Cationic Photopolymerization of Bisphenol A Diglycidyl Ether Epoxy Under 385 nm

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ABSTRACT: The cationic photopolymerization of bisphenol A diglycidyl ether epoxy (DGEBA) at $\lambda = 385$ nm was conducted by the combination of a cationic photoinitiator PAG30201 (Bis (4-isobutylphenyl) iodonium hexafluorophosphate) and a photosensitizer PSS303 (9,10-dibutoxy-9,10-dihydroanthrance). The kinetic characterization was investigated by real-time Fourier transform infrared spectroscopy. The enhancement of epoxy conversion of DGEBA was achieved by increasing temperature, adding alcohols, active monomers and radical photoinitiators. As a result, in the presence of 2 wt % PAG30201 and 1.2 wt % PSS303, the epoxy rings conversion of DGEBA has reached to more than 70% from 55.9% at room temperature; it could be increased to almost 80% if heated to 60°C. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3698–3703, 2013

INTRODUCTION

In recent decades, photopolymerization has been widely used in many fields, such as coatings, adhesives, dentistry, and others.[1] Compared with free radical photopolymerization, the cationic one has the advantages of absence of oxygen inhibition, low shrinkage, good adhesion properties, and low monomer toxicity, thus has drawn more and more attentions.[2–4]

Cationic photoinitiators play an important role in cationic photopolymerization. Usual cationic photoinitiators based on onium salts only absorb light at short wavelength ($\lambda < 300$ nm).[5,6] However, for imaging or printing, long-wavelength UV or even visible light source such as lasers and LEDs should be used.[7] Moreover, the photoinitiator systems which absorb long-wavelength UV or visible light will protect the organic coatings from sun rays.[8] It is significant to develop initiating systems for cationic photopolymerization in long wavelength.[9–15]

The monomers are also vital in cationic photopolymerization. Among the most widely used and less expensive epoxide monomers is bisphenol A diglycidyl ether epoxy (DGEBA). The price of DGEBA is only one percent of that of another widely used epoxide monomer, 3,4-epoxycyclohexylmethy-3′,4′-epoxy-cyclohexan carboxylate (EEC). DGEBA is typically employed in condensation network polymerizations with amines, amides, and anhydrides,[16–18] or even cationic polymerization induced by electron beam.[19] Unfortunately, the cationic photopolymerization of DGEBA is very sluggish.[6,16]

In this work, bis (4-isobutylphenyl) iodonium hexafluorophosphate (PAG30201) was used as a cationic photoinitiator to initiate the polymerization of DGEBA. A photosensitizer, 9,10-dibutoxy-9,10-dihydroanthrance (PSS303) was used to promote the photolysis of PAG30201 by electron transfer under 385 nm LED. Various reaction parameters, such as molar ratios of PSS303 and PAG30201, concentration of initiating system, and temperature, were carried out to investigate the photopolymerization kinetic of DGEBA. When the molar ratio of PSS303 to PAG30201 equaled to 1 : 1 and concentration of PAG30201 was 2 wt %, the epoxy conversion of DGEBA was 55.9%. The conversion can be increased to 80% when heated to 60°C. Moreover, some additives like free radical photoinitiators, vinyl ethers, and alcohols were added to the cationic photopolymerization mixture to enhance the polymerization efficiency at ambient temperature. As a result, initiated by the initiating system of 1 : 1 PSS303 and PAG30201 (2 wt % PAG30201), the conversion of epoxy has been increased from 55.9% to more than 70%.

EXPERIMENTAL

Materials

Bisphenol A diglycidyl ether epoxy (DGEBA, weight per epoxide 186 g/eq, Sanmu Chemical Industry, Jiangsu, China), was used as epoxy matrix. Dodecyl vinyl ether and n-Hexanol were purchased from the Aldrich Chemical and Tianjin Fuchen chemical reagent factory (Tianjin, China), respectively. Free radical photoinitiator 651 (2, 2-dimethoxy-2-phenylacetophenone) and

EEC were donated kindly by the Runtech Chemical Company (Changzhou, Jiangsu, China). Bis(4-isobutylphenyl)iodonium hexafluorophosphate (PAG30201) and 9,10-dibutoxy-9,10-dihydroanthracene (PSS303) were donated kindly by Tronly Electronic new material (Changzhou, Jiangsu, China). All the reagents were used as received.

