# UV Curing Behavior of Methacrylated Hyperbranched Poly(amine-ester)s

HUANYU WEI,[1] YU LU,[1] WENFANG SHI,[1] HUIYA YUAN,[2] YONGLIE CHEN[2]

[1] 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

[2] Institute of Polymer Science, Zhongshan University, Guangzhou, Guangdong 510275, People's Republic of China

**ABSTRACT:** Methacrylated hyperbranched poly(amine ester)s as oligomers in radiation curing resins have a lower viscosity and a higher cure speed. Their viscosity was reduced sharply when an amount of a monomer was added or the temperature was increased. Their polymerization rate and final conversion of the double bond differ with the variation of the chemical structure of the end group, molar mass, and monomer content. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 51–57, 2001

**Key words:** hyperbranched poly(amine-ester); dendrimer; UV curing; oligomer

## INTRODUCTION

It has been only about 10 years since the first patent of a hyperbranched polymer was granted.[1] Now, hyperbranched polymers that are homologs of dendrimers have attracted increasing attention both from a fundamental viewpoint and for the great variety of expected applications. It seems that hyperbranched polymers might be good alternatives to dendrimers, since these often omit several protection and deprotection steps between successive generations and then can be produced on a large scale at a reasonable cost. Several demonstrations suggested uses of hyperbranched polymers or dendrimers in such areas as drug delivery,[2] rheology modifiers,[3] nonlinear optics, and coatings.[4,5] Only a few studies are devoted to their behavior on UV curing.[6,7]

UV-curing technology is increasingly used in various sectors of applications, mainly in the coating industry, graphic arts, and microelectronics due to its high efficiency, environmental protection, and saving of energy. Most often, a UV-curable resin consists of oligomers and multifunctional monomers that polymerize to form a highly crosslinked polymer network, additives of various types, and a photoinitiator that yields reactive initiation species upon UV exposure.

The hyperbranched polyfunctional polyesters, as a new kind of oligomer in UV-curable resin formulations, have some superior properties. Compared with the linear oligomer of similar molecular weight, the viscosity of hyperbranched polyester is much lower due to being without the entanglement of flexible molecular chains.[6] The methacrylated hyperbranched polyester carries a number of end double bonds, so that the high reactivity of the resin formulation will be obtained. The major object of this study was to investigate the effects of the comonomer content and temperature on the viscosity of methacrylated hyperbranched poly(amine-ester) and their polymerization behavior by the measurements of the tack-free time, reaction rate, and conversion of unsaturation.

HPAE-3

X=    a) [MAA structure with O, CH3]    (—MAA)

    b) [SA structure]    (—SA)
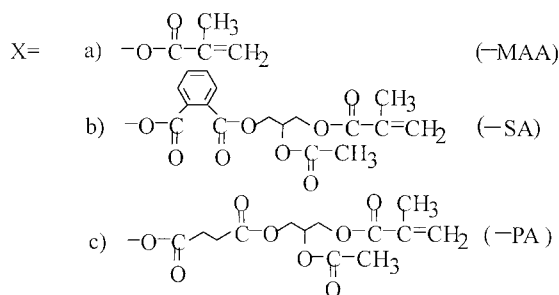
    c) [PA structure]    (—PA)
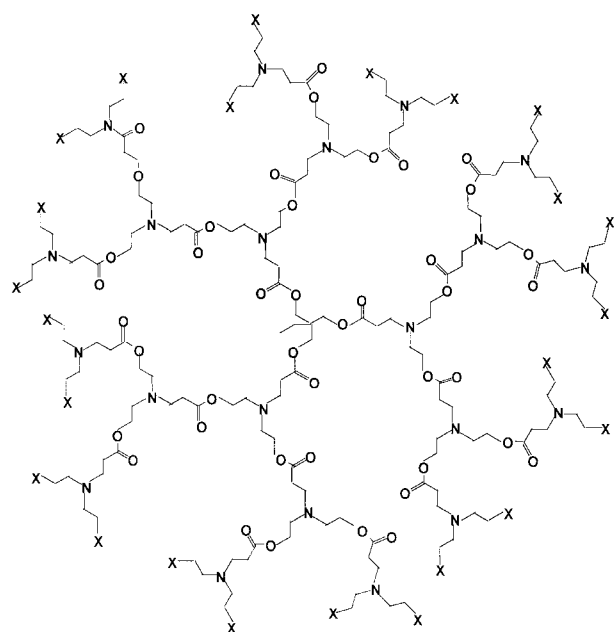
**Figure 1**   Idealized formula of the third generation of methacrylated hyperbranched poly(amine-ester).

