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SYNTHESIS AND CATIONIC PHOTOPOLYMERIZATION OF NOVEL CYCLOALIPHATIC EPOXY MONOMERS BASED ON 5,6-EPOXY-1,3-OXEPANE

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Key Words: 5,6-Epoxy-1,3-dioxepane; 3,5,8-Trioxabicyclo[5.1.0]octane; 4-Vinyl-3,5,8-trioxabicyclo[5.1.0]octane; Cationic photopolymerization

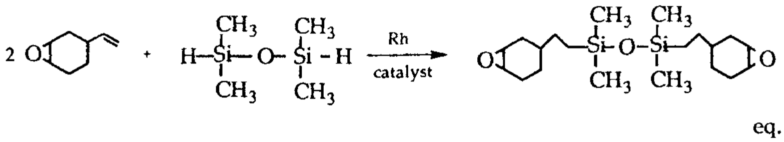
ABSTRACT

A novel series of mono-, di-, and trifunctional monomers containing 5,6-epoxy-1,3-dioxepane groups were prepared along with a similar series of epoxycyclohexane monomers. The reactivities of the monomers were compared using both differential scanning photocalorimetry and Fourier transform real-time infrared spectroscopy. The novel monomers containing 5,6-epoxy-1,3-dioxepane groups were highly reactive in photoinitiated cationic polymerization but slightly less reactive than their counterparts based on epoxycyclohexane.

INTRODUCTION

Over the past several years, research in this laboratory has centered on the investigation of the chemistry of photoinitiated polymerizations in general and in particular on the photoinduced cationic ring-opening polymerization of epoxides [1, 2]. As the commercial applications of the photoinitiated cationic polymerizations of epoxides have multiplied, there has arisen a greater need to understand the influence of the structure of these monomers on their rates of polymerization. For such applications it is often important to achieve the highest photopolymerization rates possible. During our early investigations in this area we noted that there appeared to be a wide range of reactivity between structurally diverse epoxides [3]. Specifically, for a given cationic photoinitiator it was observed that cycloaliphatic epoxides are more reactive than their open chain counterparts, and these in turn were more reactive than glycidyl ethers or glycidyl esters. Thus, while cycloaliphatic epoxides are very reactive, glycidyl esters undergo very sluggish photoinduced cationic polymerizations.

In a recent publication we described the observation that silicon-containing monomers bearing epoxycyclohexane groups possessed reactivities which were much greater than conventional cycloaliphatic epoxides and had rates of polymerization which resembled those of acrylate monomers [4, 5]. A wide variety of silicon-containing epoxides were prepared by the straightforward transition-metal-catalyzed hydrosilation of 4-vinylepoxycyclohexane [6]. Shown in Eq. (1) is the synthesis of a typical difunctional monomer using this chemistry.



eq. 1

It was the object of this investigation to extend the hydrosilation chemistry shown above in an attempt to prepare additional novel types of silicon-containing cycloaliphatic epoxy monomers and to evaluate their reactivity in photoinitiated cationic polymerization.

EXPERIMENTAL

All the organic reagents employed in this experiment were purchased from Aldrich Chemical Co. and used as received. 1,1,3,3,5,5-Hexamethyltrisiolxane was purchased from Silar Laboratories while methyl tris(dimethylsiloxy)silane was obtained from United Chemical Technology. Gas chromatographic analyses were performed on a Hewlett Packard HP-5840A Gas Chromatograph equipped with 6 ft × 1/8 in. OV-17 phenylsilicone columns and a flame ionization detector. ^{1}H-NMR spectra were obtained using a Varian XL-200 MHz spectrometer in $CDCl_3$ solvent, and chemical shifts are reported relative to tetramethylsilane as an internal standard. (4-*n*-Decyloxyphenyl)phenyliodonium hexafluoroantimonate was prepared as described previously [7]. Epoxycyclohexane functional siloxane monomers **V** and **VII** were prepared according to a published procedure [6].

Synthesis of 4,7-Dihydro-1,3-dioxepin (I) [8]

The synthesis given below for 4,7-dihydro-1,3-dioxepin (I) was also employed for the preparation of 2-vinyl-4,7-dihydro-1,3-dioxepin (**III**).

