Photopolymerization Kinetics of Hyperbranched Acrylated Aromatic Polyester

Huiguang Kou, Anila Asif, Wenfang Shi

State Key Laboratory of Fire Science and Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ABSTRACT: The influences of the irradiation temperature, comonomer content, sample thickness, and photoinitiator concentration on the polymerization kinetics of hyperbranched acrylated aromatic polyester (HAAPE) were investigated with photo-differential scanning calorimetry and IR measurements. The maximum photopolymerization rate increased with the temperature rising up to 110°C but decreased beyond 110°C. An activation energy of 16 kJ mol^{-1} for the photopolymerization was obtained below 110°C from an Arrhenius plot, but it was negative beyond 120°C. A remarkable synergistic effect between HAAPE and the comonomer trimethylolpropane triacrylate with a molar fraction of around 0.4 was observed from a photopolymerization kinetic study of the resins. The final unsaturation conversion in an ultraviolet-cured film decreased with the sample thickness, and this became more remarkable as the photoinitiator concentration increased. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1500–1504, 2003

Key words: hyperbranched; polyesters; activation energy; photopolymerization

INTRODUCTION

Ultraviolet (UV) curing has attracted increasing interest during the past decade because of the areas of its applications, such as coatings, adhesives, composites, inks, and microelectronics.[1–5] UV-curable resins usually consist of oligomers and multifunctional comonomers, which photopolymerize to form highly crosslinked polymeric networks and photoinitiators, which yield reactive initiating species when exposed to UV light. The nature of the resultant cured films, which is very important to their applications, depends not only on the properties of the components in a resin but also on the photopolymerization kinetics, that is, the photopolymerization rate (R_p), maximum photopolymerization rate (R_p^{max}), and final unsaturation conversion (P_f). The irradiation temperature, sample thickness, photoinitiator concentration, and comonomer content for a given resin affect the photopolymerization kinetics to a large extent and, therefore, the physical and mechanical properties of the cured films.[6]

As a class of UV-curable oligomers, hyperbranched acrylated polymers have attracted increasing attention both from a fundamental viewpoint and for the great variety of expected applications. Several groups are working with these materials for use as oligomers in UV-curable systems.[3,4] Hyperbranched acrylated aromatic polyester (HAAPE) was synthesized in our laboratory. HAAPE was found to have low viscosity, a low degree of shrinkage during UV curing, and good miscibility with epoxy acrylates.[7]

The aim of this work was to investigate the influences of the photopolymerization conditions, such as the irradiation temperature, sample thickness, comonomer content, and photoinitiator concentration, on the photopolymerization kinetics of an HAAPE resin with photo-differential scanning calorimetry (photo-DSC) and IR spectroscopy measurements.

EXPERIMENTAL

Materials

HAAPE, based on 5-hydroxyisophthalic acid as an AB$_2$ monomer, ethylenediaminetetraacetic acid as a core molecule, and 2-hydroxyethyl acrylate as an end-group modifier theoretically having 16 acrylic end groups and a 4.07 mmol g^{-1} unsaturation concentration, was synthesized elsewhere.[7] The weight-average molecular weight and polydispersity were experimentally measured to be 2350 g mol^{-1} and 2.01, respectively. Trimethylolpropane triacrylate (TMPTA), used as a comonomer, was supplied by Sartomer Co. (Exton, PA). 1-Hydroxy-cyclohexyl-phenyl ketone (Irgacure-184), used as a photoinitiator, was supplied by
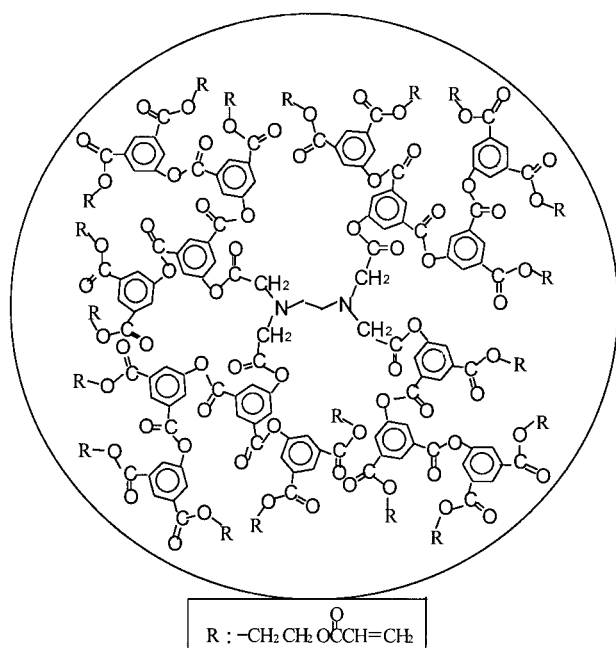
Figure 1 Idealized molecular formula of HAAPE.

