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Novel Epoxynorbornane Monomers. 2. Cationic Photopolymerization

James V. Crivello* and Ramesh Narayan

Polymer Science and Engineering Program, Department of Chemistry,
Rensselaer Polytechnic Institute, Troy, New York 12180

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ABSTRACT: The reactivity of a novel series of mono-, di-, and multifunctional monomers bearing the epoxynorbornane group in photoinduced cationic polymerization was determined using Fourier transform real-time infrared spectroscopy and differential scanning photocalorimetry. Comparisons were made between the monomers of this investigation containing the epoxynorbornane group with monomers of similar structure bearing epoxycyclohexane groups. Although the cationic polymerizations of the epoxynorborane functional monomers are rapid they, are slower than the aforementioned epoxycyclohexane analogues. This was attributed mainly to steric hindrance effects.

Introduction

In the previous paper[1] in this series, the synthesis of a variety of mono-, di-, and multifunctional monomers bearing the epoxynorbornane group (see Table 1 of the previous paper) was described. The primary objective for which this synthetic task was undertaken was to measure their rates of photoinitiated cationic epoxide ring-opening polymerization. In particular, it was of interest to compare the rates of polymerization of the new monomers with monomers of analogous structures bearing epoxycyclohexane rings. It had been shown earlier[2,3] that these latter monomers display higher rates of polymerization than other epoxy monomers such as glycidyl ethers, glycidyl esters, and epoxides of α-olefins. Since the photoinitiated cationic polymerization of epoxides is currently of considerable academic and commercial importance, it was of interest to determine those major structural and electronic factors that contribute to the the determination of their reactivity. Knowledge of the contributions of those factors would then, hopefully, lead to the design and synthesis of novel epoxide containing monomers with higher reactivities.

There are many possible parameters that affect the reactivity of epoxides in cationic polymerization. For example, recent studies conducted in this laboratory showed that the presence of ester and ether groups in such monomers tend to depress their reactivity.[4] One factor that may contribute to the reactivity of an epoxy monomer is the ring strain. Published data indicate that there is a substantial difference in the ring strain for various epoxides and that epoxy cyclohexanes possess greater ring strain than their open-chain counterparts.[5,6] What is, however, unknown is what contribution ring strain makes to the overall polymerization reactivity. For this reason, it was decided to prepare a variety of monomers and model compounds bearing epoxynorbornane groups in the hope that the anticipated increase in ring strain in the epoxynorbornane system as compared to the epoxycyclohexane monomers would give rise to higher rates of polymerization.

Experimental Section

Monomers and Reagents. The synthesis of the monomers used in this investigation were described in part 1 of this series.[1] The preparation of the photoinitiator (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate has been described previously.[7]

Table 1. FT-RTIR Data for the Photopolymerization of Epoxynorbornane Monomers

monomer[a]	$R_p[M_o]$ (s^{-1})	total epoxide conversion[b] (%)
VI	4.8 (7 s)[c]	96
IV	5.8 (7 s)	98
V	0.3 (75 s)	50
VIII	4.3 (7 s)	92
IX	4.4 (8 s)	91
VII	6.3 (6 s)	82
X	6.4 (6 s)	72
XI	2.6 (6 s)	54
XII	2.1 (6 s)	81
XIIIb	0.6 (75 s)	68
XIVb	0.3 (75 s)	73[d]
XVII	1.37 (21)	71

[a] IOC10, 1 mol %, was used as photoinitiator. [b] Measured after 300 s irradiation. [c] $R_p[M_o]$ was measured at this time. [d] The conversion after 600 s.

Photopolymerization Studies. Thin-Film Photopolymerizations. A 1.0 mol % solution of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate in the appropriate monomer was prepared in a glass vial. The vial was heated gently and vigorously agitated with a VWR-2 vortexer to dissolve the photoinitiator. The vial was then placed in a vacuum oven at room temperature to remove air trapped in the mixture. Thin (25.4 μm) films of the photopolymerizable mixture were drawn onto 8 in. × 4 in. cold rolled steel panels (Q-Panel Co.) using a BYK-Gardner AG-4301 film casting knife. The monomers were irradiated using a Fusion Systems Inc. Laboratory UV Cure Processor. The apparatus consisted of a microwave-activated 300 W UV lamp configured perpendicular to the travel of the conveyor belt and mounted at a distance of 10 cm from the belt. The radiation dose required to cure the monomers was measured using a UV Process Supply Inc. Control Cure radiometer. The maximum tack-free cure rate (ft/min or m/min) was determined by varying the speed of the conveyor belt in the processor until further increase in belt speed produced a uncured coating on the substrate when tested immediately after irradiation.

Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR). The FT-RTIR kinetic runs of photocurable epoxy monomers were carried out using a MIDAC M-1300 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. The instrument was fitted with a UVEXS Model SCU-110 mercury arc lamp which carried the light through a flexible optic wand. The end of the wand was placed at a distance of 5 cm and directed at an incident angle of 45° onto the sample window. The UV light intensity was measured using a radiometer and was found to be 15.7 mW/cm^2 . One

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drop of the photocurable formulation was placed on a NaCl plate and was drawn down, using a glass capillary, to obtain a thin film of the mixture. Infrared spectra were collected at the rate of 30 spectra/min using a LabCalc, data acquisition program obtained from Galactic Corp. and were processed using GRAMS-386 software from the same company. In all the cases, duplicate to triplicate experiments were performed to verify reproducibility.

