

Photopolymerization of Hyperbranched Aliphatic Acrylated Poly(amide ester). II. Photopolymerization Kinetics

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ABSTRACT: A hyperbranched aliphatic poly(amide ester) ending with hydroxyl groups based on 4-*N,N*-di(2-hydroxy ethyl)-4-ketobutyric acid (DKBA) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) was modified with acryloyl chloride, resulting in a radiation-curable, hyperbranched acrylated poly(amide ester). This hyperbranched polymer was characterized with respect to ultraviolet cure rate, unsaturation conversion, and mechanical properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1637–1641, 2001

INTRODUCTION

Radiation curing of thermoset resins is a technique with growing importance for thermoset applications because it offers improvements compared with thermal systems with respect to processing and environmental properties.¹ Radiation curing can be performed by different techniques, such as low-energy electron beam (EB) and ultraviolet (UV) irradiation.^{2, 3} In most cases, UV curing systems demand a photoinitiator, which decomposes when it is irradiated with UV light, forming initiator species. The formulation of the resin may affect the polymerization performances, such as curing rate and unsaturation conversion. The EB curing system is well suited to curing thicker coatings with pigments because of the strong penetration of the electron. However, the UV curing system has a lower sensitivity towards oxygen inhibition compared with the EB system.

The principal components of a radiation-curable resin are oligomers (or prepolymers) and comonomers. Important types of oligomers that give desired properties of the final cured films and that are commonly used for coatings include acrylated epoxies, acrylated polyurethanes, acrylated polyesters (or polyethers), and unsaturated polyesters.

Another kind of prepolymer that has received increasing attention during recent years is one that provides improvement of properties by changes in the macromolecular architecture. One group of these materials is dendritic polymers, comprised of dendrimers and hyperbranched polymers.^{4, 5} These two types of highly branched polymers are defined as dendrimers with regular spherical shape of the polymer molecules that have been grown from a core molecule in layers called generation, and hyperbranched polymers of irregular structure that have been grown by repeated reactions of multifunctional monomers (e.g., AB₂).⁶ It was recognized that highly branched polymers offered properties of great potential value for applications; that is, low viscosity in a melting state and in a solution, high solubility due to the compact molecular shape,

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and high reactivity due to many available functional endgroups on the surface of the molecules. Therefore, particularly hyperbranched polymers have been considered for material-consuming applications because they are more easily produced in larger scale compared with dendrimers. Several applications, such as rheological additive and toughening agents, have been suggested for hyperbranched polymers.^{7, 8} The use of a hyperbranched polymer as a thermoset resin has also been described.⁹ For the use of dendritic polymers as UV coatings and laminates, a series of polyesters with aromatic structure and poly(amine ester)s were prepared and modified with (meth)acrylate endgroups and UV cured.^{10–13}

In this paper, the hyperbranched aliphatic acrylated poly(amide ester) (HAPAE) used as a new thermoset resin for UV curing systems both by itself and in a mixture with multifunctional comonomers trimethylolpropane triacrylate (TMPTA) and hexadiol diacrylate (HDDA) is presented. The photopolymerization kinetics of HAPAE were determined by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The polymerization behaviors were also investigated by determining pendulum hardness.

EXPERIMENTAL

Materials

The second generation of hyperbranched aliphatic poly(amide ester) with hydroxyl endgroups (HAPAE-2-OH) was prepared from 4-*N,N*-di(2-hydroxy ethyl)-4-ketobutyric acid (DKBA) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) in a 9:1 ratio (theoretically 12 OH-groups per molecule). More extensive descriptions of the synthesis and characterization, combined with its modification by acryloyl chloride, are described elsewhere.¹⁴ The idealized structure of HAPAE-2-A is outlined in Figure 1. TMPTA and HDDA (supplied by Sartomer Company, PA, USA) were used as multifunctional comonomers. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) and 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure-184) were used as photoinitiators for UV curing (both supplied by Ciba-Geigy, Switzerland). All other chemicals were purchased from the Third Reagent Company of Shanghai. All the materials in this study are used as received without further purification.

