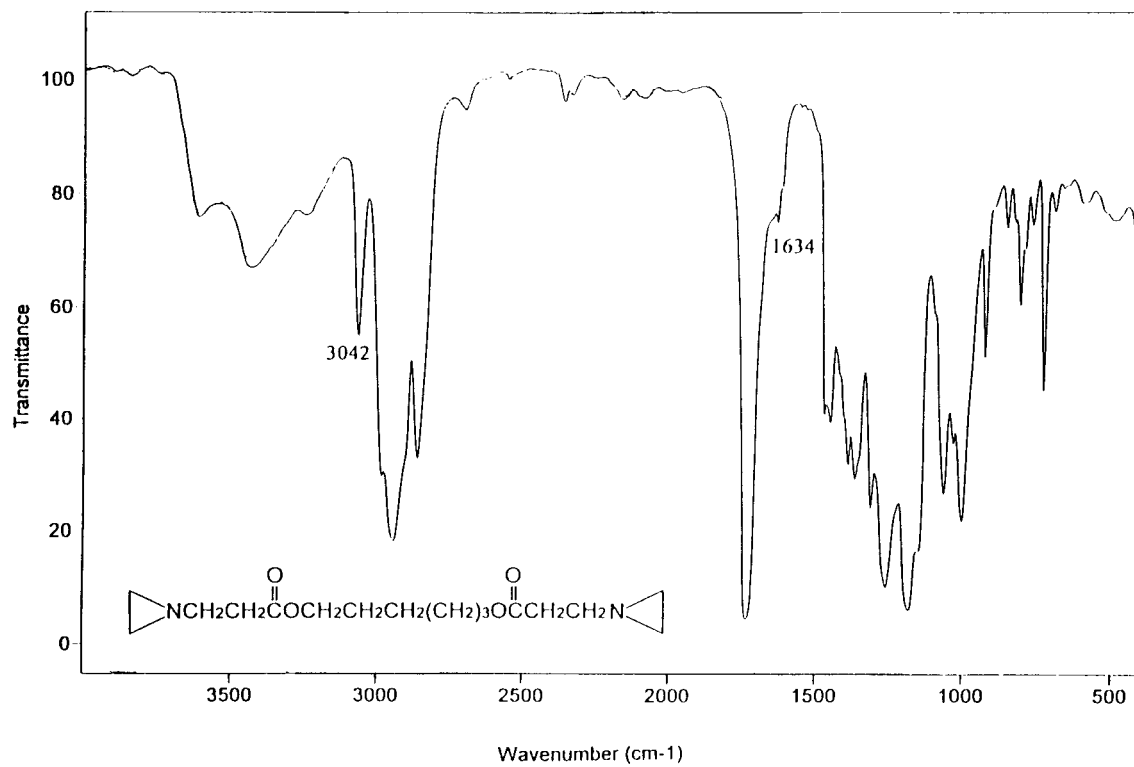


Figure 1 IR spectrum of HDDA-AZ.

