

# Photopolymerizable Hyperbranched (Meth)acrylated Poly(amine ester)

Huanyu Wei,<sup>1</sup> Huiguang Kou,<sup>1</sup> Wenfang Shi,<sup>1</sup> Kangming Nie,<sup>2</sup> Yuchuan Zhan<sup>2</sup>

<sup>1</sup>State Key Laboratory of Fire Science and Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

<sup>2</sup>Institute of Chemical Engineering, Anhui University, Hefei, Anhui 230039, People's Republic of China

Received 25 September 2001; accepted 1 February 2002

**ABSTRACT:** A hyperbranched (meth)acrylated poly(amine ester) (HPAE-2-A) was synthesized by the modification of the hydroxyl end groups of the second generation of a hyperbranched poly(amine ester) with acryloyl chloride and methacrylic anhydride. The photopolymerization kinetics were investigated with photo-differential scanning calorimetry and Fourier transform infrared. The properties of HPAE-2-A, including the dynamic viscosity, pendulum hardness, and shrinkage, were also studied in comparison with those of a hyperbranched methacrylated poly(amine ester) (HPAE-2-MA) prepared in the laboratory and tradi-

tional epoxy acrylate and epoxy methacrylate. HPAE-2-A polymerized rapidly under UV irradiation in the presence of a photoinitiator and had a higher final conversion of double bonds. The thermomechanical properties of UV-cured HPAE-2-MA films were compared with those of EB-cured films measured with a dynamic mechanical thermal analyzer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 168–173, 2003

**Key words:** hyperbranched; radiation; photopolymerization; kinetics (polym.)

## INTRODUCTION

Dendrimers with polymer molecules of regular, spherical shapes, which grow from a core molecule in layers called generations, and hyperbranched polymers with irregular molecular structures, which grow through the repeated reactions of multifunctional monomers (e.g., AB<sub>2</sub>) with or without core molecule addition, constitute a new family of dendritic macromolecules.<sup>1,2</sup> However, recently developed hyperbranched polymers are more attractive for some applications, such as adhesives,<sup>3</sup> coatings,<sup>4,5</sup> and thermoplastics,<sup>6</sup> because of their simple synthesis routes, their unique highly branched molecular structures, and their large number of functional end groups in comparison with traditional linear polymers. Although significant progress has been made in research on hyperbranched polymers for various applications,<sup>7</sup> there is still not much information on their applications in radiation-curable coating systems.<sup>8,9</sup>

In this work, we synthesized a hyperbranched (meth)acrylated poly(amine ester) (HPAE-2-MA/A) containing a maximum of 12 (meth)acrylic end groups on the molecular chains. The photopolymerization kinetics and properties of the UV-cured films of HPAE-

2-A were compared with those of HPAE-2-MA as well as traditional linear epoxy (meth)acrylates.

## EXPERIMENTAL

### Materials

A hyperbranched poly(amine ester) theoretically having 12 hydroxyl groups (HPAE-2) was synthesized from 1,1,1-trihydroxymethyl propane as a core molecule and *N,N*-diethylol-3-amine methylpropionate as an AB<sub>2</sub> monomer by a pseudo-one-pot divergent procedure.<sup>10</sup> Acryloyl chloride was prepared from the reaction of acrylic acid with benzyl chloride in our laboratory. Methacrylic anhydride was supplied by Aldrich (Germany). 2-Hydroxyl-2-methyl-1-phenyl-1-propanone (Darocur 1173) and benzoyl-1-hydroxyl-cyclohexanol (Irgacure-184), supplied from Ciba-Geigy (Switzerland), were used as photofragmenting initiators. Hexandiol diacrylate (HDDA), supplied by Sartomer Co. (United States), was used as a comonomer. Epoxy acrylate (E44-A) and epoxy methacrylate (E44-MA) were synthesized from an epoxy resin (E44) with a molar mass of about 600 (Third Reagent Co., Shanghai, China) in our laboratory.

### Synthesis

HPAE-2 (15.65 g, 0.01 mol) was mixed with 30 mL of dichloromethane and 20 mL of triethylamine. The mixture was slowly dropped into an ice-cooled reac-

Correspondence to: W. Shi (wfshi@ustc.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 2007403.

tion vessel containing 10.8 mL (0.133 mol) of acryloyl chloride and was stirred at ambient temperature until the disappearance of the hydroxyl peak ( $3500\text{--}3200\text{ cm}^{-1}$ ) in the Fourier transform infrared (FTIR) spectrum. The obtained solution was extracted stepwise with a 1M HCl solution, a 10% NaHCO<sub>3</sub> solution, and distilled water, was dried with anhydrous MgSO<sub>4</sub>, and was filtered. Finally, dichloromethane was evaporated from the solution, and this gave 20.5 g of a yellowish viscous liquid in a 92% yield.