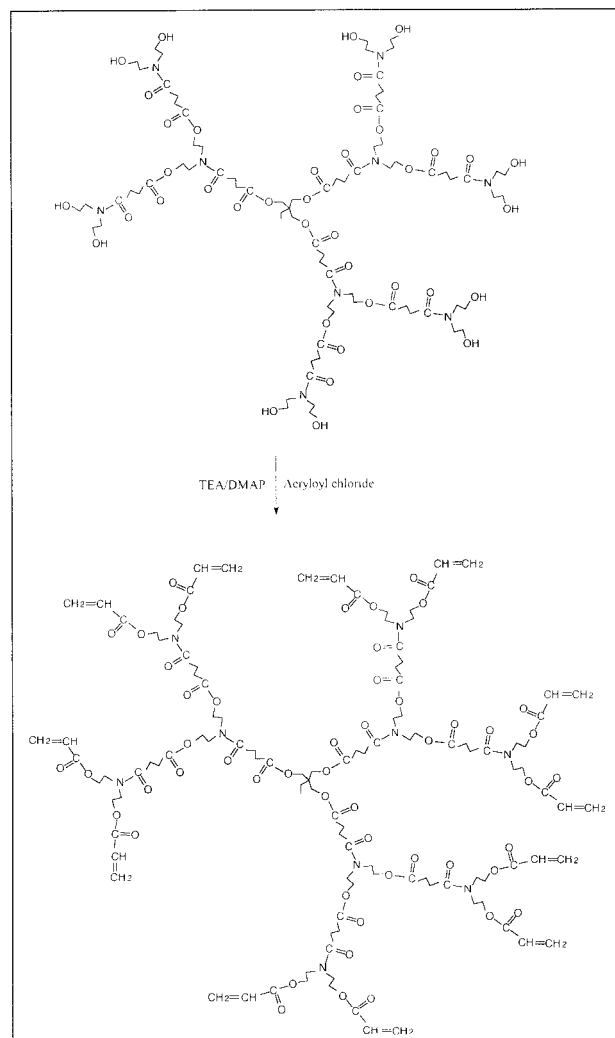


Figure 1 Schematic description of the HAPAE-2-A synthesis.

UV Curing

The mixture of HAPAE-2-A and Irgacure-184/Darocur 1173 (3 wt %), without or with TMPTA added was prepared on a glass plate with a special frame as a support. Then the sample was exposed to the UV lamp (1 kW, 80 W/cm²; made in Lantiao Company, Beijing) and cured.

Measurements

Conversion of Unsaturation

The conversion of vinyl groups measured as residual unsaturation in the UV-cured films was determined with a MAGNA-IR 750 Spectrometer (Nicolet Instrument Corp., USA) using the acrylic double bond (out of plane deformation vibration)

at 810 cm^{-1} by a baseline method. The spectra were normalized using the carbonyl peak at 1728 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%.

Pendulum Hardness

The "pendulum hardness" of the cured film was evaluated using a QBY pendulum apparatus made by the Tianjin Instrument Company, China. The films were applied on glass plates ($100 \times 90 \times 5\text{ mm}$) by a coater with a $75\text{-}\mu\text{m}$ gap.

Photopolymerization Kinetics

The photopolymerization kinetics were investigated at room temperature in a nitrogen atmosphere by a modified CDR-1 DSC (made by Shanghai Balance Instrument Plant). The digitized data based on the trace on a strip-chart recorder were analyzed by Microcal Origin 5.0 software on a personal computer. The initiator, Darocur 1173 was applied in the concentrations of 4 and 2 wt %, respectively, and TMPTA was used as reactive diluent. Polymerization was carried out in a nitrogen atmosphere. A 250 W medium-pressure mercury lamp equipped with a glass filter was used for the irradiation. The incident light intensity at a sample pan position was measured to be 2.04 mW/cm^2 .

RESULTS AND DISCUSSION

Photomerization Characteristics

The hyperbranched acrylated poly(amide ester)s containing a small amount of multifunctional comonomer are rapidly crosslinked by a free-radical polymerization mechanism in the presence of an effective photoinitiator. The curing reaction includes intermolecular crosslinking, branching growth, poly(amide ester) chain extension, intramolecular cyclization, and comonomer homopolymerization. It can be assumed that the comonomer molecules added to the resin surround the hyperbranched poly(amide ester) molecules and react largely with the acrylic double bonds on the spherical surface and form crosslinks between neighboring poly(amide ester) molecules and also homopolymerization. However, a small amount of the double bonds of the comonomers and hyperbranched acrylated poly-

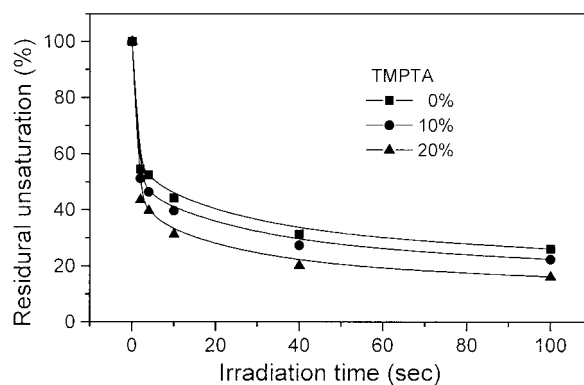


Figure 2 Residual unsaturation in the UV-cured HAPAE-2-A film determined by FTIR.