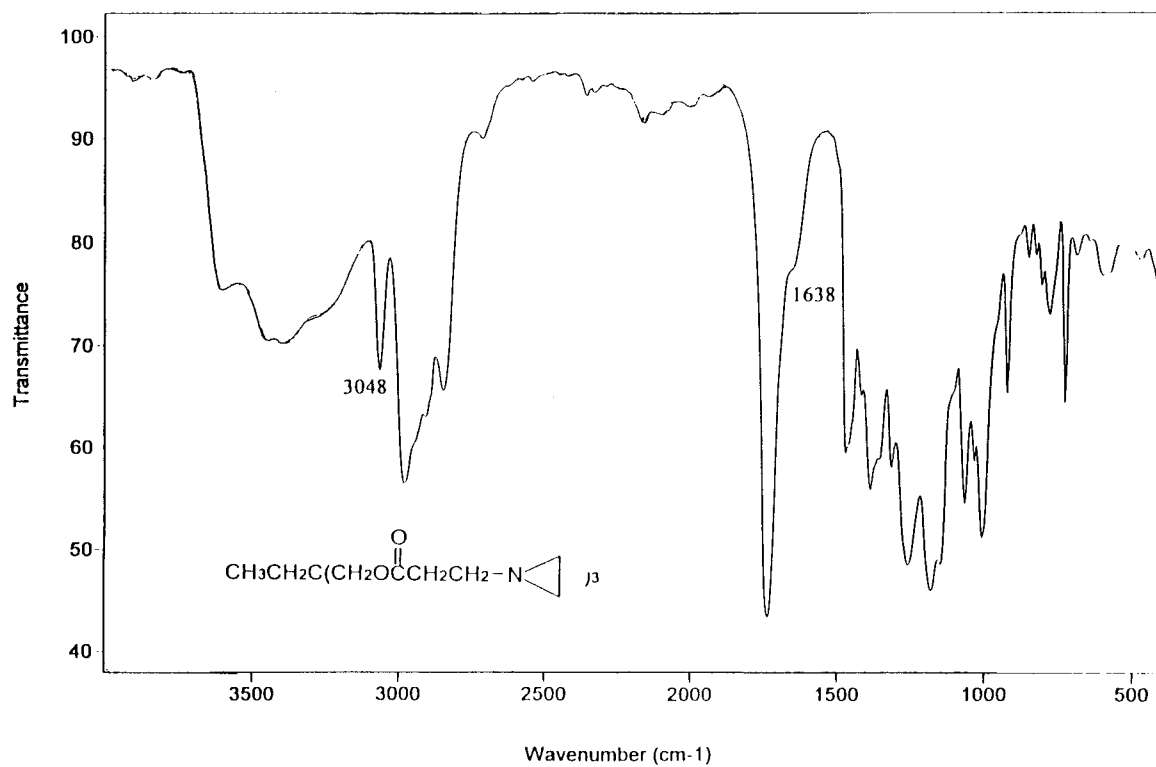


Figure 2 IR spectrum of TMPTA-AZ.