Differential Scanning Photocalorimetry. The photopolymerizations of the monomers were monitored using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with an DPA-7 ultraviolet photoaccessory. The accessory consisted of a DSC sample holder fitted with two quartz windows, through which ultraviolet light from a 100 W Hg arc lamp was directed onto 1 mg samples of various monomers in the sample compartment. The sample holder assembly was purged with nitrogen at a rate of 20 mL/min, and the samples were equilibrated for 5−10 min prior to photopolymerization.

Thermal Stability Studies. The photopolymerized films were conditioned by placing them in an oven at 65 °C for 24 h. Then thermogravimetric analyses were performed under a air flow of 40 mL/min and at a heating rate of 20 °C/min., using a Perkin-Elmer Series-7 thermogravimetric analyzer.

Results and Discussion

General Considerations. Cationic photopolymerization is an especially convenient technique for carrying out the polymerization of highly reactive epoxide monomers. This is because the photoinitiators such as diaryliodonium salts can be predissolved in the monomers to give stable, homogeneous solutions. Then, polymerization can be induced by irradiating the sample with ultraviolet light. A general scheme for these polymerizations photoinitiated by diaryliodonium salts is briefly depicted in Scheme 1.[8]

Scheme 1

$$Ar_2I^+X^- \xrightarrow{h\nu} Ar^\bullet + Ar{-}I^{\bullet+}X^- \quad (1)$$

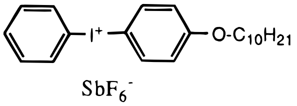
$$Ar{-}I^{\bullet+}X^- \xrightarrow{S-H} Ar{-}I + S^\bullet + HX \quad (2)$$

$$M \xrightarrow{HX} H{-}M^+\,X^- \quad (3)$$

$$H{-}M^+\,X^- + nM \rightarrow H{-}(M)_nM^+X^- \quad (4)$$

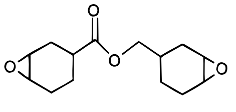
In the scheme, the diaryliodonium salt undergoes photolysis. In subsequent reactions, the intermediate species which is formed, reacts with solvent or monomer (S−H) molecules resulting in the generation of the strong acid, HX (eqs 1 and 2). Protonation of the monomer (M) gives a cationic species, $H{-}M^+X^-$ which undergoes chain growth to produce polymer (eq 4). In this scheme, X^- is a nonnucleophilic ion such as PF_6^-, AsF_6^-, or SbF_6^-.

In the present studies, we employed [4-(*n*-decyloxy)-phenyl]phenyliodonium hexafluoroantimonate (IOC10) as the photoinitiator.

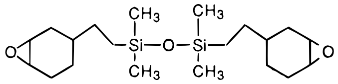


This photoinitiator is highly useful since it possesses a high quantum yield for photolysis ($\Phi = \sim 0.7$) and, due to the presence of the long decyloxy side chain, has very good solubility in all the epoxy monomers studied. On irradiation in the presence of an epoxy monomer, an oxiranium ion is formed by direct protonation of the epoxide and this species undergoes chain propagation to give a polymer having a polyether backbone.

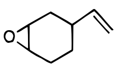
Photopolymerization of Epoxynorbornane Monomers. With a series of novel epoxynorbornane monomers and model compounds in hand, the reactivities of these novel monomers were investigated using several techniques. Where appropriate, their reactivities were compared with the four epoxycyclohexane monomers XV−XVIII.



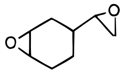
XVII



XV



XVIII



XVI

FT-RTIR Polymerization Studies. The cationic photopolymerizations of epoxynorbornane monomers and related epoxycyclohexane model compounds were followed using Fourier transform real-time infrared spectroscopy. By simultaneously irradiating a monomer−photoinitiator mixture with UV light and recording its infrared spectrum, the changes in the infrared absorption bands of a monomer undergoing photopolymerization can be monitored as a function of time. Of interest in this work are the decreases in the epoxide absorption bands in the 800−900 cm^{-1} region and the bands in the 3010−3030 cm^{-1} region corresponding to the C−H bond stretching vibration of the epoxide. Also of interest is the increase of the peaks at 1100−1170 cm^{-1} that correspond to the absorption of (C−O−C) groups in the poly(ether) which is formed upon photopolymerization. The conversion of the epoxide at any time during the UV irradiation can be obtained by calculating the peak area under the specific absorption band. With the silicon-containing monomers, because of the partial overlap of epoxy absorption and the $SiCH_3$ groups, the usual 850−870 cm^{-1} absorption band could not be employed. In these cases, a weaker band at 3020−3030 cm^{-1} was used together with a deconvoluting routine to obtain the kinetic data. The rate of the polymerization for a given monomer can be calculated using equation 5.