A given amount of an HPAE-2 solution in 30 mL of dichloromethane was end-capped with methacrylic anhydride according to the same procedure used for the preparation of HPAE-2-A, and this produced HPAE-2-MA.

### UV/EB curing

HPAE-2-A and HPAE-2-MA were mixed with Irgacure 184 (3 wt %) and then exposed to a UV lamp (1 kW, 40 mw/cm<sup>2</sup>; Lantian Co., Beijing, China) at variable conveyor speeds in air. An HPAE-2-MA sample was also irradiated with a pulsed sweeping electron beam, which was produced by a microtron accelerator with an energy of 6.5 MeV and a current of 80 mA in N<sub>2</sub> until a tack-free state was obtained.

### Measurements

The concentration of double bonds ( $C_E$ ) was determined by titration. About a 120-mg sample was dissolved in a 10-mL mixture solution of acetic acid, CCl<sub>4</sub>, methanol, and diluent sulfuric acid together with 7 mL of a 10% HgCl<sub>2</sub> solution, and then a 3-mL solution of KBr and KBrO<sub>3</sub> and 0.4 mL of hydrochloride were added and mixed homogeneously. After the mixture solution was kept in the dark for 30 min, 0.3 g of KI was added and mixed, and then it was kept in the dark for 5 min. Finally, the mixture solution was titrated with a NaS<sub>2</sub>O<sub>3</sub> standard solution and a starch solution indicator. The empty experiment was performed with the same procedure. The theoretical concentration of double bonds ( $C_T$ ) was calculated from the theoretical molar mass and double-bond number. The viscosity of the resins was detected with a QNX spinning viscometer (Tianjin Instrument Co., China) at a speed of 750 rpm at 50°C. The conversion of vinyl groups in the cured films was determined with a Magna-IR 750 spectrometer (Nicolet Instrument Corp., United States) with an absorption intensity of double bonds of  $815\text{ cm}^{-1}$  for methacrylate or  $809\text{ cm}^{-1}$  for acrylate. The spectra were normalized with the carbonyl peak at  $1728\text{ cm}^{-1}$  as an internal standard. The pendulum hardness of the cured films was determined with a QBY pendulum apparatus (Tianjin Instrument). The films were prepared on glass plates (100 mm × 90 mm × 5 mm) by an applicator with a

100- $\mu\text{m}$  gap. The shrinkage was calculated on the basis of density measurements of both the cured film and the resin by the following formula:<sup>11</sup> shrinkage (%) =  $100 \times (d_p - d_m)/d_p$ , where  $d_p$  is the density of the cured film and  $d_m$  is the density of the resin. The maximum shrinkage and theoretical shrinkage were calculated by the following formula:<sup>12</sup> maximum shrinkage (%) =  $2.58 + 3100 \times N/M$ , where  $N$  is the functionality of the oligomer,  $M$  is the average molecular weight of the oligomer, and the conversion is taken into account the theoretical shrinkage is calculated. A dynamic mechanical thermal analyzer (DMTA; Rheome Tric SCI Apparatus, Ltd., United States) was used to measure the tensile storage modulus ( $E'$ ) and the tensile loss factor ( $\tan \delta$ ) of UV/EB-cured films at a frequency of 1 Hz and at a heating rate of  $2^\circ\text{C min}^{-1}$  from 20 to 200°C.

The photopolymerization kinetics were monitored with a modified CDR-1 differential scanning calorimeter (Shanghai Balance Instrument Co.). Darocur 1173 as an initiator was applied at a concentration of 3 wt %. The digitized data, based on the trace on a strip chart recorder, were analyzed by Origin 5.0 software on a personal computer. A UV spot-cure system (BHG-250; Mejiro Precision Co., Japan) was used for the irradiation of the samples in N<sub>2</sub>. The incident light intensity at the sample pan position was measured to be  $2.04\text{ mW/cm}^2$ . The conversion of double bonds ( $P$ ) was calculated by the following formula:  $P = H_t/H_\infty$ , where  $H_t$  is the heat effect within  $t$  seconds and  $H_\infty$  is the heat effect of 100% double-bond conversion. Differential scanning calorimetry (DSC) curves were adjusted by the weight of the sample (g). The polymerization rate was defined by % s<sup>-1</sup>, that is, the variation (%) of the double bonds per second. For the calculation of the polymerization rate and  $H_\infty$ , the values of the heat of polymerization,  $\Delta H_0 = 86\text{ J/mmole}^{13}$  (per acrylic double bond), were taken.