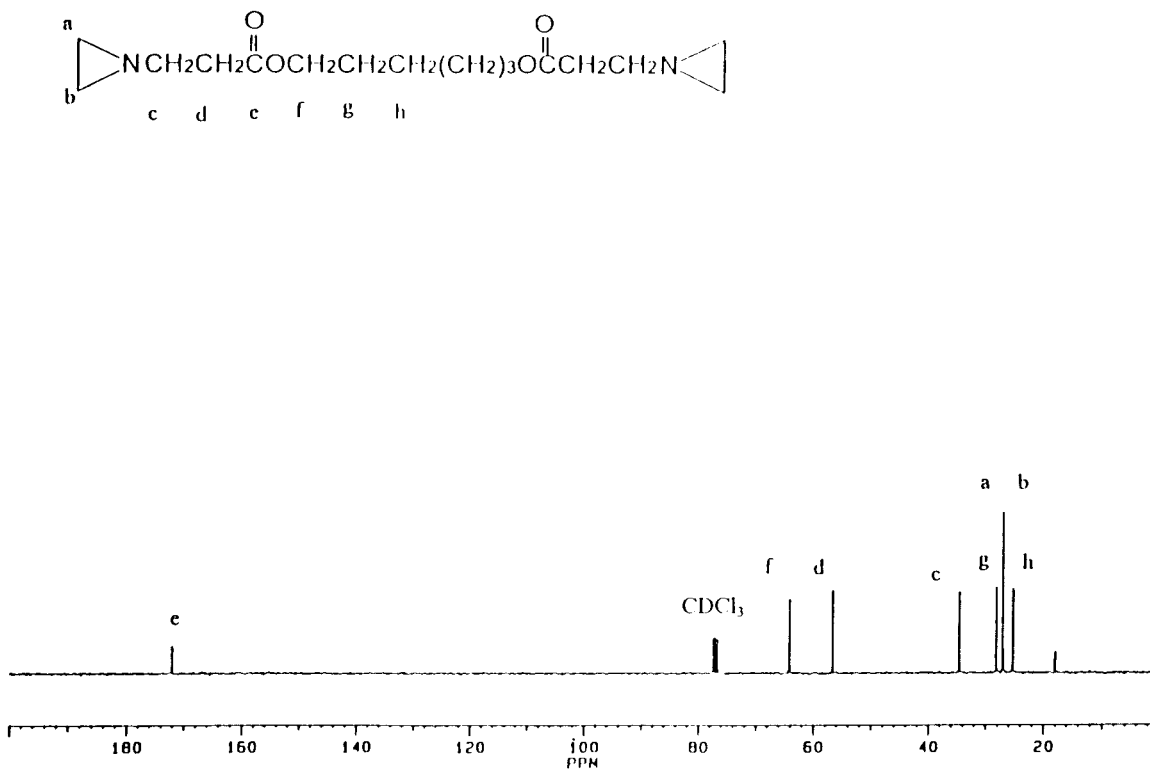


Figure 3 $^{13}\text{C-NMR}$ spectrum of HDDA-AZ.

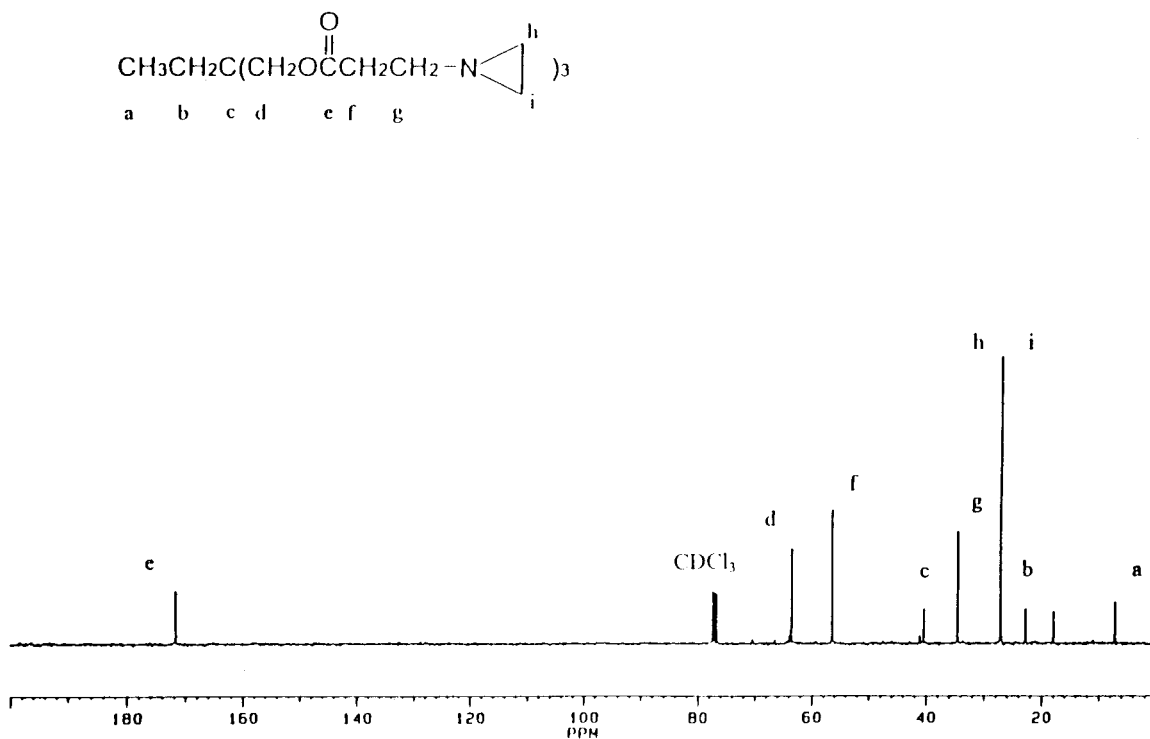
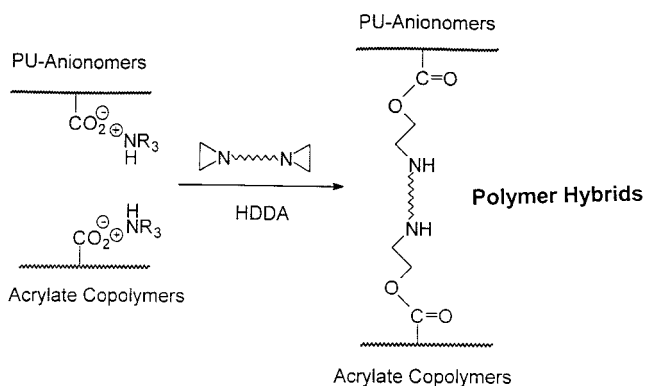


Figure 4 $^{13}\text{C-NMR}$ spectrum of TMPTA-AZ.



