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FREE RADICAL ACCELERATED CATIONIC POLYMERIZATIONS

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Abstract: The simultaneous photoinitiated cationic polymerizations of epoxides and vinyl ethers in the presence of diaryliodonium salt photoinitiators results in an acceleration of the ring-opening epoxide polymerization and a deceleration of the vinyl ether polymerization. These effects are seen both in mixtures of the two monofunctional monomers as well as in hybrid monomers which bear vinyl ether and epoxide groups in the same molecule. A combination of two mechanisms have been proposed to account for these effects. The reversible conversion of alkoxycarbenium to oxiranium ions results in a two-stage reaction in which first, the epoxide, then the vinyl ether polymerization takes place. Free radical chain induced decomposition of the diaryliodonium salt produces a large incremental number of carbenium ion species which results in the acceleration effect.

INTRODUCTION

Of special interest in this laboratory is the development of epoxide monomers with enhanced reactivity in photoinitiated cationic polymerization. Besides our general interest in the polymerizations of these monomers, they currently have many commercial applications as coatings, inks, adhesives and are potential substrates for such advanced technical areas as fiber optic coatings, optical adhesives, wave guides and in stereolithography. One approach we have recently taken for the design of new, more reactive epoxy monomers has been to incorporate other types of cationically polymerizable functional groups into these monomers. Specifically, we have prepared several such "hybrid" monomers such as allyl and crotyl glycidyl ethers containing both epoxy and vinyl (1-propenyl)[1] ether groups.[2,3] In doing so, we hoped to make use of the higher reactivity of the vinyl ether group in attempt to accelerate the polymerization of the epoxide. A considerable enhancement in the reactivity of the epoxy groups of these two monomer was observed which was ascribed to the presence of the vinyl ether moieties. It was of some interest to determine if the reactivity enhancement displayed by these compounds was unique or whether it was a general phenomenon which could be applied to even more reactive hybrid monomers bearing epoxy and vinyl ether groups. We also wished to examine whether simple mixtures of vinyl ether and epoxide monomers would display similar kinetic characteristics.

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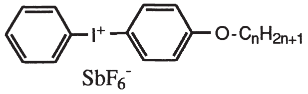
RESULTS AND DISCUSSION

Model Compound Studies

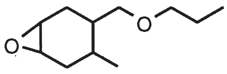
The literature contains little information concerning simultaneous epoxide ring-opening and vinyl polymerizations. For this reason, we decided to examine the concurrent photoinitiated cationic polymerizations of several vinyl ether/epoxy monomer pairs. Fourrier transform real-time infrared spectroscopy (RTIR) has proven to be an extremely useful method for monitoring the kinetics of very rapid photopolymerization reactions.[4,5,6,7] Employing this method, we have used 0.5 mol% of **IOC-10** or **IOC-11** as the photoinitiator per reactive functional group in the monomer.



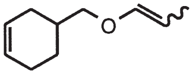
n = 10 (IOC-10), n = 11 (IOC-11)

The progress of both the vinyl ether and epoxide polymerizations were monitored separately and simultaneously by following the decrease in the absorbance of characteristic IR bands at 812 and 1669 cm^{-1} of the respective epoxide and vinyl ether groups.

Figure 1 shows a study, in which the photopolymerizations of the highly reactive cycloaliphatic epoxy monomer **MCEPr** and vinyl (1-propenyl) ether monomer **CP** were conducted.



MCEPr



CP

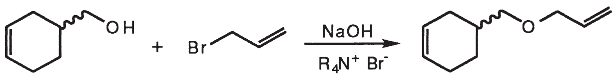
The slopes of the initial portion of the kinetic curves may be used as a measure of the reactivity of these monomers since the $R_p/[M_o]$ values so obtained are directly proportional to the rates of polymerization. While the polymerization of the cycloaliphatic epoxy monomer **MCEPr** is quite rapid ($R_p/[M_o] = 1.0 \times 10^{-2}s^{-1}$), the polymerization of vinyl ether **CP** is much faster ($R_p/[M_o] = 17 \times 10^{-2}s^{-1}$).

