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PHOTOINITIATED CATIONIC POLYMERIZATION OF EPOXY MONOMERS IN THE PRESENCE OF POLY(3,4-EPOXY-1-BUTENE)

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ABSTRACT

Hydroxyl-terminated poly(3,4-epoxy-1-butene) (polyEPB) is an interesting and highly useful agent for the acceleration of the photoinitiated cationic ring-opening polymerization of epoxide monomers. Kinetic investigations using real-time infrared spectroscopy have shown that the observed acceleration of the polymerization is due to two independent mechanisms. Crosslinking polymerization of epoxide monomers is accelerated due to an activated monomer mechanism that results in facile chain transfer due to interaction of the terminal hydroxyl groups of polyEPB with the growing oxonium ion chain ends. A second mechanism involving participation of polyEPB in a free radical chain induced decomposition of the onium salt photoinitiator is mainly responsible for the observed acceleration in the rate of polymerization. A large number of polymer-bound carbocationic species are generated by this mechanism that are capable of initiating polymerization of the epoxide monomer.

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Key Words: Poly(3,4-epoxy-1-butene); Photopolymerization; Free radical induced decomposition; Cationic ring-opening polymerization; Epoxide monomers

INTRODUCTION

Previously, we have described the development of onium salts as a class of efficient, photoinitiators for the cationic ring-opening polymerization of epoxide as well as for other types of heterocyclic and vinyl and monomers.[1] The use of epoxide monomers and oligomers for photocurable coatings is very attractive due to the excellent chemical resistance and mechanical properties of the crosslinked polymers that are produced. Furthermore, photopolymerization processes offer many additional benefits that are of considerable interest in industrial applications. For example, photopolymerizations can be conducted without the use of organic solvents thus eliminating this potential source of both air and water pollution while avoiding the initial costs associated with their use as well as their recovery. Photopolymerizations are also characterized by high production rates and high-energy efficiencies compared to the classical thermal polymerization methods. In addition, photoinitiated cationic polymerizations have the advantage of oxygen insensitivity that reduces both the cost and necessity of using an inert atmosphere. This stands in direct contrast to the free radical photopolymerization of acrylates.

Unfortunately, the rates of photopolymerization of typical epoxide monomers using the most active cationic photoinitiators available are considerably slower than the free-radical photopolymerization of multifunctional acrylates and generally too slow for some very high-speed web processes such as printing inks and overprint varnishes. In several recent papers,[2–4] we have shown that the photoinitiated cationic polymerization of multifunctional epoxide monomers can be markedly accelerated by the addition of alcohols or polyols due to a chain transfer mechanism. We have also demonstrated that an acceleration of the photoinitiated cationic polymerization of epoxides could also be achieved by a mechanism involving the free radical induced decomposition of diaryliodonium salts.[5,6] In the present work, we report the simultaneous acceleration of the photoinitiated cationic polymerization of epoxide monomers by both mechanisms using hydroxyl-terminated poly(3,4-epoxy-1-butene) (polyEPB) as a rate enhancing agent and mechanical property modifying coreactant.

EXPERIMENTAL

Materials

Hydroxyl terminated poly(3,4-epoxy-1-butene) (polyEPB) was used as received from the Eastman Chemical Company, Kingsport, TN. This oligomer was prepared by the BF_3 etherate catalyzed ring-opening polymerization of 3,4-epoxy-1-butene carried out in the presence of 1,4-butanediol. The oligomer had a 1,2/1,4 content of 95/5 and a GPC determined M_n of 1413 g/mol (polystyrene standards). Epoxy monomers were obtained from various commercial sources and purified by distillation prior to use. Photoinitiators, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10)[7] and (4-n-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10)[8] were prepared as described previously. Other reagents and solvents were used as received.

Routine infrared spectra were obtained using a Midac-M1300 Fourier transform Infrared spectrometer. Gas chromatographic (GC) analyses were performed using a Hewlett-Packard 5890 Gas Chromatograph equipped with a 10 m 5% OV-17 phenylsilicone capillary column and a flame ionization detector. ^{1}H NMR experiments were carried out using either a Varian XL-200 (200 MHz) or an Inova-300 spectrometer at room temperature using $CDCl_3$ as the solvent and employing tetramethylsilane (TMS) as an internal standard. Gel Permeation Chromatography (GPC) carried out with the aid of a Hewlett Packard, Gel Permeation Chromatograph equipped with a refractive index detector and a μ-styragel column (particle size 5 μm mixed 24–34 Å pores). $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL/min. Elemental analyses were performed by Atlantic Microlaboratories, Norcross, GA.

Synthesis of Dimethoxylated PolyEPB

Into a 500 mL, round bottom flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet were charged, 0.29 g (0.0012 mol) NaH dissolved in 30 mL freshly distilled THF. To this mixture were added dropwise, 10 g (5.1×10^{-3} mol) polyEPB dissolved in 10 mL THF. The reaction mixture was maintained at room temperature and stirred until hydrogen evolution was no longer observed. Then, 1.7 g (0.012 mol) of iodomethane dissolved in a small amount of THF was added dropwise via the addition funnel. After the addition was complete, the reaction mixture was stirred for 2 h at room temperature. The progress of the reaction was monitored by following the disappearance of the infrared band of the hydroxyl groups at 3500 cm^{-1}. Work up consisted of pouring the reaction mixture into 50 mL of distilled water, extracting with diethyl ether and then washing the organic phase with fresh distilled water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed using a rotary evaporator. Dimethoxylated polyEPB was isolated in 78.5% yield.

