

Free Radical Induced Acceleration of Cationic Photopolymerization

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Two new monomers based on α -terpineol were prepared, allyl α -terpineol ether epoxide (**III**) and 1-propenyl ether α -terpineol epoxide (**IV**). The photoinitiated cationic polymerizations of these two monomers as well as two model compounds, 1-propenyl α -terpineol ether and methyl α -terpineol ether epoxide, were studied using real-time infrared spectroscopy. Surprisingly, the rates of epoxide ring-opening polymerization of both monomers were greatly enhanced as compared to the model compounds. At the same time, the rate of polymerization of the 1-propenyl ether groups in **IV** was depressed. Two different mechanisms which involve the free radical induced decomposition of the diaryliodonium salt photoinitiator were proposed to explain the rate acceleration effects.

Introduction

Photoinitiated free radical and cationic polymerizations are in wide use today in many thin film applications such as protective and decorative coatings, printing inks, and adhesives. Among the many advantages of photopolymerizations in these particular applications is the ability to produce fully polymerized, i.e., cured, network polymers very rapidly. This permits these photopolymerizations to be carried out on a rapidly moving web in which the sample receives only a brief exposure to light. The establishment of an inert atmosphere for polymerizations taking place at high speeds on a web is both costly and problematic. Photoinitiated cationic polymerizations, on the other hand, have the advantages of oxygen insensitivity and that monomers with low toxicities can be used.¹ Of particular interest for applications such as those cited above are the photoinitiated cationic ring-opening polymerizations of epoxide monomers. This is due to the excellent chemical resistance and mechanical properties of polymers produced from these monomers. Unfortunately, the rates of polymerization of typical epoxide monomers using the most active cationic photoinitiators are considerably slower than the free radical photopolymerization of multifunctional acrylates and generally too slow for high-speed web processes. In this laboratory, we have been exploring the design and synthesis of novel epoxide monomers which exhibit high rates of photoinitiated cationic polymerization. In previous papers from this laboratory,^{2–4} we have reported on the outstanding

reactivity of enol ether monomers such as multifunctional vinyl and 1-propenyl ethers in photoinitiated cationic polymerization. Hybrid monomers such as 1-propenyl glycidyl ether containing both enol ether and epoxy groups were recently prepared, and their polymerization behavior was investigated.⁵ A considerable enhancement in the reactivity of the epoxy group was observed in these compounds which was ascribed to the presence of the 1-propenyl ether group. It was of some interest to determine whether this reactivity enhancement was specific to 1-propenyl glycidyl ether or was a general phenomenon which could be applied to the design of other even more reactive hybrid monomers bearing epoxy and vinyl ether or 1-propenyl ether groups.

In this paper, we describe the synthesis of a new hybrid monomer based on α -terpineol (1-menthen-8-ol) as well as an additional related derivative which exhibits exceptionally high rates of photoinitiated cationic polymerization.

Experimental Section

General Methods. Allyl bromide, α -terpineol, sodium hydride, potassium hydroxide, 18-crown-6 ether, acetone, Oxone (2KHSO₅·K₂SO₄·KHSO₄), methylene chloride, THF, and tris(triphenylphosphine)ruthenium(II) dichloride were purchased from the Aldrich Chemical Co. Benzene was distilled over sodium metal before use. The photoinitiators (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IO10**)⁶ and (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate were prepared as described previously.⁷ Routine infrared spectra were obtained using a Midac-M1300 Fourier transform Infrared spectrometer. ¹H NMR experiments were performed on a Unity-500 (500 MHz) spectrometer at room temperature using CDCl₃ as the solvent containing 1% tetramethylsilane as an internal standard.

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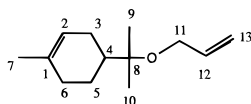
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Synthesis of Monomers and Model Compounds. *Preparation of Allyl α -Terpineol Ether (II).* A 500 mL round-bottom flask equipped with a water condenser, magnetic stirrer, nitrogen inlet, and a thermometer was charged with α -terpineol (15.0 g, 0.0972 mol), NaH (80%, 3.64 g, 0.121 mol), 15-crown-5 ether (0.4 g), and dry THF (50 mL). This mixture was heated to 55–60 °C for 30 min, then allyl bromide (16.76 g, 0.138 mol) was added and the mixture stirred at 60 °C for another 48 h. The resulting mixture was washed with three 50 mL portions of saturated aqueous NaCl solution and the organic layer dried over anhydrous Na₂SO₄. After removal of the solvent using a rotary evaporator, one-half of the liquid residue was purified by flash chromatography (silica gel, 2:25 EtAc:hexane) to give allyl α -terpineol ether, **II** (15.44 g, 92.7% yield based on reacted α -terpineol). TLC: R_f = 0.64 (1:9 EtAc:hexane). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 5.91 (m, H₁₂, 1H); 5.38 (s, H₂, 1H); 5.18 (dd, H₁₃, 2H); 3.88 (d, H₁₁, 2H); 1.2–2.1 (m, H_{3,4,5,6,7}, 11H); 1.13 (s, H_{9,10}, 6H).