Scheme 4 Polymer hybrids from PU anionomer and acrylate copolymer with aziridinylic curing agent HDDDA-AZ.

dynamic mechanical analysis measurements were carried out in bending mode with a heating rate of 3°C/min from -80 to 150°C at 1.0 Hz frequency for each sample.

Thermogravimetric analysis (TGA)

The conditioned samples were measured by a thermogravimetric analyzer with a heating rate at 20°C per minute from ambient temperature to 500°C. These were carried out under a nitrogen or air atmosphere for the measurements of polymer thermal and thermooxidative stabilities, respectively.

RESULTS AND DISCUSSION

The posttreatments of aqueous-based PU have proven to be the effective method for improving PU properties, such as the postcuring reaction of aqueous-based PU carboxyl groups with an aziridinylic curing agent¹⁻⁵ and a bivalent metallic ion (e.g., Ca²⁺, Zn²⁺, Cu²⁺, etc.) results in the formation of crosslinked polymer

networks,^{11,12} respectively. The phosphorus containing aziridinylic curing agents also serve as the reactive flame retardant.^{8,9} PU properties were modified further by the polymer hybridization of GMA-copolymer emulsion¹¹ and of aqueous-based epoxy resins,¹³ respectively. This polymer hybridization process provides an alternative for modifying aqueous-based performance properties.

The self-emulsified aqueous-based PU dispersion was prepared from a conventional PU prepolymer process.^{1,2} PU carboxyl group is the ionic center and the curing site that comes from one of PU ingredients, DMPA. The resulting PU dispersion with 30% solid content comprises 3.5×10^{-2} equivalents of carboxyl group per 100 g of solid PU resin.

Water-reducible acrylate copolymer emulsion is prepared from a free-radical copolymerization of acrylic acid, methacrylic acid, and butyl acrylate and then neutralized by triethylamine. The resulting acrylate copolymer emulsion with 30% solid content and consists of 1.1×10^{-1} equivalents of carboxyl group per 100 g solid acrylate copolymer.

These two polymer dispersions are miscible with the latent curing agent (TMPTA-AZ or HDDDA-AZ) because of their hydrophilic characters. The polymer carboxyl group is reactive toward the aziridinylic group of latent curing agent on drying and no visible phase separation was found in their final hybridized polymer films.

An equal solid weight of self-emulsified aqueous-based PU dispersion and water-reducible acrylate copolymer emulsion was blended and formulated with various dosages of prepared curing agent (HDDDA-AZ or TMPTA-AZ) (Table I). A new polymer hybrid was obtained from this polymer hybridization on drying and the performance properties of these polymer hybrids will be evaluated.

TABLE II
Thermogravimetric Analyses of Polymer Hybrids

PU/Acrylate ^b	Polymer hybrids																	
	TMPTA-AZ (phr) ^a						HDDA-AZ (phr)											
	7.7		11.5		15.3		8.4		12.7		16.9							
AZ/COOH ^c	0.7		1.1		1.4		0.8		1.2		1.6							
TGA Decomposition Temp ^d																		
1st decomposition (°C)	248	248	248	248	248	248	248	248	248	248	248	243						
2nd decomposition (°C)	313	—	—	—	—	—	—	—	—	—	—	—						
3rd decomposition (°C)	389	406	399	399	391	391	395	395	399	399	392	392						
Temperature (°C) at 80% weight left	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>	<u>N₂</u>	<u>air</u>
	305	270	327	298	331	302	336	302	313	292	318	303	309	296	309	296	309	296

^a Curing dosage based on 100 phr solid aqueous-based polymers.