A mixture of 58.15 g (0.66 mol) of 2-butene-1,4-diol, 18 g (0.6 mol) paraformaldehyde, 40 g benzene, and 0.3 g *p*-toluenesulfonic acid was placed in a round-bottomed flask equipped with a heating mantle, thermometer, Dean-Stark trap, and condenser. The reaction mixture was refluxed until the theoretical amount of water was collected in the trap. After cooling, the solvent was removed on a rotary evaporator and the oil which remained was subjected to fractional distillation. There were obtained 35 g (58% yield) of product, 4,7-dihydro-1,3-dioxepin (**I**), with a bp of 126.5-128°C.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 4.86 (s, 2H, $O-CH_2-O$); 4.30 (s, 4H, $O-CH_2-CH=$); 5.73 (m, 2H, $CH=CH$ 1,3-dioxepine ring).

In a similar fashion, 2-vinyl-4,7-dihydro-1,3-dioxepin (**III**) was isolated as a colorless liquid and purified by fractional distillation (bp 36°C/0.25 mmHg). The yield was 67%.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 4.3 (q, 4H, $O-CH_2-CH=$); 5.8 (m, 1H, $O-CH-O$); 5.42 (m, 2H, $CH_2=$); 5.63 (dd, 2H, $CH=CH$ 1,3-dioxepine ring); 5.90 (m, 1H, $CH=$).

Epoxidation of 4,7-Dihydro-1,3-dioxepin

Into a 1-liter three-neck round-bottomed flask fitted with a mechanical stirrer, pressure equalizer additional funnel, and a thermometer were placed 10 g (80 mmol) of 4,7-dihydrodioxepin, 40 mL dichloromethane, 40 mL acetone, 150 mL of a pH 7.4 phosphate buffer solution, and 0.2 g 18-crown-6 ether. The flask was cooled to below 5°C using an ice-salt mixture, and 100 g oxone (0.4 M aqueous solution) was added in small portions using the additional funnel. The pH of the solution was maintained at 7.4 by periodically adding 1 N aqueous sodium hydroxide solution. After completion of the addition of oxone, the reaction mixture was stirred for 16 hours while maintaining the temperature below 5°C. The course of the reaction was monitored using ^{1}H-NMR by following the disappearance of the olefinic protons. The layers were separated and the aqueous layer extracted with fresh dichloromethane. The combined organic layers were washed with distilled water and then dried over anhydrous sodium sulfate. Finally, the solvent was removed using a rotary evaporator, and the resulting solid recrystallized from *n*-hexane to give **II** (mp 54.5-55°C) in 30% yield.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 4.65 (dd, 2H, $O-CH_2-O$); 4.13 (dd, 4H, CH_2); 3.24 (q, 2H, epoxy$-$CH).

Chemoselective Epoxidation of 2-Vinyl-4,7-dihydro-1,3-dioxepin (III)

Into a 3-liter three-neck round-bottomed flask fitted with a mechanical stirrer, pressure equalizer addition funnel, and a thermometer were placed 30 g (0.24 mol) of 2-vinyl-4,7-dihydro-1,3-dioxepin, 120 mL dichloromethane, 120 mL acetone, 500 mL of a pH 7.4 phosphate buffer solution, and 0.6 g 18-crown-6 ether. The flask was cooled to below 5°C using an ice-salt mixture, and 320 g (0.82 mol) oxone (0.4 M aqueous solution) was added in small portions using the addition funnel. The pH of the solution was maintained at 7.4 by periodically adding 1 N aqueous sodium hydroxide solution. After completion of the addition of oxone, the reaction mixture was stirred for 16 hours while maintaining the temperature below 5°C. The course of the reaction was monitored using ^{1}H-NMR by following the disappearance of the olefinic protons. The layers were separated and the aqueous layer extracted with fresh dichloromethane. The combined organic layers were washed with distilled water and then dried over anhydrous sodium sulfate. Finally, the solvent was removed using a rotary evaporator, and the resulting material subjected to vacuum distillation to give **IV** (bp 58-59°C/0.25 mmHg) in 70% yield. **IV** was subjected to column chromatography (200-400 mesh silica gel, v/v 90:10 hexane:EtOAc) to separate the *cis* and *trans* isomers.

cis-**IV**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 5.82 (m, 1H, $CH{=}CH_2$); 5.43 (dd, 1H, *trans*-$CH{=}CH_2$); 5.37 (dd, 1H, *cis*-$CH{=}CH_2$); 5.08 (m, 1H, O—CH—O); 4.07 (dd, 8H, CH_2); 3.25 (m, 2H, epoxy—C*H*).

trans-**IV**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 5.82 (m, 1H, $CH{=}CH_2$); 5.38 (dd, 1H, *trans*-$CH{=}CH_2$); 5.29 (dd, 1H, *cis*-$CH{=}CH_2$); 4.87 (m, 1H, O—CH—O); 4.15 (dd, 8H, CH_2); 3.25 (m, 2H, epoxy—C*H*).