## EXPERIMENTAL

### Materials

Synthesis and characteristics of the second and third generations of modified methacrylated hyperbranched poly(amine-ester)s HPAE-2–methacrylic anhydride (MAA), HPAE-3–MAA, HPAE-2–succinic anhydride (SA), and HPAE-2–phthalic anhydride (PA) were described elsewhere.[8,9] The idealized chemical formula of the third generation of hyperbranched methacrylated poly(amine-ester) is given in Figure 1.

1-Benzoylcyclohexanol-2 (I-184) and 2-hydroxy-2-methyl-phenyl-propan-1-one (Darocur 1173) were used as photoinitiators (supplied by Ciba Geigy, Basel, Switzerland). The multifunctional comonomers added to the formulations were 1,6-hexanediol diacrylate (HDDA) and tripropane glycol diacrylate (TPGDA) (supplied by Sartomer Co., West Chester, PA, USA).

### UV Curing

The resin formulations were UV-irradiated with a high-pressure mercury lamp (1 kW, HPM 15 from Philips, Belgium) built into a UV CURE device constructed in our laboratory, with a distance of 10 cm from lamp to specimen and at room temperature in $N_2$.
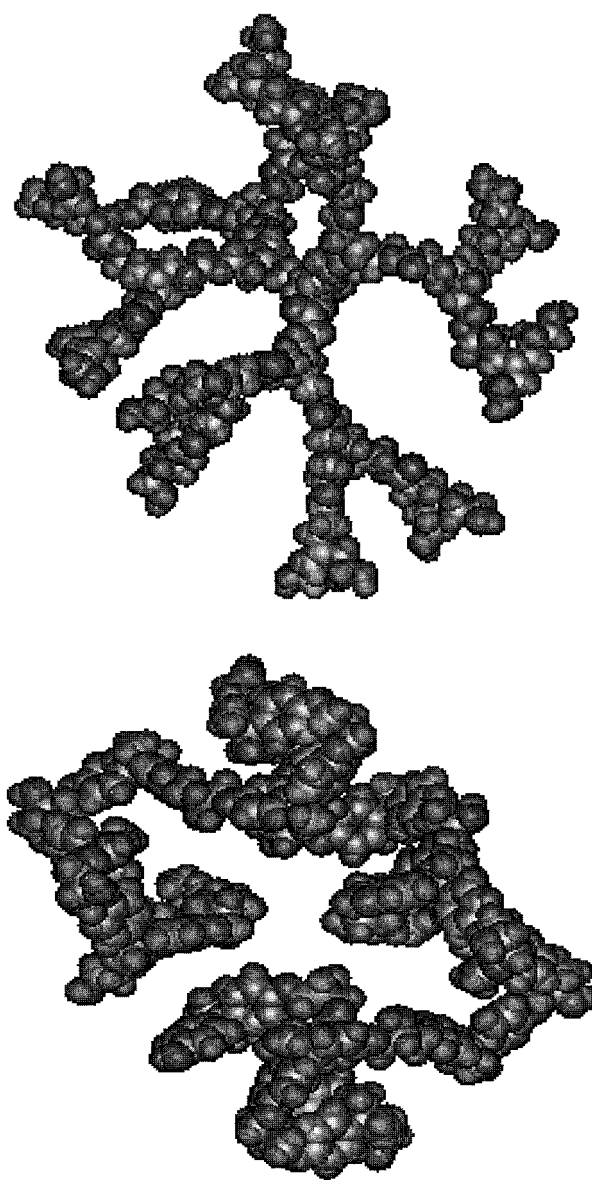