$$R_p/[M_o] = ([\%\ \text{conversion}]_{t_2} - [\%\ \text{conversion}]_{t_1})/(t_2 - t_1) \quad (5)$$

In this equation, R_p is rate of photopolymerization, $[M_o]$ is the initial monomer concentration, and t_2 and t_1 are the times between which the conversion data are collected. A plot of percent conversion versus irradiation time provides a kinetic curve for the photopolymerization. The slope of the initial linear portion of the curve corresponds to the factor $R_p[M_o]$. This value gives a measure of the relative rates of photopolymerization of the monomers. In all the FT-RTIR kinetic runs, 1 mol % of [4-(*n*-decyloxy)phenyl]phenyliodonium hexafluoroantimonate (IOC10) was used as the photoinitiator.

Figure 1 depicts a three-dimensional spectral profile of decrease in the epoxide absorption (848 cm^{-1}) with time for the cationic photopolymerization of 5-vinyl-*exo*-2,3-epoxynorbornane (**IV**). This figure clearly shows a rapid decrease in the epoxy band, indicating that this

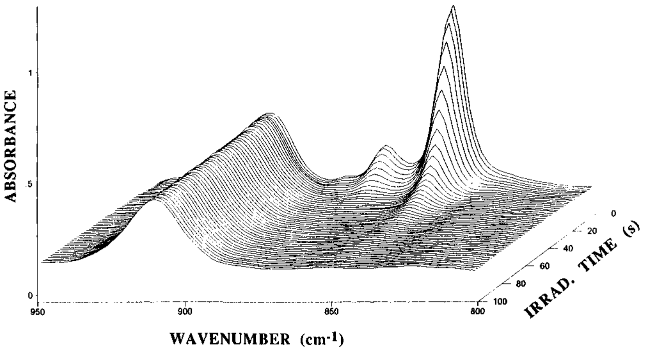


Figure 1. FTIR study of the cationic photopolymerization of **IV**.

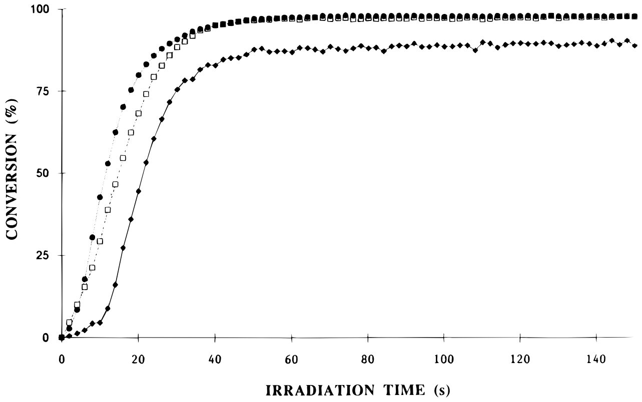


Figure 2. FT-RTIR study of the photopolymerization of ●, **IV**; □, **VI**; and ◆, **IX**.

monomer is highly reactive toward ring opening cationic polymerization. Table 1 shows the data for $R_p[M_o]$ and percent conversion data for the photopolymerization of all the epoxide monomers that were investigated in this study. Figure 2 shows the FT-RTIR kinetic curves for three monofunctional epoxynorbornane monomers **IV**, **VI,** and **IX**. The overall conversion of the epoxide groups in two of the three monomers, namely, **IV** and **VI,** was nearly quantitative (>98%). The slopes of all the three curves are nearly parallel, thereby indicating comparable reactivities for all three monofunctional monomers. For monomer **IX**, bearing the phenyl group, a short induction period and a slightly reduced, overall epoxide conversion of 91% was observed. This may be caused by trace impurities or screening effects due to the short-wavelength UV absorption of the phenyl group in this monomer.

Figure 3 illustrates the FT-RTIR curves for all the difunctional silicon-containing epoxynorbornane monomers. A similar induction period is observed in this study as in Figure 2 with the difunctional monomer **XII,** which contains a phenyl ring. This figure also shows the effect of increasing siloxane chain length on the reactivity of the bisepoxides. As the siloxane chain length increases, both the flexibility of the monomer and the distance between cross-linking sites increase. This increased freedom of motion in the medium undergoing polymerization increases the reactivity of **VII** over monomers **VIII** and **XII**, respectively. A comparison of $R_p[M_o]$ values (Table 1) clearly demonstrates that the difunctional epoxynorbornanes are more reactive than the commercially available bisepoxide **XVII**.

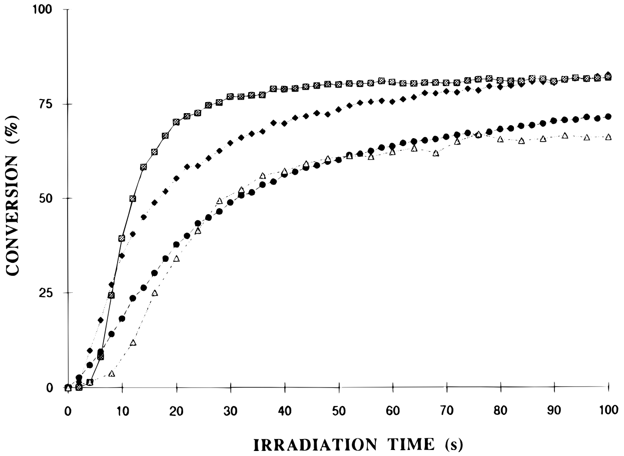


Figure 3. FT-RTIR study of the photopolymerization of difunctional monomers ◆, **VII**; □, **VIII**; △, **XII**; and ●, **XVII**.