Hydrosilation of 2-Vinyl-3,5-epoxy-1,3-dioxepane with 1,1,3,3,5,5-Hexamethyltrisiloxane; Preparation of VI

A mixture of 3.12 g (22 mmol) of 2-vinyl-5,6-epoxy-1,3-dioxepane (**IV**) and 1.83 g (17.6 mmol) of 1,1,3,3,5,5-hexamethyltrisiloxane was combined with 1 mg tris(triphenylphosphine)rhodium(I) chloride in a 25-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was heated to 80-85°C and the reaction was monitored by following the decrease of the infrared band at 2100 cm^{-1} assigned to the Si—H group of the silane. When the above band had disappeared (1 hour), the reaction mixture was cooled and then stripped of volatile starting materials under high vacuum. **VI** was isolated as a colorless oil in 85% yield.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 0.00 (s, 6H, $O{-}Si(CH_3)_2{-}O$); 0.1 (m, 12H, $-Si(CH_3)_2{-}CH_2-$); 0.55 (t, 4H, $CH_2{-}Si$); 1.60 (t, 4H, $CH{-}CH_2$); 3.2 (dd, 4H, epoxide—C*H*); 3.8 (m, 8H, $O{-}CH_2{-}O$); 4.4 (m, 2H, $CH{-}CH_2CH_2$).

Real-Time Infrared Spectroscopy (FT-RTIR)

The conversions of the monomers to polymer were measured using Fourier transform real-time infrared analysis (FT-RTIR). This method involves the monitoring of an appropriate IR band due to the polymerizing epoxide group while simultaneously irradiating a thin film sample of a monomer with UV light. Measurements were performed on a Midac, Corp. Model M1300 Fourier Transform Infrared Spectrometer equipped with a UVEXS Co SCU 110 UV lamp fitted with a flexible liquid optic cable. The end of the probe was situated so as to direct UV irradiation at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 1000 mJ/cm^2·min. Samples were prepared by placing the liquid monomers containing 0.5 mol% per epoxide equivalent of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate between two poly(ethylene) films and then mounting the resulting sandwich in 5 cm × 5 cm slide frames. The progress of the polymerizations of the monomers were determined quantitatively by monitoring the decrease of the epoxide peaks at 880-890 cm^{-1}. The data were collected on a Bit-Wise Co. 486 PC computer, reduced, and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. Grams

386, Version 3.0 software package. Light intensity measurements were made with the aid of an International Light Co. Control-Cure Radiometer.

Differential Scanning Photocalorimetry (DSP)

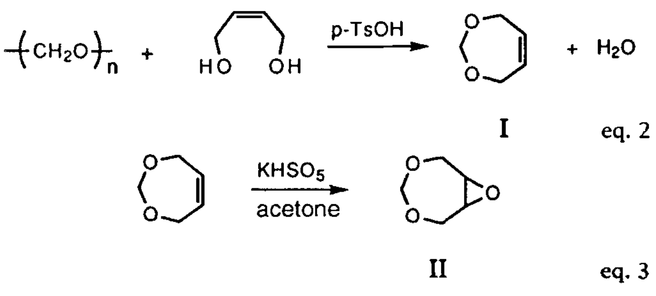
The photoinitiated polymerizations of the cyclic epoxide monomers were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a 100-W high-pressure Hg arc lamp. DSP experiments were conducted isothermally at 30°C on 0.5–1.0 mg samples of the monomer-photoinitiator solutions. The samples were placed in aluminum pans and allowed to equilibrate for several minutes. The samples were then irradiated by opening the shutter, and the course of the exothermic polymerization was followed by recording the heat evolved as a function of the irradiation time. The light flux used in these studies was 130–140 $mJ/cm^2 \cdot min$.