Photopolymerization Kinetic of DGEBA

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Real-time infrared spectra (RTIR) were used to determine the conversions of epoxy. The spectrometer was operated in the rapid mode with an average 3 scans/s^{-1} collection rate. The mixture of DGEBA, PSS303, PAG30201 and additives was applied between two KBr crystals and irradiated with a UV-LED lamp (UVEC-4, Lamplic, China) with a wavelength of 385 nm. Ten mW/cm^2 light intensity was employed. The results reported in this article were the average of three kinetic runs. All reactivity studies were conducted at ambient laboratory temperature unless otherwise noted.

Conversion data of cationic polymerization could be obtained by monitoring the decay of DGEBA epoxy peak. Upon irradiation, the decrease of the epoxy absorption peak area from 895 to 927 cm^{-1} accurately reflects the extent of cationic polymerization. Because the decrease of absorption of the peak area was directly proportional to the number of polymerized epoxide, the degree of conversion (DC) of the function group could be calculated by measuring the peak area at each time of the reaction by using the following equation:

$$DC\ (\%) = (A_0 - A_t)/A_0 \times 100 \qquad (1)$$

DC is the conversion at t time, A_0 and A_t are the peak areas of function group before irradiation and at t time, respectively. The rate of polymerization R_p was calculated from the derivative of the function of conversion versus time as follows:
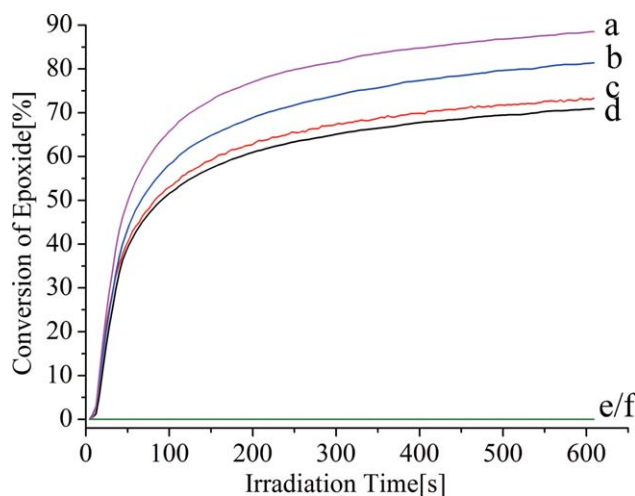
Figure 1. Effect of [PSS303] on polymerization of DGEBA. [PAG30201]= 5 wt %. The molar ratio of PSS303 and PAG30201= (a) 5/1, (b) 2/1, (c) 1/1, (d) 1/5, (e) 1/10, and (f) 0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
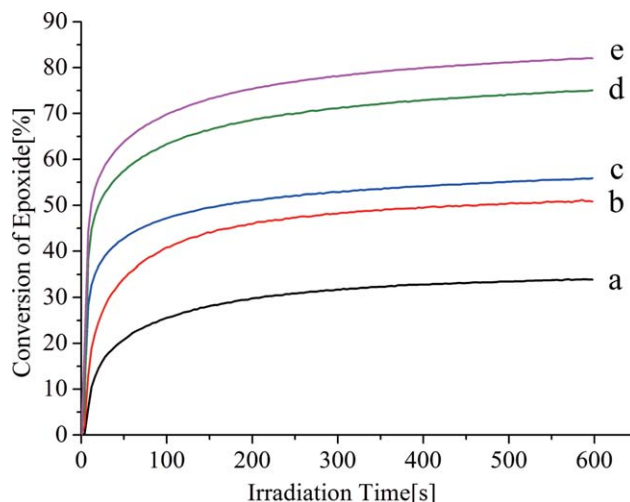
Figure 2. Effect of [PAG30201] on polymerization of DGEBA. [PAG30201]: (a) 0.5 wt %, (b) 1.0 wt %, (c) 2.0 wt %, (d) 5.0 wt %, (e) 7.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$R_p = [M]_0 \times d(DC)/dt \qquad (2)$$