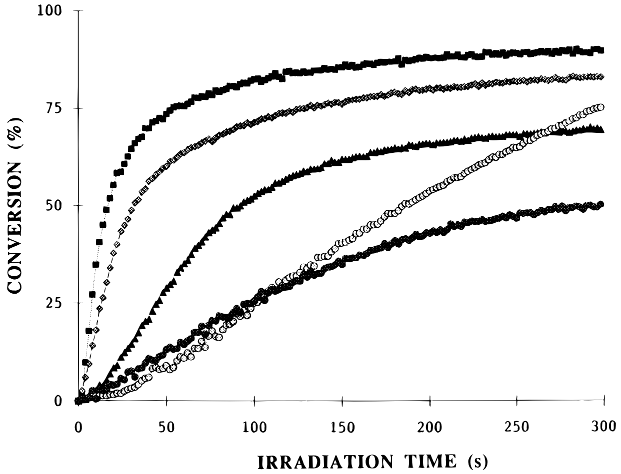


Figure 4. Comparison of the polymerization of difunctional epoxynorbornane monomers with different types of linking groups. ■, **VIII**; ◇, **VII**; ▲, **XIVb**; ○, **XIIIb**; ●, **V**.

The reactivities of a series of difunctional epoxynorbornanes with varying linking groups between the end functional epoxides were evaluated and are shown in Figure 4. Both the $R_p[M_o]$ values and the overall conversion of the siloxane-containing epoxide **VIII** are higher than that of epoxynorbornanes bearing ether (**XIIIb**), ester (**XIVb**), or hydrocarbon linking group (**V**). In monomers **XIIIb** and **XIVb**, the ether and carbonyl groups can be protonated by the Brönsted acid, in competition with the epoxide.[4] This effectively reduces the initial concentration of the initiator available for ring-opening polymerization of the epoxide, hence, photopolymerization of these monomers is slow. More importantly, these particular monomers are highly viscous. The physical effect of the photopolymerization is an increase in the molecular weight and the viscosity of the medium. Since these materials have high initial viscosities, the polymerization rate slows and becomes diffusion controlled early in the reaction. As a result, the overall conversion is also reduced in these monomers. Monomer **V** gives a polymer with a rigid backbone, and in addition, the distance between cross-links in the polymer is very short. Hence, a very densely cross-linked glassy network is formed early in the reaction, thereby greatly reducing the mobility of both the monomer and the growing polymer chains. These effects suppress the rate of propagation of the polymer chains.

The effects of variation in the photoinitiator content on the photopolymerization of **IV** was studied and the results are shown in Figure 5. At 0.1 mol % concentration of the photoinitiator (PI; IOC10), the photopolym-

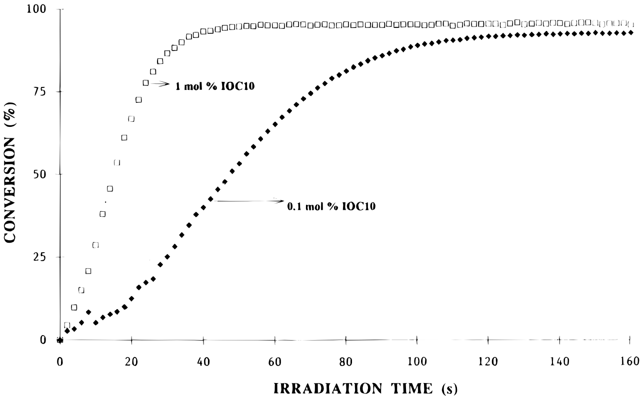


Figure 5. Effect of the photoinitiator concentration on the photopolymerization of **IV**.

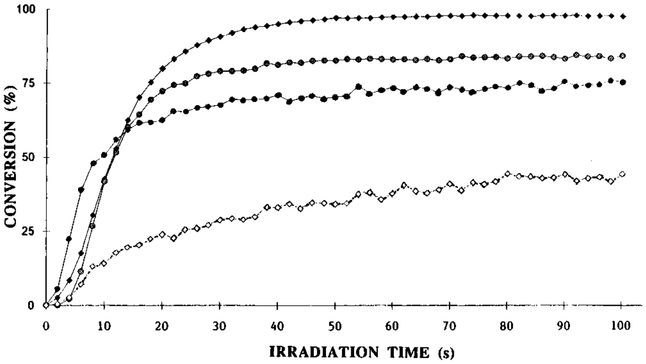


Figure 6. Effect of the functionality on the photopolymerization of various epoxynorbornane monomers: ◆, **IX**; ○, **VII**; ●, **X** and ◇, **XI**.

