

# New Crosslinked Polymer from a Rapid Polymerization of Acrylic Acid with Triaziridine-Containing Compound

Po-Cheng Chen,<sup>1</sup> Shih-Chieh Wang,<sup>1</sup> Chia-Yu Huang,<sup>1</sup> Jen-Taut Yeh,<sup>2</sup> Kan-Nan Chen<sup>1</sup>

<sup>1</sup>Department of Chemistry, Nano-tech Research Center, Tamkang University, Tamsui, Taiwan 251

<sup>2</sup>Department of Materials and Fiber, Nanya Institute of Technology, Chungli, Taiwan 320

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**ABSTRACT:** A triaziridine containing compound, trimethylolpropane tris(1-aziridinepropionate) (TMPTA-AZ), is prepared from a Michael addition of aziridine (AZ) with trimethylolpropane triacrylate (TMPTA). A rapid polymerization of acrylic acid (AA) with TMPTA-AZ occurred at ambient temperature without catalyst. This polymerization process involves three subsequent reactions are proposed: (1) An exothermic neutralization takes place between AA and TMPTA-AZ. (2) That neutralization heat triggers AZ ring-opening reaction and that carboxyl group (of AA) plays as a nucleophile

and results in an amino ester bond formation. (3) A final crosslinked polymer is obtained from that amino group reacts with its acrylic double bond via an intermolecular Michael addition reaction. These new crosslinked polymers with various performance properties are obtained from a mixture of AA and TMPTA-AZ in different ratios and post-heating. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 809–815, 2007

**Key words:** rapid polymerization; ring-opening; Michael addition

## INTRODUCTION

Aziridine (ethyleneimine, AZ) is first synthesized by S. Gabriel in 1888.<sup>1</sup> It reacts with a nucleophilic hydroxyl or carboxyl group. W. A. Reeves and coworkers use AZ derivatives for cotton fabrics.<sup>2</sup> The conformation of AZ is a triangular and its ring strain (26.9 kcal/mol) is similar to that of the oxirane (28 kcal/mol). AZ is a secondary amine with a high basicity ( $pK_a$ , 8.01) and forms an aziridinium salt with an acid and then self-polymerization by a ring-opening reaction.

A series of multi-AZ curing agents have been applied for a curing reaction of aqueous-based PU,<sup>3–11</sup> water-reducible epoxy resin,<sup>12–15</sup> aqueous-based acrylate emulsion,<sup>16,17</sup> aqueous polymeric inks<sup>18,19</sup> and their hybridized resins.<sup>20,21</sup> Moreover, phosphorus-containing multi-AZ curing agent is used as a curing agent as well as a reactive flame retardant.<sup>22–25</sup> Key of these curing processes is based on a ring-opening reaction between AZ moiety of curing agent and carboxylic acid-containing aqueous polymer on drying. The improving properties of these final cured polymers are due to the contribution of multi-AZ curing agents.

A model reaction of a mono-AZ compound, methyl 3-aziridinylpropionate (MAP), with trimethylacetic