RESULTS AND DISCUSSION

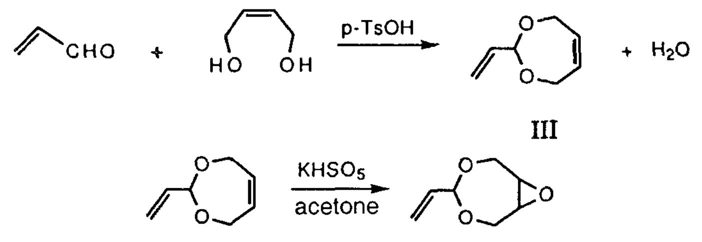
The search for a suitable cycloaliphatic epoxy ring system which could be incorporated into multifunctional monomers led us to consider many alternatives. After some initial scouting reactions we focused on the 5,6-epoxy-1,3-dioxepane (IUPAC nomenclature 3,5,8-trioxabicyclo[5.1.0]octane) ring system. This ring system is easy to prepare as shown in Scheme 1 from the readily obtained *cis*-2,3-butene-1,4-diol by condensation with paraformaldehyde (Eq. 2).

Epoxidation of **I** with oxone ($KHSO_5$) readily gives model compound 5,6-epoxy-1,3-dioxepane, **II**, as a colorless crystalline solid in good yield. The above synthetic sequence could be readily adapted to give a derivative bearing a vinyl group which could be further derivatized by hydrosilation to produce the desired monomers. The key compound, 2-vinyl-5,6-epoxy-1,3-dioxepane (4-vinyl-3,5,8-trioxabicyclo[5.1.0]octane, **IV**) was readily prepared by the analogous synthetic sequence shown in Scheme 2.

Reaction of *cis*-2,3-butene-1,4-diol reaction with acrolein yielded **III**. This latter compound underwent chemoselective epoxidation with oxone at the ring double bond to give **IV** in 70% yield. Even in the presence of excess ozone, **IV** is the major product, indicating that competitive reaction at the less reactive vinyl double



SCHEME 1.



III

eq. 4

IV

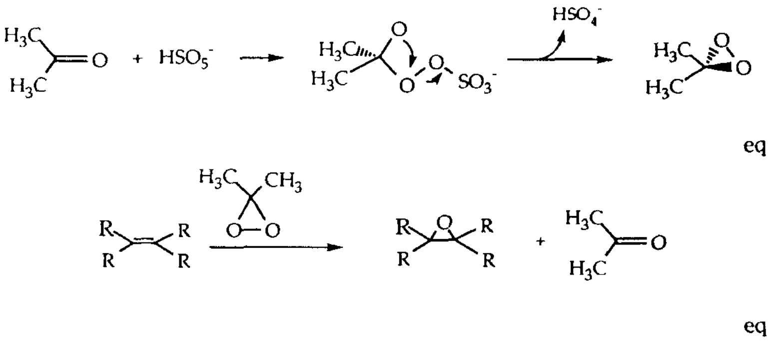
eq. 5

SCHEME 2.

bond is very much disfavored. This process involves the formation of dimethyldioxirane by interaction of oxone with acetone [9]. The transfer of oxygen from dimethyldioxirane to the alkene substrate forms the epoxide and regenerates the ketone (Scheme 3).

Figure 1 shows the ^{1}H-NMR spectra of **III** and **IV**. After the epoxidation, the double bond proton at $\delta = 5.7$ ppm had completely disappeared and new peak at $\delta = 3.2$ ppm appeared due to the protons of the epoxy group. The spectrum of **IV** shows that a mixture of geometric and stereoisomers is formed as a consequence of the presence of the epoxide and the vinyl substituent on the ring. The *cis* and *trans* isomers could be separated using column chromatography (200–400 mesh silica gel, v/v 90:10 hexane:EtOAc). These two isomers could be readily identified due to the characteristic ^{1}H-NMR chemical shifts for the acetal hydrogens (*cis*, 4.87; *trans*, 5.08 ppm).

It has been reported that the usual platinum hydrosilation catalysts cannot be employed for the hydrosilation of unsaturated epoxides due to their tendency to catalyze ring-opening polymerization of the epoxide groups [10]. In contrast, the rhodium containing Wilkinson's catalyst [$(Ph_3P)_3RhCl$] is highly selective for hydrosilation and shows no tendency toward the undesired epoxide ring-opening polymerization [6]. In the absence of a solvent, the rhodium-catalyzed hydrosilations of **IV** and 4-vinylepoxycyclohexane are very fast and the reactions are completed within approximately 30 minutes at room temperature. Using this approach, several



eq. 6

eq. 7

SCHEME 3.