Next, a 1:1 molar mixture of the above two monomers was prepared and the two monomers simultaneously photopolymerized again using **IOC-10** as the photoinitiator. A markedly different order of reactivity was observed as is shown in Figure 2. In this case, the ring-opening polymerization of the epoxide group displays a marked rate acceleration ($R_p/[M_o] = 3.1 \times 10^{-2}s^{-1}$). An epoxide acceleration factor, $AF_E = 3.1$ was calculated by taking the ratio of the $R_p/[M_o]$ values for the simultaneous versus the independent polymerizations of **MCEPr**. At the same time, the rate of the vinyl ether polymerization in the mixture was depressed ($R_p/[M_o] = 6.3 \times 10^{-2}s^{-1}$). A vinyl ether deceleration factor $DF_{VE} = 2.6$ for **CP** was calculated from the ratio of the independent and simultaneous polymerizations. It should also be noted from Figure

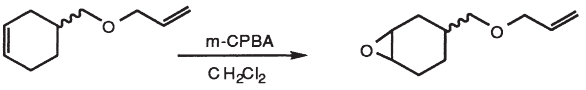
2 that the polymerization of the vinyl ether monomer is inhibited until the polymerization of the epoxide is essentially complete.

Synthesis of Hybrid Monomers

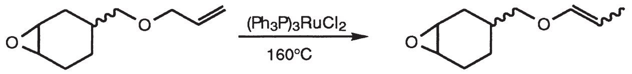
Hybrid monomers bearing vinyl ether and epoxy functionalities are readily synthesized using straightforward synthetic methods from available and easily obtained substrates. For example, monomer **CEP** was prepared by the sequence of reactions (eq. 1-3) shown below.



CA eq. 1

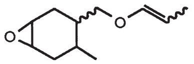


CEA eq. 2

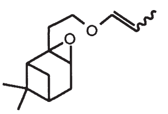


CEP eq. 3

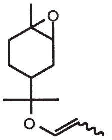
CA was prepared in high yield by the Williamson ether synthesis using a phase transfer catalyst (eq. 1). Epoxidation of **CA** using m-chloroperbenzoic acid (eq. 2) takes place regioselectively at the cyclohexene double bond to give **CEA**. Ruthenium catalyzed isomerization of the double bond of **CEA** (eq. 3) proceeds smoothly to give high yields of **CEP**. Similar methodology was employed for the preparation of the three hybrid monomers **MCEP**, **NEP** and **TEP** shown below.



MCEP



NEP



TEP

The cationic photopolymerization of **CP** is displayed in Figures 3. Analogous behavior is displayed by all the monomers. In each case, the polymerization of the epoxide functional group in the molecule proceeds at a markedly higher rate than the vinyl ether group. This is in direct contrast to the usual situation in which the rate of polymerization of vinyl ethers is typically much faster than that of epoxides. In every case, the polymerization of the epoxide group of the hybrid monomer proceeds to high conversion while that of the vinyl ether group in the same molecule takes place more slowly and to comparatively low conversion. Both polymerizations take place without the usual induction period.