Newsun Co. (Changsha, China). Each formulation contained 3 wt % Irgacure-184, unless otherwise stated.

Measurements

Photo-DSC measurements

R_p was monitored with a modified CDR-1 differential scanning calorimeter (Shanghai Balance Instrument Co., Shanghai, China). The photopolymerization was carried out in an atmosphere of N_2. A UV spot-cure system (BHG-250, Mejiro Precision Co., Tokyo, Japan) was used for the irradiation of the samples. The incident light intensity at the sample pan was measured to be 3.12 mW cm^{-2}. The unsaturation conversion (P_t) was calculated with the formula $P_t = H_t/H_\infty$, where H_t is the heat effect within time t (s) and H_∞ is the heat effect for $P_t = 100\%$. Differential scanning calorimetry curves were adjusted by the weight of the sample (g). The polymerization rate was defined as mmol$_{C=C}$ g^{-1} s^{-1}, that is, the variation of the unsaturation concentration (mmol$_{C=C}$ g^{-1}) per second. For the calculation of the polymerization rate and H_∞, the value for the heat of polymerization ($\Delta H_0 = 86$ J mmol^{-1} per acrylic unsaturation) was taken.[8]

IR measurements

IR analysis was carried out with a Magna 750 instrument (Nicolet Instrument Co., WI). For the depth profile analysis of the cured films, HAAPE resin containing 3 wt % Irgacure-184 was smeared on a 50-μm-thick polypropylene (PP) film with a coater to yield a film of a given thickness, such as 0.5 mm. On top of this coated PP, a second PP film was attached. This sandwiched coating was used as the top layer of the UV-curable system. Another sandwiched coated with a 10-μm-thick resin was used as the bottom layer of the UV-curable system. The first sandwiched coating was put on top of the second sandwiched coating and exposed to UV light from the BHG-250 spot-cure system.[9] Then, the IR spectrum of the second sandwiched coating was recorded once every each 5 s. P_t was indicated by a decrease in the peak intensity at 815 cm^{-1} and calculated with the following formula: $P_t = 1 - A_t^{815}/A_0^{815}$, where A_t^{815} is the area of the peak at 815 cm^{-1} at time t (s) and A_0^{815} is the initial area of the peak at 815 cm^{-1} before irradiation.[10] Finally, the curve of P_t versus the irradiation time at a 0.5-mm depth of the film was obtained. In the same procedure, P_t curves at different depths (1.0, 1.5, 2.0, 2.5, and 3.0 mm) were obtained. In this experimental setup, the UV light transmission in the wavelength range of 250–390 nm was almost 100% for the PP film.[9]

