

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

STUDY OF THE PHOTOINITIATED CATIONIC POLYMERIZATION OF 3,4-EPOXY-1-BUTENE

M. Sangermano^a; S. N. Falling^b; J. V. Crivello^a

^a Department of Chemistry, New York Center for Polymer Synthesis, Rensselaer Polytechnic Institute, Troy, NY, U.S.A. ^b Research Laboratories, Eastman Chemical Company, Kingsport, TN, U.S.A.

Online publication date: 31 August 2001

To cite this Article Sangermano, M. , Falling, S. N. and Crivello, J. V.(2001) 'STUDY OF THE PHOTOINITIATED CATIONIC POLYMERIZATION OF 3,4-EPOXY-1-BUTENE', *Journal of Macromolecular Science, Part A*, 38: 9, 919 – 932

To link to this Article: DOI: 10.1081/MA-100104944

URL: <http://dx.doi.org/10.1081/MA-100104944>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

STUDY OF THE PHOTOINITIATED CATIONIC POLYMERIZATION OF 3,4-EPOXY-1-BUTENE

M. Sangermano,¹ S. N. Falling,² and J. V. Crivello^{1,*}

¹Department of Chemistry, New York Center for Polymer Synthesis,
Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180

²Eastman Chemical Company, Research Laboratories, P.O. Box 1972,
Kingsport, TN 37662-5150

ABSTRACT

The photopolymerization of 3,4-epoxy-1-butene (**1**) was investigated using Fourier transform real-time infrared spectroscopy (FT-RTIR). The effects of photoinitiator structure and concentration and light intensity on the photopolymerization were investigated. Compared to related epoxide monomers, **1** was shown to be more reactive and this was ascribed to stabilization of the growing cationic chain end by the double bond during the ring-opening polymerization. Epoxide **1** was also shown to be useful as a reactive diluent in the photopolymerization of multifunctional epoxides and was observed to accelerate the polymerization of less reactive epoxy monomers.

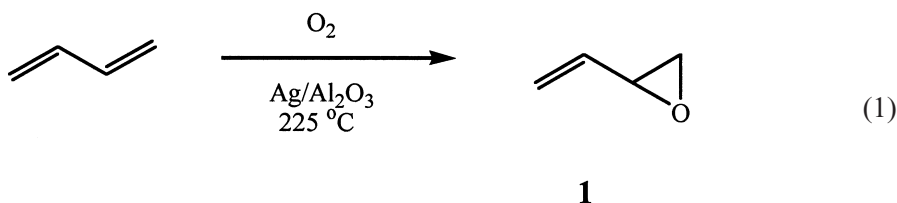
Key Words: 3,4-Epoxy-1-butene; Cationic photopolymerization; Cationic ring-opening polymerization; Epoxides; Onium salt photoinitiators; Vinyl oxirane.

INTRODUCTION

Until recently, the best available route for the preparation of 3,4-epoxy-1-butene (vinyl oxirane, **1**) was the addition of hypochlorous acid to 1,3-butadiene followed by treatment of the resulting chlorohydrin with base [1]. However, this reaction is complicated by the formation of butadiene diepoxide and other by-

*Corresponding author.

products so that high yields of **1** have not been obtained by this method. The development by Monnier [2] of a novel, high yield synthesis of **1** by the catalytic, vapor-phase epoxidation of 1,3-butadiene (Equation 1) has made this compound attractive as a versatile, low cost, difunctional monomer with reactive epoxy and vinyl groups.



Epoxide **1** has been found to be a highly reactive compound that can be converted to a wide range of interesting compounds by specific reaction at either the epoxy group, the double bond or simultaneously at both functional groups [3]. One rapidly emerging technology upon which this monomer may have an impact is cationic UV curing, a process which involves the rapid photoinduced polymerization of liquid multifunctional monomers to give solid, crosslinked films useful for coatings, printing inks and adhesives. Typically, onium salt photoinitiators such as diaryliodonium and triarylsulfonium salts are employed in this process [4]. Polymerization of the monomer results from the attack of a strong protonic acid generated from the photolysis of these photoinitiators on the monomer. Monomers containing the epoxide group undergo facile ring-opening polymerization when irradiated with UV light in the presence of an onium salt photoinitiator. In the case of **1**, polyethers bearing pendant vinyl groups may result by simple ring-opening polymerization. In addition, there was the possibility that the double bond could also interact with the neighboring epoxy group during polymerization to produce polymers in which all four-carbon atoms of the monomer are incorporated into the polymer backbone [5, 6].

Accordingly, a study of the cationic photopolymerization of **1** was conducted. This article reports the results of this study as well as the determination of the structure of the polymer that is formed. In addition, the cationic photopolymerizations of several related compounds were studied to determine the effect of the vinyl group on the rate of photopolymerization of **1**.

EXPERIMENTAL

Materials

3,4-Epoxy-1-butene (**1**), 3,4-dibromo-1,2-epoxybutane and 3,4-dichloro-1,2-epoxybutane were obtained as gifts and used as received from Eastman Chemical Company, Kingsport, TN. 1,2-Epoxybutane was used as purchased from

the Aldrich Chemical Co., Milwaukee, WI. The diaryliodonium salt photoinitiators employed in this investigation were prepared as described previously [7]. $^1\text{H-NMR}$ spectra were obtained using a Varian, Inova 500 MHz Spectrometer.