erization rate was slow with a $R_p[M_o]$ value of only 1.4 s^{-1}. Increasing the PI concentration to 1 mol % markedly increased the value to 4.1 s^{-1}. As the photoinitiator concentration is increased, a larger number of polymer chains are initiated and the initial rate increases. However, it should be noted that the overall conversion of the epoxide in both instances approaches the same value. In Figure 6, the effect of increasing functionality can be seen in a series of related epoxynorbornane monomers. As the epoxide functionality increases, the overall conversion of the epoxide decreases in the order **IV** > **VII** > **X** > **XI**. This effect has been noted previously[9] and can be ascribed to the lowering of the mobility of the epoxynorbornane groups as an increasingly higher cross-link density network is formed. It should be noted, however, that the initial rates of the polymerization of these four monomers are comparable.

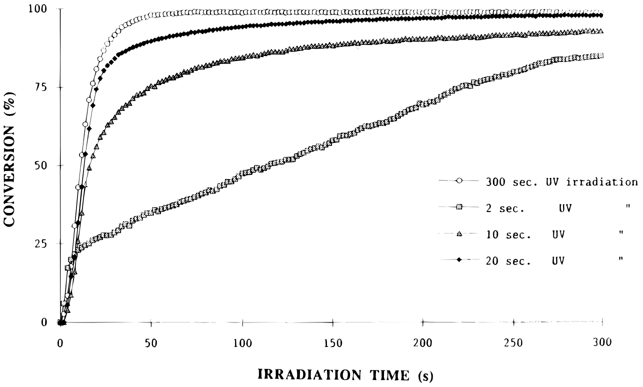


Figure 7. FT-RTIR study of the postcure effect in the polymerization of **XI** in the presence of 1.0 mol % IOC10.

Table 2. Extent of the Dark Reaction in the Photopolymerization of 5-Vinyl-2,3-epoxynorbornane

irradiation time (t_x) (s)	% conversion at time t_x (C_{t_x})	% ultimate conversion[a] ($C_{t_{300}}$)	% dark polymerization[b]
2	6	85 (300)[c]	93
10	26	93 (270)[c]	72
20	74	99 (200)[c]	25
300	99	99 (50)[c]	0

[a] Measured at 300 s. [b] Calculated as $[\{1 - (C_{t_x})/(C_{t_{300}})\}100]$. [c] Time in seconds to reach ultimate conversion.

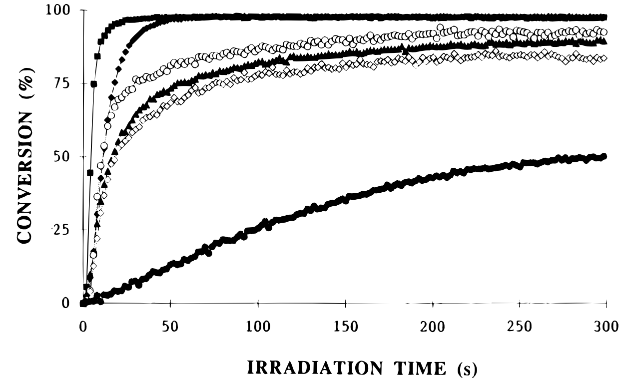


Figure 8. FT-RTIR study of the comparison between epoxynorbornane monomers ■, **XVIII**; ◆, **IV**; ○, **XV**; ▲, **VIII**; ◇, **XVI**; and ●, **V** using 1.0 mol % IOC10.

Table 3. Comparison of Photopolymerization Reactivity of Monomers Based on Epoxycyclohexane and Epoxynorbornane

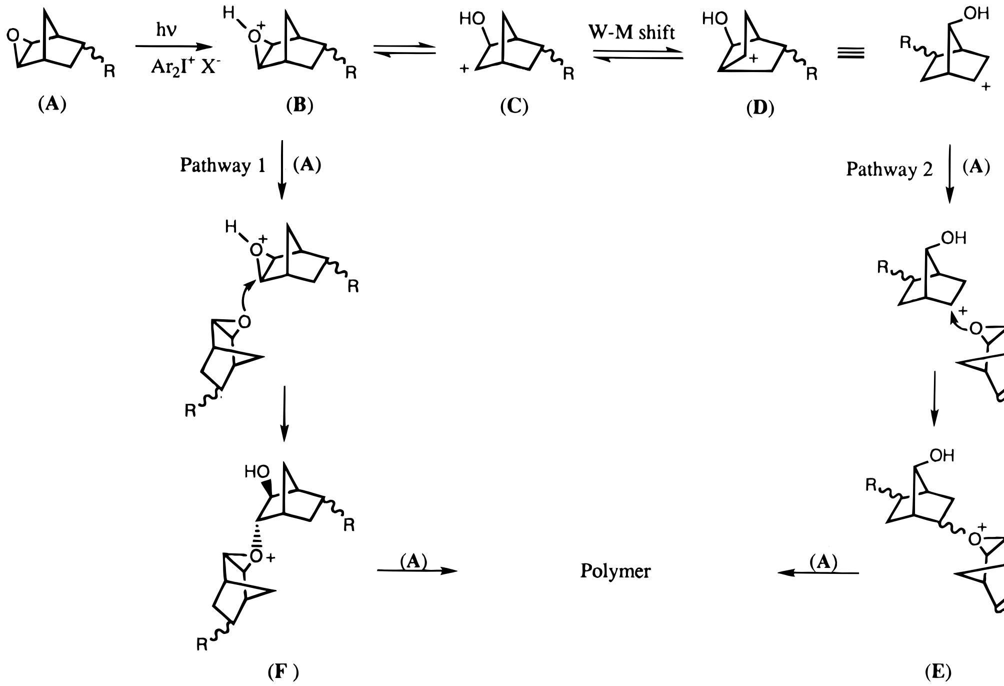
monomer[a]	$R_p[M_o]$ (s^{-1})	conversion of epoxide[b] (%)
XVIII	7.5 (6 s)[c]	98
IV	5.8 (7 s)	98
XVI	4.5 (8 s)	79
V	0.3 (75 s)	50
XV	8.7 (7 s)	94
VIII	4.3 (8 s)	92