Cationic Photopolymerizations

Photopolymerizations of all the monomers and oligomers in this work were monitored using Fourier transform real-time infrared spectroscopy

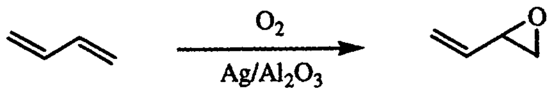
(FT-RTIR). A Midac M-1300 FTIR spectrometer (Midac Corp., Irvine, CA) equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector was used. The instrument was fitted with a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a flexible liquid optic wand. The end of this wand was placed at a distance of 5 cm and directed at an incident angle of 45° onto the sample window. UV light intensities were measured with the aid of a UV Process Supply, Inc. radiometer (Chicago, IL) at the sample window. All photopolymerizations were conducted at a light intensity of 600 mJ/cm^{2}min (10 mW/cm^2).

Photopolymerizations were carried out at room temperature in solutions of the epoxide monomers containing various concentrations of IOC10 or SOC10 as the photoinitiator. All concentrations reported in this paper are given in units of mol% with respect to the epoxide monomer unless otherwise noted. Homogeneous solutions of 2.0 mol% of photoinitiator dissolved in the indicated monomer were prepared. The mixtures also contained 1:2 molar ratio of polyEPB or tetraethylene glycol (TEG), where molar ratio refers to the ratio: mol OH groups/mol epoxy groups. The solutions were spread as a thin film between two oriented and corona treated 12 μm polypropylene films (General Electric Capacitor Dept., Hudson Falls, NY). The peak-to-peak distance taken by the interferometer of the FT-IR spectrometer was held at a constant value.

Kinetic curves were obtained by following the decrease in the intensity of the epoxy peak. The maximum of this peak occurred at different spectral positions for the various monomers (ERL, 750 cm^{-1}; LDO, 800 cm^{-1}; DEO, 780 cm^{-1}) used in this investigation. Infrared spectra were collected at a rate of 1 spectrum per second using LabCalc, data acquisition software obtained from Galactic Industries Corp. (Salem, NH) and were processed using GRAMS-386 software from the same company. Three to five runs were performed for each kinetic study and the results averaged. Variations in the experimental conditions such as the light intensity, humidity and temperature from one day to another result in slight differences in the kinetic curves, particularly in the induction period. For this reason, all kinetic curves contained within a given figure were determined on the same day and under the same conditions. Under these conditions, there was excellent run-to-run reproducibility.

RESULTS AND DISCUSSION

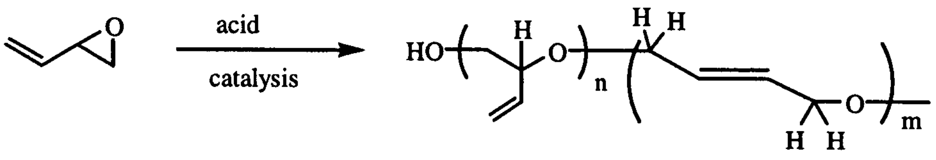
3,4-Epoxy-1-butene (EPB) is an interesting compound and potential monomer with dual vinyl and epoxide functionality. EPB has been prepared in low yields by two groups by the direct epoxidation of 1,3-butadiene with various oxidizing agents.[9,10] The discovery in the mid-1980's of an efficient silver promoted selective epoxidation of 1,3-butadiene to EPB (Eq. (1)) provides a facile route to this highly reactive and potentially inexpensive monomer.[11]



EPB

(1)

The chemistry of EPB is extremely versatile and this compound undergoes a wide variety of reactions both at the double bond and by ring-opening of the epoxide group.[12] Polymerization of EPB takes place under either acid or base catalysis to yield the corresponding hydroxyl-terminated polyether (polyEPB). While the main pathway for the base-catalyzed polymerization of EPB takes place by epoxide ring-opening generating repeating units bearing pendant vinyl groups (1,2-polymerization), some 1,4-polymerization (5–30%) also takes place under acid catalysis with the cooperative involvement of both the epoxide and vinyl groups (Eq. (2)).[13] Polymerization of EPB by an activated monomer mechanism in the presence of alcohols yields di- and multifunctional hydroxyl-terminated poly-EPB.[15] Typical molecular weights of these polymers range from 350 to 5000 g/mol.



polyEPB

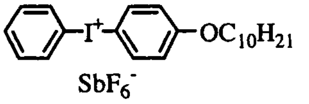
(2)

The structure of polyEPB has two important features that potentially make it of interest for use in the photoinitiated cationic polymerization of epoxide monomers. First, the polymers contain terminal hydroxyl groups that can participate in cationic ring-opening polymerizations. The second structural feature of importance is the presence of readily abstractable secondary and tertiary α-allylic ether protons in every repeat unit along the backbone of polyEPB that can take part in a free radical induced decomposition of certain onium salt cationic photoinitiators. We have examined both of these possible accelerating mechanisms and now report the details of the results of our investigations.