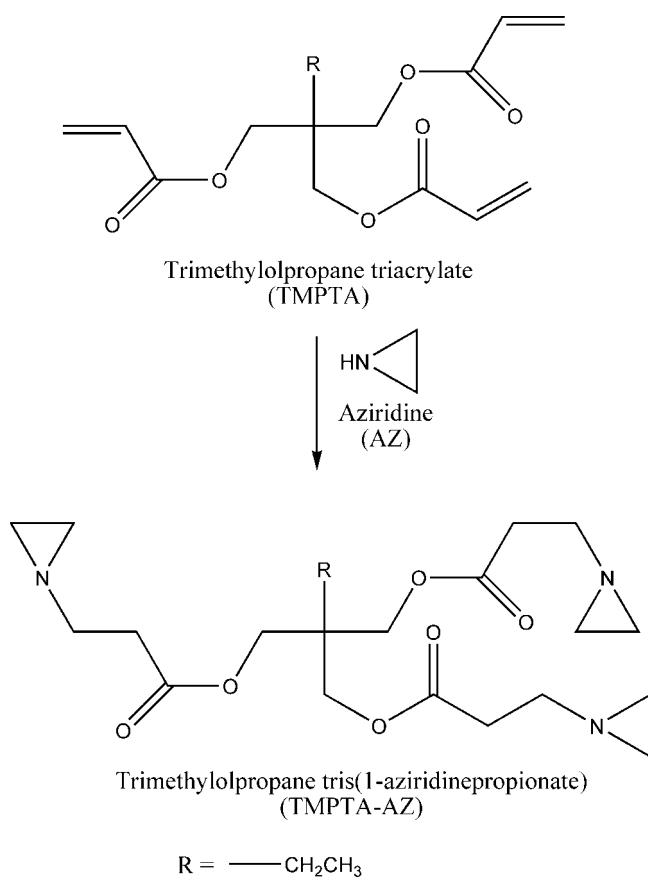
acid (TMAA) demonstrates that a series of reactions take place stepwise—neutralization, and then a ring-opening for an amino-ester bond formation, and this amino group reacts toward an acrylic double bond of ethyl acrylate (EA) monomer via a Michael addition reaction for a second  $\beta$ -amino-ester formation.<sup>26</sup> A polymerization of acrylic acid (AA) with a multi-AZ containing compound, e.g., trimethylolpropane tris(1-aziridinepropionate) (TMPTA-AZ), occurs immediately at ambient temperature, and it results in the formation of crosslinked polymers. The polymerization mechanism is proposed which is similar to the model reaction. A polymerization of AA with TMPTA-AZ takes place immediately at mixing, and it provides a convenient process for preparing a highly networked polymer. The polymerization process and performance properties of these new polymers are evaluated in this report.

## EXPERIMENTAL

### Materials

Trimethylolpropane tris(1-aziridinepropionate) (TMPTA-AZ) was synthesized in our laboratory. Trimethylolpropane triacrylate (TMPTA) and acrylic acid (AA) were supplied by Lancaster Co. All solvents were purified according to the published method before use.

Correspondence to: K.-N. Chen (knchen@mail.tku.edu.tw).



**Scheme 1** Preparation of TMPTA-AZ.

### Synthesis of Trimethylolpropane tris(1-aziridinepropionate)

Aziridine (AZ) was prepared from 2-aminoethanol by a modified process of published method.<sup>2</sup> Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution (30 mL) of AZ (0.33 mol) was added dropwise into CH<sub>2</sub>Cl<sub>2</sub> solution (100 mL) of trimethylolpropane triacrylate (TMPTA, 0.1 mol) through an addition funnel in an ice bath. The reaction mixture was kept at room temperature for an additional 12 h after addition. TMPTA-AZ was obtained in 97% yield (Scheme 1, Figs. 1–4) after CH<sub>2</sub>Cl<sub>2</sub> and an excess amount of AZ are removed under reduced pressure.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.83 (3H), 1.45(2H), 1.02(6H), 1.59(6H), 2.31(6H), 2.43(6H), 3.88(6H).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ = 7.0, 22.5, 27.0, 34.4, 40.4, 56.4, 63.6, 171.4.

### Polymerization of acrylic acid and TMPTA-AZ

A suitable equivalent ratio of AA was added slowly into TMPTA-AZ with agitation in an ice-bath. The cooled reaction mixture was cast on glass plate and a polymerization reaction occurred immediately at ambient temperature. The resulting tough polymers were

treated further at different temperatures, respectively (Scheme 2).