RESULTS AND DISCUSSION

The idealized molecular formula of HAAPE is shown in Figure 1. It is well known that all acrylate resins polymerize rapidly when exposed to UV light in the presence of a photoinitiator. Their photopolymerization shows a complex behavior. One of the most characteristic features is autoacceleration, that is, an increase in R_p despite the consumption of unsaturation. This occurs because of the extremely restricted diffusion of the radicals in the highly crosslinked polymeric network. However, autodeceleration occurs because the propagation eventually becomes diffusion-controlled along with the termination. Both these processes lead to the appearance of $R_p^{\max}$.[6]
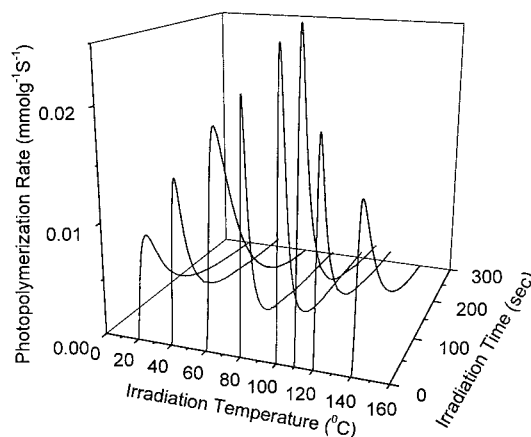

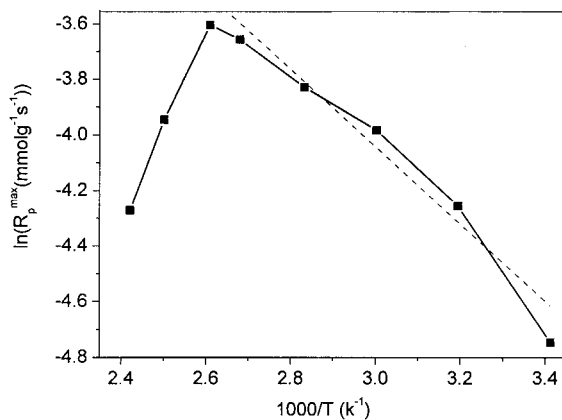**Figure 2** R_p versus the irradiation time of HAAPE at different irradiation temperatures.

Figure 3 Arrhenius plots for R_p of HAAPE. The dotted line shows an approximation to Arrhenius plots for calculating the activation energy.

Influence of the irradiation temperature

Figure 2 shows R_p of HAAPE versus the irradiation time at different temperatures obtained by photo-DSC measurements. R_p at each irradiation temperature shows a steep increase in the beginning of photopolymerization, which is followed by a rapid drop after R_p^{max} is reached. R_p^{max} increases with the temperature rising up to 110°C but decreases beyond 110°C. Figure 3 gives the temperature dependence of R_p^{max} of HAAPE drawn as an Arrhenius plot. The activation energy of the photopolymerization for HAAPE below 110°C is about 16 kJ mol^{-1}, but it is negative beyond 120°C. Broer and Mol[11] observed a similar phenomenon. This photopolymerization behavior below 110°C can be explained by the fact that the photopolymerization reactivity of acrylic groups is promoted along with the viscosity reduction of the resin by the rising temperature. However, it is assumed that the reason for the photopolymerization behavior beyond 110°C is that a chain-transfer reaction and thermal degradation or depolymerization take place at a high temperature.
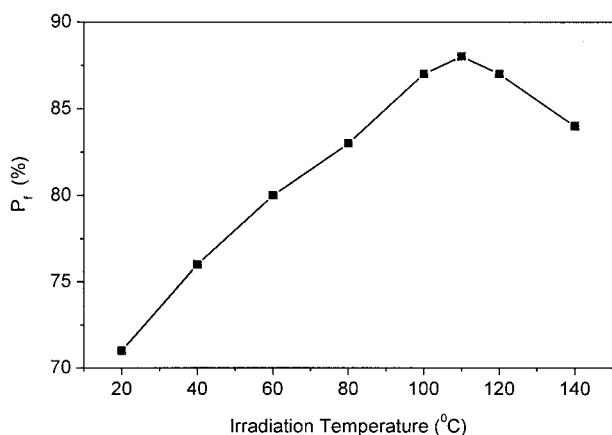