[a] IOC10, 1 mol %, was used as the photoinitiator. [b] Measured after 300 s UV irradiation. [c] $R_p[M_o]$ was measured at this time.

In photoinitiated cationic polymerization, irradiation is necessary only to initiate the polymerization. The propagation or chain-growth step of the polymerization is a nonphotochemical (i.e., "dark") process. This process can continue well after the light source has been removed. In theory, in the absence of termination reactions, the polymerization can continue until all the available monomer has been consumed. To evaluate the extent of the dark polymerization in epoxynorbornane monomers, a 1.0 mol % solution of IOC10 in **IV** was irradiated for various time periods while the polymerization by FT-RTIR was monitored. The plots and the data corresponding to these experiments are presented in Figure 7 and Table 2. From these data, the following observations can be made. First, the overall conversion in all cases is high (>90%). Second, the shorter the irradiation time, the longer the dark time required for the samples to reach their ultimate conversions. Optimally, a 10 s. irradiation at a UV light intensity of 15.7 mW/cm^2 followed by a dark period of 270 s is sufficient to quantitatively polymerize all the epoxynorbornane groups. Finally, the data in the above table show that up to 93% of the consumption of the monomer can occur as a dark process. This clearly demonstrates the presence of long-lived propagating species in the cationic photoinitiated polymerization of epoxides.

Shown in Figure 8 and Table 3 is a FT-RTIR study comparing three different epoxynorbornane monomers

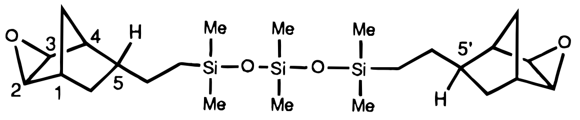
Scheme 2



(**V**, **VI**, **VIII**) with their very closely related epoxycyclohexane counterparts (**XV**, **XVI**, **XVIII**). From these data it is clear that although epoxynorbornanes are by themselves very reactive cationically photopolymerizable monomers, they are less reactive than the structurally related monomers derived from epoxycylcohexanes. It is also apparent that the contribution of the higher ring strain in epoxynorbornanes must be offset by other factors which detract from the rates of polymerization of these monomers. Shown in Scheme 2 is the mechanism we propose for the cationic ring-opening polymerization of epoxynorbornanes. The first step toward obtaining a polymer is the generation of a strong Brönsted acid upon irradiation of the photoinitiator. In the next step (B), the strong acid protonates the epoxide oxygen. In most epoxides, further monomer addition to this protonated species occurs by a S_N2-type mechanism resulting in the formation of an trialkyloxonium ion (F), which is the chief propagating species. It should be noted in the case of the epoxynorbornane monomers of this paper, the epoxide is in the *exo* position. This requires that the nucleophile (i.e., the bulky monomer) must approach from the very sterically hindered *endo* side of the bicyclic ring. We suggest that this sterically unfavorable situation is the main reason for the decreased rate observed in cationic polymerization of epoxynorbornanes as compared to epoxycyclohexanes.

Other factors also play a role in determining the rate of the polymerization of epoxynorbornanes. In addition to the above pathway, it has been shown that upon exposure to strong acids such as perchloric acid, epoxynorbornanes undergo alkyl shifts (i.e., Wagner–Meerwin rearrangements) such as those shown in Scheme 1 (C → D).[10,11] These rearrangements give rise to other structures in the polymer backbone via pathway 2. Further, from an analysis of ^{13}C NMR, J_{C-H} coupling constants, and other spectroscopic and molecular modeling data, it has been shown that the basicity of the epoxide group in epoxynorbornane (pK_b = 6.99) is slightly lower than that of epoxycyclohexane (pK_b = 6.24).[12] Another study also revealed that the percent s character of the C–H bond of the epoxide group and the electron density on the epoxide carbon atom were higher in epoxynorbornane than that of epoxycyclohexane.[13] This suggests that the protonation or alkylation at the oxygen atom of the epoxide group in epoxynorbornanes is more difficult and that they are also poorer nucleophiles than epoxycyclohexanes. Lastly, other workers[14] have observed that only low molecular weight products (M_n <1000) were obtained in the thermally initiated cationic polymerization of 2,3-epoxynorbornane using trityl hexafluoroantimonate.