### Properties of crosslinked polymers

#### Gel content

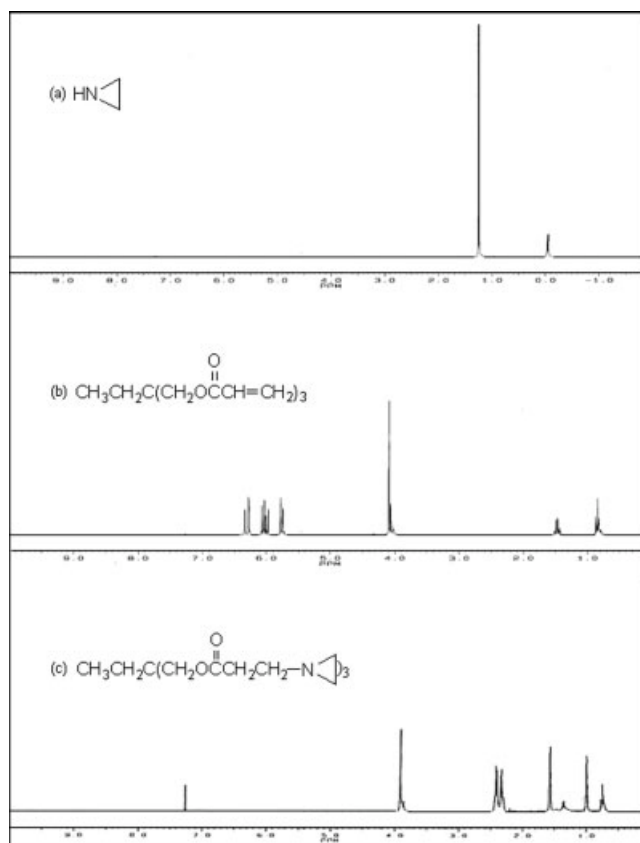
A known weight of oven-dried polymer ( $W_1$ ) was put into a Soxhlet extractor for continuous extraction with tetrahydrofuran (THF) for 24 h. The polymer gel remains after extraction was dried ( $W_2$ ) and calculated according to the test result. Three tests were carried out and averaged for each polymer sample.

$$\text{Gel content \%} = (W_2/W_1) \times 100\%$$

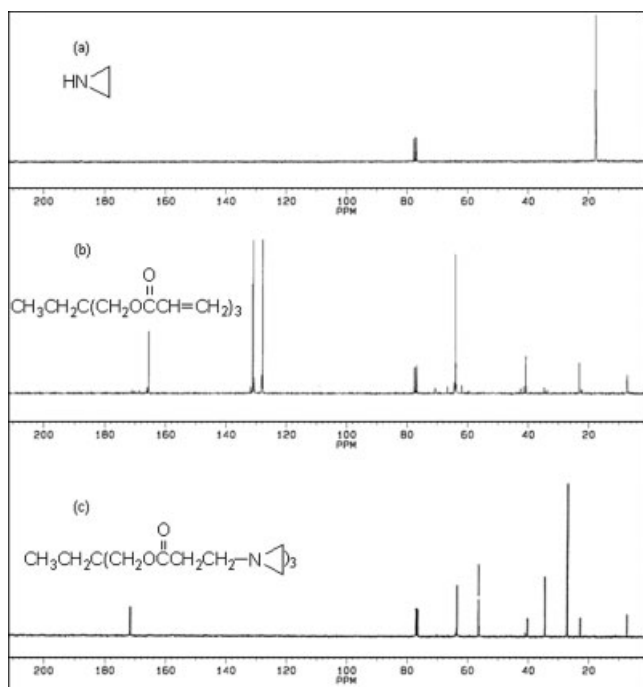
#### Water uptake

A known weight ( $W_0$ ) of dried polymer sample with a dimension of  $60 \times 60 \times 1 \text{ mm}^3$  was immersed in deion water bath for 7 days. The towel-dried sample weight ( $W_1$ ) and the oven-dried sample weight ( $W_2$ ) were obtained. Water uptake ( $W_w\%$ ) and weight loss ( $W_x\%$ ) of polymer in water were calculated according to the following equations:

$$W_w\% = [(W_1 - W_2)/W_2] \times 100\%$$



**Figure 1** <sup>1</sup>H-NMR spectra of (a) AZ; (b)TMPTA and (c)TMPTA-AZ.



**Figure 2**  $^{13}\text{C}$ -NMR spectra of (a) AZ; (b) TMPTA and (c) TMPTA-AZ.

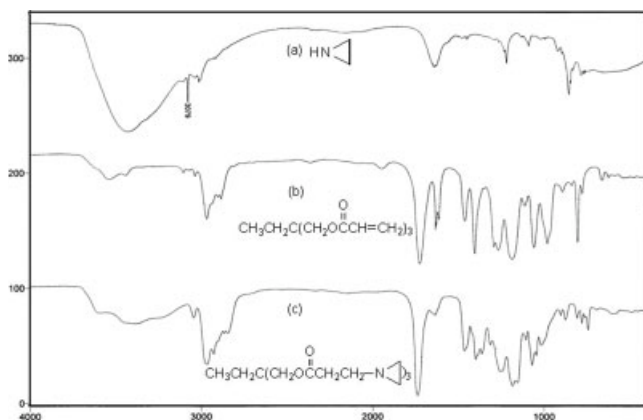
where  $W_w$  is the amount of water uptake by polymer, and