## RESULTS AND DISCUSSION

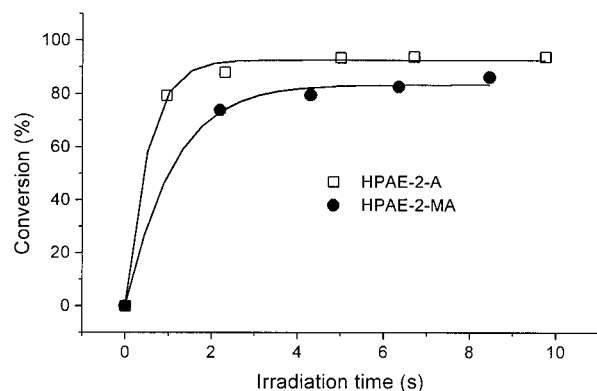
### Characteristics

The idealized formulae of HPAE-2, HPAE-2-A, and HPAE-2-MA are shown in Figure 1. The concentrations of double bonds of HPAE-2-A and HPAE-2-MA, determined by titration, are given in Table I. The results show that the substitution degree of hydroxyl groups with both acrylic and methacrylic groups,  $C_E/C_T$ , where  $C_E$  is the value obtained from experiment measurements and  $C_T$  is the value obtained from the theoretical calculation, reached approximately 90%, which was close to the values of linear oligomers.

### Viscosity

The viscosity of an oligomer is an important parameter for a UV-curing coating system because it affects





**Figure 4** Unsaturation conversion of HPAAE-2-A and HPAAE-2-MA as a function of the irradiation time as measured by FTIR.

photopolymerization kinetics of a multifunctional oligomer are the rate at peak maximum ( $R_p^{\max}$ ) and the final degree of double-bond conversion ( $P^f$ ). The photopolymerization kinetics of an HPAAE-2-A resin by photo-DSC measurements are given in Figure 3.  $R_p^{\max}$  for the HPAAE-2-A resin is  $2.82\% \text{ s}^{-1}$ ; that is, 2.82% of the double bonds are reacted per second, and 12 s is needed to reach  $R_p^{\max}$ .  $P^f$  of HPAAE-2-A is 82%, which is very close to that of traditional acrylate oligomers. The higher  $P^f$  for the HPAAE-2-A resin indicates that the acrylic end groups located on the outer layer of the spherulike structure are only slightly trapped in the network and are highly accessible for polymerization.

The conversion of double bonds of HPAAE-2-A and HPAAE-2-MA was also determined by the monitoring of the IR absorption intensity of acrylic and methacrylic groups (out-of-plane deformation vibration), respectively. In Figure 4, it can be seen that both the UV-curing rate and the conversion of double bonds of the HPAAE-2-A resin are higher than those of HPAAE-2-MA. After 2 s of irradiation, over 85% conversion of the double bonds is obtained for HPAAE-2-A, and then the conversion levels off. However, over 70% conversion of the double bonds is obtained for HPAAE-2-MA after 4 s of irradiation. After 8 s of irradiation, double-bond conversions over 90 and 85% for HPAAE-2-A and HPAAE-2-MA, respectively, are obtained. The higher curing rate and conversion of double bonds of

HPAAE-2-A are attributable to the higher reactivity of its acrylic groups.

### Shrinkage

Shrinkage is usually generated with fast cured films, especially for UV/EB-cure systems, and this affects the adhesion of films to substrates. Shrinkage always occurs during polymerization and results from the replacement of relatively weak, long-distance intermolecular van der Waals bonds by stronger, shorter covalent bonds between the carbon atoms of different units. The theoretically calculated and experimentally determined data of shrinkage are listed in Table II. The acrylated HPAAE-2 has lower shrinkage than methacrylated HPAAE-2, and this is different from conventional linear oligomers. It may be explained that the large numbers of acrylic end groups of HPAAE-2-A, which have higher reactivity than methacrylic end groups, make vitrification easier. Magny et al.<sup>12</sup> already observed that conversion continues but shrinkage remains constant when a given value of the double-bond conversion is reached for highly functionalized acrylates. This means that early vitrification limits shrinkage to some degree. The lower shrinkage usually contributes to stronger adhesion to the matrix. Therefore, it is expected that better adhesion to the matrix can be obtained with HPAAE-2-A as an oligomer of UV-curable coatings.