^b Blend of PU and acrylate copolymer without curing.

^c The equivalent ratio of aziridinylic group and carboxyl group in polymer hybrid curing system.

^d Thermal decomposition temperature of each polymer is measured under nitrogen atmosphere.

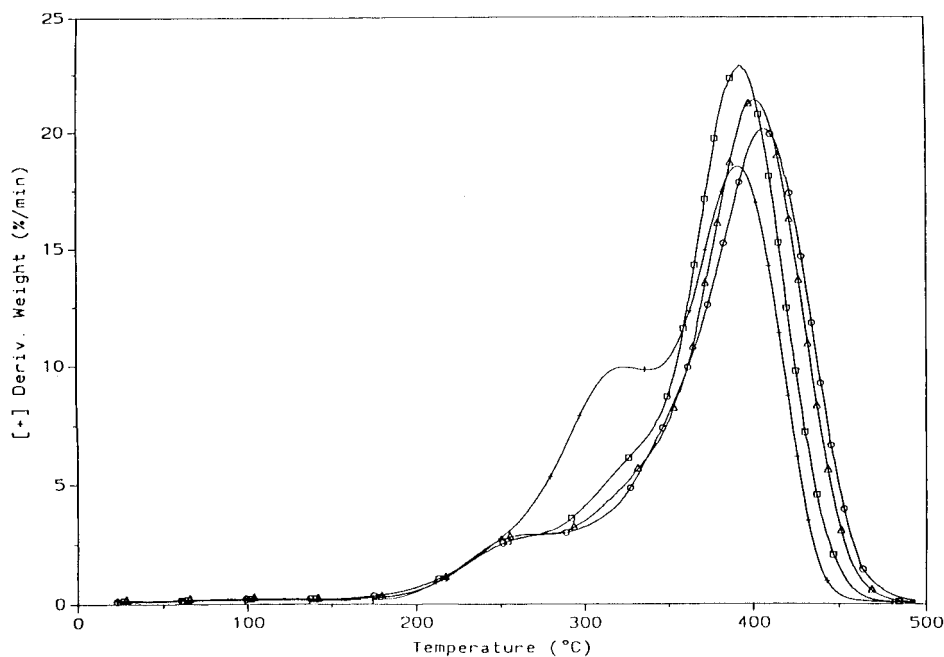


Figure 5 Differential thermogravimetric analyses of polymer hybrids with various curing dosages of TMPTA-AZ.

Aziridinyl latent curing agent

The latent curing agents were prepared from the Michael addition reaction of aziridine with diacrylate (HDDA) or triacrylate (TMPTA) (Scheme III). The disappearance of acrylate double bond stretching vibration frequency at 1634 cm^{-1} in IR (Figs. 1 and 2) and the chemical shifts at 128 and 132 ppm in ^{13}C -NMR (Figs. 3 and 4) indicate the completion of the addition reaction. The resulting aziridinyl latent curing agent,

HDDA-AZ or TMPTA-AZ, is water soluble and miscible with these aqueous polymer dispersions.

Monitoring polymer curing by infrared spectra

The curing reaction of aqueous-based PU with TMPTA-AZ is proved by infrared (IR) spectroscopy.³⁻⁵ The absorption peaks at 1654 and 1723 cm^{-1} belong to the carbonyl ($\text{C}=\text{O}$) stretching of carboxylic ion and urethane group of PU anionomer, respectively.