where $[M]_0$ is the initial concentration of epoxy (mol^{-1}). In the following section, $R_{p,max}$ represents the maximum rate of polymerization for different samples.
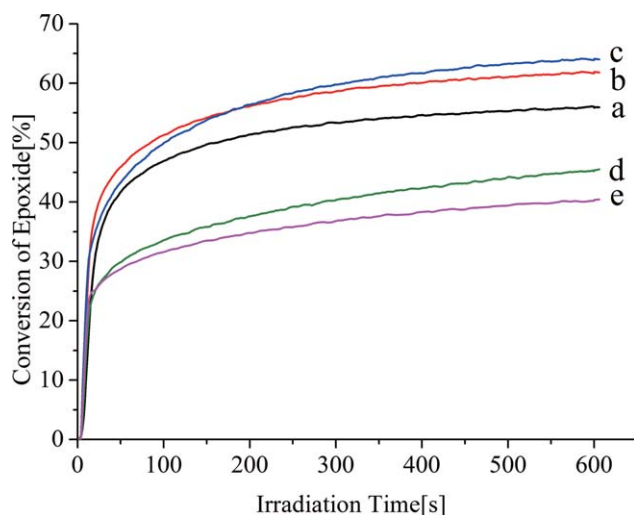
RESULTS AND DISCUSSION

Polymerization of DGEBA Initiated by PAG30201 and PSS303

In order to examine the effect of concentration of the photosensitizer PSS303 on the photopolymerization, various molar ratios of PSS303 and PAG30201 (from 1/10 to 5/1) were used in epoxy mixture containing 5.0 wt % PAG30201. As exhibited in Figure 1, no conversion of epoxy was found when the ratio was too low, such as 1/10 (curve c) and the sample without PSS303 (curve d). Because PAG30201 has no absorbance in wavelengths longer than 300 nm, while the irradiation wavelength was 385 nm, in this case, the PAG30201 could not decompose to form reactive species to induce polymerization of epoxide. When the concentration of photosensitizer increased, it could absorb 385 nm light to sensitize the decomposition of PAG30201 to produce reactive species to induce the polymerization of epoxide. Although in tested samples, higher molar radio of PSS303 and PAG30201 was good for polymerization, for reasons of solution problem and high price of PSS303, the mixture of PSS303/PAG30201 = 1/1 (molar ratio) was used as an initiating mixture in the later experimental.

As showed in Figure 2, five samples contained different concentrations of PAG30201 and PSS303, and the molar ratio of them was 1/1. When the concentration of PAG30201 increased from 0.5 to 7 wt % (the concentration of PSS303 increased from 0.3 to 4.2 wt %), the conversion of epoxy increased from 33.9% to more than 80%. It is a quite efficient method to increase the concentration of initiating system to enhance the polymerization. Because more cationic reactive species would be produced by more PAG30201, then, more DGEBA would be initiated and polymerized. Although more initiators resulted in higher

Figure 3. Effect of temperature on polymerization of DGEBA: (a) 30°C, (b) 40°C, (c) 50°C, and (d) 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 1. Mechanism of photopolymerization of epoxides initiated by diaryliodonium salt.

room temperature. But once ring-opening took place, a considerable amount of heat was released because of the relief of ring strain in the monomer. This energy was available for the next reaction in eq. 4, the polymerization would proceed smoothly and produce the polymer film.[16] So when the polymerization took place in high temperature, the reaction stage 3 and 4 could go quickly. And also the viscosity of DGEBA decreased when heated. So increasing reaction temperature was of advantage to the cationic polymerization.

conversion of epoxy, the polymers became more but shorter and less cross-linked, the properties of cured films reduced; another issue is also that the price of PSS303 is very high. In the following experimental work all samples contained 2 wt % PAG30201 and 1.2 wt % PSS303. It was noticed that, in the presence of 2 wt % PAG30201 and 1.2 wt % PSS303, the conversion of epoxy was only 55.9% (curve c), then several methods were employed to enhance the polymerization efficiency of DGEBA.