**Figure 2**   Computer simulations of HPAE-3-SA (MW 3300) and linear epoxy acrylate (MW 4000).
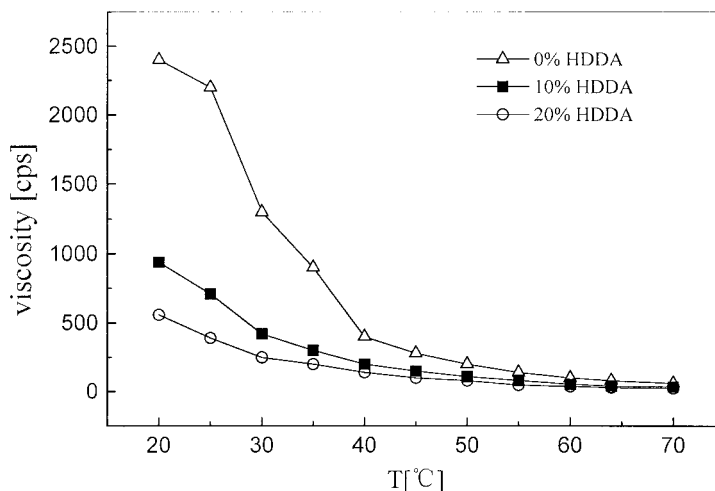
**Figure 3** Function of viscosity of HPAE-2-MAA as the temperature and the comonomer content.

## Measurements

### Viscosity

The viscosity of the obtained products was measured with a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) with the speed of 750 rpm.

### Tack-free Time

The tack-free time was evaluated as the exposure time required to reach a completely tack-free state by touching the surface with a cotton ball under a weight of 200 g for 30 s after UV exposure.

### Conversion of Unsaturation

The conversion of unsaturation in the UV-cured films was determined with a MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA) using the methacrylic double bond at 810 cm$^{-1}$ (out-of-plane deformation vibration) by a baseline method. The spectra were normalized with the carbonyl peak at 1719 cm$^{-1}$ as an internal standard to account for variations in sample thickness and instrument recording. The double-bond content of the uncured formulation was defined as 100%.

### Photopolymerization Kinetics

The photopolymerization kinetics were monitored by a modified CDR-1-type DSC (made by the Shanghai Balance Instrument Plant, Shaihai, China). The digitized data based on the trace on a strip chart recorder were analyzed by software Microcal Origin 5.0 on a personal computer. The initiator Darocur 1173 was applied in a concentration of 3 wt %. A 250-W medium-pressure mercury lamp equipped with a quartz glass filter was used for the irradiation. The incident light intensity at a sample pan position was measured to be 0.48 mW/cm$^2$. Polymerization was carried out in an inert atmosphere.

## RESULTS AND DISCUSSION

### Viscosity

The viscosity of an oligomer is an important parameter in UV-curing technology that affects the cure process and properties of the cured films. The viscosity of a polymer is related to the dynamic extension of the molecules and the segment density within the volume of a molecule and in-

**Table I   Tack-free Time for Resins with Different Oligomers and Photoinitiators**

| Photoinitiator | HPAE-2-MAA | HPAE-2-PA | HPAE-2-SA | HPAE-3-PA |
|---|---|---|---|---|
| I-184 (4 wt %) | < 1.5 s | < 1.5 s | < 1.5 s | < 1.5 s |
| BP (5 wt %) | 4 s | 8 s | 7 s | 9 s |

**Table II   Concentrations of Double Bonds of Different Oligomers (mmol/g)**

| | Oligomer | | | |
| --- | --- | --- | --- | --- |
| | HPAE-2-MAA | HPAE-2-PA | HPAE-2-SA | HPAE-3-SA |
| Theoretical ($C_T$) | 5.04 | 2.16 | 2.4 | 2.30 |
| Experimental ($C_E$) | 4.54 | 1.86 | 2.16 | 2.15 |
| $C_E/C_T$ | 0.90 | 0.86 | 0.90 | 0.94 |

termolecular chain entanglement. There is an important structural difference between linear oligomers and hyperbranched polymers. A linear oligomer of sufficient molecular weight contains an entanglement of flexible molecular chains, while a hyperbranched polymer is a compact molecule with many branches which carry a high number of terminal functional groups on each molecule, and no entanglement of the chains was observed. The computer simulations of both are given in Figure 2.