Monomer **VII** was prepared from **IV**, which consists of an approximately 80:20 isomeric mixture of *exo*-2,3-epoxy-*exo*-5-vinylnorbornane and *exo* 2,3-epoxy-*endo*-5-vinylnorbornane Upon hydrosilylation of **IV** with 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS), three isomers of **VII** are possible (5-*endo*-5′-*endo*, 5-*exo*-5′-*exo* and 5-*endo*-5′-*exo*). The structure of one such diastereomer (5-*endo*-5′*exo*) is shown.



When **VII** was purified by chromatography, three fractions were isolated, each enriched in a different diastereomer. Using ^1H NMR, the proportions of 5-*exo* to *endo* substitution for each of the fractions could be determined (see Experimental Section for spectral assignments). They were 13:87, 52:48, and 71:29, respectively. The photoinduced cationic polymerizations of each of the fractions was carried out and analyzed using FT-RTIR. The results of these experiments are presented in Figure 9. The figure shows that there is a clear difference in reactivity between the three fractions. The fraction with a higher proportion of the 5-*exo* substituent was much more reactive ($R_p[M_o] = 8.4\ s^{-1}$, 87% combined conversion) than the fraction with higher 5-*endo* content ($R_p[M_o] = 3.2\ s^{-1}$, 76% combined conversion). The fraction possessing approximately equal amounts of the *endo* and *exo* isomers showed intermediate reactivity ($R_p[M_o] = 6.3\ s^{-1}$, 81% combined conver-

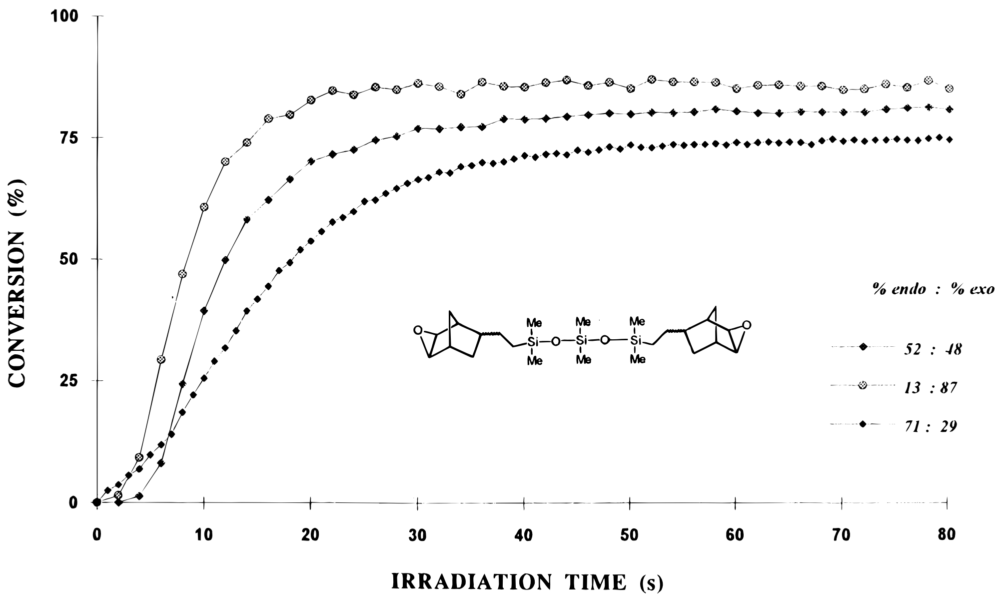


Figure 9. Photopolymerization of three mixtures of diastereomerically enriched epoxynorbornanes obtained from monomer **VII** using 1.0 mol % IOC10.

Table 4. Tack-Free Cure Speeds and Peak Polymerization Times of Epoxynorbornane Monomers

monomer[a]	peak time (t_{peak}) (s)[b]	tack-free cure speed ft/min (m/min)[c]	radiation dose (mJ/cm^2)
XV	7	>160 (49.0)	<57
VIII	11	>160 (49.0)	<57
X	13	>160 (49.0)	<57
VII	18	>160 (49.0)	< 57
XII	28	100 (30.4)	92
XVI		50[d] (15.2)	552

[a] IOC10, 1 mol %, was used as the photoinitiator. [b] Time to reach peak polymerization rate in the DSP curves. [c] Obtained using one 300 W Hg arc UV lamp. [d] Three passes were required to obtain a tack-free film.

sion). This difference in reactivity between the diastereomerically enriched fractions can again be attributed to the steric hindrance in the vicinity of the epoxide. The 5-*endo* substituents offer greater steric hindrance to the approach of a new epoxide monomer to the growing alkyloxonium ion chain end than the corresponding 5-*exo* substituents. Hence, the reactivity of the fraction richer in the *exo*-substituted isomer should be more reactive than the *endo*-rich fraction.