Effect of Temperature on Polymerization of DGEBA
Figure 3 showed the conversion at different irradiation time and curing temperatures, it could be seen that conversion reached to 78.5% at 60°C while it only 58.7% at 30°C. On the other hand, the maximum polymerization rate in 60°C was more than twice of that in 30°C (Table I).

The generally accepted mechanism for the cationic photopolymerization of epoxides initiated by diaryliodonium salt was depicted in scheme 1.[16,20] In the first step, the diaryliodonium salt yielded the superacid (H^+X^-) under light irradiation, then the photogenerated superacid rapidly protonated the cyclic ether to generate the secondary oxonium ions (as depicted in eq. 2). The two steps took place readily at room temperature with little or no activation energy.[16] In eq. 3, the monomer attacked the secondary oxonium ion to generate the tertiary oxonium ion. If the aliphatic glycidyl ethers such as DGEBA were used as the monomers at room temperature, in this step, only a little portion of or no monomers could yield the tertiary oxonium ion, since the activation energy of this reaction was hard to overcome for aliphatic glycidyl ethers at

Effect of Alcohol on Polymerization of DGEBA
For cationic ring-opening polymerization of epoxides, the hydroxyl groups of alcohols may act as functional reactive groups by interacting with the cationic growing chain through an activated monomer mechanism.[2,21–25] In this article, n-Hexanol was chosen to test the effect of alcohol on cationic photopolymerization of DGEBA. As showed in Figure 4, when different concentrations of n-Hexanol was added to the cationic photopolymerization mixture of DGEBA, the conversion of epoxy changed, the optimal concentration of n-Hexanol was 1 wt %. If the content of n-Hexanol was more than 1.0 wt %, the high hydroxyl concentration could inhibit the initiation stage or propagating species were immediately consumed by the reaction

Table I. Polymerization Rate at Different Temperatures

Temperature (°C)	30	40	50	60
$R_{p,max}$ (s^{-1})	1.54	1.72	2.69	3.92

Figure 4. Effect of n-Hexanol on polymerization of DGEBA. [n-Hexanol]: (a) 0, (b) 1.0 wt %, (c) 2.0 wt %, and (d) 5.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
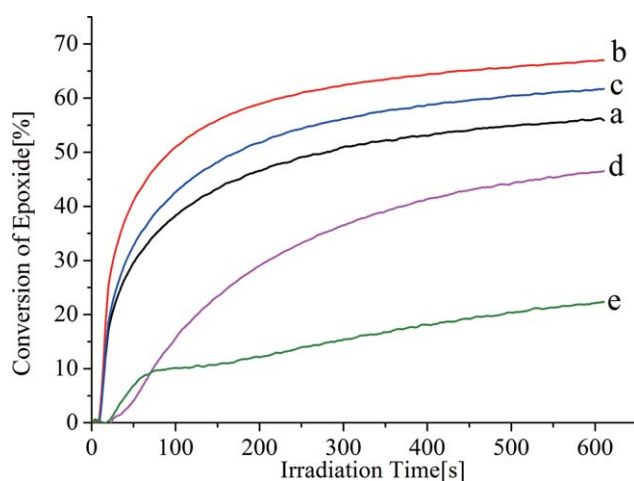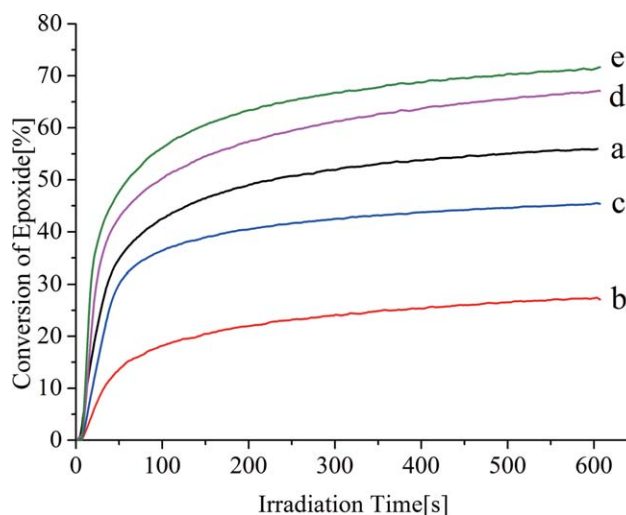
Figure 5. Effect of EEC on polymerization of DGEBA. [EEC]: (a) 0, (b) 2.0 wt %, (c) 5.0 wt %, (d) 10.0 wt %, and (e) 20.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with hydroxyl group and the sufficient chain growth was not ensued.[21]