Bulk Photopolymerization of 3,4-Epoxy-1-butene (1)

A 3 mL solution of **1** containing 1.0 mol% IOC10 was prepared. The solution was sealed with a rubber cap in a 15 mm dia. quartz reaction tube, the tube placed in an ice bath and irradiated for two minutes in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company, Hamden, CT). After this time, chloroform was added to the reaction mixture and the polymer solution poured into methanol. The polymer was isolated by filtration and once again dissolved in chloroform and reprecipitated into methanol. This process was repeated one more time. The resulting polymer was dried in a vacuum oven at 50°C , and then the $^1\text{H-NMR}$ spectrum recorded.

Real-Time Infrared Spectroscopy (RTIR) Photopolymerization Studies

The thin film photopolymerizations of all the monomers 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 4-20 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.

Photopolymerizations were carried out at room temperature using unfiltered UV light from a Hg arc source in bulk monomers containing various concentrations of the indicated photoinitiator. All concentrations in this paper are given in units of mol% with respect to the epoxide monomer. The monomer/photoinitiator solutions were coated onto a $12\ \mu\text{m}$ oriented and corona treated polypropylene films (General Electric Capacitor Dept., Hudson Falls, NY), covered with an identical polypropylene film, and then mounted in $5\ \text{cm} \times 5\ \text{cm}$ slide frames. The thickness of the liquid monomer films was estimated at 10-25 μm . Infrared spectra were collected at a rate of 1 spectrum per second using LabCalc data acquisition software obtained from the Galactic Industries Corp., Salem, NH and were processed using GRAMS-386 software from the same company. During irradiation, the decrease of the IR absorbance due to the vinyl group at $1640\ \text{cm}^{-1}$ and/or the epoxy groups between $790\text{-}915\ \text{cm}^{-1}$ of the monomers were monitored. In all cases, three to five runs were recorded and the results averaged. Data reduction and subsequent conversion versus time plots were obtained using Excel software (Microsoft Corp., Redmond, WA).

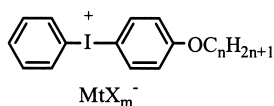
The kinetic parameter, $R_p/[M_0]$, for selected kinetic runs was determined from the initial slopes of the irradiation time-conversion curves according to Equation 2.

$$R_p/[M_0] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1}) / (t_2 - t_1) \quad (2)$$

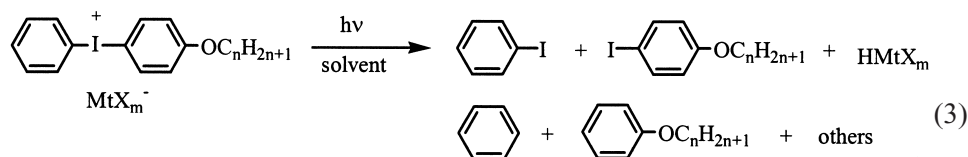
where R_p and $[M_0]$ are respectively the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times t_1 and t_2 .

RESULTS AND DISCUSSION

Figures 1 and 2 show respectively, the $^1\text{H-NMR}$ spectra of neat monomer **1** and its polymer (in CDCl_3) prepared by solution cationic photopolymerization using (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) as the photoinitiator. The structures of IOC10 ($\text{C}_n\text{H}_{2n+1} = \text{C}_{10}\text{H}_{21}$, $\text{MtX}_m^- = \text{SbF}_6^-$) and other related diaryliodonium salt photoinitiators used in this investigation are shown below. These photoinitiators were selected for their good solubility in **1**, as well as in the other monomers used in this investigation. Furthermore, it has been previously shown that these photoinitiators possess high quantum yields of photolysis and are extraordinarily efficient photoinitiators of both vinyl ether and epoxide cationic polymerizations. [8, 9] On photolysis (Equation 3), diaryliodonium salts undergo irreversible fragmentation to give a variety of organic products together with a protonic acid, HMtX_m , derived by hydrogen abstraction reaction from the monomer or solvent [4].



The $^1\text{H-NMR}$ assignments shown in Figure 2 were made on the basis of model compounds and on the published spectra of structurally similar polymers [5, 6, 10]. The spectrum of the polymer obtained on cationic photopolymerization is indicative of mainly a straightforward epoxide ring-opening polymerization as shown in Equations 4 and 5. In addition, there are also some repeat units involving addition to both the double bond and the epoxide groups. These repeat units can be rationalized as arising via an $\text{S}_{\text{N}}2'$ conjugate addition mechanism as depicted in Equation 6.