As Figure 3 shows, the viscosity of HPAE-2–MAA is reduced sharply as the monomer HDDA
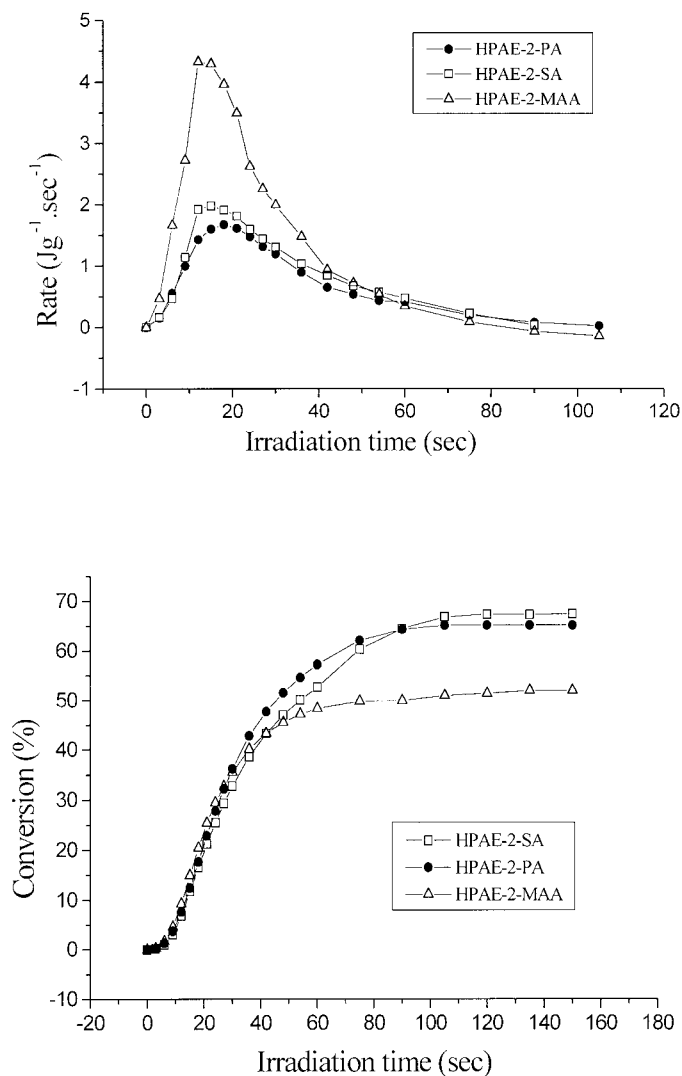