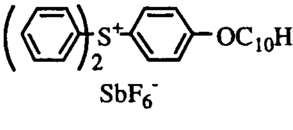
Kinetic investigations of the reactivity of various epoxy monomers, in the presence of polyEPB, were carried out using Fourier transform real-time infrared spectroscopy (FT-RTIR), a technique pioneered by Decker and Moussa.[16,17] We have used this technique for the determination of the rates of very rapid cationic photopolymerizations that are completed on a time scale of a few seconds.[18,19] This analytical technique involves monitoring the decrease of an IR band characteristic of the epoxy functional group present in the monomer that undergoes cationic ring-opening polymerization. The photopolymerization studies reported in this communication were conducted using the cationic photoinitiators, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) and (4-n-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10). The structures of these photoinitiators and the monomers used in this investigation are shown in Table 1. Both photoinitiators were soluble in all the monomers studied and have high quantum yields ($\Phi = 0.5-0.7$).[20] The epoxide monomers were coated onto a thin polypropylene film, mounted in a 2 cm × 2 cm slide holder and irradiated with UV light at room temperature. Polymerizations were carried out open to the air and also covered with a thin film of polypropylene. The conversions of the epoxide functional group to polymer were monitored by following the decrease in the intensity of the epoxide infrared absorption bands upon UV exposure as a function of time. The band that was monitored depends on the specific epoxide monomer employed (ERL = 750 cm^{-1}; LDO = 850 cm^{-1}; DEO = 660 cm^{-1}). Since many of these substrates were found to be highly reactive, it was found necessary to adjust the light intensity (10 $\mathrm{mW/cm^2 \cdot sec}$) to slow the polymerization sufficiently to allow data collection and to facilitate a direct comparison of the rates between the monomers in the presence and absence of polyEPB.

Table 1. Structures of Photoinitiators and Monomers

Photoinitiators

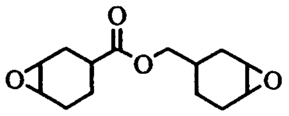


IOC10
(4-n-decyloxphenyl)phenyl-iodonium hexafluoroantimonate

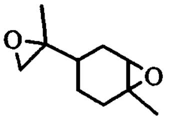


SOC10
(4-n-decyloxyphenyl)diphenyl-sulfonium hexafluoroantimonate

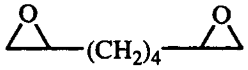
Monomers



ERL
3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate



LDO
limonene dioxide



DEO
1,2,7,8-Diepoxyoctane

Acceleration of Epoxide Photopolymerization Due to Hydroxyl Groups in PolyEPB

Figures 1–4 show the FT-RTIR curves for the photopolymerization of three different epoxy monomers in the presence of polyEPB. Each of the monomeric mixtures investigated, contained either IOC10 or SOC10 as the photoinitiator. Comparative kinetic curves appear in each figure for the

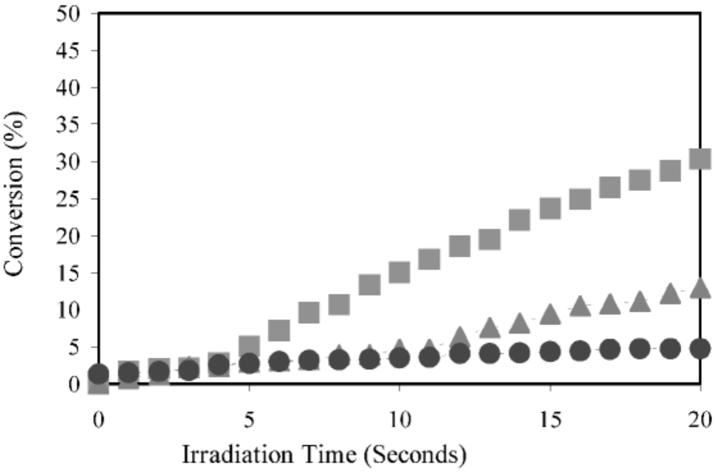


Figure 1. Study of the cationic photopolymerization of 3,4-epoxycyclohexane-3′,4′-epoxycyclohexanecarboxylate (ERL) under various conditions. (●) using 2.0 mol% IOC10, (■) 0.5 mol% polyEPB and 2.0 mol% IOC 10 and (▲) 0.5 mol% polyEPB and 2.0 mol% SOC10.

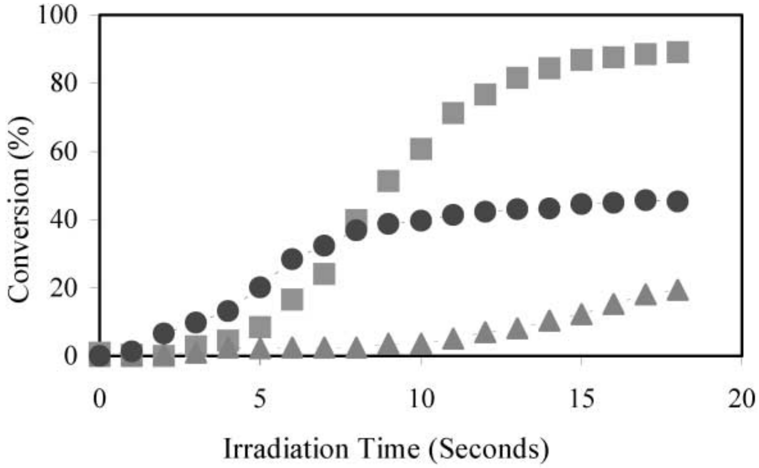


Figure 2. Study of the cationic photopolymerization of limonene dioxide under various conditions. (●) using 2.0 mol% IOC10, (■) 0.5 mol% polyEPB and 2.0 mol% IOC10, and (▲) 0.5 mol% polyEPB and 2.0 mol% SOC10.