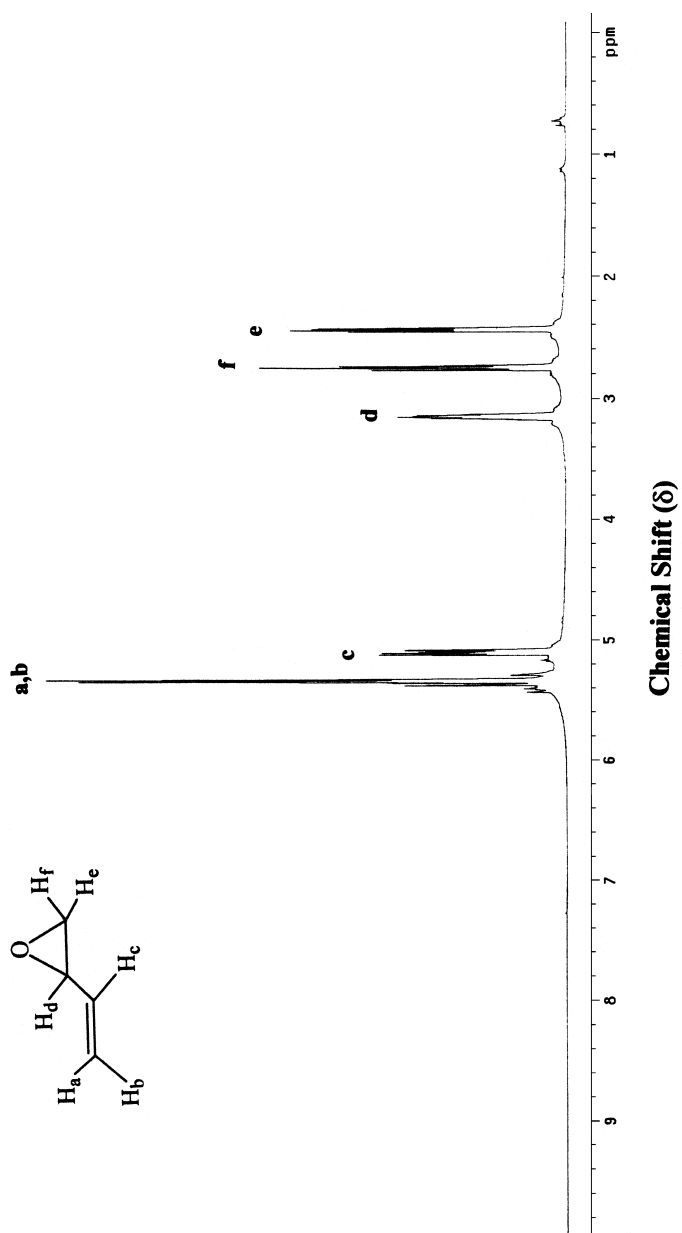


Figure 1. ¹H-NMR spectrum of neat 3,4-epoxy-1-butene (I).

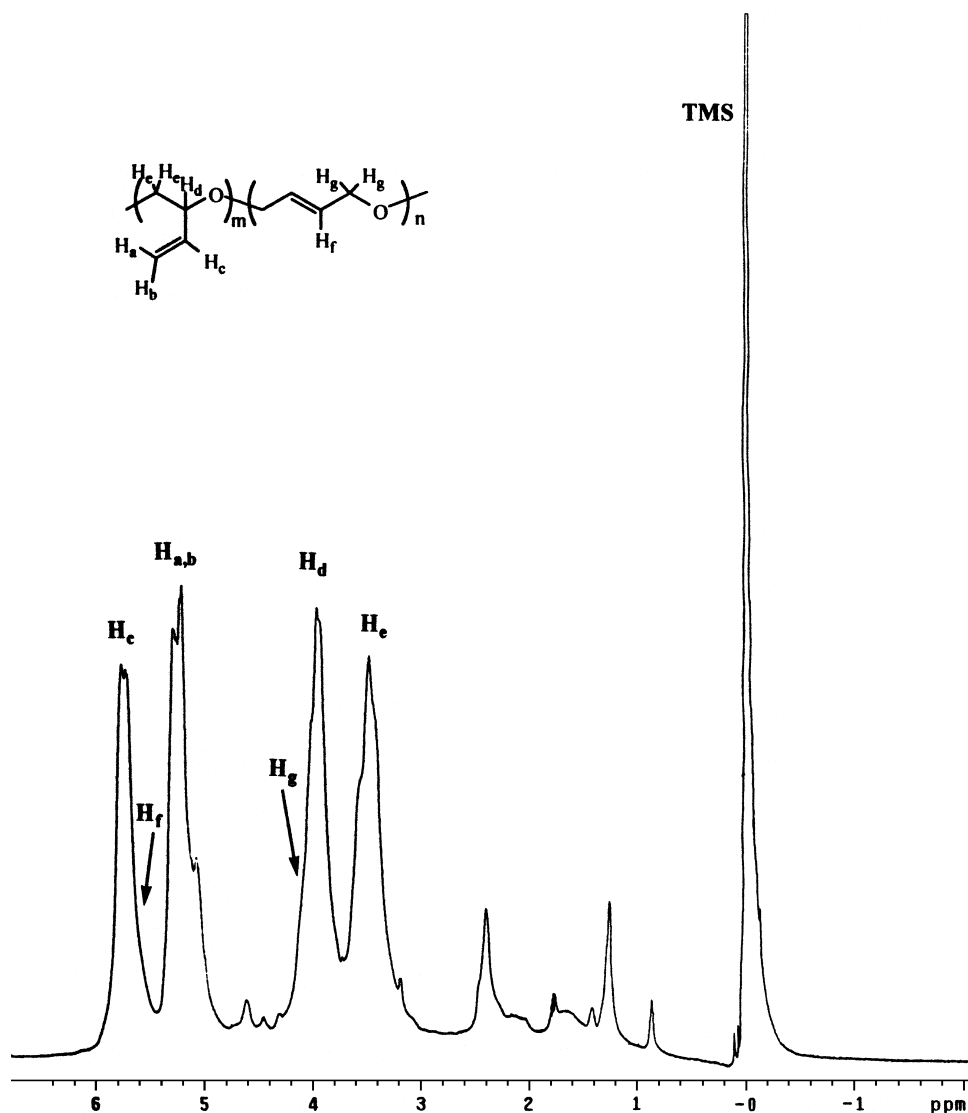
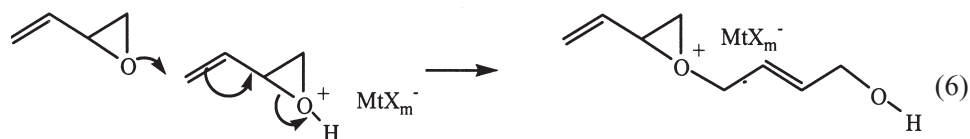
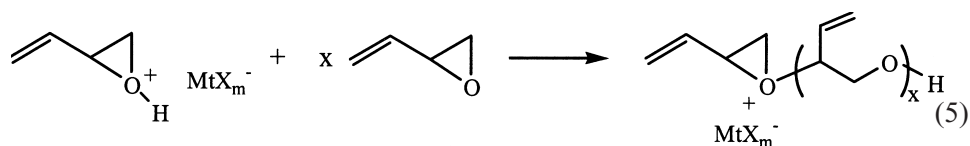
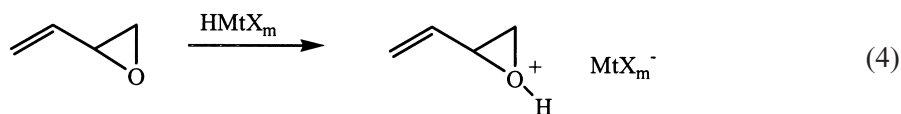


