Effect of Temperature on the Cationic Photopolymerization of Epoxides

James V. Crivello[a]

[a] Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York

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JAMES V. CRIVELLO

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York

The effects of temperature on the photoinitiated cationic ring-opening polymerizations of a number of different epoxide monomers were studied with the aid of a modified optical pyrometer instrument. Depending on the structures of the epoxide monomer, various behaviors were observed. The results were interpreted as due to steric and electronic features inherent in the structures of the monomers that affect the stabilization of the secondary oxonium ions, which are formed as intermediates in these polymerizations. At one extreme, cycloaliphatic epoxides such as cyclohexene oxide give highly reactive oxonium intermediates that exhibit high rates of polymerization even at subambient temperatures. At the other extreme, alkyl glycidyl ethers produce oxonium ion intermediates, which are so stable that they do not spontaneously react to form polymer at room temperature. By manipulation of the structure of the epoxide monomer, novel monomers with tailored reactivities can be prepared.
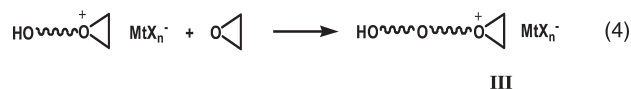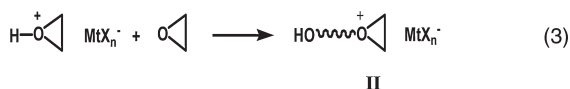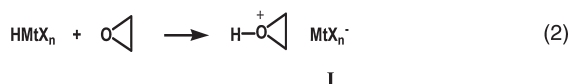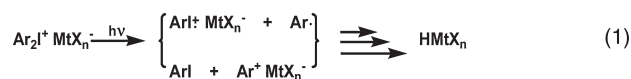
Keywords: cationic polymerization; photopolymerization; epoxide monomers; reactivity studies; temperature effects

1 Introduction

It has long been known that in contrast to free-radical polymerizations in which there is little impact of temperature on the overall rates, the rates of cationic vinyl polymerizations are highly sensitive towards variations in the temperature (1). The rates of cationic ring-opening polymerizations of many heterocyclic monomers are also markedly accelerated when they are carried out at high temperatures (2). Work in this laboratory has similarly reported that these same temperature effects apply to the respective cationic photopolymerizations (3). Our interest lies primarily in the ring-opening cationic photopolymerizations of epoxide (oxirane) monomers and epoxide-functional reactive oligomers. As depicted in Scheme 1, the photopolymerizations of these monomers take place by the photolysis of photoinitiators such as diaryliodonum salts that generate strong Brønsted acids (HMtX$_n$, Eq. (1)) such as HSbF$_6$, HPF$_6$ or HBF$_4$. The acids react with the epoxide groups Eq. (2) to initially form secondary oxonium ion intermediates (I). These latter species react with monomer (Eqs. (3) and (4)) to give tertiary oxonium ions (II and III) that proceed further to give polymer.

We and others have reported that oxirane monomers display a wide range of reactivity in cationic photopolymerizations (4–6). Generally, it has been found that the overall rate by which a photopolymerization of an epoxide monomer proceeds depends primarily on the stability of the secondary oxonium ion (I) which is less reactive than the tertiary oxonium ion intermediates (II and II) (7). The stabilities of these species are profoundly affected by steric and electronic factors associated with their structures. Most reactive are those epoxides that react with photogenerated Brønsted acids to generate unstable secondary oxonium intermediates. Examples of such monomers are terminal alkyl and cycloaliphatic epoxides that do not bear other heteroatom-containing functional groups. Typically, such photopolymerizations proceed rapidly and exothermically on irradiation. Such photopolymerizations also display little or no induction period. Since the polymerizations of these monomers are highly exothermic, they often exhibit marked thermal autoacceleration effects. In contrast, epoxides that possess substituents containing basic heteroatoms situated so that they can stabilize the secondary oxonium intermediates typically display sluggish photopolymerization rates. In some cases, such as with alkyl glycidyl ethers, the oxonium ions that are generated are sufficiently stable to be directly observed by ^{1}H and ^{13}C-NMR spectroscopy (8). Alternatively, the presence of these species can be inferred by the analysis of the products of ion-trapping reactions. In those latter specific instances, the stability of the secondary oxonium

Address correspondence to: James V. Crivello, Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy 12180, New York. E-mail: crivej@rpi.edu

$$Ar_2I^+ \ MtX_n^- \xrightarrow{h\nu} \left\{ \begin{array}{l} ArI^{+\cdot} \ MtX_n^- \ + \ Ar\cdot \\ ArI \ + \ Ar^+ \ MtX_n^- \end{array} \right\} \Longrightarrow \ HMtX_n \qquad (1)$$

$$HMtX_n \ + \ O\triangleleft \ \longrightarrow \ H{-}\overset{+}{O}\triangleleft \ MtX_n^- \qquad (2)$$