Preparation of Allyl α -Terpineol Ether Epoxide (III). Into a 2 L three-necked round-bottom flask fitted with an efficient mechanical stirrer, a Claisen adapter, two addition funnels, and a pH meter electrode were placed allyl α -terpineol ether **II** (7.72 g, 0.0397 mol), methylene chloride (50 mL), acetone (50 mL), phosphate buffer (pH = 7.4, 200 mL), and 18-crown-6 ether (0.4 g). The flask was cooled to 5 °C using an ice bath. Then, 34.0 g (0.0553 mol) of Oxone as a 1 M aqueous solution was added dropwise over the course of 1 h. At the same time, a solution of KOH (12.0 g) in 100 mL of H₂O was also added dropwise to neutralize the acid and maintain the pH between 7.1 and 7.5. Upon the completion of the addition of the Oxone, the reaction mixture was stirred at 5 °C for an additional 4 h. The resulting mixture was filtered and extracted with three 50 mL aliquots of dichloromethane, and the combined organic layers were washed with brine and dried over anhydrous MgSO₄. After removal of the solvents on a rotary evaporator, the resulting oil was subjected to further purification using flash chromatography (silica gel, 3:20 EtAc:hexane). There was obtained 7.94 g (95.0% yield) of **III**. TLC: R_f = 0.28 (1:9 EtAc:hexane). The ¹H NMR spectrum of **III** is shown in Figure 1A. Elemental Analysis for C₁₃H₂₂O₂: C, 74.24; H, 10.54. Found: C, 74.02; H, 10.38.

Preparation of 1-Propenyl α -Terpineol Ether Epoxide (IV). A 25 mL round-bottom flask equipped with a magnetic stirrer, a thermometer, nitrogen inlet, and a water condenser was charged with ((C₆H₅)₃P)₃RuCl₂ (0.0159 g, 0.0756 mmol) and **II** (3.50 g, 16.65 mmol). When the temperature of the reaction mixture reached 120 °C, it was blanketed with nitrogen and maintained at that temperature for 2 h. After this time, TLC analysis showed that nearly all of the starting material **III** had reacted. Reaction was continued for an additional 20 min. Then, the reaction mixture was cooled to room temperature and subjected to purification by flash chromatography (silica gel, 1:9 EtAc:hexane). There were obtained 3.38 g (96.6% yield) of **IV**. TLC: R_f = 0.53 (1:10 EtAc:hexane). The ¹H NMR spectrum of **IV** is shown in Figure 1B. Elemental Analysis for C₁₃H₂₂O₂: C, 74.24; H, 10.54. Found: C, 74.41; H, 10.61.

Preparation of 1-Propenyl α -Terpineol Ether (V). **V** was synthesized by the ((C₆H₅)₃P)₃RuCl₂-catalyzed isomerization of **II** using the same method as employed for **IV**. After purification by flash chromatography (silica gel, 1:10 EtAc:hexane) a 96.0% yield of **V** was obtained. TLC: R_f = 0.76 (1:9 EtAc:hexane). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.20 (d,d, H₁₁, 1H); 5.39 (s, H₂, 1H); 4.96 *E* and 4.44 *Z* (m, H₁₂, 1H); 1.67 (s, H₁₃, 3H); 1.09 (m, H_{9,10}, 6H); 1.10–2.10 (m, H_{3,4,5,6}, 7H).

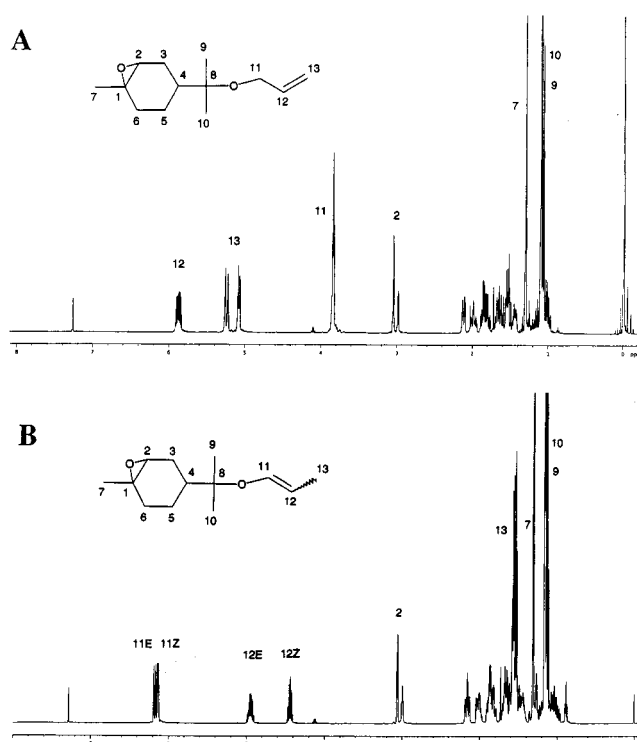
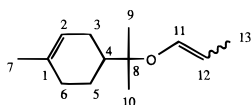
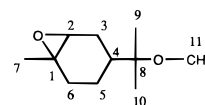


Figure 1. (A) ¹H NMR of monomer **II** in CDCl₃. (B) ¹H NMR of monomer **IV** in CDCl₃.

Elemental Analysis for C₁₃H₂₂O: C, 80.35; H, 11.41. Found: C, 79.32; H, 11.14.

Preparation of Methyl α -Terpineol Ether Epoxide (VI). **VI** was synthesized by similar methods to those used for **II** and **III**, except no purification was carried out between the two steps. Flash chromatography (silica gel, 1:10 EtAc:hexane) gave pure **VI** (91.5% total yield for two steps). TLC: R_f = 2.9 (1:9 EtAc:hexane). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 3.16 (m, H₁₁, 3H); 3.06–3.00 (m, H₂, 1H); 1.31 (s, H₇, 3H); 1.07 (m, H_{9,10}, 6H); 0.9–2.2 (m, H_{3,4,5,6}, 7H).