### Pendulum hardness

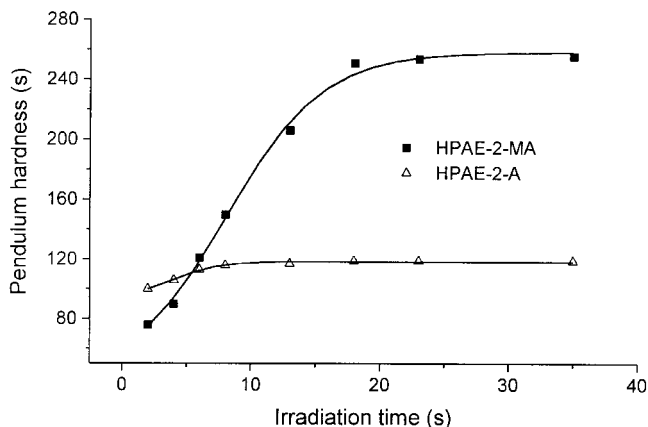
The hardness of the UV-cured films is also an important parameter in their applications. The pendulum hardnesses of HPAAE-2-A and HPAAE-2-MA are given in Figure 5. The pendulum hardnesses of the two resins exhibit different increasing tendencies with the UV irradiation time. HPAAE-2-MA needs 18 s to reach the maximum value, but for HPAAE-2-A, only 8 s is needed. The final pendulum hardness of HPAAE-2-A is about 50% lower than that of HPAAE-2-MA because of the increase in the rigidity of the network resulting from the large number of methyls in HPAAE-2-MA.

**TABLE II**  
Shrinkage of the UV-Cured HPAAE-2-A and HPAAE-2-MA Films

Sample	Unsaturation conversion <sup>a</sup> (%)	Maximum shrinkage (%)	Theoretical shrinkage <sup>b</sup> (%)	Experimental shrinkage (%)
HPAAE-2-MA	85	13	11	8.9
HPAAE-2-A	94	19	18	5

<sup>a</sup> Measured by FTIR.

<sup>b</sup> Calculated by taking conversion into account.



**Figure 5** Pendulum hardness of UV-cured films of HPAE-2-A and HPAE-2-MA as a function of the irradiation time.

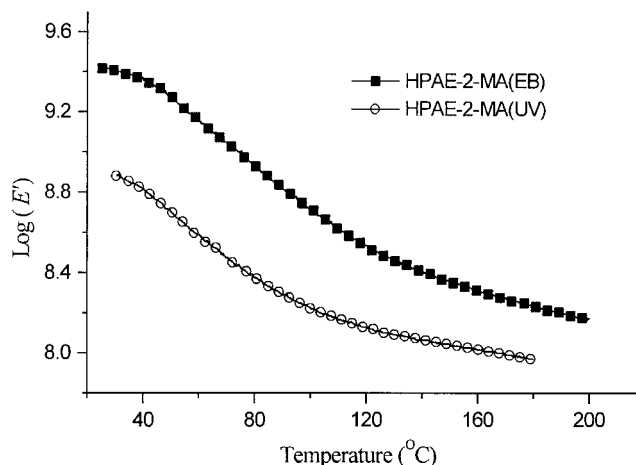
### Thermal mechanical properties

The dynamic mechanical thermal properties of UV/EB-cured films were measured with the DMTA. The softening point ( $T_s$ ) is defined as the extrapolated onset of the drop of  $\log(E')$ . The glass-transition temperature ( $T_g$ ) is defined as the peak of the  $\tan \delta$  curve. The  $T_s/T_g$  ratio expresses the width of the  $\tan \delta$  peak; a higher  $T_s/T_g$  ratio usually leads to a narrower  $\tan \delta$  peak. The crosslink density ( $V_e$ ) was calculated from the following formula:  $V_e = E'/3RT$ ,<sup>15</sup> where  $R$  is the gas constant and  $T$  is the temperature in kelvins. The results obtained from the DMTA measurements are listed in Table III.