**Figure 4**   Reaction rate and unsaturation conversion of polymers with different molecular structures.
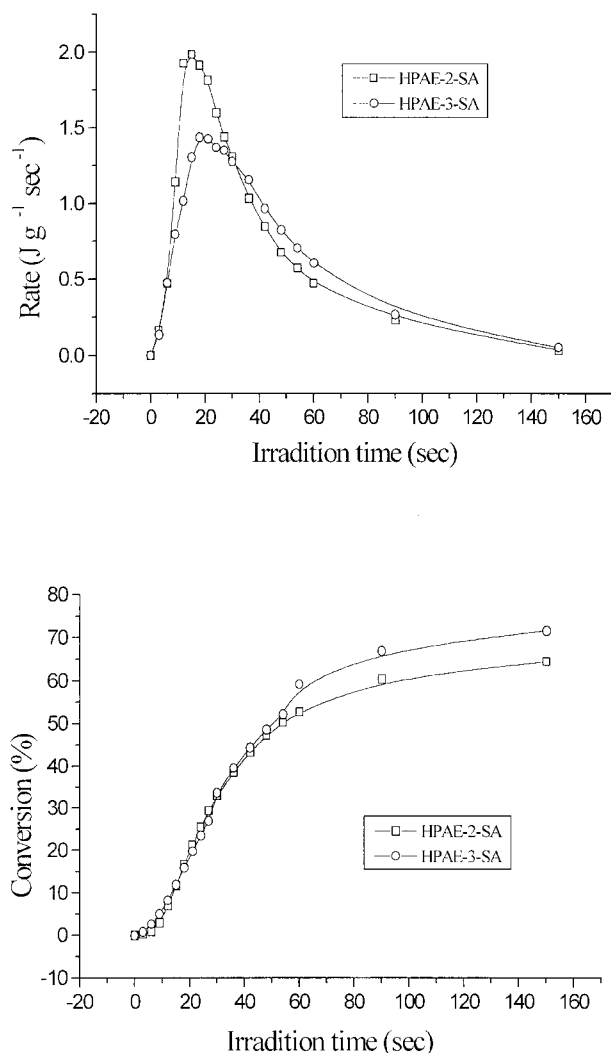
**Figure 5** Reaction rate and unsaturated conversion of the second and third generations of hyperbranched polymer.

is added into the system at the same temperature. However, the melt viscosity of HPAE-2–MAA without HDDA addition is also reduced rapidly as the temperature increases. This is a characteristic of the spherelike molecule. When the monomer is added or the temperature increases, the interaction between spherelike molecules is obviously reduced and the viscosity is observed to decrease.

## Photopolymerization Characteristics

The cure rate of the resin system is of great importance as time and energy consumption is of concern in applications. The tack-free time is evaluated as the exposure time required to obtain a completely tack-free state. It was found that the resins with oligomer HPAE-2–MAA,

HPAE-2–PA, HPAE-2–SA, and HPAE-3–PA in the presence of I-184 (4 wt %) were rapidly polymerized within 1.5 s curing time under 1 kW lamp exposure to obtain a tack-free state. However, in the case of 5% benzophenone (BP), the four resins were cured in 4, 8, 7, and 9 s, respectively (Table I).

## Photopolymerization Kinetics

The concentrations of the double bond of different HPAE oligomers are given in Table II. The rate of polymerization depends first of all on the reactivity of the functional groups, on their concentration, and on the viscosity of the resin, whereas the chemical structure and functionality of both the oligomer and the monomer determine the degree of polymerization. Although the mobility of the polymer network plays a dominant role in determining the value of final conversion, the diffusional limitations caused by a high initial viscosity of the formulation are the crucial factors.

The most important parameters characterizing the cure kinetics of multifunctional oligomers are the rate at peak maximum and the final degree of double-bond conversion. The discussion of the results in this sector is based mainly on the values of these parameters obtained for the polymerization of the individual formulation.