$$W_x\% = [(W_0 - W_2)/W_0] \times 100\%$$

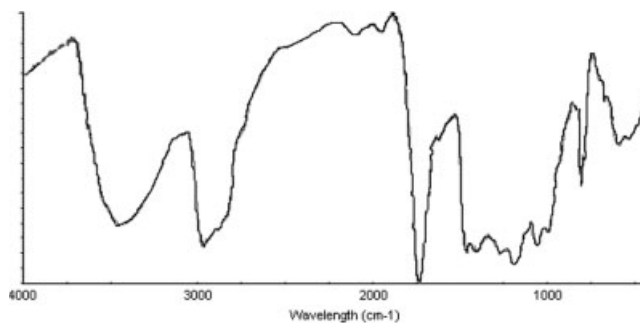
where  $W_x$  is the amount of polymer dissolved into water.

#### Ethanol swollen

A known weight ( $W_0$ ) of dried polymer sample with a dimension of  $60 \times 60 \times 1 \text{ mm}^3$  was immersed in a 95% ethanol bath for 24 h. The towel-down dry sample weight ( $W_1$ ) and the oven-dried sample weight



**Figure 3** FTIR spectra of (a) AZ; (b) TMPTA and (c) TMPTA-AZ.



**Figure 4** FTIR spectrum of the polymer with postcuring at  $100^\circ\text{C}$  for 24 h.

( $W_2$ ) were obtained. The ethanol-swollen ( $W_e\%$ ) and the weight loss ( $W_y\%$ ) of polymer in ethanol was calculated according to the following equations:

$$W_e\% = [(W_1 - W_2)/W_2] \times 100\%$$

where  $W_e$  is the amount of ethanol absorption by polymer, and

$$W_y\% = [(W_0 - W_2)/W_0] \times 100\%$$

where  $W_y$  is the amount of polymer dissolved into ethanol.

#### Hardness

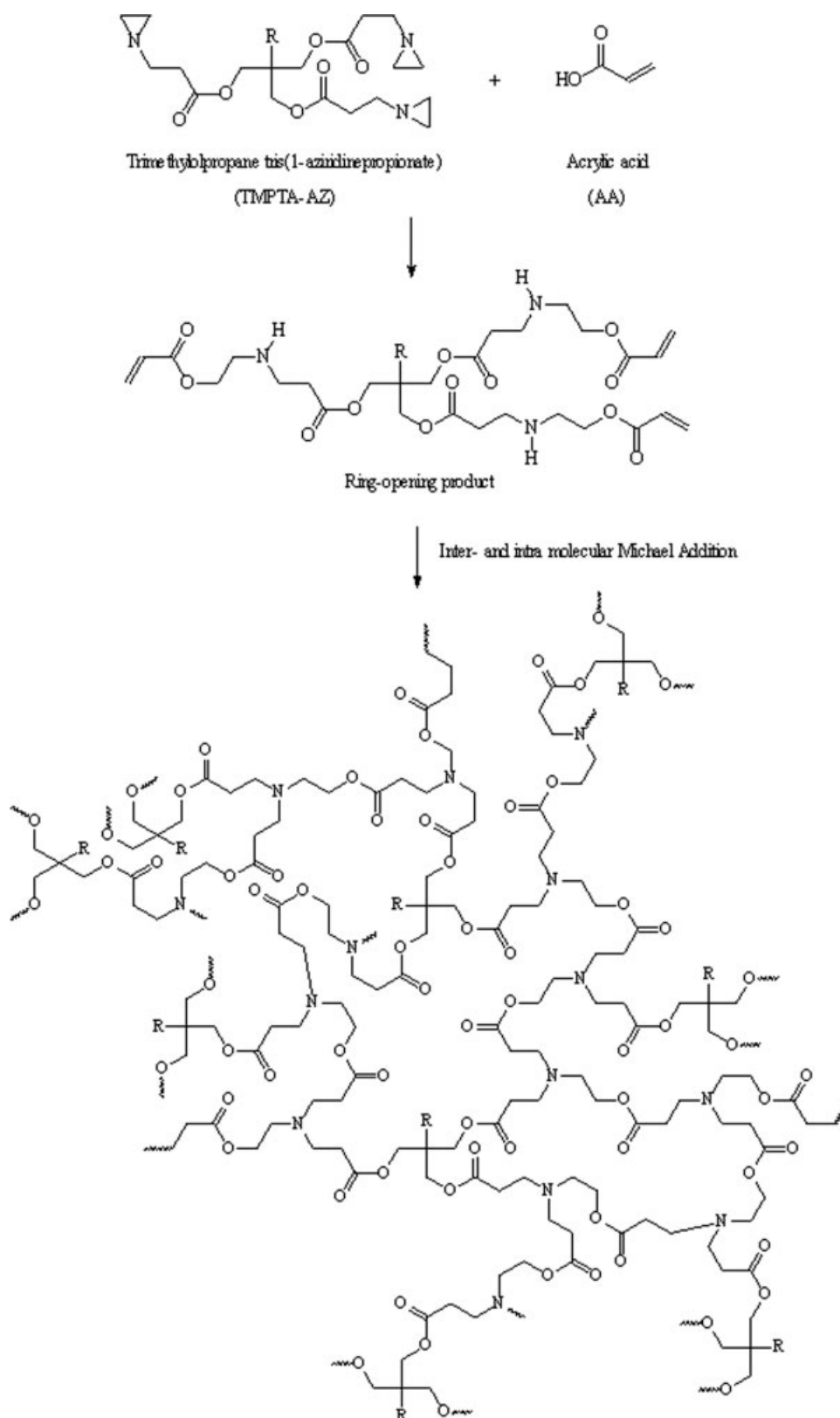
Hardness of each polymer was measured by a Shore a Durameter according to ASTM D2240.