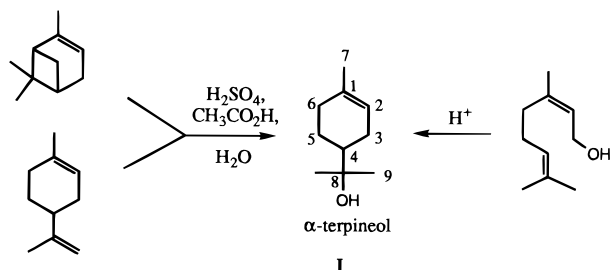
Elemental Analysis for C₁₁H₂₀O₂: C, 71.70; H, 10.94. Found: C, 71.90; H, 10.92.

Photopolymerization: Fourier Transform Real-Time Infrared (FT-RTIR) Measurements. Samples of the monomers containing 0.5 mol % of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate for each polymerizable functional group were coated onto a 12 μ m polypropylene film. A second polypropylene film was placed over the sample and this sandwich mounted in a 5 cm \times 5 cm slide frame. The samples were then placed into the sample holder of the spectrometer. The RTIR measurements were performed on a Midac Corp. Model M-1300 Fourier transform infrared spectrometer equipped with an UVEXS Co. SCU 110 UV lamp fitted with a flexible liquid optic cable. The end of the probe was positioned to direct the UV irradiation at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 254 \pm 3 mJ/cm² min. Light intensity measurements were made with an International Light Co. Control-Cure Radiometer. Data were collected at a rate of one full spectrum per second. The progress of the polymerizations was monitored by following the decrease in the intensity of the 760 cm⁻¹ (epoxy) or 1668 cm⁻¹ (1-propenyl ether) absorption bands upon UV exposure as a function of time. The percent conversions were determined by integration of the peak areas at a given time as compared to the areas of those same peaks at the start of the polymerization. Calcula-

tions were made with the aid of a Galactic Industries Corp. Grams 386, Version 3.0 software package.

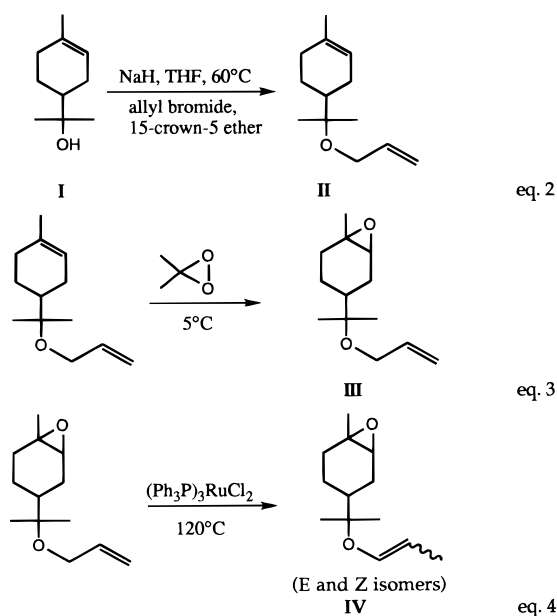
Results and Discussion

Monomer Design and Synthesis. α -Terpineol (**I**) is a naturally occurring terpene alcohol with a lilac odor isolated from pine oil.⁸ Alternatively, **I** can be readily prepared from either α -pinene or limonene by acid-catalyzed hydration and rearrangement⁹ or by the acid-catalyzed cyclization of geraniol or nerol.¹⁰



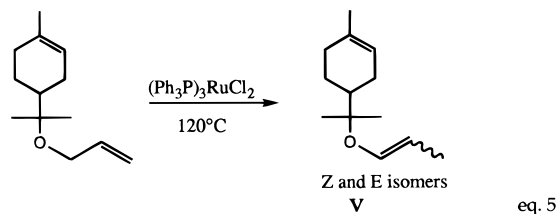
As a result of its widespread natural occurrence and ready preparation from commodity terpene precursors, α -terpineol is a potentially interesting biorenewable and inexpensive substrate for the synthesis of monomers and polymers. α -Terpineol bears both cycloalkene and hydroxyl groups which are potential sites for the attachment of various types of polymerizable functional groups. We have employed the three-step synthetic strategy shown in Scheme 1 for the preparation of hybrid monomer **IV** bearing both an epoxy group and a 1-propenyl ether. Since enol ethers react under the usual epoxidation conditions to give a variety of undesirable products, it was necessary first to introduce the epoxy group and then the 1-propenyl ether group.

Scheme 1



α -Terpineol (**I**) undergoes allylation (eq 2) under phase transfer catalytic conditions to give the allyl ether **II** in high yield (95%). Thereafter, allyl α -terpineol ether (8-(2-propenoxy)-1-*p*-menthene), **II**, was regioselectively epoxidized (eq 3) using Oxone (2KHSO₅·K₂SO₄·KHSO₄) with acetone to give **III**. Montgomery¹¹ recognized that at neutral pH acetone catalyzes the decomposition of caroic acid (H₂SO₅) with the liberation of oxygen gas. Edwards et al.¹² have definitively shown that the primary reaction of caroate with acetone generates dimethyldioxirane (DMDO) as an intermediate. DMDO has proved to be a powerful and selective epoxidizing agent for alkenes at nearly neutral pH. We have modified the conventional procedures¹³ used in this reaction to minimize solvents and to markedly improve the yields. Only a small amount (<4%) of the diepoxy side product is formed resulting from epoxidation at both unsaturated double bonds of **II**. Under the buffered and controlled pH conditions of the epoxidation reaction, epoxide ring-opening reactions were minimized and the yield of desired monoepoxide **III** was 95.0%. The ¹H NMR spectrum of **III** is shown in Figure 1A. The allylic double bond of epoxide **III** can be isomerized by heating for 2 h at 120 °C in the presence of tris-(triphenylphosphine)ruthenium(II) dichloride (eq 4).¹⁴ Under these conditions, the epoxide ring remains unaffected. Thus, **IV** [8-(1-propenoxy)-1,2-epoxymenthane] containing both an epoxide and a 1-propenyl ether functional group was prepared in 96.6% yield (after purification) as a ~50:50 mixture of *E* and *Z* isomers about the 1-propenyl ether carbon-carbon double bond. The ¹H NMR spectrum of **IV** is shown in Figure 1B.