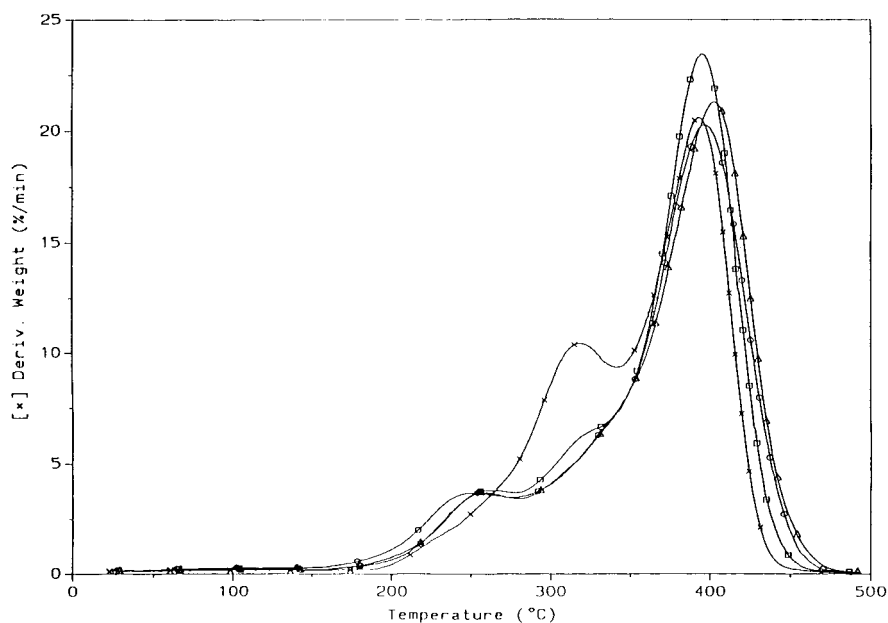


Figure 6 Differential thermogravimetric analyses of polymer hybrids with various curing dosages of HDDA-AZ.

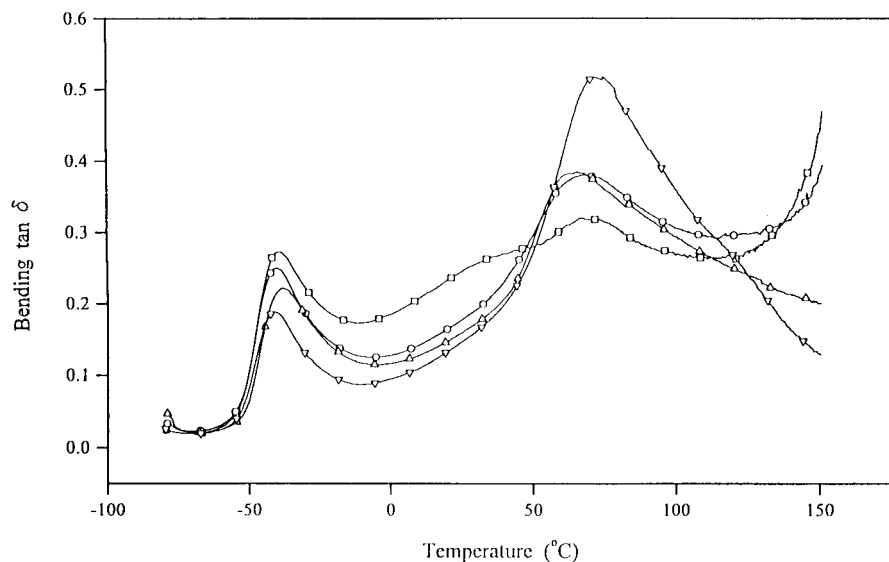


Figure 7 Dynamic mechanical thermal analyses of polymer hybrids with various curing dosages of TMPTA-AZ.

The blending of aqueous-based PU anionomer and water-reducible acrylate copolymer both contain carboxylic ions at high pH (e.g., pH > 8.0). These ionic centers stabilize the aqueous polymer dispersion and serve as the curing sites of these two blended polymers on drying.

The intensity of carboxylic ion carbonyl stretching on 1654 cm^{-1} weakens ester and urethane carbonyl stretching frequencies centered at 1723 cm^{-1} increase in IR spectra of polymer hybrids. These indicate that the curing reaction takes place among the polymer carboxyl groups with aziridiny curing agent and results in the formation of amino ester linkage³ on final polymer hybrids (Scheme IV).