Figure 2. ¹H-NMR spectrum of poly(3,4-epoxy-1-butene) produced by photopolymerization of **1** using 1 mol% IOC10 as the photoinitiator.

The polymer formed in this polymerization was found to be lightly crosslinked. Crosslinking took place whether the polymerization was carried out in air or nitrogen. In contrast, the cationic polymerization of **1** by trifluoromethanesulfonic acid has been reported to yield soluble, linear polymers.^[5] Photolysis of diaryliodonium salt photoinitiators also yields free radicals that can result in the production of sites for crosslinking either by hydrogen abstraction-coupling reactions or by direct addition polymerization of the pendant double bonds.



A brief, systematic investigation of the effects of various experimental parameters on the rate of the photoinitiated cationic polymerization of **1** was carried out. In this study we have employed Fourier transform real time infrared spectroscopy (FT-RTIR) [11, 12] to monitor the rates of the photopolymerization. We have described the technique and the configuration of our apparatus in previous publications [8, 13] from this laboratory.

Figure 3 shows a FT-RTIR study of the polymerization of bulk **1** containing 2.0 mol% of IOC10 as photoinitiator. Depicted in this figure are two conversion

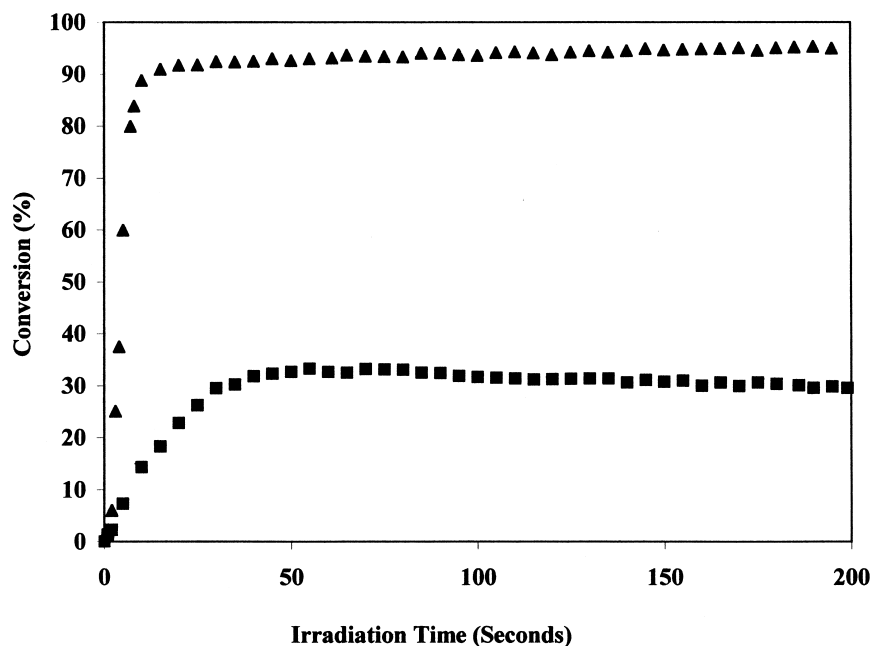


Figure 3. FT-RTIR study of the photopolymerization of **1** in the presence of 2.0 mol% IOC10: (▲) epoxy groups; (■) vinyl groups. (light intensity 15 mW/cm²).

versus time curves; one for the epoxy group at 820 cm^{-1} and the other at 1640 cm^{-1} for the disappearance of the vinyl group of **1** [14]. The results support the conclusion drawn from the $^1\text{H-NMR}$ spectrum (Figure 2) mentioned above. While the conversion of the epoxy groups is nearly quantitative, only approximately 35% of the vinyl groups are consumed during the course of the polymerization reaction (250 seconds irradiation).

Effect of Light Intensity

The photopolymerizations of bulk samples of **1**, containing 1.0 mol% of IOC10 as photoinitiator were investigated using FT-RTIR. Shown below in Figure 4 are the kinetic curves obtained at UV light intensities of 10 and 5 mW/cm^2 . The kinetic parameters $R_p/[M_0]$ taken from the initial slopes of these two curves are respectively, $12 \times 10^2\text{ s}^{-1}$ and $1.1 \times 10^2\text{ s}^{-1}$. A considerably faster polymerization rate was observed at the higher light intensity. These results suggest that at the lower light intensity, the rate of polymerization is light limited.