As will be discussed in the following sections, it was also necessary to prepare several model compounds for comparative reactivity studies. As a model compound for a 1-propenyl ether containing the α -terpineol ring system, 1-propenyl α -terpineol ether [8-(1-propenoxy)-1-menthene] **V** was prepared using the ruthenium-catalyzed isomerization reaction shown in eq 5.



Methyl α -terpineol ether epoxide (8-methoxy-1,2-epoxymenthane), **VI**, was also prepared as a model compound for comparative and mechanistic studies. This compound was readily synthesized in good yield according to the two-step sequence shown in eq 6.

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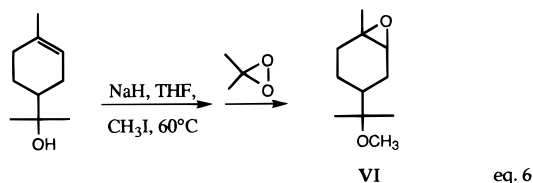
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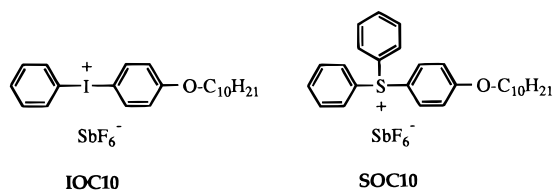
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VI was isolated as a colorless oil in 92.6% overall yield.

It should be noted that α -terpineol is a chiral molecule and also that compounds **II–VI** are also chiral and are composed of a racemic mixture of the two enantiomers. At the same time, compounds **III–VI** also contain geometric isomers as a result of cis–trans isomerization about either the 1-propenyl ether double bond or the epoxy group or both. No attempt was made during the course of this investigation to separate or resolve the isomers. In all cases, therefore, the monomers and model compounds were employed as their isomeric mixtures in the subsequent cationic photopolymerization studies.

Cationic Photopolymerization Studies. Owing to the high reactivity of the monomers investigated in this study, we have elected to monitor the course of their cationic photopolymerizations using real-time infrared spectroscopy (RTIR). We^{15,16} and others¹⁷ have reported the use of this technique for the determination of the rates of very rapid photopolymerizations which are completed on a time scale of a few seconds. This technique consists of following in real time the disappearance of specific infrared bands characteristic of the functional groups undergoing polymerization. The photopolymerization studies reported in this paper were conducted using the cationic photoinitiators (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC10**) and (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (**SOC10**), at concentrations of 0.5 mol % per functional group present. Both of these photoinitiators are soluble in all the monomers studied and have high quantum yields ($\Phi = \sim 0.7$).



For example, in the case of the hybrid monomer **IV**, 1.0 mol % of the photoinitiators were used due to presence of the two different polymerizable functional groups. The monomers were coated onto a polyethylene film and irradiated with UV light at room temperature. Simultaneously, the conversions of each functional group to polymer were monitored by following the decrease in the intensity of either the 760 cm^{-1} (epoxy) or the 1664 cm^{-1} (1-propenyl ether) infrared absorption bands upon UV exposure as a function of time. Since many of the monomers were found to be highly reactive,

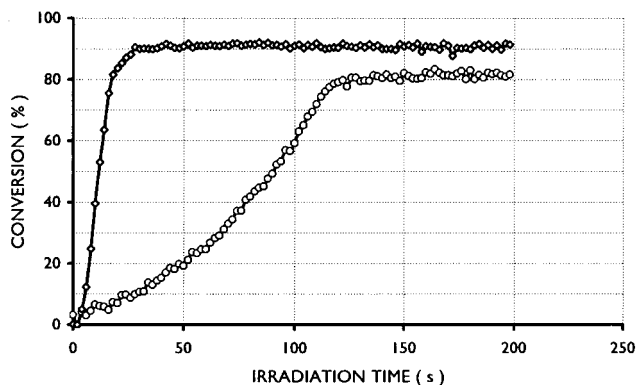


Figure 2. RTIR study of the cationic photopolymerization of model compounds: **V**, \diamond , 1-propenyl ether groups (1668 cm^{-1}) and **VI**, \circ , epoxy groups (760 cm^{-1}).

it was found necessary to adjust the light intensity to a very low level ($254 \pm 3 \text{ mJ/cm}^2 \text{ min}$, 4.2 mW/cm^2) to slow the polymerization sufficiently to allow comparison of the rates.

To provide a baseline for the studies of the hybrid monomer **IV**, the cationic photopolymerizations of model compounds **V** and **VI** were conducted and the corresponding RTIR curves are shown in Figure 2. A comparison of the curves shows that the rate of polymerization of the epoxy group as indicated by the slope of the initial portion of the RTIR curve is considerably lower than that of the 1-propenyl ether group. We have noted in the past that the cationic vinyl polymerizations of enol ether monomers in general¹⁸ and 1-propenyl ether monomers¹⁹ in particular are much more rapid than the most reactive epoxide ring-opening polymerization reactions and are among the most rapid polymerizations known. The IR spectra of the polymerization of **IV** as well as the other epoxy compounds reported in this paper show evidence of the simultaneous formation of a carbonyl absorption at 1715 cm^{-1} . This can be attributed to the well-known²⁰ rearrangement of epoxides under acidic conditions to give ketones. This side reaction appears to occur to a very minor extent during the course of the polymerization reactions.