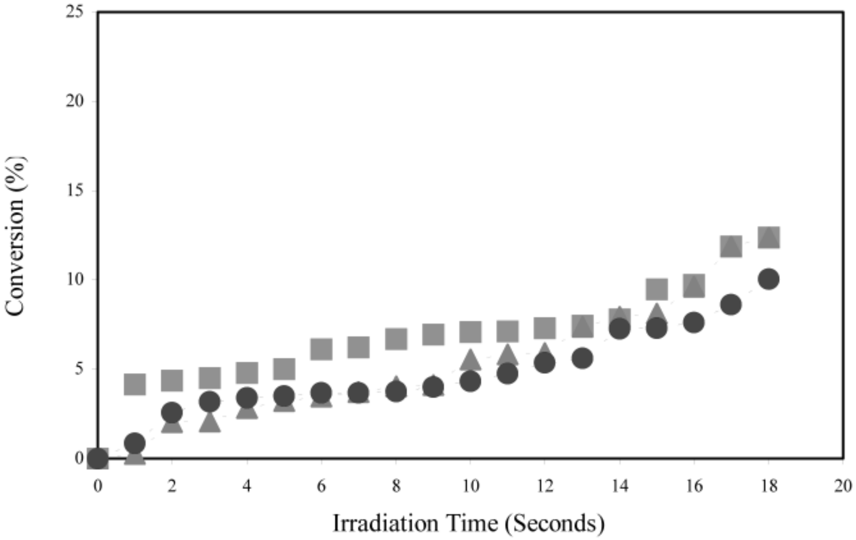


Figure 3. Kinetic study of the cationic photopolymerization of 1,2,7,8-diepoxyoctane (DEO) under various conditions. (●) using 2.0 mol% IOC10, (■) 0.5 mol% polyEPB and 2.0 mol% IOC10, and (▲) 0.5 mol% tetraethylene glycol and 2.0 mol% SOC10.

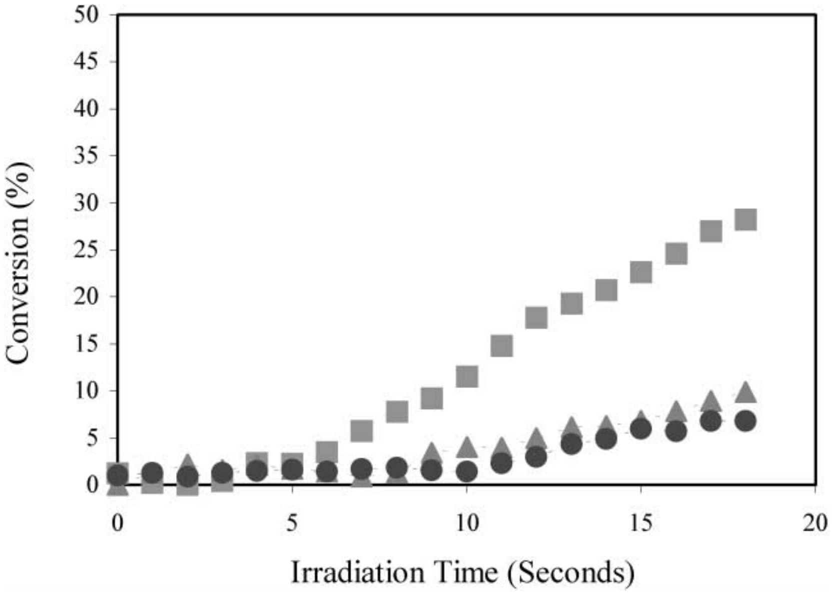


Figure 4. FT-RTIR study of the cationic photopolymerization of 3,4-epoxycyclohexane-3′,4′-epoxycyclohexanecarboxylate (ERL) with 2.0 mol% IOC10. (●) pure (ERL), (■) 0.5 mol% polyEPB, and (▲) 0.5 mol% polyEPB and 2.0 mol% tetraethylene glycol.

photopolymerizations of the corresponding pure monomers conducted in the absence of polyEPB. In all cases, the rates of ring-opening polymerization are enhanced when polyEPB is added to epoxide monomers in the presence of IOC10. The effect is greatest when either the more reactive LDO or ERL (Figs. 1 and 2) are used than if DEO (Fig. 3) is employed as monomers. Only a modest rate enhancement is observed when SOC10 is employed as the photoinitiator. Figure 4 shows the effect of the concentration of polyEPB on the rate and extent of the conversion of the ring-opening polymerization of ERL. From this study, it appears that a marked increase in the polymerization rate takes place only at concentrations of polyEPB that give a hydroxyl content above 10 mol%. It should be noted that since significant dilution of the epoxy monomer takes place at the higher concentrations of polyEPB, the actual rate enhancement is greater than it appears in Fig. 4.

To determine whether the rate enhancement effects of polyEPB are due to the presence of the terminal hydroxyl groups, polyEPB was replaced with an equivalent molar ratio (0.5 molar) of tetraethylene glycol (TEG) as the polyol and the same the same kinetic investigations were repeated. The results are given in Figs. 5–7. As before, these curves were always accompanied by a "baseline" curve of the pure monomer for comparison.

The relative reaction rate of the photopolymerization for a given monomer can be calculated from the RTIR data using the following equation:

$$\frac{R_p}{[M_o]} = \frac{(\%\text{conversion})t_2 - (\%\text{conversion})t_1}{t_2 - t_1}$$