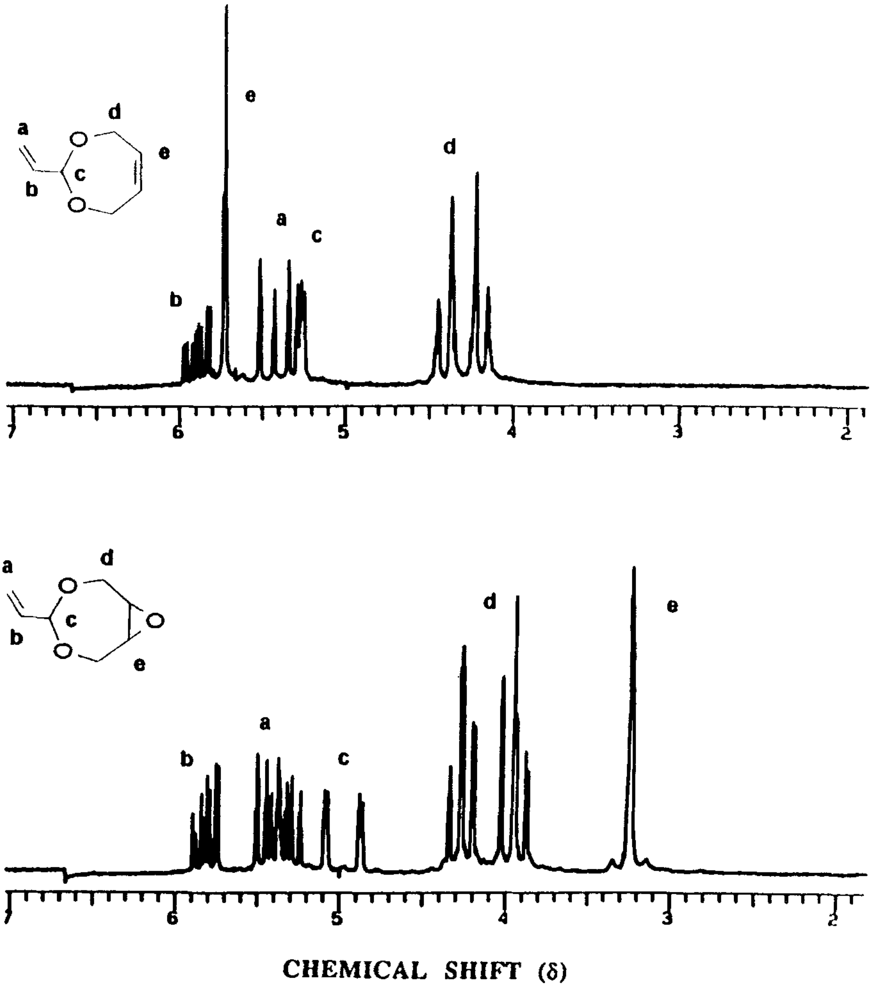
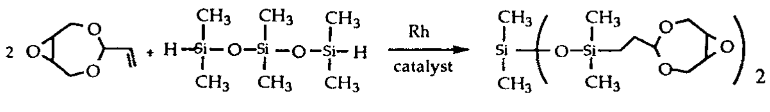


FIG. 1. ^{1}H-NMR spectrum of **III** and a mixture of *cis*-**IV** and *trans*-**IV** in $CDCl_3$.

different di- and trifunctional epoxy monomers shown in Table 1 were prepared. Equation (8) shows the synthesis of difunctional monomer **VI**.

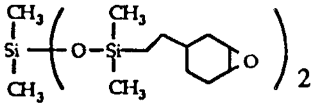
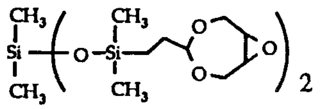
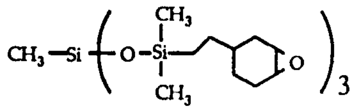
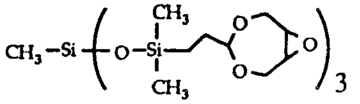


VI

eq. 8

The hydrosilations proceed quantitatively, and the pure monomers could be obtained by simply removing traces of unreacted starting materials under vacuum after completion of the reaction. A similar set of monomers based on 4-vinylepoxy-

TABLE 1. Synthesis of Epoxide Monomers

Structure	Notation		Elemental analysis	
			% C	% H
	**II**	Calcd:	51.72	6.94
		Found:	51.88	6.88
	**IV**	Calcd:	59.15	7.09
		Found:	59.22	7.05
	**V**	Calcd:	57.84	9.71
		Found:	57.63	9.26
	**VI**	Calcd:	48.75	8.12
		Found:	48.44	7.84
	**VII**	Calcd:	58.07	9.43
		Found:	57.48	9.18
	**VIII**	Calcd:	48.38	7.83
		Found:	48.24	7.69

cyclohexane was prepared in the same manner [6]. Table 1 gives the structures and the elemental analyses of these monomers.