#### Thermogravimetric Analyses

Each polymer sample (about 10 mg) was measured by a Hi-Resolution TGA 2950 TG-DTA thermogravimetric analyzer with a heating rate of  $20^\circ\text{C}/\text{min}$  from room temperature to  $600^\circ\text{C}$  under nitrogen atmosphere.

## RESULTS AND DISCUSSION

A polymerization of acrylic acid (AA) with a monoaziridine-containing compound, methyl 3-(aziridiny)propanoate (MAP), results in a linear poly( $\beta$ -amino ester) formation at ambient temperature. And, a reaction mechanism is proposed according to a modeling reaction of MAP with trimethylacetic acid (TMAA); each stage reaction product is characterized by NMR spectra.<sup>26</sup> The model reaction of MAP with TMAA is started from an exothermic acid-base neutralization of carboxylic acid (of TMAA) with AZ (of MAP) and results in a quaternary aziridinium salt adduct. A ring-opening reaction is triggered by the neutralization heat and forms an amino-ester bond. And, this amino



**Scheme 2** Rapid Polymerization Process of AA with TMPTA-AZ.

group reacts further with acrylic C=C double bond of ethyl acrylate (EA) via a Michael addition and results in a second  $\beta$ -amino-ester bond formation.<sup>26</sup>

A triaziridine-containing compound, e.g., trimethylolpropane tris(1-aziridine-propionate) (TMPTA-AZ), is synthesized for replacing MAP. A polymerization

takes place immediately at mixing of AA with TMPTA-AZ, and it results in a new crosslinked polymer formation at ambient temperature. The performance properties of these resulted polymers are dependent on the equivalent ratio of COOH/AZ and post-heating.

### Preparation of TMPTA-AZ

A triaziridine containing compound (TMPTA-AZ) is synthesized (Scheme 1) for replacing monoaziridine compound, MAP. Its chemical shift of  $^1\text{H-NMR}$  spectra at 0.05 and 1.23 ppm indicate the proton next to nitrogen atom of AZ and four methylene protons on AZ ring [Fig. 1(a)]. The chemical shifts around from 5.72 to 6.33 ppm indicate nine protons on acrylate double bonds of TMPTA [Fig. 1(b)]. Proton chemical shifts of C=C double bond (on 5.72–6.33 ppm) disappear on the product of TMPTA-AZ after a Michael addition reaction of AZ to TMPTA. It results in two new chemical shifts at 2.31 and 2.43 ppm, which show six methylene protons next to nitrogen atom of AZ and six methylene protons adjacent to carbonyl groups, respectively, [Fig. 1(c)].