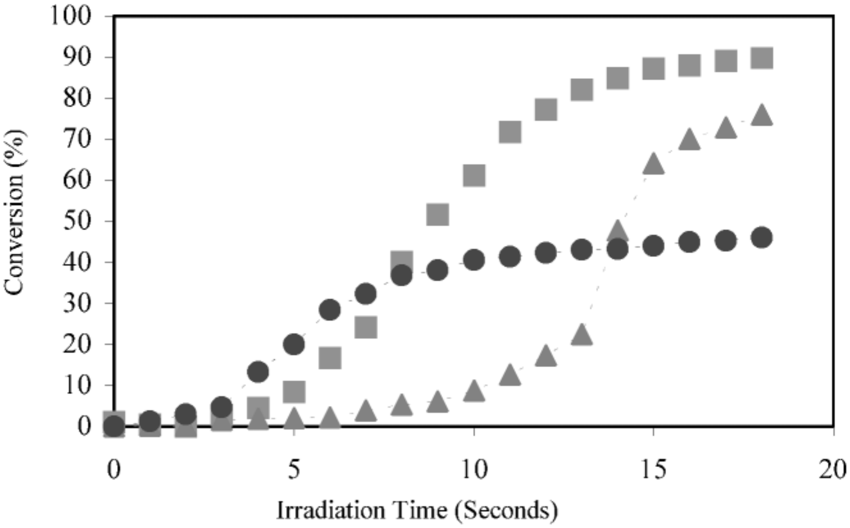


Figure 5. Study of the cationic photopolymerization of limonene dioxide (LDO) with 2.0 mol% IOC10. (●) pure (ERL), (■) 0.5 mol% polyEPB, and (▲) 0.5 mol% tetraethylene glycol.

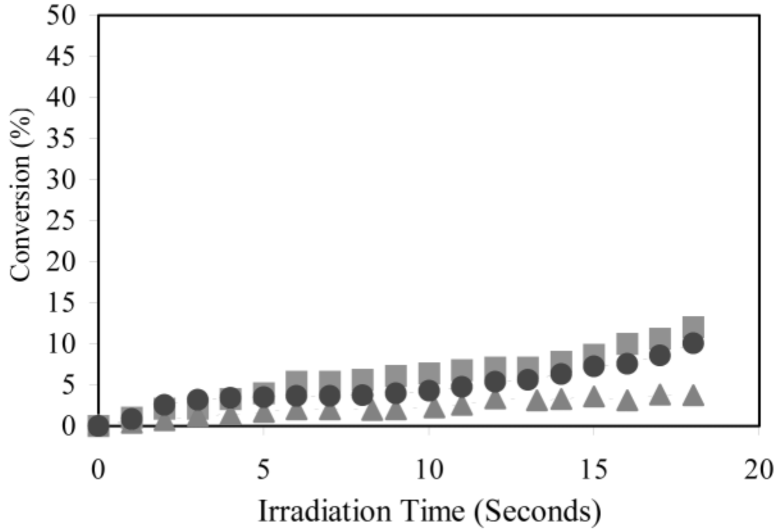


Figure 6. Kinetic study of the cationic photopolymerization of 1,2,7,8-diepoxyoctane (DEO) under various conditions. (●) using 2.0 mol% IOC10, (■) 0.5 mol% polyEPB and 2.0 mol% IOC10, and (▲) 0.5 mol% tetraethylene glycol and 2.0 mol% SOC10.

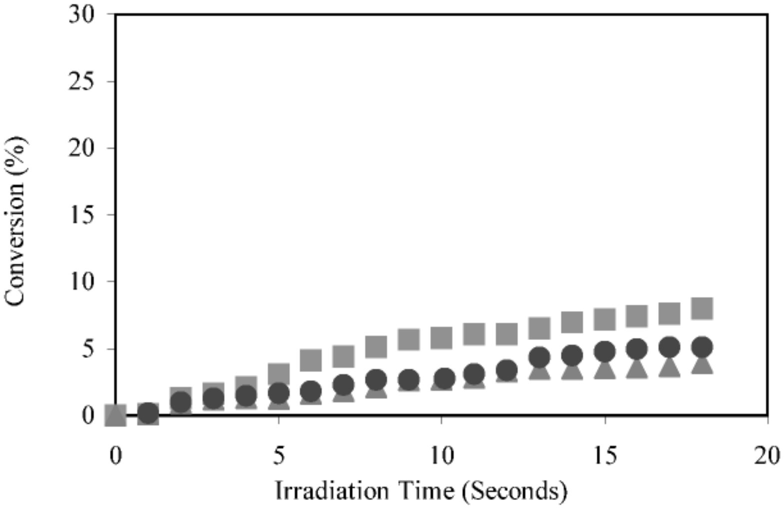


Figure 7. FT-RTIR comparison of the cationic photopolymerization of ERL. (●) 2.0 mol% IOC10, (■) 2.0 mol% IOC10 and 0.5 mol% dimethoxy polyEPB, and (▲) 2.0 mol% SOC10 and 0.5 mol% dimethoxy polyEPB.

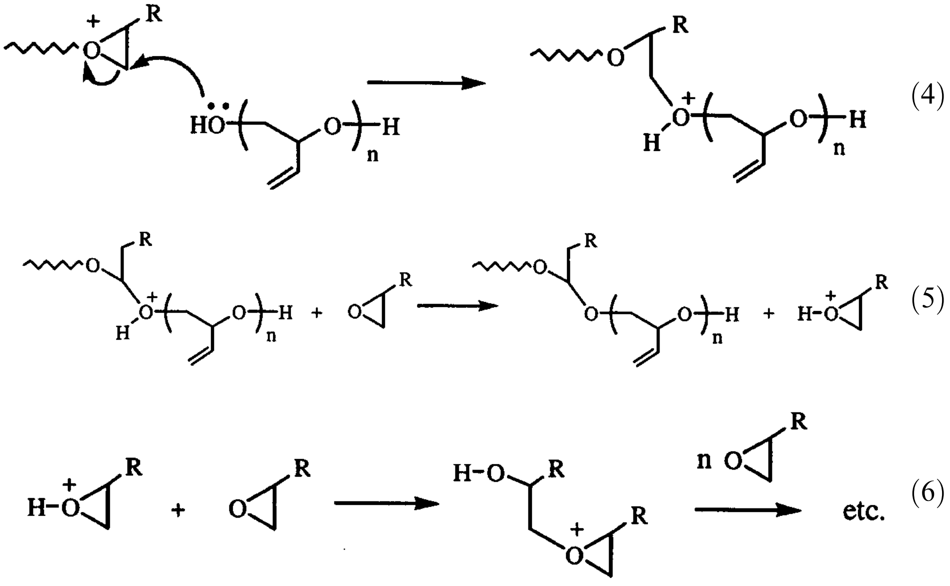
where R_p is the rate of polymerization, $[M_0]$ is the initial monomer concentration, and t_1 and t_2 are the times between the collection of conversion data. The ratio $R_p/[M_0]$ can be calculated from the initial slopes of the FT-RTIR kinetic curves. In Table 2 is presented a tabulation of the $R_p/[M_0]$ data