Photoinitiator Concentration

The effect of the photoinitiator concentration on the rate of the cationic ring-opening polymerization of **1** was investigated at a UV light intensity of 5 mW/cm^2 using FT-RTIR. The photopolymerizations were carried out in bulk **1**, containing 1.0 mol% and 2.0 mol%, respectively, of IOC10 as the photoinitiator. The conversion versus time curves for the two different photoinitiator concentrations are reported below in Figure 5. A higher polymerization rate was obtained at the

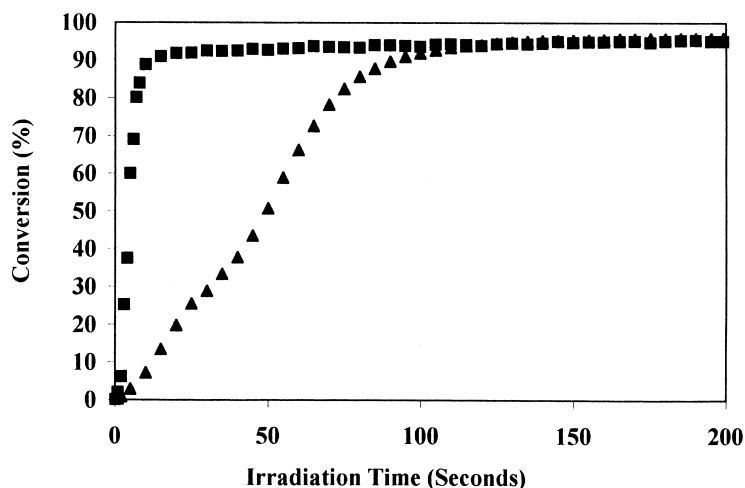


Figure 4. Study of the effect of UV light intensity on the rate of the epoxide ring-opening polymerization of **1** in the presence of 1.0 mol% IOC10: 5 mW/cm^2 (▲); 10 mW/cm^2 (■).

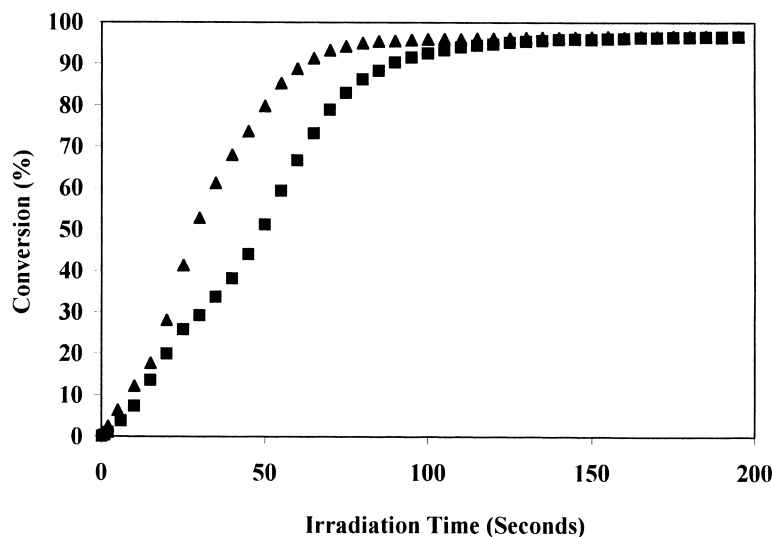


Figure 5. Effect of the concentration of IOC10 on the rate of the ring-opening photopolymerization of **1**: 1.0 mol% (■); 2.0 mol% (▲) (light intensity 5 mW/cm²).

greater photoinitiator concentration. This is indicative of the generation of a greater number of active initiator species when the optical density of the photoinitiator in the polymerization mixture is doubled. Previously, [15] we have observed generally that the maximum rate of most epoxide ring-opening photopolymerizations was achieved at a photoinitiator concentration of 2-3 mol%.

Based on the results obtained in the above two studies, a UV light intensity of 10 mW/cm² and a photoinitiator concentration of 2.0 mol% were adopted for all of the subsequent studies of the cationic ring-opening photopolymerization of **1**.

Comparison of Different Cationic Photoinitiators on the Photopolymerization of **1**

Several different diaryliodonium salts were employed as cationic photoinitiators for the polymerization of **1**. In each case, the concentration of the photoinitiator was 2.0 mol% with respect to the monomer. Initially, three related hexafluoroantimonate salts were employed, with different length side chain alkoxy groups on the phenyl ring. Using IOC8, IOC10, and IOC11 (C_nH_{2n+1} = C₈H₁₇, C₁₀H₂₁, C₁₁H₂₃, respectively), no difference in the kinetic behavior of the **1** photopolymerization was observed (Figure 6). However, major differences were observed when the counterion of IOC10 was varied as shown in Figure 7. As expected, [16] the polymerization rate increases according to the following sequence: SbF₆⁻ > AsF₆⁻ > PF₆⁻.