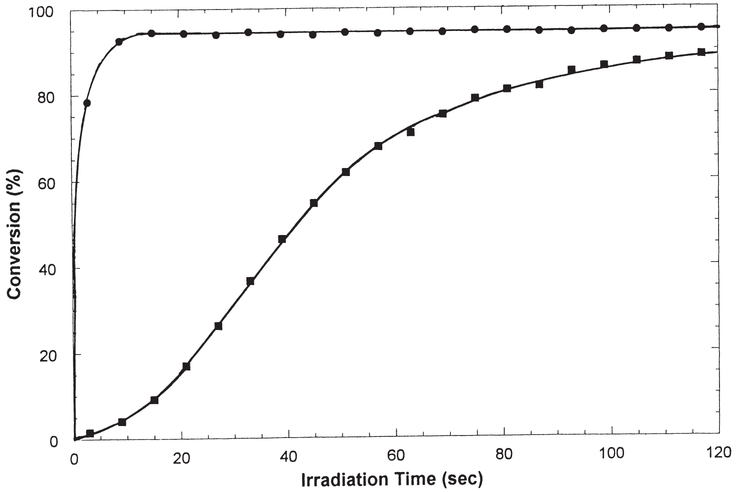


Figure 1. Comparison of the epoxide ring-opening photopolymerization of ■, **MCEPr** and ●, **CP** using 1 mol% **IOC-10** as photoinitiator (light intensity 2150 mJ/cm^2·min).

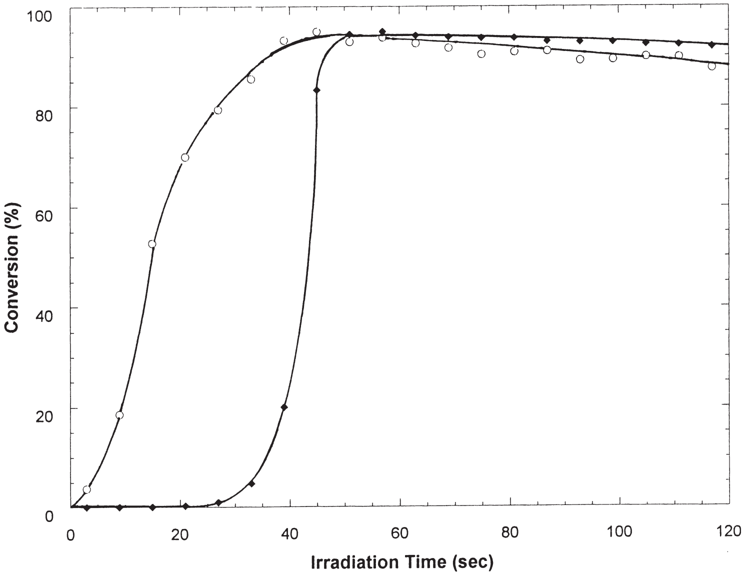


Figure 2. RTIR study of the photopolymerization of a 1:1 molar mixture of ○, **MCEPr** (epoxide) and ◆, **CP** (1-propenyl ether) using 1 mol% **IOC-10** as photoinitiator (light intensity 2100 mJ/cm^2·min).

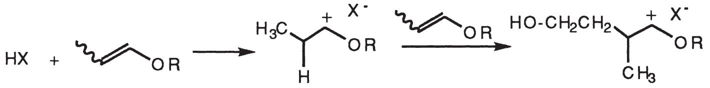
Mechanistic Interpretation of the Results

To explain the above phenomena observed with mixed vinyl ether/epoxy monomer systems and with the corresponding hybrid monomers, we propose two mechanistic schemes. The photolysis of diaryliodonium salts as shown in equation 4 takes place by both heterolytic (dominant process) and homolytic cleavages of a carbon-iodine bond and produces a number of reactive species including: radicals, cations and cation-radicals.[8,9,10]

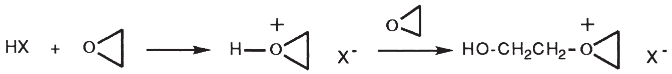
$$Ar_2I^+\ MtX_n^- \xrightarrow{h\nu} \left\{ \begin{array}{l} ArI^{+\cdot}\ MtX_n^- \ +\ Ar\cdot \\ ArI^+\ MtX_n^- \ +\ ArI \end{array} \right\} \longrightarrow HMtX_n$$

eq. 4

Highly reactive aryl cations and aryliodine cation-radicals generated during this photolysis react further with solvents, monomers or impurities to give protonic acids, $HMtX_n$. In this laboratory, we have employed diaryliodonium salts as photoacid generators and used them to photoinitiate the cationic polymerizations of vinyl ethers and epoxides.[11] These two polymerizations proceed respectively, via the formation and propagation of alkoxycarbenium ions and oxiranium ions (eq. 5 and 6).