Table 2. Kinetic Data for the Photopolymerization of Epoxy Monomers

Monomer/ Accelerator (Photoinitiator)	Conversion% @ 20 sec	$Rp/[M_0]$ ($\times 10^{-2} s^{-1}$)	AF
ERL	7	0.35	–
ERL/polyEPB (IOC10)	30	1.5	4.3
ERL/polyEPB (SOC10)	13	0.65	1.8
ERL/TEG (IOC10)	10	0.5	1.4
LDO	47	2.35	–
LDO/polyEPB (IOC10)	90	4.5	1.9
LDO/polyEPB (SOC10)	20	1	0.42
LDO/TEG(IOC10)	75	3.75	1.6
DEO	10	0.5	–
DEO/polyEPB (IOC10)	13	0.65	1.3
DEO/TEG (IOC10)	5	0.25	0.5

taken from the FT-RTIR kinetic curves. Also shown in Table 2 are the acceleration factors (AF); determined for the different mixtures of the epoxide monomers with polyEPB or TEG as compared to the corresponding pure epoxy monomer.

When the cationic ring-opening photopolymerization of epoxide monomers is carried out in the presence of polyEPB, using I0C10 as the photoinitiator there is a significant increase in the rate of polymerization and an increase in the conversion. In some cases, a reduction of the induction period was also noted (Figs. 1 and 4). This is reflected in the larger acceleration factors for these polymerizations given in Table 2. One explanation for the observed rate acceleration and enhanced conversion in the presence of polyEPB is that there is extensive chain transfer due to the hydroxyl end groups. We have previously observed this phenomenon for many alcohols, diols and polyols.[2] In fact, polyols are now commonly added to commercial photocurable epoxy formulations to both enhance the rate of crosslinking polymerization and to modify the mechanical characteristics of the polymers that are formed.[20] This effect can be explained as shown in Eqs. (4)–(6) of Scheme 1 by the aforementioned activated monomer mechanism in which the growing oxonium chain end is intercepted by the nucleophilic terminal hydroxyl groups of polyEPB (Eq. (4)). For the sake of simplicity, only the majority (95%) repeat units derived from the epoxide ring-opening polymerization are depicted for polyEPB in this scheme and in the other schemes that appear in this article. Deprotonation of the intermediate by monomer (Eq. (5)) generates an adduct in which the polyether is now linked through an ether bond to polyEPB. The protonated monomer generated during this process can start a new polymer chain by attack of the epoxide monomer on the oxonium ion (Eq. (6)).

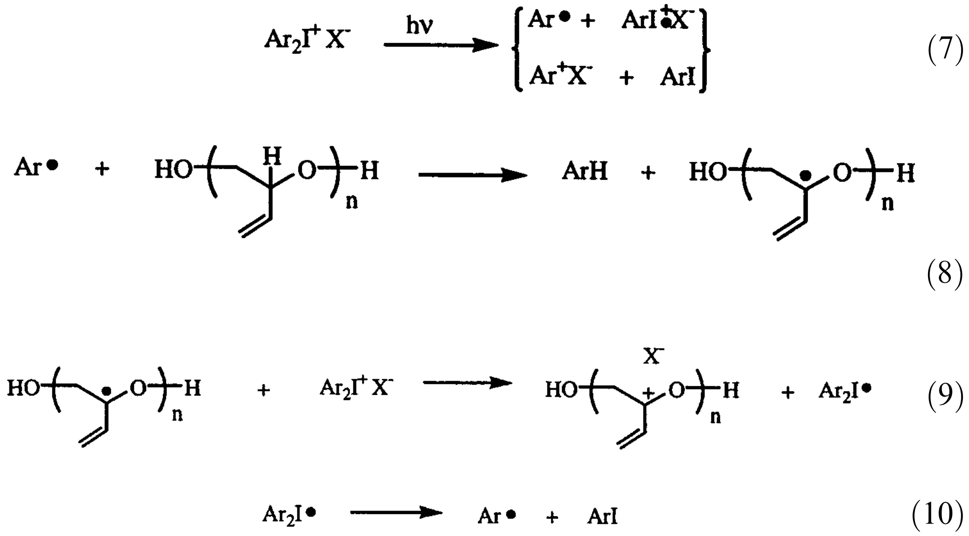


Scheme 1.

The rapid chain transfer that occurs as a result of the activated monomer mechanism contributes to an increase in the observed overall rate and to the conversion in crosslinking polymerizations. Both effects are due to rapid chain transfer by highly mobile protons that move the growing species from the crosslinked polymer chains to the monomer during the polymerization. This effect becomes more and more important as the viscosity of the reaction medium increases and the polymerization progresses towards the gel and vitrification points.