Figure 8 shows a comparison of the photopolymerization of **1** with several closely related compounds and derivatives. Monomer **1** exhibits considerably higher

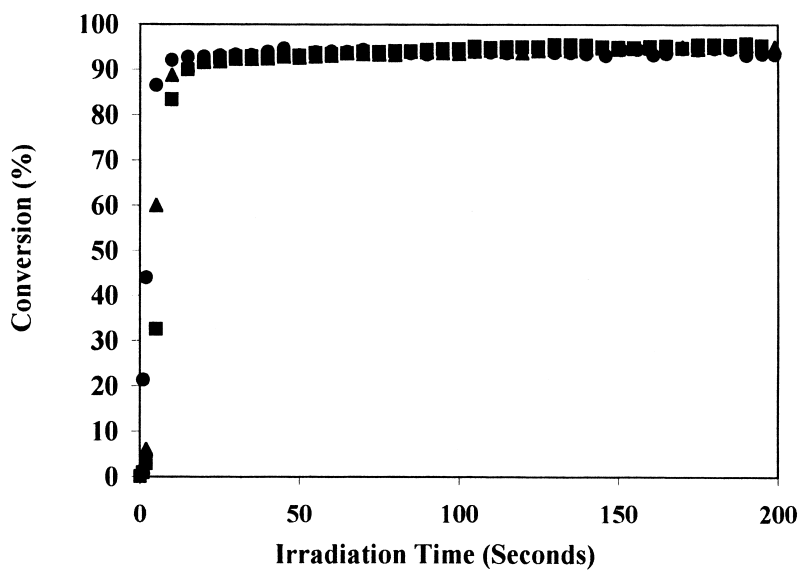


Figure 6. Effect of the structure of the photoinitiator (2.0 mol%) on the rate of the photopolymerization of **1**: IOC8 (4-*n*-octyloxyphenyl)phenyliodonium SbF_6^- (■); IOC10 (4-*n*-decyloxyphenyl)phenyliodonium SbF_6^- (▲); IOC11 (4-*n*-undecyloxyphenyl)phenyliodonium SbF_6^- (●) (light intensity 10 mW/cm^2).

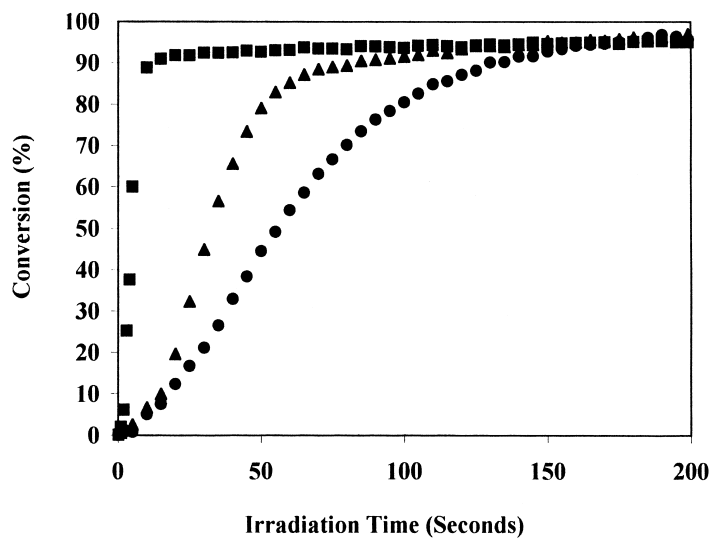
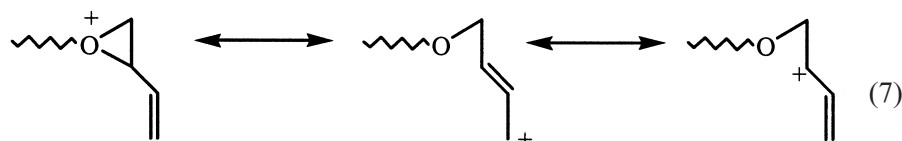


Figure 7. FT-RTIR study of the influence of the counter ion of the photoinitiator (2.0 mol%) on the rate of the photopolymerization of **1**: IOC10 (4-*n*-decyloxyphenyl)phenyliodonium SbF_6^- (■); AsF_6^- (▲); and PF_6^- (●) (light intensity 10 mW/cm^2).

reactivity in cationic photopolymerization than its saturated analogue, 1,2-epoxybutane, and is also more reactive than its dibromo and dichloro derivatives (3,4-dibromo-1,2-epoxybutane and 3,4-dichloro-1,2-epoxybutane). This suggests that the neighboring vinyl group of **1** exerts an activating influence on the epoxide group. One way in which this may occur is through resonance stabilization of the propagating oxonium ion end group of the polymer chain as depicted in Equation 7.



Thus, equilibration between the oxonium and allylic cations would be expected to provide a strong driving force for the polymerization of **1** and also accounts for the observed formation of repeat units arising from 1,4-conjugate addition.

Epoxide **1** as Reactive Diluent in Epoxide Photopolymerizations

Monomer **1** was employed as a reactive diluent in the crosslinking photopolymerization of mono- and difunctional epoxides such as phenyl glycidyl ether (PGE, 1,2-epoxy-3-phenoxypropane) and the bicycloaliphatic epoxy com-