Figure 3 presents an RTIR study of the cationic photopolymerization of monomer **IV**. Astonishingly, this hybrid monomer shows quite different polymerization behavior from that predicted by the model compound studies described above. The polymerization of the epoxide functional group in **IV** is much faster than that of the 1-propenyl ether group in the same molecule. These results are similar to our reported previous observations in the polymerization of the hybrid monomer 1-propenyl glycidyl ether.⁵ However, in this case, the rate of epoxide ring-opening polymerization is exceptionally rapid due, in part, to the highly strained nature of the epoxycyclohexane ring system. It is also worth noting that the polymerization of the epoxy groups is nearly complete before appreciable polymerization of the 1-propenyl ether groups sets in. Further,

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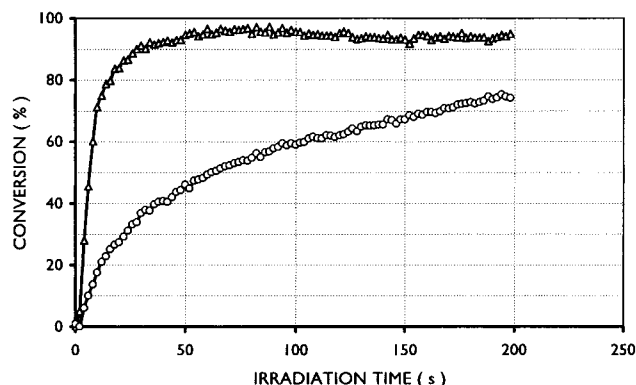
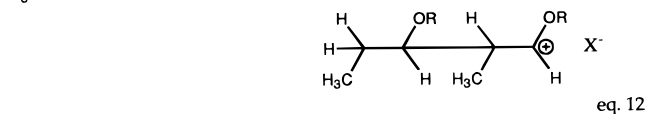
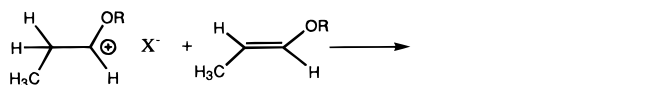
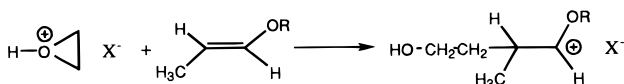
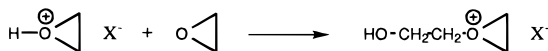
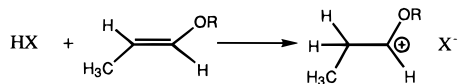
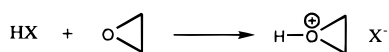
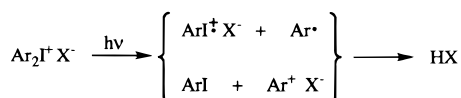


Figure 3. Photopolymerization of **IV**: (Δ) epoxy groups; (\circ) 1-propenyl ether groups.

it may be noted that while the conversion of the epoxide groups is nearly quantitative, the polymerization of the 1-propenyl ether groups reaches only approximately 75% (after 200 s irradiation). Examination of the polymer obtained after polymerization showed that it was insoluble in all common solvents, indicating that it is cross-linked.

To explain the anomalous behavior of **IV** during its photopolymerization, we propose the mechanism shown in Scheme 2.

Scheme 2

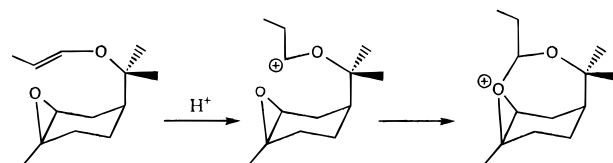


Photolysis of the diaryliodonium salt photoinitiator (eq 7) results in the generation of a number of reactive species, including aryl radicals, aryl cation-radicals, aryl cations, and the superacid HSbF_6 .²¹ Initiation of cationic polymerization can occur by protonation or attack of aryl cations on either the epoxide (eq 8) or 1-propenyl ether

(eq 9) groups of **IV**. In eqs 8 and 9 only the attack by protons is shown, since these are overwhelmingly the most abundant species involved in initiation. While cationic polymerization of the protonated epoxide (oxiranium ion) can take place by the nucleophilic attack of another epoxide group (eq 10), attack by a 1-propenyl ether group (eq 11) either does not occur or takes place very slowly due to the relatively high stability of the oxiranium ion as compared to the carbocation which would be formed. Similarly, the carbocation which is generated by the initial protonation of the 1-propenyl ether groups can induce the polymerization of either another 1-propenyl ether or an epoxide group (eq 12 and 13). Using the same rationale, the crossover reaction (eq 13) would be expected to take place rapidly to convert the carbocation to the more stable oxiranium ion.

One would also predict that crossover from 1-propenyl ether to epoxide polymerization would also be facilitated in α -terpineol-derived hybrid monomer **IV**, due to the proximity of the two functional groups in this molecule. Molecular models show that conformations exist in this monomer which bring the 1-propenyl ether and epoxy groups within bonding distance. As shown in eq 14, an intramolecular cyclization via a seven-member intermediate would convert the initially formed carbocation to an oxiranium ion which can then propagate by ring-opening polymerization.