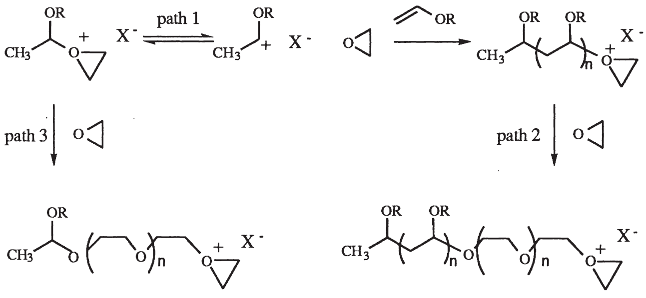
eq. 5



eq. 6

When both reactive species are generated together in the presence of the two different monomers, an equilibrium can be set-up between the two species as shown in Scheme 1.

Scheme 1



If epoxides of low reactivity such as glycidyl ethers are present, their rate of cationic ring-opening polymerization are comparatively slow. Thus, there will be a small but finite concentration of alkoxycarbenium ions present which can propagate by addition of vinyl ether molecules (path 1). Reversible termination by oxirane molecules and reinitiation may occur many times as vinyl ether polymerization proceeds. Eventually, nucleophilic attack by the oxirane monomer takes place resulting in the start of a polyether chain (path 2) which can no longer equilibrate to form alkoxycarbenium ions and vinyl ether polymerization ceases. In such cases, simultaneous vinyl ether and epoxide polymerizations take place. However, as previously noted, the rate of the vinyl ether polymerization is depressed as compared to the independent polymerization of that monomer. This is due to the rapid conversion of propagating alkoxycarbenium ions to the more stable and less reactive oxiranium ions.

In contrast, if highly reactive epoxide monomers such as those containing epoxycyclohexyl groups are used (path 3), the initially formed oxiranium ions are rapidly converted to growing polyether chains which do not equilibrate with alkoxycarbenium ions. In such cases, all of the polymerization is diverted to epoxide ring-opening and vinyl ether polymerization is delayed until the epoxide concentration falls to a low level at which competition of epoxide monomers for the growing chain end is no longer favorable. In this case, homopolymerization of the two monomers is observed.

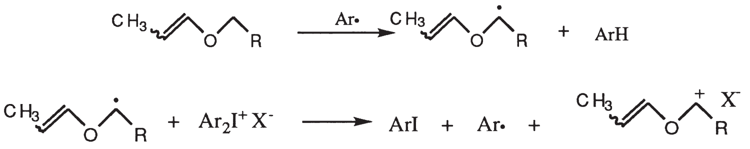
The mechanism shown in Scheme 1 bears a striking resemblance to the mechanism proposed by Percec and his coworkers[12,13,14] for the living cationic polymerization of vinyl ethers in the presence dimethylsulfide. These workers have suggested that an alkoxycarbenium ion is in equilibrium with an alkoxymethylsulfonium species and that the propagation and chain transfer reactions are slowed by rapid termination by ion-trapping with dimethylsulfide. For reasons of simplicity, the usual chain transfer and back-biting reactions have not been included in Scheme 1 although the authors acknowledge the presence of these side reactions in the present studies as well. While this mechanism allows us to rationalize the fact that epoxides and vinyl ethers do not undergo any substantial copolymerization, and that in certain cases there is a marked temporal separation between the two homopolymerizations, it does not offer a full explanation for those instances in which an increase in the rate of epoxide ring-opening polymerization in the presence of the vinyl ether monomer is observed. Accordingly, we propose an additional mechanism to explain this latter effect.