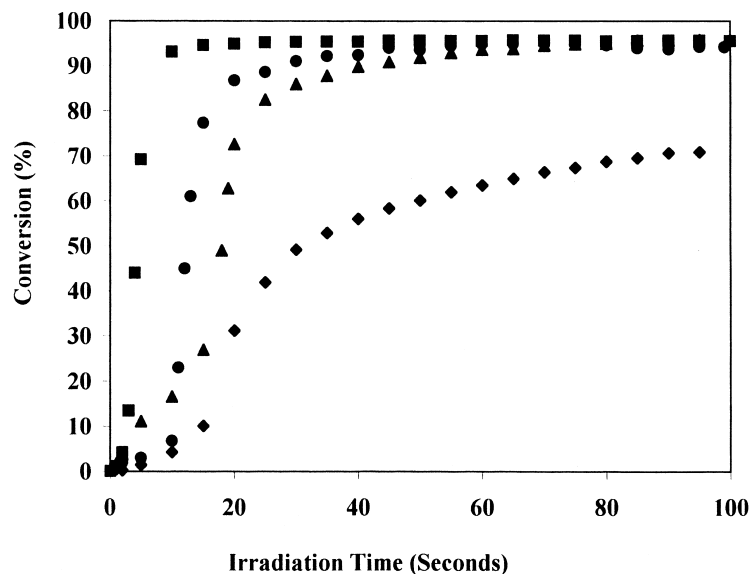
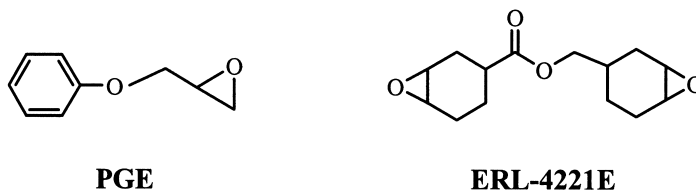


Figure 8. Comparison of the reactivity of **1** (■) with 1,2-epoxybutane (◆); 3,4-dibromo-1,2-epoxybutane (▲); and 3,4-dichloro-1,2-epoxybutane (●) (2.0 mol% IOC10, light intensity 15 mW/cm²).

pond, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (ERL-4221E, Union Carbide Corporation).



In all cases, a 1:1 molar ratio with respect to the epoxy groups of the two monomers with **1** was employed. It was possible to simultaneously follow the photopolymerization of both of the two monomers in the mixtures using FT-RTIR because they have different and characteristic IR epoxy bands. The results are shown in Figures 9 and 10. For comparison, in each kinetic study, the kinetic curves for the photopolymerization of the pure monomers is also included in these two studies. As can be seen in Figure 9, the polymerization of **1** takes place much more rapidly than ERL-4221E. The addition of **1** to ERL-4221E substantially increases the rate of polymerization of the epoxide groups of ERL-4221E, while depressing the rate for **1** in the mixture. Similar, but very much smaller effects are observed for the polymerization of a 1/1 molar mixture of **1** and PGE (Figure 10).

The results of these studies show that **1** is a highly reactive monomer under the conditions of photoinitiated cationic polymerization. The reactivity of this monomer is qualitatively greater than the "high reactivity" bicycloaliphatic

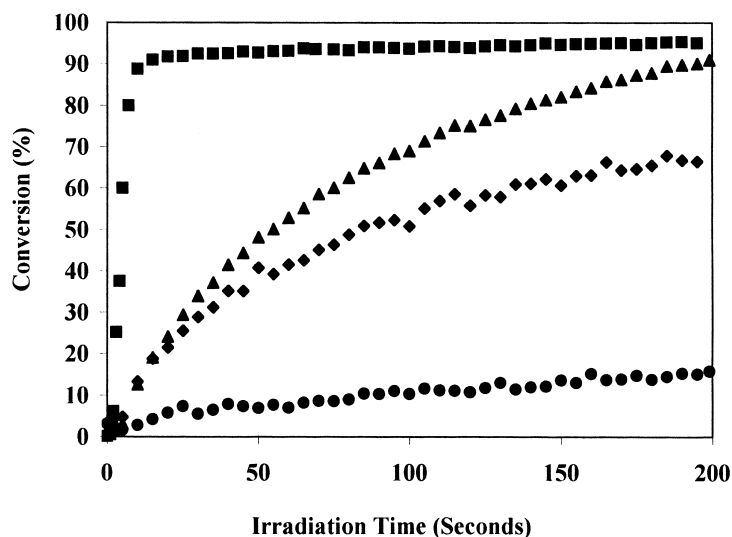


Figure 9. FT-RTIR study of the photopolymerization of pure **1** (■), ERL-4221E (●), **1** (820 cm⁻¹ band) in a 1/0.5 mixture with ERL-4221E (▲) and ERL-4221E (750 cm⁻¹ band) in a 1/0.5 mixture with **1** (◆) (2.0 mol% IOC10, light intensity 10 mW/cm²).

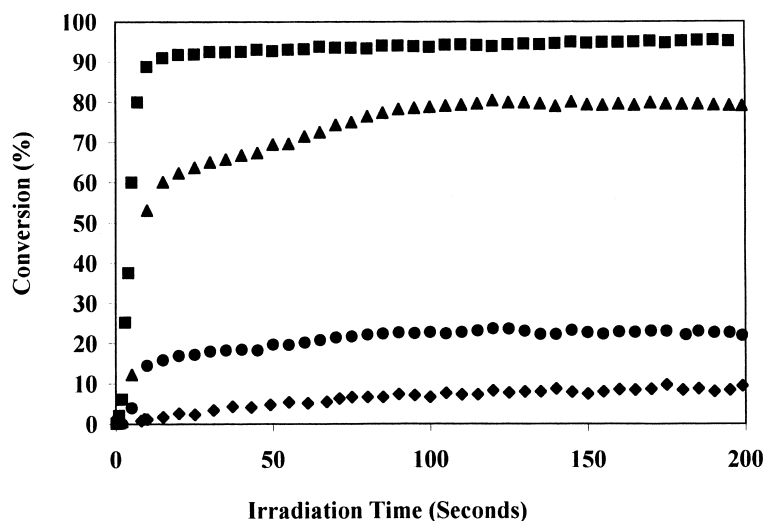


Figure 10. FT-RTIR study of the photopolymerization of pure **1** (■), PGE (◆), **1** (820 cm^{-1} band) in a 1/1 mixture with PGE (▲) and PGE (760 cm^{-1} band) in a 1/1 mixture with **1** (●) (2.0 mol% IOC10, light intensity 10 mW/cm^2).