However, while intramolecular reaction may contribute to the acceleration of epoxide polymerization by diverting the initiation process exclusively to epoxide polymerization, this cyclization reaction does not appear to contribute substantially to the main propagation reaction. This statement can be justified on the basis of three separate pieces of evidence. First, the consumption of the two functional groups appears to take place sequentially rather than simultaneously. Second, cyclization as depicted in eq 14 requires that equal



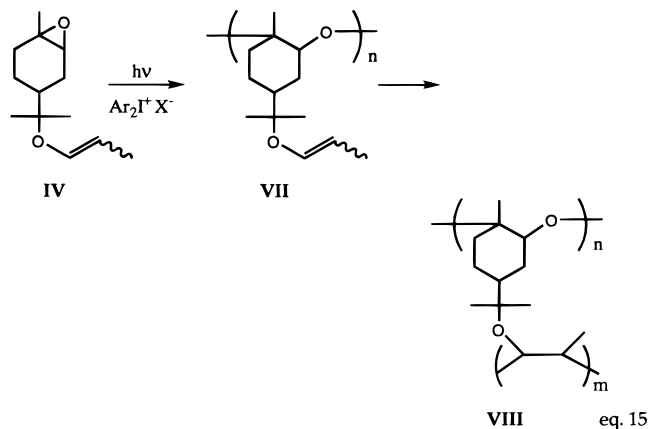
eq. 14

numbers of epoxy and 1-propenyl ether groups react. Instead, as noted in Figure 3, while nearly 100% of the epoxy groups react, only 75% of the 1-propenyl ether groups are consumed during the photopolymerization. Last, as we have noted earlier, the polymer which is obtained by photopolymerization of **IV** is cross-linked. If the cyclization process shown above was involved in the main propagation reaction, one would expect to obtain a linear, soluble polymer. For these reasons, we propose that the major process involves an intermolecular mechanism involving interaction of the 1-propenyl and epoxy groups on different molecules.

Since rapid crossover from 1-propenyl ether to epoxide takes place while the reverse cross-propagation reaction either occurs slowly or does not take place, ring-opening homopolymerization of the epoxide proceeds until virtually all these functional groups are exhausted. After

(21) Crivello, J. V. In: *UV Curing: Science and Technology*, Pappas, S. P., Ed.; Technology Marketing: Stamford, CN, 1978; p 24.

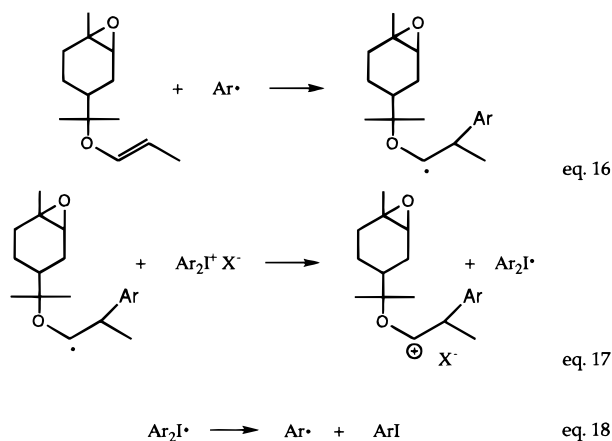
this has taken place, 1-propenyl ether polymerization rapidly sets in. These two separate stages of the polymerization have a direct impact on the structure of the polymer which is formed. This is depicted in eq 15.



In the first stage, the polymer **VII** formed is substantially a linear polyether bearing pendant 1-propenyl ether groups. In the second stage, this polymer undergoes cross-linking to give **VIII** by subsequent reaction of the pendant groups. Thus, the epoxide conversion proceeds to very high conversions, since linear, soluble polymer is produced. However, while the initial stages of the 1-propenyl ether polymerization proceed at a high rate, the polymerization slows and stops as the density of the cross-linked network increases and the glass transition temperature rises. Due to the immobility of the remaining 1-propenyl ether groups, an ultimate conversion of only 70% is attained.

While rapid chain transfer from 1-propenyl ether to epoxide polymerization explains why the polymerization of the epoxide group in **IV** takes place before that of the 1-propenyl ether group, it does not offer an adequate rationale for the apparent rate acceleration of the epoxide polymerization of this monomer. Shown in Scheme 3 is a mechanism which we propose to explain this latter phenomenon.

Scheme 3



As noted previously, the photolysis of diaryliodonium salts generates not only cationic species (protons and cation-radicals) but also free radical species as well. Aryl radicals can interact with **IV** via the pathway shown in eq 16. In this reaction, a secondary radical species is generated by addition of the aryl radical to the propenyl

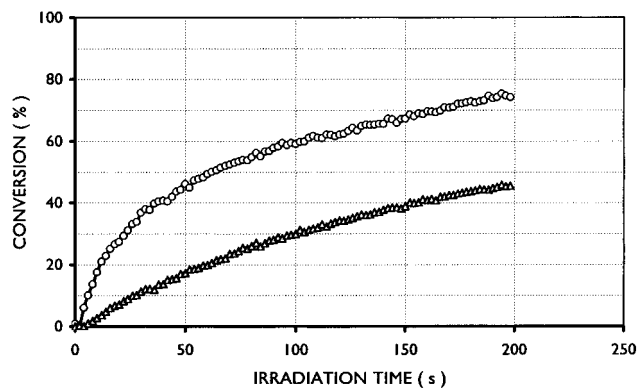


Figure 4. Comparison of the RTIR curves for the 1-propenyl ether polymerizations of **IV** in the presence of **IOC10** (○) alone and (△) in the presence of 4% nitrobenzene.

ether double bond. Redox interaction of these radical species with the diaryliodonium salt gives rise to a carbocation and a diaryliodonium radical (eq 17). In a subsequent reaction (eq 18), the diaryliodonium radical decays irreversibly to generate an aryl iodide and an aryl free radical. The reactions shown in eqs 16–18 constitute a free radical chain reaction in which the diaryliodonium salt photoinitiator is consumed by a nonphotochemical process. At the same time, carbocations are generated that ultimately initiate cationic polymerization. Consideration of Scheme 3 leads to the overall conclusion that the photochemically induced decomposition of the diaryliodonium salt photoinitiator is greatly amplified by the redox cycle of eqs 16–18. This results in the very rapid and efficient generation of a large number of initiating species by a nonphotochemical process which is manifested by a high apparent rate of consumption of the epoxide groups.