### *Influence of the Chemical Structure of the End Group*

Methacrylated hyperbranched poly(amine-ester) is obtained by two methods[9]: One is directly esterified with MAA; the other is first esterified with SA (or PA), then reacted with glycidyl methacrylate. As shown in Figure 4, the reaction rate of the oligomer (HPAE-2–MAA) produced by the first method is much higher than that of the oligomers (HPAE-2–SA and HPAE-2–PA) produced by the second method and also less time is needed to reach the maximum rate. This is because the former has a higher concentration of double bonds, higher reactivity of double bonds because of its less steric hindrance, and higher molecular mobility because of its lower viscosity. Although the viscosity of HPAE-2–SA and HPAE-2–PA are nearly the same, HPAE-2–SA has a higher concentration of double bonds and a higher reactivity than has HPAE-2–PA. As a result, the rate of HPAE-2–SA is a little higher than that of HPAE-2–PA. However, when a comparison is made of the conversion of double bonds of these three oligomers, the opposite result is obtained.
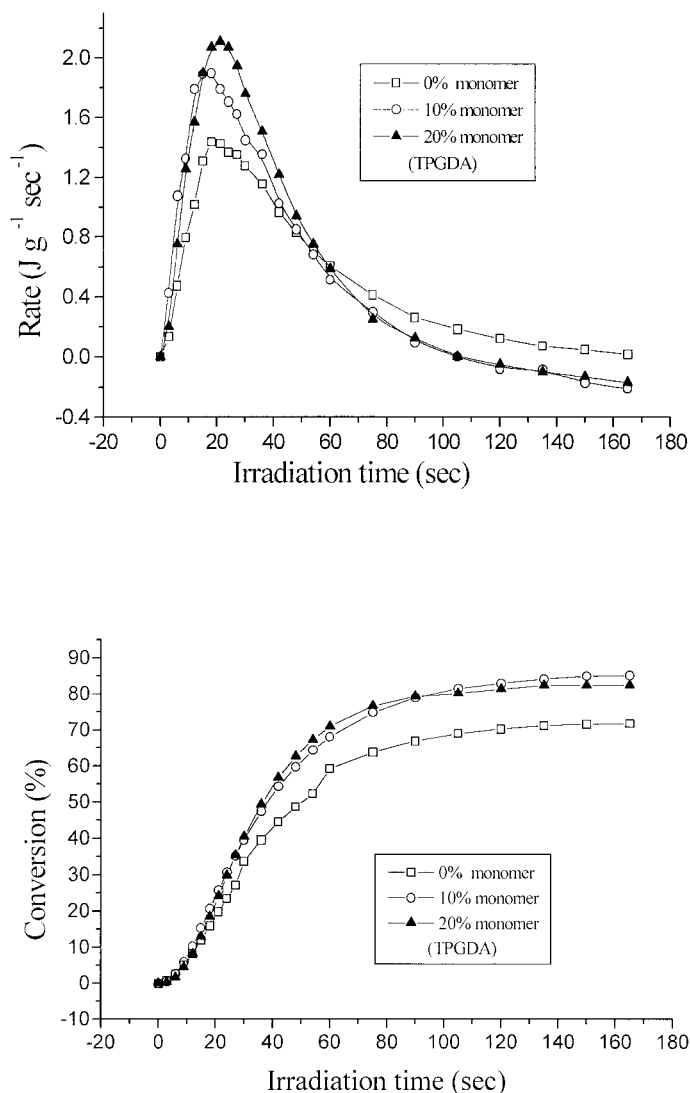
**Figure 6** Reaction rate and unsaturation conversion of different comonomer contents.

This is because the polymer network formed by HPAE-2–MAA has a higher crosslink density and lower mobility because of its higher initial concentration of double bonds, which leads to some double bonds being trapped and unable to react in the three-dimension polymer network.

### Influence of Molar Mass

HPAE-2–SA and HPAE-3–SA are, respectively, the second generation and the third generation of hyperbranched methacrylated poly(amine-ester)s with the same end group. As seen from Figure 5, HPAE-2–SA has higher reaction rate compared with HPAE-3–SA and also needs a shorter time to reach the maximum rate. It can be interpreted that the viscosity of the oligomer determines the reaction rate when the concentration and reactivity of the double bonds of the two oligomers are nearly the same. The lower viscosity of HPAE-2–SA makes the molecule mobilize more easily. The same tendency can be observed and the final conversion of the double bonds of HPAE-3–SA is higher when observing the conversion of the double bonds of these two oligomers. This is because the diffusional limitation of long chain radicals caused by the higher initial viscosity of HPAE-3–SA makes termination of the two radicals difficult.