Photoinitiated Cationic Polymerization

We have conducted a study of the photoinitiated cationic polymerizations of the silicon-containing epoxide monomers shown in Table 1. The polymerization rates of the 5,6-epoxy-1,3-dioxepanes and the corresponding epoxycyclohexane monomers were compared in an effort to determine the effect of the change in the structure of the epoxide. In these studies the diaryliodonium salt photoinitiator, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate, was used because of its high quantum yield ($\Phi = 0.7$) and excellent solubility in various monomers.

One experimental technique employed for following the course of the cationic photopolymerizations was differential scanning photocalorimetry. This method involves monitoring the heat liberated on polymerization of the monomer as a function of time as the sample is being irradiated with ultraviolet light. The time from the start of the irradiation to the maximum of the exothermic peak gives a measure of the relative reactivity of the monomer. Figure 2 shows the differential photocalorimetry curves from which the photoinitiated cationic polymerization of the vinyl

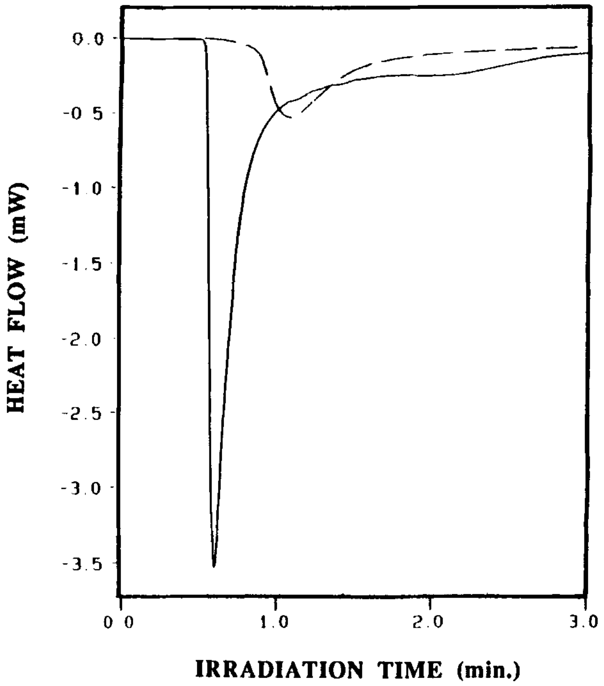


FIG. 2. DSP study of the cationic photopolymerization of (- -) **IV** and (——) **IX**.

starting materials for the two classes of monomers are compared. As shown in Fig. 2, 3-vinyl-7-oxabicyclo[4.1.0]heptane (**IX**) is more reactive than **IV**, which displays an induction period at the beginning of the UV exposure followed by a comparatively broad exothermic peak. In contrast, **IX** gives a very sharp, rather narrow exotherm, although some tailing is noted. This initial study indicated that the epoxycyclohexane moiety is more reactive than the 5,6-epoxy-1,3-dioxepane moiety. After polymerization, transparent films were obtained in both cases. The solubilities of these two polymers were determined by immersing them in chloroform. While the polymer from **IX** displays good solubility, the polymer from **IV** showed almost completely insolubility in this and other solvents. This suggested that the latter polymer was crosslinked.

We have also employed Fourier transform real-time infrared spectroscopy (FT-RTIR) to investigate the reactivities of two types of cyclic epoxide monomers. This was achieved by monitoring the decrease of the characteristic epoxide band at 870–880 cm^{-1} of the monomers while continuously irradiating them with broadband UV light. Figure 3 shows the conversion versus irradiation time curves for the diaryliodonium salt photoinitiated cationic polymerization of the *cis*- and *trans*-**IV** isomers. A comparison of the initial slopes of the curves leads us to conclude that 1) these compounds are surprisingly reactive and 2) there is no appreciable difference in reactivity between these two isomers. The longer induction period observed for the *cis*-**IV** isomer indicates that this compound contains a slightly greater amount of trace impurities than the corresponding *trans*-**IV** isomer. It should be noted that