(amide ester)s may be buried inside the crosslinked networks of the cured resins and remain unreacted during the curing.¹⁵

The decrease of the IR absorption band (out-of-plane deformation vibration) at 810 cm^{-1} as a function of the irradiation time allows an evaluation of the number of acrylic double bonds in the resin during curing. Plots of residual unsaturation versus irradiation time are shown in Figure 2. The residual unsaturation in all the cured HAPAE-2-A films decreased extensively, to ~55% in the cured pure HAPAE-A film, 51% in the film containing 10 wt % TMPTA, and 45% in the film containing 20wt % TMPTA after 2 s of irradiation, respectively. The high UV cure rate of HAPAE-2-A can be interpreted as being due to the numerous double bonds at the surface of the molecule, which are prone to react. But when the cure time was up to 100 s, there were ~32, 28, and 20% double bonds remaining in the cured films in the three cases, respectively. Complete unsaturation conversion is never obtained, especially when the viscosity is high. There are numerous reports showing that ~25% unreacted double bonds remain in acrylate prepolymer films after UV curing because of some residual acrylic groups being trapped and unable to react in the three-dimensional polymer matrix formed.¹⁶

On the other hand, it also can be seen that the more TMPTA is added, the higher is the final unsaturation conversion. This result is because TMPTA not only acts as a diluent for reducing the viscosity but also assists in forming the crosslinking network by homopolymerization and copolymerization with the acrylic group of HAPAE-2-A, which forms extra crosslinking with the restricted double bond of HAPAE-2-A.

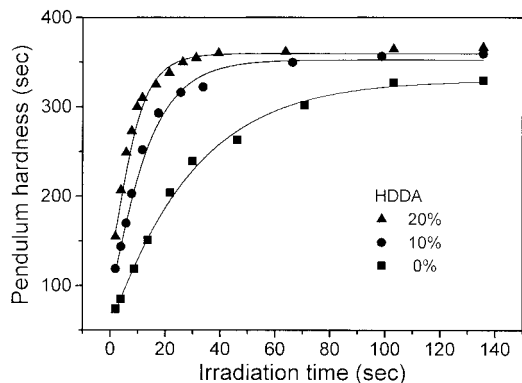


Figure 3 Pendulum hardness of the UV-cured HAPAE-2-A film with 3 wt % I-184.

Pendulum hardness is one of the important properties of UV-cured film that is taken into account for applications. The pendulum hardness is related to the crosslinking network density and the conversion of double bonds at the molecular chain. The pendulum hardness of HAPAE-2-A films without or with HDDA addition versus irradiation time is shown in Figure 3. It can be seen that prolonging the irradiation time leads to the increase of pendulum hardness because more light energy causes higher conversion of double bonds. However, the more HDDA added, the higher is the pendulum hardness of the cured film. This result can be explained by the fact that comonomer addition increases the concentration of the double bond in the resin; that is, the density of crosslinking of the film increases, which leads to the higher pendulum hardness. It also can be seen that the resins with more HDDA addition need shorter irradiation time to obtain the maximum.

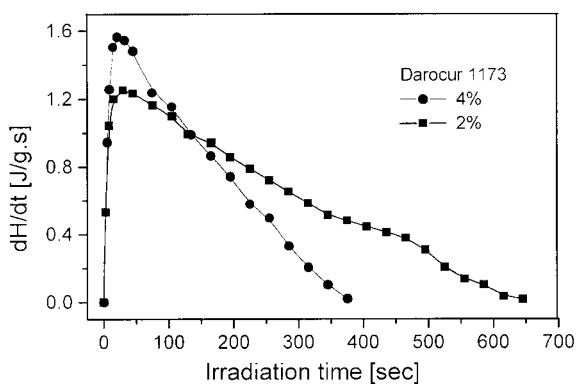


Figure 4 Function of reaction rate as the initiator content as determined by DSC.