<center>I</center>

$$H{-}\overset{+}{O}\triangleleft \ MtX_n^- \ + \ O\triangleleft \ \longrightarrow \ HO\text{\textbackslash\textbackslash}\overset{+}{O}\triangleleft \ MtX_n^- \qquad (3)$$

<center>II</center>

$$HO\text{\textbackslash\textbackslash}\overset{+}{O}\triangleleft \ MtX_n^- \ + \ O\triangleleft \ \longrightarrow \ HO\text{\textbackslash\textbackslash}O\text{\textbackslash\textbackslash}\overset{+}{O}\triangleleft \ MtX_n^- \qquad (4)$$

<center>III</center>

Sch. 1. Mechanism of the photoinitiated cationic ring-opening polymerization of epoxides".

intermediates is manifested in a pronounced induction period during which the concentration of these species builds up in the reaction mixture as the photoinitiator is decomposed by light. Polymerization does not proceed spontaneously at room temperature in such systems. However, if a point heat source is applied to the sample during this induction period, polymerization starts rapidly at that locus and proceeds as a well-defined reaction front that propagates in all directions to consume the entire irradiated sample (9).

The frontal behavior described above is a consequence of the presence of strong thermal accelerating effects in the photoinitiated cationic ring-opening polymerization of alkyl glycidyl ether monomers. It was of interest to determine whether other classes of epoxide monomers can be made to undergo frontal polymerizations. At low temperatures, it may be possible to stabilize the oxonium intermediates of other types of epoxide monomers sufficiently to observe frontal polymerization behavior. While studies have been conducted on the effects of high temperatures on the cationic photopolymerizations of oxirane monomers, no equivalent studies have been reported on such systems at sub-ambient temperatures. The present communication reports on the development of a novel method for conveniently carrying out these studies and reports some preliminary results derived from them.

2 Experimental

2.1 Materials

1,2-Epoxydecane was received as a gift, from the Viking Chemical Co., Minneapolis, MN. Cyclohexene oxide (1,2-epoxycyclohexane), glycidyl 4-methoxyphenyl ether (GMPE) and n-butyl glycidyl ether were purchased from the Aldrich Chemical Co. (Milwaukee, WI). Glycidyl phenyl ether and glycidyl 4-methylphenyl ether (CGE) were purchased respectively from Fluka Chemical Corp. (Milwaukee, WI) and Wilmington Chemical Co. (Wilmington, DE). The

diaryliodonium salt photoinitiators (4-n-octyloxyphenyl) phenyliodonium hexafluoroantimonate (IOC-8 SbF$_6$) and (4-n-decyloxyphenyl)phenyliodonium hexafluorophosphate (IOC-10 PF$_6$) used in this work were prepared as described in earlier publications (9).

2.2 Monitoring Photosensitized Cationic Polymerizations Using Optical Pyrometry (OP)

The basic optical pyrometry apparatus and sampling methods employed for monitoring the photopolymerizations carried out in this investigation were described in a recent communication from this laboratory (10). The OP instrument is capable of remotely measuring temperatures of samples in the range of -23 to 400°C $\pm$ 1°C while they are undergoing photopolymerization. Thin film samples for analysis were prepared by placing monomer solutions containing a photoinitiator and a prospective photoinitiator between two 5 µm DuPont fluorinated poly(ethylene-propylene) copolymer films together with an open mesh polyester spacer and mounting the samples in 2 cm × 2 cm plastic slide frames and then inserting them into the sample holder of the Optical Pyrometer instrument for analysis. The average thickness of the liquid samples was 0.40–0.45 mm. Irradiation with UV light for a specific time was accomplished using a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a liquid optic cable. Measurements of UV radiation intensity were carried out using a UV Process Supply Inc. Control Cure Radiometer.

3 Results and Discussion

3.1 Low Temperature Photopolymerization Studies Using Optical Pyrometry

Previously, we have described the use of a new analytical technique that we call optical pyrometry (OP) to monitor the course of photopolymerizations (11,12). Briefly, this technique involves the remote monitoring of the temperature of a sample undergoing photopolymerization in real-time by means of an infrared camera (optical pyrometer). Using this method of analysis, it is possible to study the effects of monomer reactivity, photoinitiator concentration, atmosphere, elevated temperatures, substrates, pigments and dyes and fillers on the course of free radical and cationic photopolymerizations. In the present investigation, the OP instrument was further modified to enable the study of photopolymerizations at low (-20 to 0°C) temperatures. This has been achieved as depicted in Figure 1 through the use of a large (2 kg brass) insulated thermal mass cooled to the appropriate temperature. The cooled thermal mass makes contact with the liquid monomer sample placed between two thin polymer films by means of a plate mounted on its surface. The optical pyrometer records the temperature only of the top polymer film of the sample sandwich, which is in direct
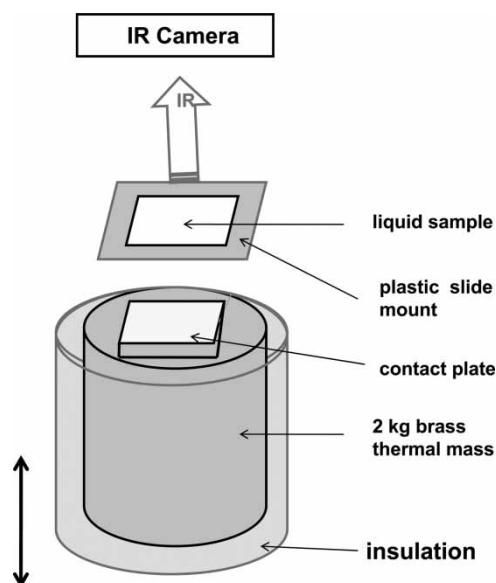
Fig. 1. Schematic drawing of the cooling apparatus for optical pyrometry.