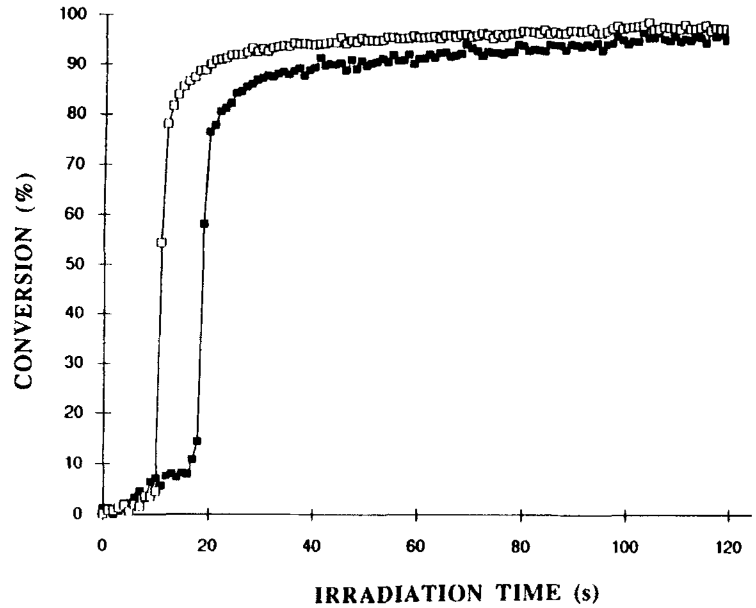


FIG. 3. FT-RTIR study of the photopolymerization of **IV** isomers: (□) *trans*, (■) *cis*.

these polymerizations were conducted under ambient conditions. Thus, the monomers were briefly exposed to the laboratory environment before polymerization took place, during which they may have absorbed water and other inhibiting agents. Due to the very low light intensity under which the FT-RTIR were conducted, one can observe that the acid generated on photolysis first interacts with these agents and, after they are consumed, polymerization ensues very rapidly. It should be noted that a direct comparison between the FT-RTIR and DSP studies of these monomers cannot be made since the light intensity used in the studies were very different (18–19 vs 130–140 mJ/cm^2·min). An FT-RTIR study of the reactivities of mono-, di-, and trifunctional epoxycyclohexane monomers **V**, **VII**, and **IX** is given in Fig. 4. While the reactivities and conversions of the mono- and difunctional monomers are nearly the same, the polymerization of trifunctional monomer, **VII**, shows a slightly lower reactivity and conversion. This has been noted before [11] and has been attributed to the increasing crosslink density in these monomers which limits conversion due to a decrease in the mobility and diffusion of the reactive functional groups during polymerization. Figure 5 shows a similar study for the photopolymerization of 5,6-epoxy-1,3-dioxepane monomers **IV**, **VI**, and **VIII**. As previously mentioned, the monofunctional epoxide shows a very high polymerization rate. The di- and trifunctional monomers, by comparison, undergo a slower polymerization and proceed to lower conversions of the epoxide groups.

Since Figs. 4 and 5 are on the same scale, the two types of cyclic epoxide monomers may be directly compared. Although they are very reactive monomers, in all cases the 5,6-epoxy-1,3-dioxepane monomers have lower reactivities than the analogous epoxycyclohexane monomers. The limiting conversions of the former monomers are also lower than the latter ones. We have sought to find explanations

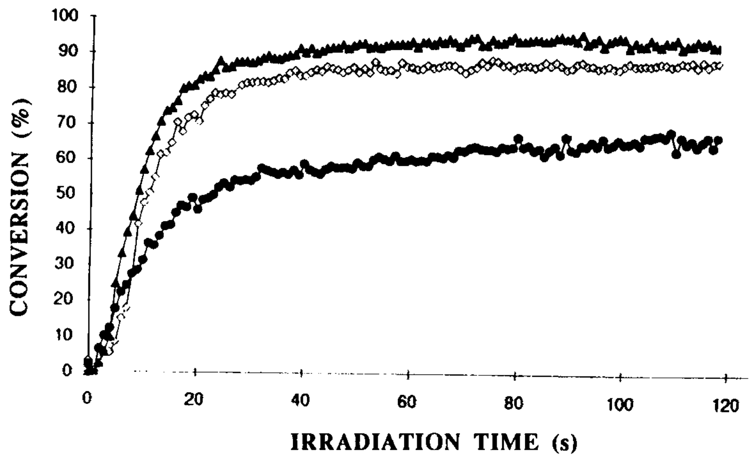


FIG. 4. FT-RTIR study of the photopolymerization of epoxycyclohexane monomers: (▲) IX, (◇) V, (●) VII.