Effect of Active Monomers on Polymerization of DGEBA

Figure 5 showed the effect of a cycloaliphatic epoxy resin EEC on the polymerization of DGEBA. The EEC has highly strained rings, the activation energy for the reaction in eq. 3 of scheme 1 of EEC was relatively small and was thermally accessible at room temperature.[16] In the polymerization of DGEBA containing a small amount of EEC, the energy released by the reaction in eq. 3 of scheme 1 of EEC was available for DGEBA to process the same reaction in room temperature, therefore, relatively more DGEBA overcame the activation energy to generate the tertiary oxonium ion, finally gave the polymer, the conversion of epoxy was increased. It was increased by almost 10% arriving at 64.0% (curve c) when the concentration of EEC was 5 wt %.

Table II. Polymerization Rate of Different Concentration of Dodecyl Vinyl Ether

[dodecyl vinyl ether] (wt %)	0	2	5	10	20
R_p (s^{-1})	1.38	2.02	1.50	–	–

However, as shown in Figure 5, too much EEC was harmful to the polymerization of DGEBA. In fact, there was a competition between EEC and DGEBA for the secondary oxonium, large amount of EEC consumed too much active site with higher activity resulting in the decrease of the conversion of DGEBA. This result agreed with the conclusion of Crivello's work.[16,25,26]

Figure 6 showed the effect of dodecyl vinyl ether on the polymerization of DGEBA. The conversion of epoxy was 66.9% in the presence of 2 wt % dodecyl vinyl ether (curve b) while it was 55.9% without dodecyl vinyl ether, which increased more than 10%. The maximum polymerization rate increased from 1.38 to 2.03 s^{-1} by adding 2 wt % dodecyl vinyl ether. There were two reasons. One was same to that of EEC, the energy released by the reaction of dodecyl vinyl ether helped DGEBA overcame the activation energy of eq. 3 in scheme 1, so that epoxy conversion of DGEBA was increased. On the other hand, the dodecyl vinyl ether was more active than DGEBA whether in eqs. 2 or 3 in scheme 1, the alkoxy carbenium ions formed by vinyl ethers were more active than oxonium ions formed by DGEBA, they were much easier to be attacked by DGEBA,[26] that was why dodecyl vinyl ether could increase the polymerization rate obviously while EEC cannot (Table II). However, too much dodecyl vinyl ether (10 or 20 wt %) consumed almost all of the active sites with extra high activity while only a little active sites react with DGEBA. So conversion of epoxy decreased dramatically (curves d and e), and $R_{P,max}$ could not be obtained in higher dodecyl vinyl ether concentration (Table II).