The chemical shift of  $^{13}\text{C-NMR}$  spectra at 17.3 ppm indicates two carbons on AZ [Fig. 2(a)], and chemical shifts at 127.8 and 130.9 ppm reveal four carbons on C=C double bonds of TMPTA [Fig. 2(b)]. The chemical shifts of C=C double bond disappear instead of three new chemical shifts at 27.0, 34.4, and 56.4 ppm for TMPTA-AZ [Fig. 2(c)]. These are two carbons on AZ, two carbons adjacent to nitrogen atom of AZ, and two carbons adjacent to carbonyl, respectively.

AZ has an absorption peak at  $3079\text{ cm}^{-1}$  [Fig. 3(a)], and TMPTA has acrylic C=C bond absorption peak at  $1631\text{ cm}^{-1}$  on FTIR spectra [Fig. 3(b)]. The absorption peak at  $1631\text{ cm}^{-1}$  disappears, and the absorption peak of AZ remains on the addition product, TMPTA-AZ [Fig. 3(c)].

### Polymerization of AA with TMPTA-AZ

A rapid polymerization occurs immediately at the mixing of AA with TMPTA-AZ. The reaction mechanism is similar to a model reaction of trimethylacetic

acid (TMAA) and a monoaziridine-containing compound, methyl 3-(aziridiny)-propanoate, (MAP). The polymerization is similar to that of AA with MAP and results in the formation of a linear poly( $\beta$ -amino ester). The polymerization takes place in three consecutive reaction stages: neutralization of AA with MAP with exothermic neutralization heat, which triggers a ring-opening, followed by an intermolecular Michael addition reaction, and then, the mixing of AA and a triaziridine-containing compound, TMPTA-AZ, for replacing MAP; the polymerization occurs immediately at ambient temperature, which results in a crosslinked poly( $\beta$ -amino esters) formation. This rapid polymerization process of these two monomers AA and TMPTA-AZ has the potential for use as instant adhesive, sealant, composite material or other applications.<sup>27</sup>

### Properties of crosslinked polymers

#### Gel content

Gel content of crosslinked polymers, which are obtained from a polymerization of AA with TMPTA-AZ at ambient temperature, which increases slightly from 60 to 70% with increasing the equivalent ratio of carboxylic acid/aziridine (COOH/AZ) (Table I). However, it decreases to 66% when its COOH/AZ is equal to 1.2/1, because a resulting crosslinked solid material provides stereo hindrance, preventing further crosslinking reaction. And, an excess of acrylic acid is neutralized with secondary amine group of the ring-opening product, which inhibits the intermolecular Michael addition reaction. Polymeric solid obtained from a ratio of COOH/AZ = 0.8/1, which has almost the highest performance properties with different posttreatments (Table II). A posttreatment at  $100^\circ\text{C}$  for 24 h offers a highest gel content (84%). High gel content indicates a highly branched and crosslinked polymeric networks formation (Scheme 2). A crosslinked polymer is obtained from the polymerization of AA with TMPTA-AZ in a COOH/AZ equivalent ratio of 0.8 or 1.0. The physical properties including gel content and hardness also reach to a maximum for the formation of highly crosslinked polymer by this rapid polymerization process.

TABLE I  
Physical Properties of Polymer with Various [CO<sub>2</sub>H]/[AZ] Ratios at Ambient Temperature

Properties	[CO <sub>2</sub> H]/[AZ] ratio			
	0.6/1.0	0.8/1.0	1.0/1.0	1.2/1.0
Gel content (%)	60	68	70	66
Water-uptake (%)	10	24	37	38
Weight-loss in water (%)	4	4	4	4
Ethanol swollen (%)	50	36	31	32
Weight-loss in ethanol (%)	13	8	6	7
Hardness (Shore A)	70	78	76	70

**TABLE II**  
Physical Properties of Polymer with  $[\text{CO}_2\text{H}]/[\text{AZ}] = 0.8/1.0$  with Various Postcuring Conditions