for this difference in behavior between the two types of monomers. One factor which might contribute to the observed differences is the potential higher functionality of the 5,6-epoxy-1,3-dioxepane monomers as compared to the epoxycyclohexane monomers. It has been shown that 1,3-dioxepanes undergo cationic ring-opening polymerization [12]. Further, we have observed that on photoinitiated cationic polymerization, both monomers II and IV give crosslinked polymers. This

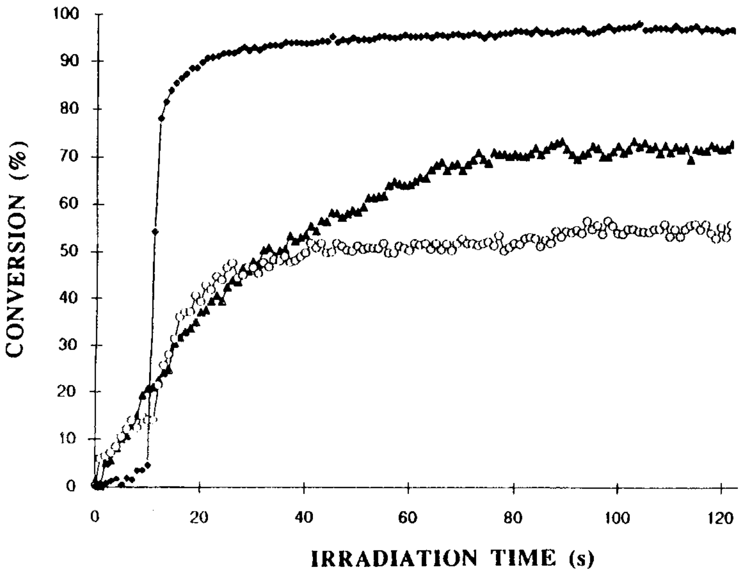
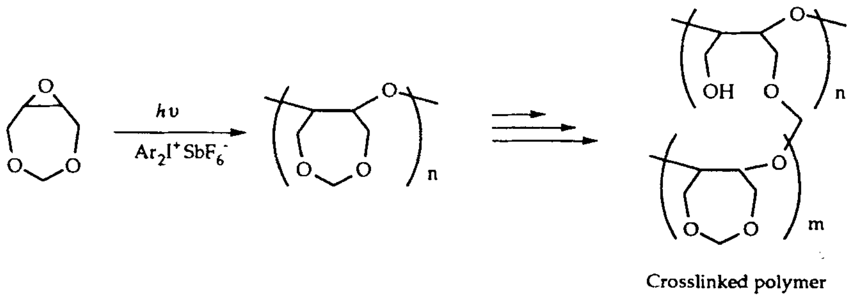


FIG. 5. Comparison of the photopolymerizations of 5,6-epoxy-1,3-dioxepane monomers: (■) *trans*-IV, (▲) VI, (○) VIII.

suggests that while the primary reaction of these monomers involves polymerization of the epoxide group, some amount of simultaneous ring-opening of the 1,3-dioxepane ring also takes place, resulting in crosslinking. This is depicted in Eq. (9) for monomer **II**.



eq. 9

The extent of crosslinking has not been directly measured but is presumed to be rather low. This is however, sufficient to render the polymer insoluble in all solvents.

Thus, the higher actual functionality of the 5,6-epoxy-1,3-dioxepane monomers causes these monomers to reach the vitrification point at lower conversions than the corresponding epoxycyclohexanes. Hence, the polymerization slows since it becomes diffusion controlled earlier for these former monomers. An additional consideration is the presence of the acetal oxygens in the former monomers. It has been shown that the incorporation of slightly basic ether or acetal oxygens into a monomer has a deaccelerating effect on the cationic photopolymerization rate of that monomer [13].

CONCLUSIONS

In this study the synthesis and cationic photopolymerization of multifunctional 5,6-epoxy-1,3-dioxepanes and epoxycyclohexanes have been described. Both differential scanning calorimetry and real-time infrared spectroscopic studies show that the 5,6-epoxy-1,3-dioxepane monomers are highly reactive but slightly less reactive than those based on epoxycyclohexane It was also found that during polymerization some amount of ring-opening of the 1,3-dioxepane ring occurs in the case of the former monomers which contributes to a higher functionality for these materials. We expect that these novel cycloaliphatic epoxide monomers will find uses in coatings as well as in many other applications.

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