There is considerable precedent for the mechanism shown in Scheme 3. We have previously reported that the photoinitiated cationic polymerization of 1-propenyl ether monomers is accelerated by a very similar mechanism involving a free radical induced decomposition of a diaryliodonium salt photoinitiator.²² In addition, we have also proposed that the electron-beam induced cationic polymerization of epoxy monomers occurs by such a process.²³ To obtain some evidence for involvement of this mechanism with the present monomer, the photoinitiated cationic polymerization of **IV** was carried out in the presence of nitrobenzene as a free radical retarder. The results are shown in Figure 4 in which the 1668 cm^{-1} 1-propenyl ether IR absorption band was monitored. When the free radical induced decomposition reaction is retarded by nitrobenzene, the polymerization displays a marked deceleration, as may be noted by a decrease in the slope of the RTIR curve. Diaryliodonium salts are effective in the mechanism depicted in Scheme 3 because they possess very low reduction potentials, which allow them to be readily reduced by the carbon-centered free radicals generated during the reaction. Figure 5 shows a RTIR study of the polymerization of **IV** in which the triarylsulfonium salt **SOC10** is used as the photoinitiator. Since the redox potential of this photoinitiator (−28 kcal/mol) is more

(22) Crivello, J. V.; Bratslavsky, S. A. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2755.

(23) Crivello, J. V.; Fan, M.; Bi, D. *J. Appl. Polym. Sci.* **1992**, *44*, 9.

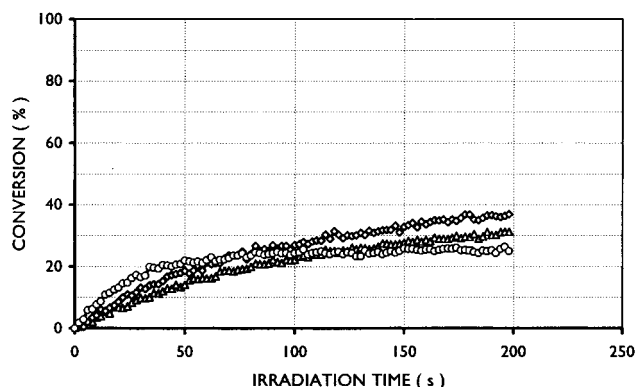


Figure 5. RTIR study of the cationic photopolymerization of **III** and **IV** in the presence of **SOC10**: \diamond , **IV** epoxide groups; \triangle , **IV** 1-propenyl ether groups; \circ , **III** epoxide groups.

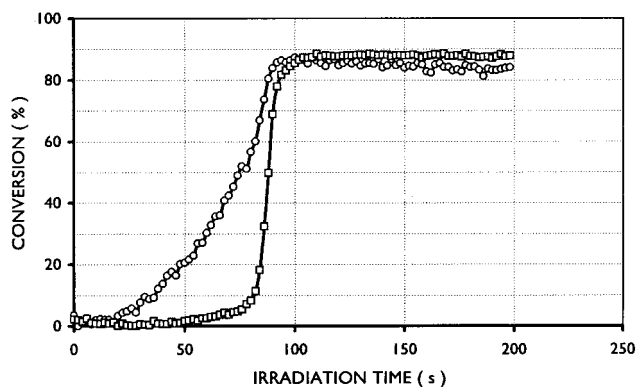


Figure 6. Comparison of the RTIR curves for the photopolymerizations of an equimolar mixture of (\square) **V** (1-propenyl ether), and (\circ) **VI** (epoxide) in the presence of 0.5 mol % **IOC10**.

than 5 times higher than that of **IOC10** (-5 kcal/mol), it is not reduced by free radicals produced in the reaction.²⁴ Hence, the redox cycle is not operative and the apparent rate of polymerization of both the 1-propenyl ether and epoxide groups is markedly slowed. It is, however, worth noting that in accordance with the mechanism shown in Scheme 2, the rate of epoxide polymerization exceeds that of the 1-propenyl ether. Also included in this figure is the epoxide polymerization of allyl α -terpineol ether epoxide **III**. Comments regarding behavior of this compound will be made later in this paper.

Consideration of the mechanisms depicted in Schemes 2 and 3 suggested that acceleration of epoxide polymerization should be noted even when the 1-propenyl ether and epoxide groups are not located in the same molecule. Figure 6 confirms this. In this figure, an equimolar mixture of model compounds **V** and **VI** were simultaneously photopolymerized in the presence of 0.5 mol % **IOC10**. Again, comparison with the results shown in Figure 2 shows that the polymerization of the epoxide group of **VI** displays a marked acceleration, while at the same time the polymerization of the 1-propenyl ether groups of **V** is depressed.