### Influence of the Monomer Content

As shown in Figure 6, the reaction rate and the final conversion of the double bonds of HPAE-
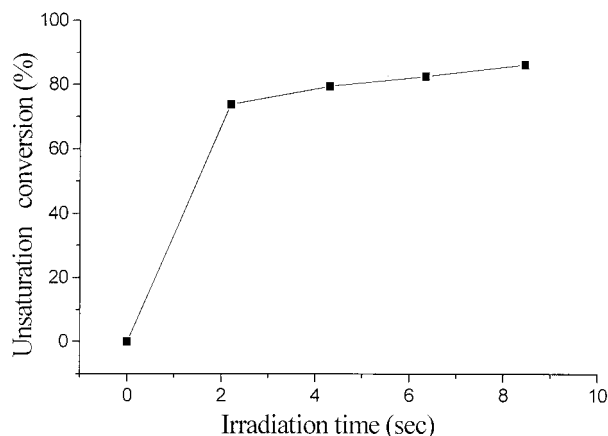
**Figure 7**  Unsaturation conversion in the UV-cured HPA-2-MAA film by FTIR.

3–SA were promoted in different degrees when an amount of TPGDA as the monomer was added. The reason for this is that the concentration of double bonds and the mobility of the molecule increased because of reduction of the viscosity when TPGDA was added. As for the final conversion of double bonds, the TPGDA molecules dispersed the approximately spherical HPAE-3–SA molecules and formed a polymer network between TPGDA and HPAE-3–SA molecules. The polymerization reaction is mainly between TPGDA and HPAE-3–SA, not only between HPAE-3–SA. As a result, the mobility of the polymer network increased. Some HPAE-3–SA molecules, which were trapped in the absence of a comonomer, were released upon the addition of the comonomer and took part in the polymerization reaction and conversion of the double bonds.

**Residual Unsaturation**

The residual unsaturation in the UV cured HPAE-2–MAA film with 3 wt % of Darocur 1173, as a function of the irradiation time, is shown in Figure 7. The residual unsaturation in the HPAE-2–MAA film cured for 2 s is less than 30%. As the irradiation time reaches 8 s, the residual unsaturation decreases to 15%. It can be seen that, after curing, certain amounts of double bonds still

remain in the film substrate. This is interpreted that some residual methacrylic double bonds will be trapped and unable to react in the three-dimensional polymer network formed.[10]

## CONCLUSIONS

The viscosity of hyperbranched methacrylated poly(amine-ester)s as oligomers in radiation curing resins was reduced sharply when an amount of the monomer was added or the temperature was increased. Their polymerization reaction rate and final conversion of double bonds differ with the variation of the chemical structure of the end group, molar mass, and monomer content. HPAE-2–MAA has the highest reaction rate and the lowest final conversion of double bonds. HPAE-2–SA compared with HPAE-3–SA has a higher reaction rate and a lower final conversion of double bonds. The reaction rate and the final conversion of the double bonds of HPAE-3–SA were promoted when an amount of TPGDA as the monomer was added.

## REFERENCES

1. Kim, Y. H. U.S. Patent 4 857 630, 1987.
2. Liu, H.; Uhrich, K. E. Polym Prepr 1997, 38, 582.
3. Garret, D. F. U.S. Patent 5 136 014, 1992.
4. Kuhne, K.; Nuyken, O. Werkst. Informationstech., Symp.1, Werkstoffwoche'96, 1996; p 53.
5. Hardeman, G.; Misev, T. A.; Heyenk, A. WO 9 318 079, 1993.
6. Rånby, B.; Shi, W. F. WO 96 107 688, 1996.
7. Hult, A.; Malmström, E.; Johansson, M.; Sörensen, K. Swed Patent SE 468 771B, 1993.
8. Lu, Y.; Lin, D.; Wei, H. Y.; Shi, W. F. Acta Polym Sin, 2000, 4, 411.
9. Shi, W. F.; Wei, H. Y.; Huang, H. Chin Pat Appl 99 117 623.5, 1999.
10. Rabek, J. F. In Radiation Curing in Polymer Science Technology; Fouassier, J. P.; Rabek, J. F., Eds.; Elsevier: London, New York, 1993; Vol. I, p 329.