Figure 6. Effect of dodecyl vinyl ether on polymerization of DGEBA. [dodecyl vinyl ether]: (a) 0, (b) 2.0 wt %, (c) 5.0 wt %, (d) 10.0 wt %, and (e) 20.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
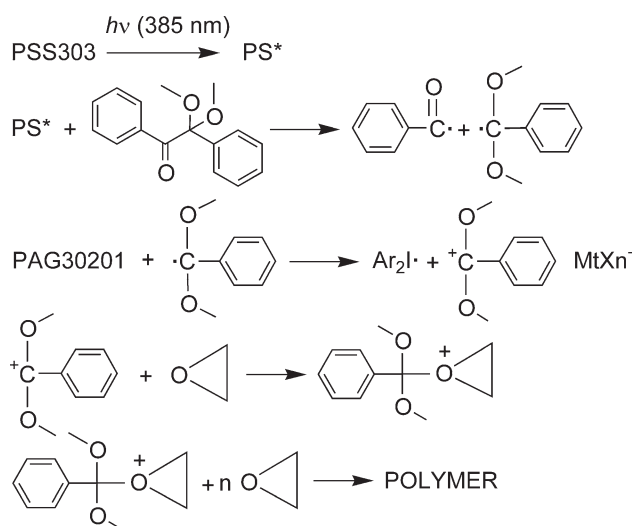

Figure 7. Effect of 651 on polymerization of DGEBA. [651]: (a) 0, (b) 0.5 wt %, (c) 1.0 wt %, (d) 1.5 wt %, and (e) 2.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[651] (wt %)	0	0.5	1.0	1.5	2.0
R_p (s^{-1})	1.38	0.55	0.95	2.29	3.50

Effect of Free Radical Photo Initiators on Polymerization of DGEBA

Free radical photoinitiators have been used to accelerate cationic photopolymerization in several researches.[12,14,16,27–29] The effect of free radical photoinitiators on polymerization of DGEBA was investigated in this work. As showed in Figure 7 and Table III, increase concentration of the free radical photo initiator 651 resulted in the higher conversion of epoxy and faster polymerization rate. The conversion of epoxy was 71.7% and the maximum polymerization rate was 3.50 s^{-1}, when the concentration of 651 was 2.0 wt % (curve e). But it should be noticed that at a lower concentration of 651, both the conversion of epoxy and the polymerization rate was lower than the control sample.

As shown in scheme 2, when the mixture of DGEBA, PAG30201, PSS303, and 651 was irradiated by light of 385 nm, in the first step, PSS303 absorbed light and then sensitized 651 to generate two free radical species, the acyl radical and the dimethoxybenzyl radical[16]; then the iodonium salt oxidized this latter free radical species readily to give a dimethoxybenzyl carbenium ion.[16,29] The dimethoxybenzyl carbenium ion attacked the oxygen of epoxy rings of DGEBA to directly generate the tertiary oxonium ion, which was more reactive than the secondary oxonium ions formed in eq. 2 of scheme 1.[16] However, PAG30201 which should have initiated the polymerization of DGEBA was consumed in the redox reaction. It was only the dimethoxybenzyl carbenium ion that initiated the polymerization of DGEBA in presence of 651. So compared to control sample, higher conversion of epoxy and faster polymerization rate were obtained in curves e and d. But in samples b and c, because of too small amount of dimethoxybenzyl carbenium ions generated by small

concentration of 651, the conversion of epoxy and the polymerization rate was lower than the control sample.

CONCLUSION

The initiating system of PAG30201 : PSS303 = 1 : 1 was proved to be efficient for cationic photopolymerization of DGEBA in 385 nm. When the concentration of PAG30201 was 2.0 wt % and concentration of PSS303 was 1.2 wt %, the conversion of epoxy was 55.9%. Heating is the most effective method for enhancing the polymerization of DGEBA. Rising temperature from 30°C to 60°C, the conversion of epoxy was increased by almost 25% and polymerization rate doubled. At room temperature, the conversion of epoxy reached to 71.7% in the presence of just 2 wt % free radical initiator 651. Adding suitable amount EEC, n-Hexanol, and dodecyl vinyl ether could also increase the polymerization of DGEBA.

Scheme 2. Mechanism of photopolymerization of DGEBA initiated by PSS303, PAG30201 and 651.

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