However, chain transfer processes alone do not explain all the observed effects of polyEPB in the ring-opening polymerization of epoxide monomers. Specifically, a marked reduction of the induction period as compared to the polymerization of the pure monomer is observed in the presence of polyEPB and IOC10. At the same time, this effect is not observed in the presence of identical formulations in which polyEPB was replaced with TEG. In these latter two studies, both polyEPB and TEG were employed in the same molar ratio, so that the number of terminal hydroxyl groups was identical in both cases. Further, the influence of polyEPB on epoxide photopolymerizations in the presence of SOC10 are very much reduced as compared to when IOC10 is used. To explain these latter phenomena, an additional mechanism must be invoked.

The reduction of the inhibition period can be explained on the basis of the free-radical induced photoinitiator decomposition process that is depicted in Scheme 2. The photolysis of diaryliodonium salts (Eq. (7)) generates not only cationic species, but also free-radical species as well. These radicals can abstract the highly labile tertiary and allylic ether protons present at almost

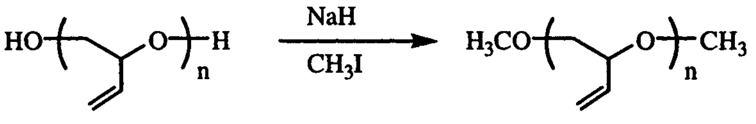


Scheme 2.

every repeat unit along the polyEPB backbone (Eq. (8)). Thereafter, the carbon-centered radical that is formed is subsequently oxidized by the diaryliodonium salt (Eq. (9)), which affords the corresponding polymer-bound carbocation species and a diaryliodine free radical. The polymeric cation can initiate the ring-opening polymerization of epoxide and other types of monomers. The entire above process is driven by the facile and irreversible decomposition of the diaryliodine free radical (Eq. (10)) to regenerate the aryl radical and a neutral aryl iodide.

The above mechanism constitutes a free-radical chain reaction in which the diaryliodonium salt is consumed by a non-photochemical process. In the course of this process, many carbocationic species are generated that are subsequently capable of initiating cationic polymerization. Consideration of this reaction scheme leads to the overall conclusion that the photochemical induced decomposition of the diaryliodonium salt photoinitiator is generally amplified by the above thermally driven redox cycle. This is manifested by a high apparent rate of consumption of the epoxide groups and by a reduction of the inhibition period. Diaryliodonium salts participate very effectively in this mechanism because they possess very low reduction potentials. This allows them to be readily reduced by the carbon-centered free radicals generated during the reaction. In the presence of SOC10, the redox cycle is not operative, since the redox potential of this photoinitiator (—28kcal/mol) is more than 5 times higher than that of IOC10 (—5kcal/mol). The redox cycle is also suppressed somewhat by replacing polyEPB with TEG in which the hydrogen abstraction process, although operative, is less effective.

To obtain further evidence for the involvement of the above free-radical mechanism, dimethoxylated polyEPB was prepared by the reaction of polyEPB with excess iodomethane, according the following reaction.



(11)

This reaction was monitored by IR spectroscopy by following the disappearance of the hydroxyl band at 3500 cm^{-1}. The photopolymerization of the difunctional epoxy monomer, ERL, was carried out in the presence of the methoxylated oligomer. In this case, the hydroxyl chain transfer mechanism should be suppressed and it should be possible to evaluate the contribution of only the free radical acceleration process. The dimethoxylated polyEPB obtained was used in a 1:2 molar ratio with respect to the epoxide groups present in the monomer. Both IOC10 and SOC10 (2.0 mol%) were employed as photoinitiators. The kinetic curves were recorded and compared with the corresponding curve for pure ERL. The results are reported in Fig. 7. It can be observed that in the presence of IOC10, the induction period is strongly reduced due to the redox cycle shown in Scheme 2. Additional support for this mechanism was obtained by adding 4% nitrobenzene as a free radical retarder to the mixture. In Fig. 8, the kinetic curves of the mixture of ERL in the presence of dimethoxylated polyEPB and IOC10 as photoinitiator either in the presence and absence of nitrobenzene are reported. Also included in this figure for comparison is the kinetic curve for the photopolymerization of the pure monomer, ERL, in the presence of IOC10. It was observed that in the presence of nitrobenzene the initial rate acceleration is depressed and the inhibition period is lengthened further confirming the proposed free-radical acceleration mechanism.

CONCLUSION

PolyEPB was employed as a reactive additive to increase the overall rate of the cationic photopolymerization of various epoxide monomers. In the presence of 0.5 mol% of polyEPB, an increase in the total epoxide conversion and a decrease of the induction period were observed. These results have been interpretated on the basis of two effects that can be attributed to the unique structure of polyEPB. First, the hydroxyl endgroups of polyEPB participate in the polymerization through an activated monomer mechanism that gives rise to rapid chain transfer. Second, polyEPB accelerates cationic photopolymerization by inducing the free-radical chain decomposition of diaryliodonium salt photoinitiators. The mechanistic studies performed during the