Thin-Film Photopolymerizations and Differential Scanning Calorimetry Measurements. A rapid and qualitative means of evaluating the reactivity of various multifunctional monomers is to determine the rates at which thin films of the liquid monomer containing a photoinitiator are converted to a solid cross-linked films by exposure to ultraviolet irradiation of a known intensity. These measurements were made by simply placing 25 μm films coated on a substrate on a conveyor and then under a 300 W medium-pressure Hg arc lamp. The highest conveyor speed that can be measured is termed the "tack-free cure speed". The data collected for several epoxynorbornane difunctional siloxane monomers and their corresponding epoxycyclohexane analogues are provided in Table 4. In the first four entries in the table, the tack-free times exceed the maximum rate of the conveyor (160 ft/min; 49 m/min). The minimum dose required to cure these monmers was less than 57 mJ/cm^2. Monomers **XII** and **XVI** gave considerably lower tack-free times.

The cationic photopolymerization of these same monomers was monitored using differential scanning photocalorimetry (DSP) in an isothermal mode at 25 °C. An example is given in Figure 10 in which the polymerization of epoxynorbornane monomer **VIII** and epoxycyclohexane monomer **XV** are compared. In these experiments, the irradiation was started after a 0.5 min equilibration period. The time to reach the peak of the exotherm (t_{peak}) for each of the monomers is a measure of the reactivity of that monomer and is recorded in Table 4. The shorter the value of the t_{peak}, the more reactive the monomer. In Figure 10 it can be seen that the t_{peak} for **XV** is shorter than for **VIII** and that the polymerization exotherm is broader for this latter monomer. The DSP data in Table 4 serve to support and confirm the results obtained from the FT-RTIR and tack-free time studies, i.e., the order of reactivity of the monomers being **XV** > **VIII**, **X**, **VII** > **XII** ≫ **XVI**.

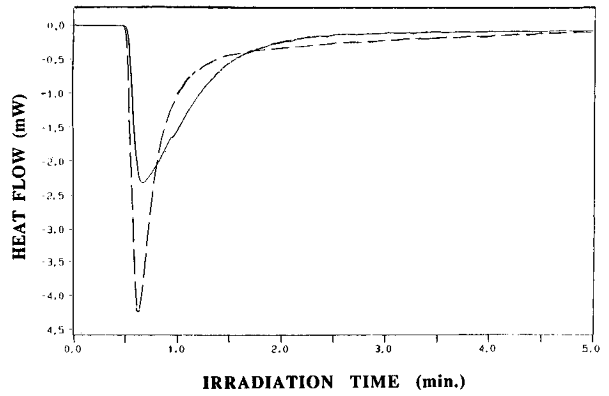


Figure 10. Comparative DSP study of the photopolymerization of epoxynorbornane monomer **VIII** (—) with epoxycyclohexane monomer **XV** (– –).

Thermal Analysis of Photopolymerized Epoxynorbornane Monomers. To ensure that of most of the epoxide groups present in polymers obtained by photopolymerization had reacted, films of the polymers were heated in an oven at 70 °C for 24 h. Attempts to measure the T_g of the polymers from epoxynorbornane functional siloxanes using DSC in the temperature range of −40 to +220 °C were unsuccessful. The T_g of polymers obtained by the thermally initiated cationic polymerization of epoxynorbornane was reported to be 72−80 °C.[14] Since polymerization of monomer **V** would result in cross-linked polymer with essentially infinite molecular weight, its T_g would be expected to be higher than that for the linear polymer obtained from the polymerization of 2,3-epoxynorbornane. Indeed, for monomer **V,** a T_g of 117 °C was measured.

Thermogravimetric analysis studies of polymers derived from the photopolymerization of three representative epoxynorbornane monomers, **V**, **VII**, and **XI**, were carried out in air at a heating rate of 20°C/min. Similar results were obtained for the three polymers The polymers were stable in air up to 280−320 °C. A 10% weight loss in these polymers occurred at 315, 305, and 280 °C, respectively. After these temperatures, there is rapid and stepwise weight loss due to thermal degradation of these polymers. The polymer obtained from **V** was completely decomposed at 605 °C, whereas 12 and 8% char was obtained for the siloxane-containing polymers **VII** and **XI** at higher temperatures, presumably due to the formation of SiO_2.

Conclusions

A new series of multifunctional monomers bearing reactive epoxynorbornane groups were synthesized using straightforward methods. The photoinitiated cationic polymerization of the new monomers was studied using Fourier transform real-time infrared spectroscopy and differential scanning photocalorimetry and by determining their tack-free times. The epoxynorbornane functional siloxanes displayed the highest reactivity toward cationic ring-opening polymerization. These particular monomers were slightly less reactive than monomers with analogous structures with the epoxycyclohexane functional group. The difference in the reactivities between these two classes of monomers was ascribed to the greater steric hindrance present in the former monomers. Epoxynorbornane monomers have many potential applications in the areas of coatings and adhesives.

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