Figure 4 P_f in the cured films versus the irradiation temperature.
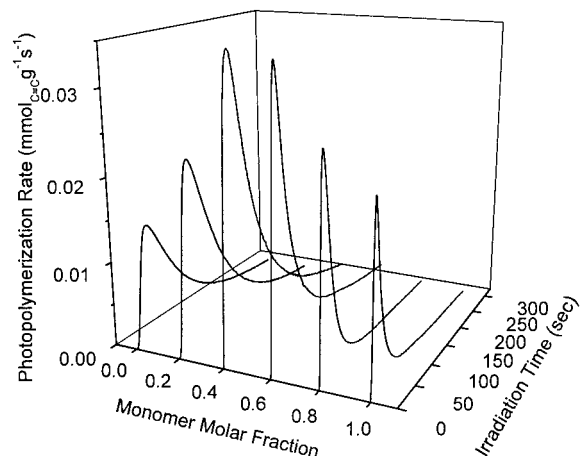

Figure 5 R_p of HAAPE resins versus the irradiation time at different TMPTA molar fractions.

All these reactions suppress the autoacceleration. An increase of P_f in the UV-cured film from 72% at 20°C to 88% at 110°C is achieved (Fig. 4). This remarkable effect may be explained by the fact that the segmental motion of the polymeric chains is promoted at a high temperature. This makes more residual unsaturation sites accessible to photopolymerization. However, P_f decreases beyond 110°C. This is also due to a chain-transfer reaction and thermal degradation or depolymerization at a high temperature.

Influence of the comonomer content

Figures 5 and 6 show the dependence of R_p and P_f, respectively, on the comonomer TMPTA molar fractions (calculated with unsaturation) in HAAPE resins at room temperature. R_p^{max} reaches a maximum at a 0.4 molar fraction and then decreases with the addition of TMPTA. This is because the reactivity of acrylic end groups is promoted by the reduced viscosity, which is due to comonomer addition in the resin. However, a higher initial unsaturation concentration
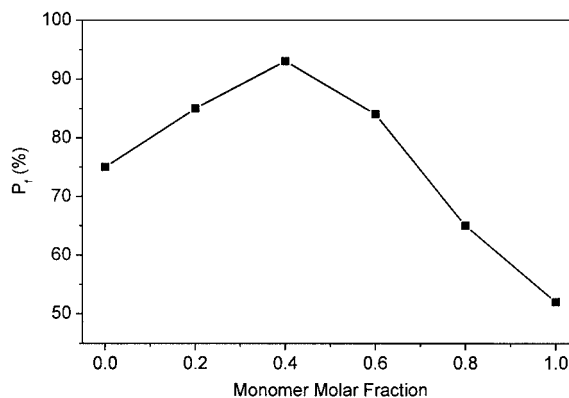

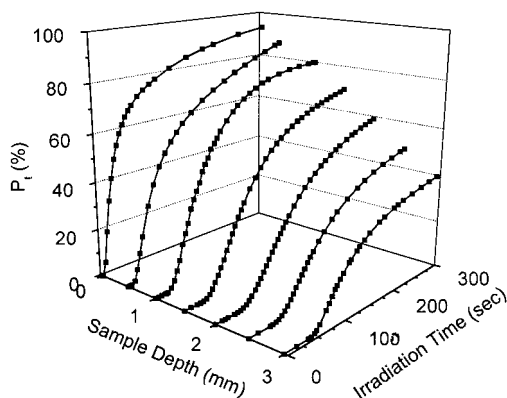**Figure 6** P_f in the cured films versus the TMPTA molar fraction.

Figure 7 P_t in the cured films versus the irradiation time at different sample depths.

(TMPTA molar fraction > 0.4) leads to a lower network mobility, resulting in the reduction of the reactivity of the residual unsaturation. Moreover, the time for reaching R_p^{max} is shortened by the addition of TMPTA. It can also be seen that P_f reaches a maximum at a 0.4 molar fraction of TMPTA and then decreases with increasing TMPTA content. It can be concluded that TMPTA disperses HAAPE and reacts to form polymeric networks with HAAPE. Some acrylic groups trapped in the HAAPE networks are released and take part in photopolymerization because of TMPTA addition at a TMPTA molar fraction below 0.4. However, a higher initial unsaturation concentration (TMPTA molar fraction > 0.4) leads to a lower mobility of the polymeric network, which straps some unreacted acrylic groups. As a result, a remarkable synergistic effect between HAAPE and the comonomer TMPTA is obtained at a TMPTA molar fraction of about 0.4.