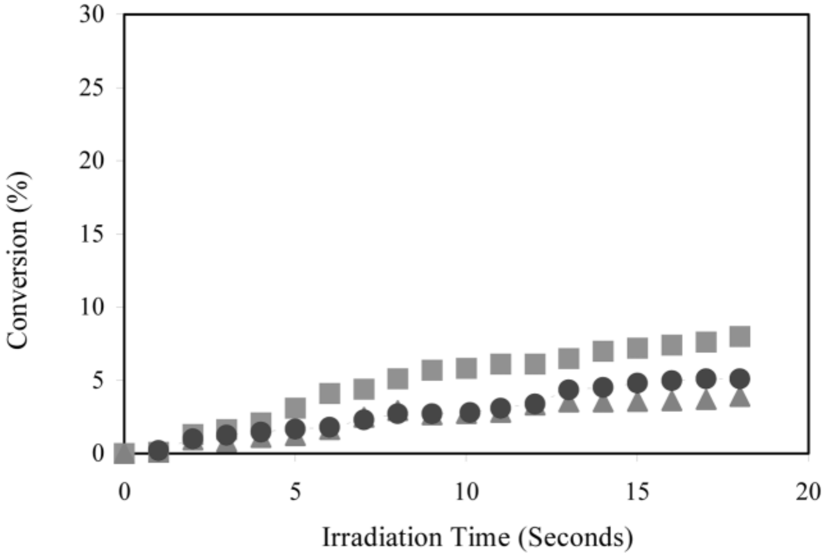


Figure 8. FT-RTIR comparison of the cationic photopolymerization of ERL with 2.0 mol% IOC10. (●) pure ERL, (■) 2.0 mol% IOC10 and 0.5 mol% methoxy polyEPB, and (▲) 2.0 mol% IOC10, 0.5 mol% dimethoxy polyEPB and 4.0 mol% nitrobenzene.

course of this investigation have isolated and confirmed the presence of both of these mechanisms. Lastly, because polyEPB becomes bound into the structure of the network, it can intrinsically modify the mechanical properties of the resulting UV-cured films.

These results suggest that polyEPB may be a very attractive substrate for use in cationically photocurable coatings, inks and adhesives. Not only are the rates of polymerization of epoxy monomers enhanced in the presence of this oligomer, but also the oligomer is incorporated into the matrix resin curing by two independent mechanisms. First, the terminal hydroxyl groups of polyEPB react with the epoxide groups during cationic polymerization to give ethers during reaction. In addition, grafting of the epoxide monomer occurs at the tertiary sites along the backbone by a combined free radical and cationic mechanism. Therefore, we suggest that polyEPB may have an appreciable potential market as a rate and matrix modifier in these applications.

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REFERENCES

1. Crivello, J.V. In *Ring-Opening Polymerization*; Brunelle, D.J., Ed.; Hanser: Munich, 1993; p. 157.
2. Crivello, J.V.; Conlon, D.A.; Olson D.R.; Webb, K.K. J Radiat. Curing **1986**, *13* (4), 3.
3. Crivello, J.V.; Liu, S. J Polym. Sci., Polym. Chem. Ed. **2000**, *38* (3), 389.
4. Chakrapani, S.; Crivello, J.V. J. Mac. Sci., Pure and Appl. Chem. **1998**, *A35* (4), 691.
5. Mowers, W.A.; Crivello, J.V.; Rajaraman, S.K. J Polym. Sci., Polym. Chern. Ed. **1999**, *37* (21), 4007.
6. Rajaraman, S.K.; Mowers, W.A.; Crivello, J.V. *PMSE Preprints* 1999, *81*, 116. ACS Meeting New Orleans, LA, August 1999.
7. Crivello, J.V.; Lee, J.L. J. Polym. Chem Ed. **1989**, *27*, 3951.
8. Akhtar, S.R.; Crivello, J.V.; Lee, J.L. J. Org. Chem. **1990**, *55*, 4222.
9. Thomsen, D.S.; Schoitt, B.; Joergnsen, K.A. J. Chern. Soc., Chem. Commun. **1992**, *15*, 1072.
10. Maples, K.R.; Lane, J.L.; Dahl, A.R. J. Labelled Compd. Radiopharm. **1992**, *31* (6), 469; Chem. Abstr. **1992**, *117*, 90057k.
11. Monnier, J.R.; Muehlbauer, P.J. US Patents 4,897,498,1990; 4,950,773,1990 to Eastman Chemical; Monnier, J.R. Applied Catalysis A, **2001**, *221*, 73.
12. Eastman Chemical Company Technical Brochure, EFC-18, Dec. 1997; Denton, D.; Falling, S.; Stavinoha, Jr., J.; Watkins, W. Chemica Oggi, May 1996, p. 17.
13. Matayabas, Jr., J.C.; Falling, S.N. US Patent 5,434,314, Jul. 18, 1995, to Eastman Chemical Co.
14. Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. In Polym. Sci.*; 68/69, Springer-Verlag: Berlin, 1985; p. 63.
15. Falling, S.N.; Godleski, S.A.; Lopez-Maldonado, P.; MacKenzie, P.B.; McCullough, J.L.G.; Matayabas, C., Jr. US Patent 5,652,328, Jul. 29, 1997; Matay-bas, Jr., J.C.; MacKenzie, P.B.; Hyatt, J.A. US Patents 5,502,137, Mar. 26, 1996; 5,536,809, Jul. 16, 1996, to Eastman Chemical Co.
16. Decker, C.; Moussa, K.J. Polymer Sci.: Part A: Polym. Chem. **1990**, *28*, 3429.
17. Decker, C.; Moussa, K. Makromol. Chem. **1990**, *191*, 963.
18. Crivello, J.V.; Bratslavsky, S.A. J. Mac. Sci., Pure and Appl. Chem. **1994**, *A31* (12), 1927.
19. Crivello, J.V.; Lohden, G. Chem. Mater. **1996**, *8* (1), 209.
20. Crivello, J.V. In *Ring-Opening Polymerization*; Brunelle, Ed; Hanser Pub.: Munich, 1993; p. 157.
21. Eaton, R.F.; Hanrahan, B.D.; Braddock, J.K. Proceedings, RadTech '90 North American, Chicago, Il, Mar. 25–29, p. 384.

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