When the cationic photopolymerization of allyl α -terpineol ether epoxide, **III**, was carried out in the presence

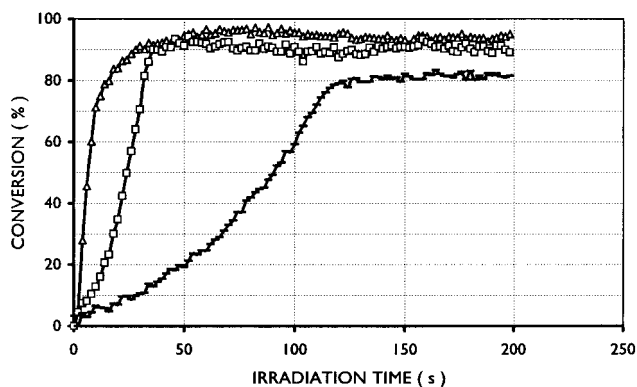
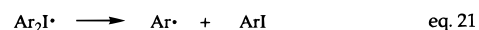
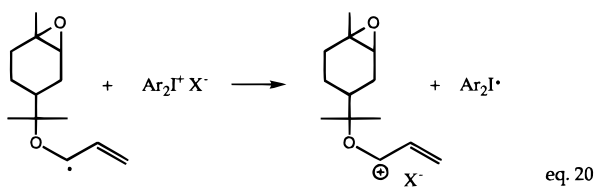
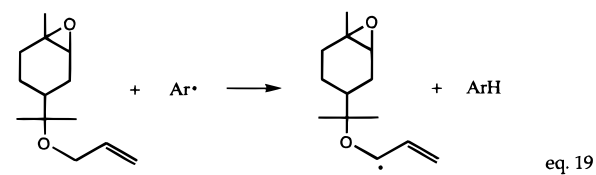


Figure 7. RTIR study of the photoinduced cationic ring-opening epoxide polymerizations of (\square) **III**, (\triangle) **IV**, and (—) **VI**.

of 0.5 mol % **IOC10** as a photoinitiator, we were surprised to note that the epoxide polymerization also displays an apparent acceleration effect. This can be seen in Figure 7 in which the curve for the epoxide polymerization of **III** is compared with those of the model compound **VI** and with hybrid monomer **IV**. While the acceleration effect for **III** is not quite as marked as for **IV**, the polymerization is greatly accelerated over that of **VI**. On closer examination of the curves in Figure 7, it may be noted that there is essentially no induction time required for **IV** to reach the maximum rate of polymerization (i.e. slope) while a more pronounced induction time is observed for **III**. Once polymerization is underway, slopes of the curves (i.e. the rates) are nearly the same. This phenomenon can again be explained by invoking a very similar mechanism to that shown in Scheme 3. In Scheme 4 is the mechanism that we propose is operative in the polymerization of allyl ether functional epoxy monomer **III** and which is responsible for the observed rate acceleration.

Scheme 4



During photolysis, free radical species generated by the homolytic cleavage of one of the carbon-iodine bonds of the diaryliodonium salt photoinitiator (eq 7) interact with **III** by abstraction of the weakly bonded hydrogen on the methylene carbon of the allylic ether group, as depicted in eq 19. The resulting allylic free radical is stabilized by both resonance interaction with the double bond and by the neighboring electron-rich oxygen atom. This allylic free radical can react further (eq 20) by a redox reaction with the diaryliodonium salt

(24) Crivello, J. V. In *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser Pub., Munich, 1993; p 175.

(an oxidant) to give the resonance-stabilized carbocation shown and a diaryliodonium free radical. As noted previously, rapid decomposition of the diaryliodonium free radical (eq 21) gives an aryl iodide and at the same time, regenerates the aryl free radical. The reactions shown in eqs 19–21 also constitute a free radical chain reaction in which the diaryliodonium salt is consumed by a nonphotochemical process. At the same time, carbocations are generated that subsequently initiate cationic polymerization. Thus, from the mechanism of Scheme 4 it can be concluded that the rate of the photochemically induced polymerization of **III** is amplified by the redox cycle of eqs 19–21.

Because more cationic chain carriers are generated per photon, the induction time that is required to overcome trace amounts of basic impurities (e.g. water) which are always present is also reduced for allyl α -terpineol ether epoxide, **III**. When the radical chain induced decomposition is not present as shown in Figure 2 for epoxy monomer **VI**, there is a long induction period which is followed by rapid consumption of the monomer. To offer further proof for the mechanism shown in Scheme 4, the radical retarder, nitrobenzene, was added to monomer **III** and the photopolymerization carried out once again. As predicted, when nitrobenzene is present, the induction time is lengthened and the entire polymerization profile of **III** now resembles that of **VI**.

Monomers **III** and **IV** constitute new types of epoxy monomers in which the monomer contains functional groups which interact with the initiator to synergistically accelerate the rate of cationic polymerization. The general mechanistic concepts presented here have been applied to the synthesis of additional types of activated epoxy monomers. The results of these studies will be reported in forthcoming papers from this laboratory.

Conclusions

α -Terpineol is a convenient, inexpensive, and biorenewable substrate from which new monomers for photoinitiated cationic polymerization can be constructed. This paper reports the synthesis of two potentially interesting highly reactive epoxide monomers which can be prepared from α -terpineol by simple, straightforward synthetic methods. Allyl α -terpineol ether epoxide **III** and its isomer, 1-propenyl α -terpineol ether epoxide **IV**, were prepared in high yields and characterized. Key synthetic steps in the preparation of these monomers were the use of dimethyldioxirane to selectively epoxidize the cycloalkene carbon-carbon double bond of allyl α -terpineol ether, **II**, to give epoxy monomer **III**, followed by ruthenium-catalyzed double bond isomerization to afford **VI**.

Studies of the photoinitiated cationic polymerization of monomers **III** and **IV** and comparison with appropriate model compounds revealed that the rate of epoxide ring-opening polymerization of hybrid monomer **IV** and monomer **III** exhibited marked rate enhancements. These observations were attributed to a free radical induced decomposition of the photoinitiator which increases the apparent polymerization rate by increasing the number of chain carriers. These new monomers based on α -terpineol provide a novel approach and a demonstration that the apparent rates of photopolymerization of epoxy monomers can be considerably accelerated. This chemistry may have many potential practical applications. In addition, the methods and observations made here may be similarly applied to the design and synthesis of other highly reactive epoxy monomers.

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