Influence of the film depth and photoinitiator concentration

Photo-DSC is frequently used to monitor the photopolymerization process. However, this technology is used for studying only the average P_t value in a block of a film but not the photopolymerization profile at different depths of a thick sample.[10] Figure 7 shows P_t in a UV-cured HAAPE film versus the irradiation time at different sample depths obtained from IR measurements. The P_t curve for each depth profile increases rapidly until P_f is reached, whereas P_f decreases along with the depth from the film surface to a 3-mm depth. This can be explained by the higher incident UV light intensity at the top of the resin than in the other layers. The low UV light intensity leads to low P_f. Moreover, the starting time of photopolymerization is delayed by about 5, 10, 15, 25, 30, and 40 s at 0.5-, 1.0-, 1.5-, 2.0-, 2.5-, and 3.0-mm depths, respectively. This can be interpreted as being due to no or few photons reach-

ing the bottom layers for initiating the polymerization at the beginning of irradiation until the top layer is cured.

Figure 8 shows P_f in UV-cured films versus the photoinitiator concentration at different sample depths obtained from IR measurements. P_f in the film decreases along the sample depth from the surface up to 3 mm for each photoinitiator concentration. The reduction of P_f with the photoinitiator concentration becomes more remarkable as the sample depth increases. P_f reaches 90% at approximately a 1 wt % photoinitiator addition. Increasing the photoinitiator concentration does not result in a higher P_f value for sample depths below 0.5 mm, whereas an obvious reduction with P_f is obtained when the sample thickness is greater than 0.5 mm. Furthermore, the reduction of P_f with the sample depth becomes more remarkable as the photoinitiator concentration increases. This can be interpreted as follows: the absorption of UV light by the photoinitiator becomes stronger as the sample thickness or photoinitiator concentration increases. It may be concluded that a distinct photoinitiator concentration can be observed corresponding to the maximum of P_f and that it moves to lower values as the sample depth increases. Woods et al.[12] obtained similar results.

CONCLUSIONS

The photopolymerization kinetics of HAAPE strongly depend on the irradiation temperature, comonomer molar fraction, sample thickness, and photoinitiator concentration. R_p^{max} increases with the temperature rising up to 110°C but decreases beyond 110°C. An activation energy of 16 kJ mol^{-1} for the photopolymerization has been obtained below 110°C from an Arrhenius plot, but it is negative beyond 120°C. A synergistic effect between the HAAPE resin and comonomer has been observed from R_p^{max} during the
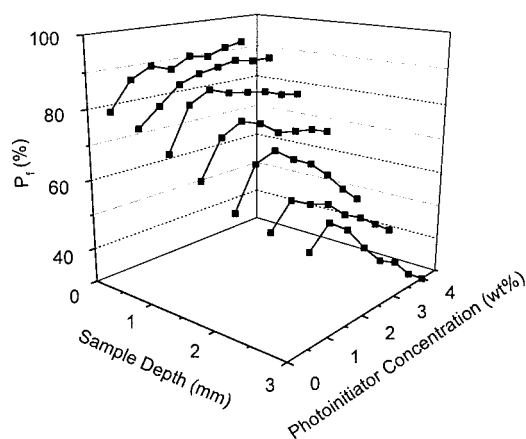

Figure 8 P_f in the cured films versus the photoinitiator concentration at different sample depths.

photopolymerization and P_f in the UV-cured films. The photopolymerization of HAAPE is most promoted by a 0.4 molar fraction comonomer addition. As a result, the strongest synergistic effect occurs for a comonomer molar fraction of about 0.4. P_f decreases with increasing photoinitiator concentration. This becomes more remarkable as the sample depth increases. As a result, the optimum photoinitiator concentration for a film of a particular thickness can be determined, and it moves to a lower value as the film thickness increases.

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