epoxy resin ERL-4221E that is commonly employed for commercial applications in coatings, printing inks and adhesives. There are several explanations for the high reactivity of **1** as a monomer in these polymerizations. First, as mentioned before, the neighboring vinyl double bond may serve to activate the epoxy group towards ring-opening polymerization. The presence of 1,4-enchainment in the isolated polymer demonstrates that the double bond is reactive in these polymerizations. In addition, we have shown that the reactivity of epoxide monomers decrease when nucleophilic groups are present in the molecule such as the ester groups in ERL-4221E [17, 18]. Lastly, epoxide **1** is a liquid monomer with low viscosity. It has been observed that the rates of photopolymerizations are decreased in media of high viscosity [19].

CONCLUSION

3,4-Epoxy-1-butene (**1**) is a very reactive monomer in photoinitiated cationic polymerization. Using typical diaryliodonium salt cationic photoinitiators, rapid ring-opening epoxide polymerization of this monomer takes place. We have observed that the polymerization of this monomer is subject to the same experimental parameters as other epoxy monomers and that there is an optimum light intensity and photoinitiator concentration necessary to achieve the highest rate. Diaryliodonium salt photoinitiators bearing the hexafluoroantimonate anion are the most reactive for the photopolymerization of **1**. The addition of **1** was found to increase the rate of polymerization of other typical epoxy monomers. Specifically, **1** may have utility as a reactive diluent in UV curable epoxy systems employed for coatings, printing inks and adhesives.

ACKNOWLEDGMENT

Financial support of this work was gratefully received from Eastman Chemical Company, Kingsport, Tennessee.

REFERENCES

1. Lee, H.; Neville, K. *Handbook of Epoxy Resins*, McGraw Hill: New York, 1982, p. 3-3.
2. Monnier, J.R.; Muehlbauer, P.J. U.S. Patents, 4,897,498 (Jan. 30, 1990) and 4,950,773, (Aug. 21, 1990) to Eastman Kodak Company.
3. Eastman Chemical Company. Publication P-264A (2000); Denton, D.; Falling, S.; Monnier, J.; Stavinoha, J., Jr.; Watkins, W. *Chemica Oggi*, 17 (May, 1996); Turner, S.R.; Falling, S.N.; Blevins, R.W. *Journ. Mac. Sci., Pure & Appl. Chem.* **1997**, *A34*, 1857.
4. Crivello, J.V. *Ring-Opening Polymerization*, Brunelle, D.J., Editor, Hanser: Munich, 1993, p. 157.
5. Matayabas, J.C., Jr.; Falling, S.N. U.S. Patents, 5,434,314 (July, 18, 1995) and 5,536,882 (July 16, 1996) to Eastman Chemical Company.
6. Matayabas, J.C., Jr.; Falling, S.N. U.S. Patents, 5,393,867 (Feb. 28, 1995) and 5,608,034 (Mar. 4, 1997) to Eastman Chemical Company. Falling, S.N.; Godleski, S.A.; Lopez-Maldonado, P.; MacKenzie, P.B.; McCullough, L.G.; Matayabas, J.C., Jr. U.S. Patent, 5,608,034 (March, 4, 1997) to Eastman Chemical Company.
7. Crivello J.V.; Lee, J.L. *J. Polym. Sci., Polym. Part A: Chem. Ed.* 1989, *27*, 3951.
8. Rajaraman, S.K.; Mowers, W.A.; Crivello, J.V. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1999**, *37*, 4007.
9. Mowers, W.A.; Crivello, J.V.; Rajaraman, S.K. *RadTech Report*, March/April, 2000.
10. Wagener, K.B.; Brzezinska, K.; Bauch, C.G. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 75.
11. Decker, C.; Moussa, K. *Makromol. Chem.* **1990**, *191*, 963.
12. Decker, C. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1992**, *30*, 913.
13. Hua, Y.; Crivello, J.V. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2000**, *38*, 3697.
14. Belamy, L.J. *The Infra-red Spectra of Complex Molecules*, Methuen & Co.: London, 1962, p. 36.
15. Crivello, J.V.; Lee, J.L. *Polymer Journal* **1985**, *17*, 73.
16. Crivello, J.V. *Advances in Polymer Science*, Springer Verlag, Vol. 62, 1984, p. 1.
17. Crivello, J.V.; Varlemann, U. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1995**, *33* (14), 2463.
18. Crivello, J.V.; Linzer, V. *Polimery* **1998**, *68*, 661.
19. Moorjani, S.K.; Rangarajan, B.; Scranton, A.B. *Photopolymerization Fundamentals and Applications*, Scranton, A.B.; Bowman, C.N.; Peiffer, R.W., Eds. ACS Symposium Series No. 673, American Chemical Society, Washington, D.C., 1997, p. 95.

Received April 10, 2001