Properties	$[\text{CO}_2\text{H}]/[\text{Aziridine}] = 0.8/1.0$					
	50°C			100°C		
	6 h	12 h	24 h	6 h	12 h	24 h
Gel content (%)	78	78	78	82	83	84
Water-uptake (%)	24	24	24	19	19	15
Weight-loss in water (%)	4	4	4	4	3	4
Ethanol swollen (%)	35	35	35	33	28	25
Weight-loss in ethanol (%)	9	8	5	6	3	0
Hardness (Shore A)	80	81	82	90	96	97

### Hardness

Hardness indicates the elasticity and density of polymeric material. Hardness is 78 Shore A for a polymer obtained from these two monomers with an equivalent ratio of  $\text{COOH}/\text{AZ} = 0.8/1.0$  at ambient temperature. However, its hardness increases with increasing the posttreatment. Its hardness increases to 80 and 90 after posttreating at 50 and 100°C for 6 h, respectively, and it reaches 96 after treating at 100°C for 12 h. The posttreatment at a higher temperature drives further curing reaction, and until 100°C it achieves a maximum crosslinking density. These results coincide with the gel contents of these polymerized materials. These phenomena show that the post-heat treatment provides additional energy to drive a Michael addition reaction toward completion and results in higher crosslinking density. A higher crosslinking density reduces free volume of the polymer, and therefore, the resulting polymer demonstrates a high hardness.

### Water uptake

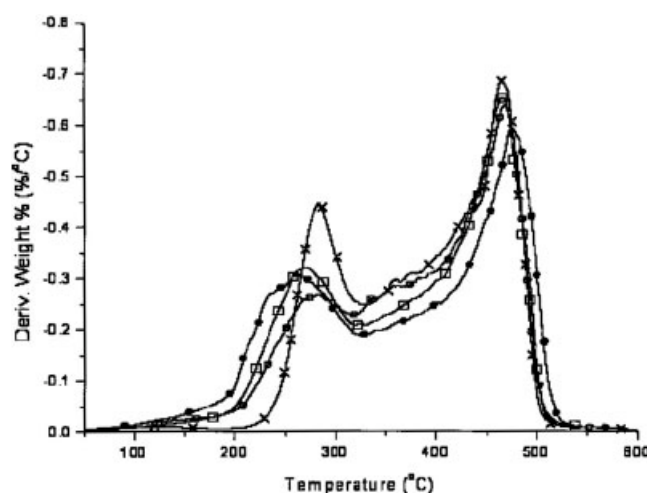
Both of AA and TMPTA-AZ are soluble in water. However, weight-loss in water of the resulted polymers is below 4%, which are obtained from the composition of two monomers in different  $\text{COOH}/\text{AZ}$ , because AA triggers the polymerization reaction and proceeds further for a crosslinked polymeric network formation. There is only a little amount of unreacted material left that dissolves in water.

Water uptake of this polymer reaches a minimum value at a ratio of  $\text{COOH}/\text{AZ} = 0.6/1.0$ , and it increases with increasing AA usage (Table I). For example, for ratios 0.8/1.0 and 1.0/1.0, water uptake of the resulting polymers increase to 24 and 37%, respectively. However, increasing the amount of AA to an equivalent ratio ( $\text{COOH}/\text{AZ}$ ) does not increase the water uptake of polymer, because of a highly networked structure of the final polymer that inhibits further Michael addition and leaves some unreacted carboxylic acid, which is hydrophilic. Less free molecular mobility of polymer limits further crosslinking

reaction at ambient temperature. Water uptake decreases after a prolonged posttreatment at 100°C. The increased post-heating drives further the curing reaction of the crosslinked polymer. For example, water uptake is 24% for a polymer obtained from an equivalent ratio of  $\text{COOH}/\text{AZ} = 0.8/1.0$  at ambient temperature, and this value decreases to 15% after posttreatment at 100°C for 24 h (Table II).