Physical and mechanical properties

The gel content and ethanol uptake of polymer hybrid also demonstrate the relative degree of polymer crosslinking density. The gel content of original PU anionomer is 85.4%, and the gel content of polymer hybrid increases with increasing curing dosage. For example, their gel contents are 90.6 and 91.7% cured with 7.7 and 15.3 phr TMPTA-AZ, respectively; their aziridiny group and carboxyl group ratios are 0.7 and 1.5. In HDDA-AZ curing system, their gel contents are 92.8 and 95.8% with 8.4 and 16.9 phr HDDA-AZ (Table I). HDDA-AZ curing system has a higher gel content with a similar equivalent ratio of aziridiny and

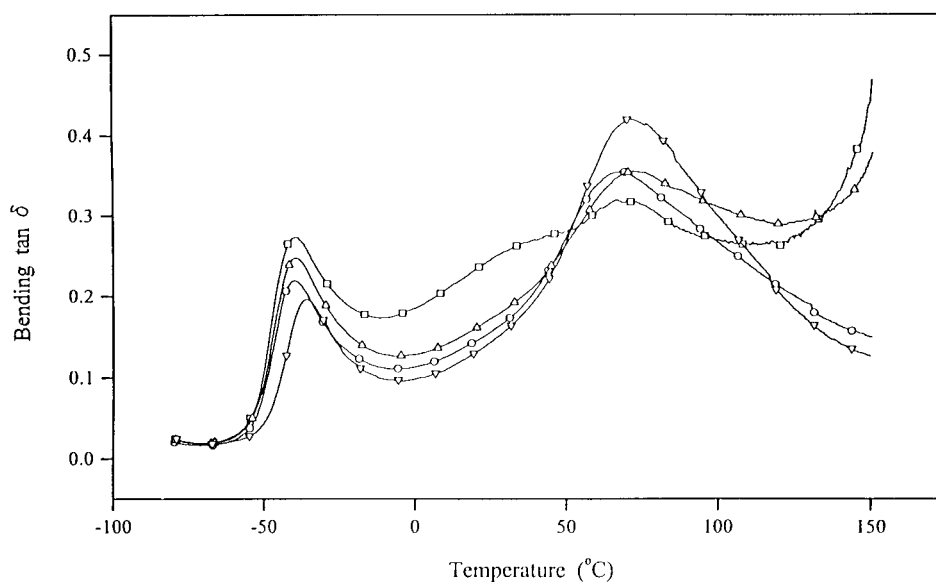


Figure 8 Dynamic mechanical thermal analyses of polymer hybrids with various curing dosages of HDDA-AZ.

carboxyl groups (AZ/COOH) because of the trifunctional TMPTA-AZ, causing the steric hindrance from further crosslinking reaction. The increasing gel content and the decreasing ethanol uptake of polymer hybrids with curing agent (Table I) are also evidence that crosslinking reaction of HDDA-AZ is better than TMPTA-AZ.

The tensile stress at 4.0 kg/cm² with 100% elongation of original PU and its value of polymer hybridization increases with the curing dosage increase. The tensile strength changes from original 20.0 kg/cm² at 559% elongation to 22.5 kg/cm² at 515% elongation of PU/acrylate copolymer blend (without curing). This physical blend of these two polymers has no crosslinking reaction between these two. However, the final polymer hybrid becomes 10.3 kg/cm²/206% after the treatment with 7.7 phr TMPTA-AZ or 8.4 phr HDDA-AZ and the tensile stress at 7.2, 9.4, and 11.4 kg/cm² with 100% elongation of polymer hybrids with 9.2, 11.5, and 15.3 phr TMPTA-AZ dosages, respectively. The similar results of polymer hybrids were obtained from curing with various HDDA-AZ curing dosages (Table I).

Thermal behavior

The thermal decomposition temperature under nitrogen of two polymers blends without curing has three decomposition temperatures at 248, 313, and 389°C (Table II). The second decomposition temperature does not show up on the polymer hybrids because of the crosslinking reaction. The third decomposition temperature increases from the original 389°C of polymer blend to 406 or 399°C of polymer hybrids with 7.6 and 11.5 phr TMPTA-AZ, respectively (Table II and Fig. 5). For the HDDA-AZ curing system, its third decomposition temperature of polymer hybrid increases to 395 or 399°C after the treatment of 8.4 or 12.7 phr HDDA-AZ (Table II and Fig. 6). The crosslinking reaction occurred between PU and acrylate copolymer via the curing agent and these two types of polymers hybridized into a new polymer hybrid. However, the curing dosage increases to their equivalent AZ/COOH ratio well over 1.0 and their thermal stability decreases to 391 and 392°C for 15.3 phr TMPTA-AZ and 16.9 phr HDDA-AZ, respectively (Table II), due to the addition of excess curing agent, but lacks available polymer carboxyl group to react with completely.