As shown in equation 4, free radical species are generated by photolysis of diaryliodonium salts. For this reason, these compounds can be employed to initiate free radical polymerizations. Further, simultaneous, photoinduced free radical and cationic polymerizations can be conducted using diaryliodonium salts.[15,16,17] It is also important to recognize that diaryliodonium salts, due to presence of iodine in the +3 oxidation state, are oxidants.[18] During photolysis, the excited diaryliodonium salt undergoes a formal reduction at the iodine atom. As a result, the solvent, monomer or impurities are oxidized. Diaryliodonium compounds can be reduced in other ways as well. For example, we have employed various photosensitizers (PS) to broaden the spectral response of diaryliodonium salt photoinitiators. The photosensitizers serve as reducing agents in their excited states reducing and the overall mechanism of photosensitization involves an electron transfer or redox process.[19,20]

Hypervalent iodine compounds, including diaryliodonium salts can also be reduced chemically employing a wide variety of chemical reducing agents.[18] In this laboratory, we have employed ascorbate[21] and tin[22] reducing agents together with diaryliodonium salts to conduct redox initiated cationic polymerizations. In two seminal papers, Ledwith, et al.[23,24] demonstrated that electron-rich free radicals produced either by photolysis or by thermolysis are capable of reducing diaryliodonium salts. Yagci and his coworkers[25,26,27] have continued this work in recent years using other types of onium salts. Bi and Neckers[28] have recently reported the use of a dye to photosensitize the visible light cationic polymerization of cyclohexene oxide in the presence of a diaryliodonium salt. These workers reported that the mechanism involved the generation of free radicals by the Norrish Type II abstraction of a hydrogen atom from an amine by the photoexcited dye.

In this laboratory, during the cationic photoinitiated polymerization of 1-propenyl ethers, it was observed that there was a marked rate acceleration and a depression of the induction period when diaryliodonium salts were used as photoinitiators but not when triarylsulfonium salts were employed.[29] In accord with the earlier proposal of Ledwith, et al.,[14,15] we suggested that the observed effects could be explained by the mechanism shown in Scheme 2 involving the abstraction of the α-ether hydrogen atoms by aryl free radicals (eq. 7) followed by the free-radical induced reduction of the diaryliodonium salt by these latter radicals (eq. 8).

Scheme 2



It is also possible, as proposed by Ledwith,[13] that the aryl radicals can add to the vinyl ether double bond to produce an electron-rich and easily oxidized α-ether free radical.

The free radical induced chain reaction represented by equations 7 and 8 results in the dark (i.e. non-photochemical) decomposition of a diaryliodonium salt together with the transformation of an equivalent number of free radicals into cationic centers which can initiate cationic polymerization. Thus, besides the usual direct cationic photoinitiation process, the additional free radical chain induced decomposition of diaryliodonium salts in the presence of vinyl ethers results in the production of substantially more active polymerizing cationic centers and consequently, an increase in rate.

Since the rate acceleration of the epoxide polymerization observed in our studies is a free radical process, it should be inhibited or retarded by free radical traps. We have conducted experiments to verify this hypothesis. Marked reductions in the rates of epoxide polymerizations were observed when nitrobenzene was added to mixed vinyl ether and epoxide systems or to the polymerizations of hybrid monomers. Similar results were noted when these polymerizations were carried out in the presence of oxygen. In addition, the onsets of the vinyl ether polymerization are lengthened in the presence of these retarders. The cationic photopolymerizations of epoxides were not accelerated in the presence of vinyl ethers when triarylsulfonium salt photoinitiators are used. Due to their higher redox potential than diaryliodonium salts, triarylsulfonium salts are not reduced by a-ether radicals.[11] Thus, in this case, cationic polymerization occurs only as a result of the photolysis of the triarylsulfonium salt and without an incremental component due to the free radical induced decomposition of the photoinitiator.