As shown in Figures 6 and 7, the UV and EB-cured films exhibit the same thermal behaviors. However,  $T_s$  and  $T_g$  of the film by EB irradiation shift upward from 40 and 73°C to 43 and 86°C, respectively, in comparison with those of the film by UV irradiation. It is well known that an almost 100% double-bond conversion is usually obtained with EB-curing systems, whereas in UV-cured films, about 20% of residual double bonds can be detected. For HPAE-2-MA, the double-bond conversion is about 85%, as described previously. Lower residual unsaturation generally leads to higher  $V_e$ . Moreover, because of the high energy of the EB system, in addition to the double-bond conversion, extra crosslink reactions can occur between radicals resulting from bond fracture. Therefore, 8.3 mmol/cm<sup>3</sup> for the UV-cured film goes to 12.8 mmol/cm<sup>3</sup> for the EB-cured film according to the calculation of  $V_e$ . As a result, higher  $T_s$  and  $T_g$  values of the EB-cured

**TABLE III**  
DMTA Results of the UV/EB-Cured HPAE-2-MA Films

Sample	$T_s$ (°C)	$T_g$ (°C)	$T_s/T_g$	$V_e$ (mmol/cm <sup>3</sup> )
HPAE-2-MA (EB)	40	83	0.88	12.8
HPAE-2-MA (UV)	38	73	0.90	8.3

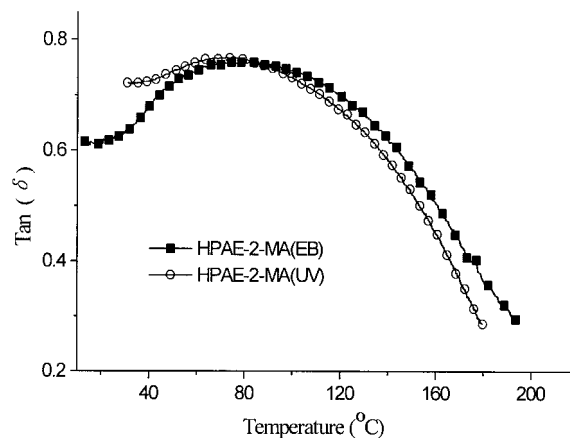


**Figure 6**  $\log(E')$  versus temperature for UV/EB-cured films of HPAE-2-MA.

film in comparison with those of the UV-cured film were obtained from the same resin. The wide  $\tan \delta$  peaks of the two films indicate both have inhomogeneous crosslink networks resulting from the reaction of not only intermolecules but also intramolecules.

### CONCLUSIONS

HPAE-2-A exhibits a higher photopolymerization rate and a higher conversion of double bonds than HPAE-2-MA according to both photo-DSC and FTIR measurements. HPAE-2-A has a lower viscosity than E44-A and E44-MA without and with HDDA addition but is much more flexible and has lower shrinkage than HPAE-2-MA.  $V_e = 8.3$  mmol/cm<sup>3</sup> for the UV-cured HPAE-2-MA film goes up to  $V_e = 12.8$  mmol/cm<sup>3</sup> for the EB-cured HPAE-2-MA film. According to the properties observed in this study, HPAE-2-A has potential for use in radiation-curable coatings, adhesives, and composite systems.



**Figure 7**  $\tan \delta$  versus temperature for UV/EB-cured films of HPAE-2-MA.

**References**

1. Kim, Y. H. *J Polym Sci Part A: Polym Chem* 1998, 36, 1685.
2. Chow, H. F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* 1998, 54, 8543.
3. Nummelin, S.; Skrifvars, M. R. K. *Top Curr Chem* 2000, 210, 1.
4. Lange, J.; Stenroos, E.; Johansson, M.; Malmström, E. *Polymer* 2001, 42, 7403.
5. van Benthem Rolf, A. T. M. *Prog Org Coat* 2000, 40, 203.
6. Ratna, D.; Simon, G. P. *Polymer* 2001, 42, 8833.
7. Hult, A.; Johansson, M.; Malmström, E. *Adv Polym Sci* 1999, 143, 1.
8. Wei, H. Y.; Kou, H. G.; Shi, W. F.; Yuan, H. Y.; Chen, Y. L. *Polymer* 2001, 42, 6741.
9. Wei, H. Y.; Lu, Y.; Shi, W. F. *J Appl Polym Sci* 2001, 80, 51.
10. Lu, Y.; Lin, D.; Wei, H. Y.; Shi, W. F. *Acta Polym Sinica* 2000, 4, 411.
11. Acham, N.; Crisp, J.; Holman, R.; Kakkar, S.; Kennedy, R. *Proceedings of the RadTech Europe '97 Conference, Maastricht, The Netherlands, 1995*; p 71.
12. Magny, B.; Muzeau, E.; Pezron, E. *Proceedings of the RadTech Europe '97 Conference, Lyon, France, 1997*; p 29.
13. Andrzejewska, E.; Andrzejewski, M. A. *J Polym Sci Part A: Polym Chem* 1998, 36, 665.
14. Karen, L. W.; Fréchet, J. M. J. *Polymer* 1994, 35, 4489.
15. Gillham, J. K. *Polym Eng Sci* 1986, 26, 1429.