The DMTA curves of the two-polymer blend (without curing) has a low temperature damping peak at -40°C, and this peak intensity decreases as increasing TMPTA-AZ or HDDA-AZ curing dosage. The polymer blend softens around 120°C and the resulted polymer hybrids remain rubbery up to 150°C on their DMTA curves. A broad damping peak centered at

70°C and its intensity increases as the increasing curing dosage, possibly due to the amino ester bond formation between polymers. As this peak intensity sharply increases with 15.3 phr TMPTA-AZ or 16.9 phr HDDA, it may be caused partially by the homopolymer formation from excess curing agent (Figs. 7 and 8).

CONCLUSION

Self-emulsified PU dispersion and water-reducible acrylate copolymer emulsion are compatible with each other in the water phase. These two polymers are blended with an equal weight ratio and various dosages of the latent curing agent, TMPTA-AZ and HDDA-AZ, respectively, as the self-curable single component polymer hybrid. Properties of these polymer hybrids are modified according to the curing dosage. For example, the gel content increases from 80.1% of polymer blend to 95.8% of polymer hybrid with HDDA-AZ (16.9 phr); ethanol uptake decreases from 2269% of polymer blend down to 250% of polymer hybrid with TMPTA-AZ (15.3 phr). The thermal properties of the polymer hybrids are better than any of these original polymers. These improvements show the benefits of new polymer hybrid formation. This polymer hybridization process of self-emulsified PU and water-reducible acrylate copolymer via a postcuring reaction offers an alternative for polymer modification and cost effectiveness of more expensive aqueous-based PU.

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References

1. Ramesh, S.; Tharanikkarasu, K.; Mahesh, G. N.; Radhkrishnan, G. *J Macromol Sci, Rev Macromol Chem Phys* 1998, C38, 481.
2. Dieterich, D. in *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: New York, 1985; Chapter 2.
3. Chen, G.-N.; Chen, K.-N. *J Appl Polym Sci* 1997, 63, 1609.
4. Chen, G.-N.; Liu, P.-H.; Chen, M.-S.; Chen, K.-N. *J Polym Res* 1997, 4, 165.
5. Chen, G.-N.; Chen, K.-N. *J Appl Polym Sci* 1998, 67, 1661.
6. Kim, J. W.; Suh, K.-D. *J Appl Polym Sci* 1998, 69, 1079.
7. Vabrik, R.; Czalik, I.; Tury, C.; Ruzsna, I.; Ille, A.; Vig, A. *J Appl Polym Sci* 1998, 68, 111.
8. Wang, T.-Z.; Chen, K.-M. *J Appl Polym Sci* 1999, 74, 2499.
9. Shao, C.-H.; Wang, T.-Z.; Chen, G.-N.; Chen, K.-J.; Yeh, J.-T.; Chen, K.-N. *J Polym Res* 2000, 7, 41.
10. Ling, H.-J.; Chen, K.-N.; J.-Z.; Lai, Lin, Y.-S. U.S. Pat. 6,077,960, 2000.
11. Chen, G.-N.; Chen, K.-N. *J Appl Polym Sci* 1999, 71, 903.
12. Ling, H.-J.; Chen, G.-N.; Chen, K.-N. *Adv Eng Mater* 1999, 2, 114.
13. Chen, T.-W.; Yeh, J.-T.; Chen, K. N.; Lin, Y.-S. U.S. Pat. 6,291,554, 2001.
14. Reeves, W. A.; Drake, Jr., G. L.; Hoffpauir, C. L. *J Am Chem Soc* 1951, 73, 3522.