Because the polymerization of epoxide group in hybrid monomers preceeds that of the vinyl ether group in the same molecule, initially a linear polyether polymer is formed. This reaction proceeds to high conversion. When substantially all of the epoxide groups have reacted, the crosslinking polymerization of the pendant vinyl ether groups sets in. This latter polymerization proceeds more slowly since it is essentially a crosslinking reaction. As the reaction takes place, the network becomes more and more highly crosslinked and the reaction rate is retarded by a simultaneous increase in the glass transition temperature. Due to the immobility of the remaining vinyl ether groups, a maximum conversion of only 35% is attained.

CONCLUSIONS

Based on these studies, it can be concluded that the rate of cationic photopolymerization of a given monomer can be influenced not only by such factors as the experimental parameters and the nature of photoinitiator, but also by structural factors within the monomer itself which are remote from site of polymerization. We have taken advantage of this concept to design more reactive monomers by incorporating functional groups which can participate in the free radical induced decomposition of the photoinitiator. In this paper, we have described the synthesis of hybrid monomers which incorporate both vinyl ether and epoxide functional groups in the same molecule. Hybrid monomers **CEP**, **NEP**, **MCEP** and **TEP** represent a new class of highly reactive substrates in which the epoxide group polymerizes more rapidly than the vinyl ether group. These new, low-viscosity high-reactivity monomers have many potential applications involving UV curing. In addition, this work also suggests alternative methods by which photoinduced cationic polymerizations of epoxides may be accelerated through rational design of monomers.

EXPERIMENTAL

Photopolymerization Studies Using Real-Time Infrared Spectroscopy (RTIR)

Photopolymerizations of all the monomers were monitored using real-time infrared spectroscopy (RTIR) employing an apparatus and procedures as previously described.[3]

Synthesis of Model Compounds and Monomers

The following experimental procedures are typical of those employed during the course of this investigation for the synthesis of model compounds and hybrid monomers.

Synthesis of (2-Oxapent-4-enyl)cyclohex-3-ene (**CA**)

Into a 500 mL round bottom flask equipped with an overhead stirrer, thermometer and a nitrogen inlet were placed 56.085 g (0.5 mol) of distilled 1,2,3,6-tetrahydrobenzylalcohol, 90.75 g (0.75 mol) of allyl bromide, 100 mL of toluene and 30 g (0.75 mol) of sodium hydroxide. The reaction mixture was stirred at room temperature for 15 minutes. Then, 3 g (0.01 mol) of tetra-n-butylammonium bromide was added and the reaction mixture slowly heated to reflux (65 °C) and maintained at that temperature for eight hours. The reaction mixture was cooled and filtered to remove the sodium bromide which precipitated during the reaction. The filtrate was poured into 500 mL of distilled water, the organic layers were separated and the aqueous layer extracted with fresh toluene. The combined organic layers were washed with three 200 mL portions of distilled water and the organic phase was dried over anhydrous sodium sulfate. Then, the excess allyl bromide and toluene were removed using a rotary evaporator and the reaction mixture subjected to vacuum distillation. The clear liquid distillate amounted to 62.32 g (82 % recovered yield). Fractional vacuum distillation gave pure **CA** with a boiling point of 22 °C at 0.05 mm Hg. Elemental Analysis. Calculated for $C_{10}H_{16}O$: C, 78.90 %; H, 10.59 %. Found: C, 78.82%; H, 10.52%.

Synthesis of (2-Oxapent-3-enyl)cyclohex-3-ene (**CP**)

To 19 g (0.125 mol) of **CA** in a 100 mL round bottom flask equipped with a magnetic stirrer, reflux condenser and a nitrogen inlet were added 0.008 g (0.0075 mmol) of tris(triphenylphosphine)ruthenium(II) dichloride. The reaction mixture was heated at 160 °C for

2 h. The ^{1}H NMR spectrum showed that the bands assigned to the allyl groups (d ppm 5.1-5.4, CH_2= ; 5.8-6.1, CH= ; 3.8-4.1, CH_2) had been completely replaced by new bands (d ppm 1.58, CH_3; 4.25-4.45, cis-CH_3-C$\underline{H}$= ; 4.65-4.85, trans-CH_3-C$\underline{H}$= ; 5.9-6, cis-CH-O; 6.15-6.3, trans-O-CH) assigned to the 1-propenyl ether groups. Pure **CP** (mixture of *d,l-cis* and *d,l-trans* isomers) was isolated by fractional vacuum distillation (b.p. 156 °C at 20 mm Hg) in 92 % yield. Elemental Analysis. Calculated for $C_{10}H_{16}O$: C, 78.9 %; H, 10.59 %. Found: C, 78.79 %; H, 10.53 %.