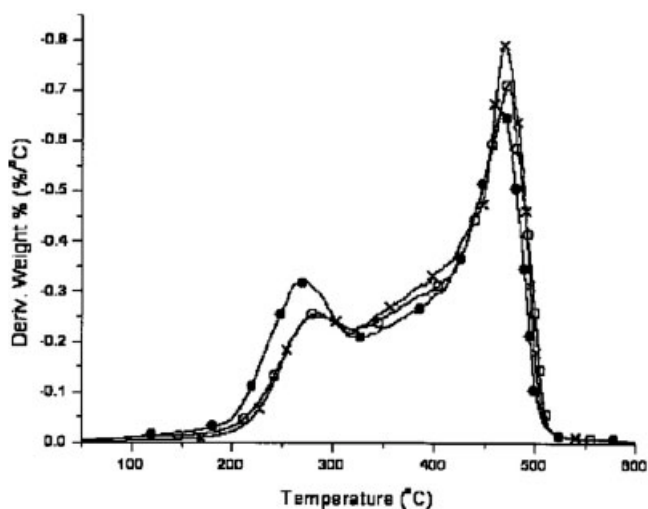
### Ethanol swollen

Weight loss of polymer in ethanol decreases slightly from 13 to 7% with increasing AA usage that is the polymeric material obtained from a rapid polymerization process at ambient temperature (Table I). However, weight loss of polymer in ethanol (with  $\text{COOH}/\text{AZ} = 0.8/1.0$ ) reaches to 3.0% and to 0% after treatment at 100°C for 12 and 24 h, respectively. In the meantime, ethanol swelling of polymer decreases from 35 to 25% after it is posttreated at 100°C/24 h. These indicate that the higher polymeric network formation by a prolonged posttreatment at 100°C (Table II).



**Figure 5** DTA thermogram of polymers obtained from a polymerization at ambient temperature with different ratios of  $\text{CO}_2\text{H}/\text{AZ}$ .  $\text{CO}_2\text{H}/\text{AZ} = 0.6/1.0$  ( $\times$ );  $0.8/1.0$  ( $\square$ );  $1.0/1.0$  ( $\bullet$ );  $1.2/1.0$  ( $\circ$ ).





**Figure 6** DTA thermogram of polymers with  $\text{CO}_2\text{H}/\text{AZ} = 0.8/1.0$  at different post-heating conditions. RT (●);  $50^\circ\text{C}/24\text{ h}$  (○);  $100^\circ\text{C}/24\text{ h}$  (×).

#### Thermogravimetric analysis

Polymeric materials obtained from a rapid polymerization of these two monomers AA and TMPTA-AZ at ambient temperature demonstrate a two-stage degradation on a differential thermogravimetric analysis (DTA) under nitrogen. A first-stage degradation of polymer appears at the range between  $260$  and  $285^\circ\text{C}$ , and a second-stage degradation at  $471$ – $484^\circ\text{C}$  on DTA. The intensity of first degradation peak decreases and that of the second degradation peak increases with increasing COOH/AZ ratio. A higher ratio of COOH/AZ results in low-temperature shift on the first degradation stage. These indicate that the curing reaction of these two monomers at ambient temperature is not quite completed yet (Fig. 5). The first degradation peak indicates amino-ester polymer branch with a less crosslinking density. The polymer curing reaction proceeds further at  $100^\circ\text{C}$  for 24 h via a Michael addition. In the meantime, its second degradation peak intensity becomes higher than that before heating. These DTA thermograms of polymeric materials show that the post-heating treatment promotes a higher crosslinking density of polymer, which is also demonstrated by gel content and other physical properties (Fig. 6).

#### CONCLUSIONS

A new crosslinked polymeric material is obtained from a polymerization process of a  $\alpha,\beta$ -unsaturated double-bond-containing compound, such as acrylic acid (AA) with trimethylolpropane tris(1-aziridinepropionate) (TMPTA-AZ). An exothermic neutralization of carboxylic acid of AA with aziridine of

TMPTA-AZ at mixing of these two monomers triggers a ring-opening reaction, resulting in an amino-ester bond formation, and then the amino group reacts further with  $\alpha,\beta$ -unsaturated acrylic double bond via a Michael addition reaction in continuous stepwise polymerization process. This polymerization process of AA with TMPTA-AZ takes place immediately on mixing at ambient temperature and then leads to the formation of crosslinked polymeric materials. Its polymerization and curing reaction are driven further by post-heat treatment. This rapid polymerization process of AA and TMPTA-AZ leads to a highly crosslinked polymer, which has the potential for use as instant adhesive, sealant, composite material or other applications.<sup>27</sup>

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