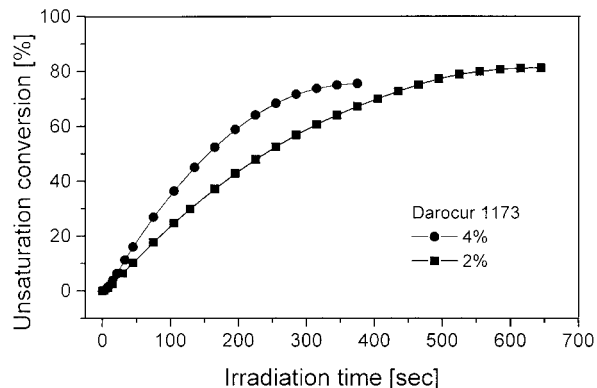


Figure 5 Function of unsaturation conversion as the initiator content as determined by DSC.

Photopolymerization Kinetics

Influence of the Photoinitiator Content

The effects of the photoinitiator content on curing rate and unsaturation conversion of the HAPAE-2-A are shown in Figures 4 and 5. The resin containing 4 wt % Darocur 1173 takes less time to arrive at the maximum conversion than that containing 2 wt % Darocur 1173. This result accounts for the higher maximum polymerization rate ($R_{p_{max}}$) and the shorter time needed to reach $R_{p_{max}}$ due to a larger number of free radicals coming forth in the autoacceleration stage of the 4 wt % initiator system than that of 2 wt % system. However, it also can be seen that the latter gives a higher conversion than the former. This result is interpreted as being due to an increased radical combination that is a second-order reaction, resulting in termination of the polymerization, whereas initiation is a first-order reaction.

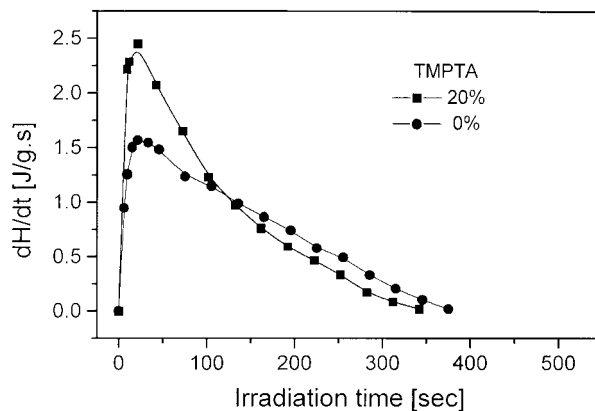


Figure 6 Function of reaction rate as the comonomer content as determined by DSC.

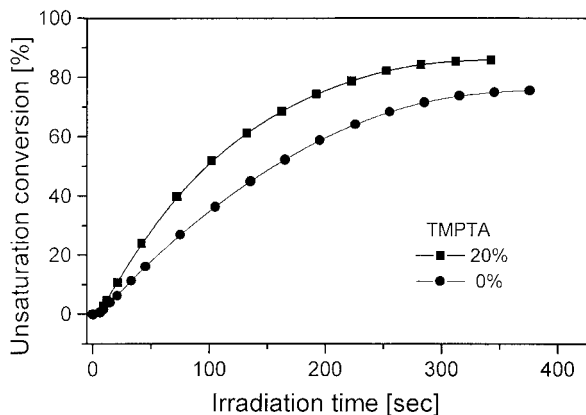


Figure 7 Function of unsaturation conversion as the comonomer content as determined by DSC.

Influence of the Comonomer Content

Another factor for affecting the curing rate is the comonomer that is often used in a UV curing system. The cure kinetics of HAPAE-2-A systems without and with TMPTA added are shown in Figures 6 and 7. As we can see, the $R_{p_{max}}$ of the resin with 20 wt % TMPTA added is higher than that of the resin without TMPTA, and the double-bond conversion of the former is also higher than that of the latter. There are more double bonds remaining in the film of the resin without TMPTA than in that with 20 wt % TMPTA because of reduced mobility. This reason is the same as that mentioned in the previous paragraph and indicates that proper dilution with comonomer for the highly functionalized HAPAE-2-A system may give a higher cure rate and unsaturation conversion.

CONCLUSION

It has been shown that hyperbranched aliphatic acrylated poly(amide ester) is a versatile scaffold for UV curing. Photopolymerization characteristics can be obtained by varying the content of

the photoinitiator and comonomer. The hyperbranched acrylated poly(amide ester) resins polymerized readily with ~20–30% residual unsaturation after curing. The acrylate endgroups are accessible for polymerization. Additionally, the curing rate and unsaturation conversion increase along with the comonomer added.

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