Synthesis of (2-Oxapent-4-enyl)-3,4-epoxycyclohexane (**CEA**)

Into a 1 L round bottom flask equipped with an overhead stirrer, an addition funnel and a thermometer were placed 32.3 g of m-chloroperoxybenzoic acid (0.1205 mol) and 300 mL methylene chloride. The flask was cooled to 0-3 °C using an ice bath. **CA** (20 g, 0.1205 mol) in 150 mL dichloromethane was added dropwise so that the temperature did not rise above 10 °C. The addition required approximately 90 minutes. The reaction was allowed to warm to room temperature and then stirred overnight. The reaction mixture was filtered using a Büchner funnel to remove m-chlorobenzoic acid and the filtrate washed with 100 mL quantities of saturated sodium bicarbonate solution until the evolution of carbon dioxide ceased. The organic layer was dried over anhydrous sodium sulfate. Then, the excess methylene chloride was removed using a rotary evaporator and the reaction mixture subjected to vacuum distillation. The volatile clear liquid amounted to 13.96 g (69 % recovered yield). Fractional distillation gave pure **CA** as a mixture of isomers with a boiling point of 30 °C at 0.1 mm Hg. Elemental Analysis. Calculated for $C_{10}H_{16}O_2$: C, 71.39 %; H, 9.59 %. Found: C, 71.36 %; H, 9.55 %.

Synthesis of (2-Oxapent-3-enyl)-3,4-epoxycyclohexane (**CEP**)

CEA was isomerized using a procedure identical to that used for **CP**. The isomerization reaction was complete after 9 h at 160 °C. A yield of 93 % was obtained. **CEA** (mixture of 8 isomers) had a boiling point of 165 °C at 22 mm Hg. Elemental Analysis. Calculated for $C_{10}H_{16}O_2$: C, 71.39 %; H, 9.59 %. Found: C, 71.39 %; H, 9.53 %.

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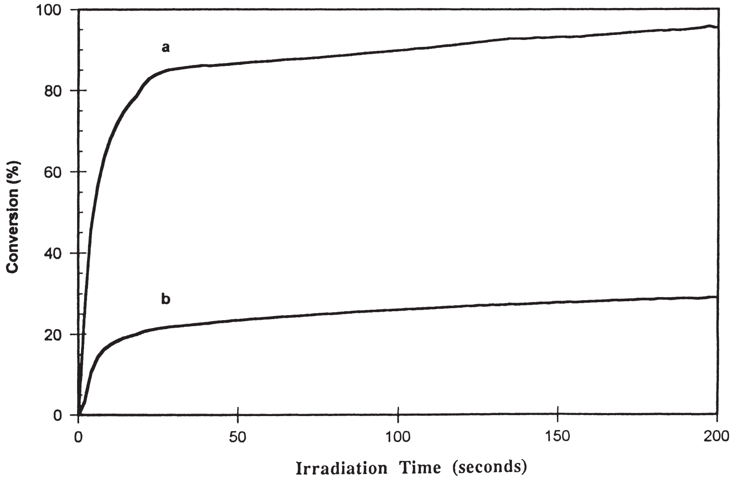

Figure 3. RTIR study of the photoinitiated cationic polymerization of **CEP** using 1 mol% **IOC-11** as photoinitiator. (a), epoxide; (b); 1-propenyl ether (light intensity 2100 mJ/cm^2·min).