contact with the liquid monomer sample. The thermal mass can be raised to cool the sample or lowered to allow the photopolymerizations to be conducted under ambient (23–26°C) laboratory temperature conditions. Further, the apparatus allows us to modify the temperature conditions as desired during the course of a photopolymerization. Since the sample consists of a very low thermal mass thin liquid monomer film, cooling is very fast and efficient. Using this modified OP apparatus, the effects of low temperatures on the course of both free radical and cationic photopolymerizations can be readily examined. In this communication, the photopolymerizations were conducted under comparatively

low UV light intensities (350–710 mJ/cm min, 5.8–11.8 mW) to slow the reactions sufficiently to facilitate the analysis of the various temperature-dependant processes. It is important to note that the UV light used in this instrument is delivered to the sample by means of a liquid optical cable. Consequently, the irradiating light contains only wavelengths in the UV and visible regions. Infrared wavelengths (i.e. heat) are absent. Thus, the reactive species of interest in this study are generated by photolysis of their respective photoinitiators under essentially "cold" conditions.

3.2 Comparison of Free Radical and Cationic Photopolymerizations Conducted at Low Temperatures

Depicted in Figure 2 is a comparison of the free radical photo-polymerization of trimethyolpropane triacrylate conducted at 24°C and −6°C. As may be noted, the thermal profiles of these two photopolymerizations are very similar, substantiating the observation that these acrylate photopolymerizations exhibit little temperature dependence. The results further support the earlier finding (13) that the propagation reactions for free radical polymerizations take place via very low activation energy processes. The sharper profile of the photopolymerization carried out at −6°C is due to the very rapid cooling of the sample provided when the low temperature apparatus is used.

For comparison, Figure 3 shows a similar study in which the cationic photopolymerization of cyclohexene oxide was carried out using (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8 SbF_6) as the photoinitiator. Lowering the temperature of the sample by 20°C does not appreciably slow the onset of the polymerization of this monomer. In this case, as expected, the maximum
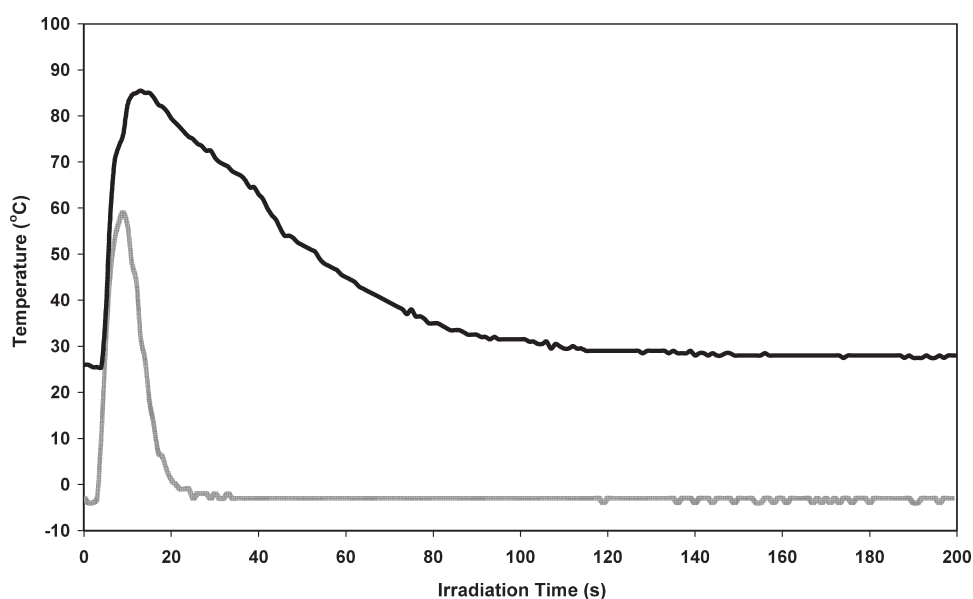

Fig. 2. Photopolymerization of trimethylolpropane triacrylate with 2 wt% 2,2-diethoxy-2-phenylacetophenone (light intensity 422 mJ/cm² min).
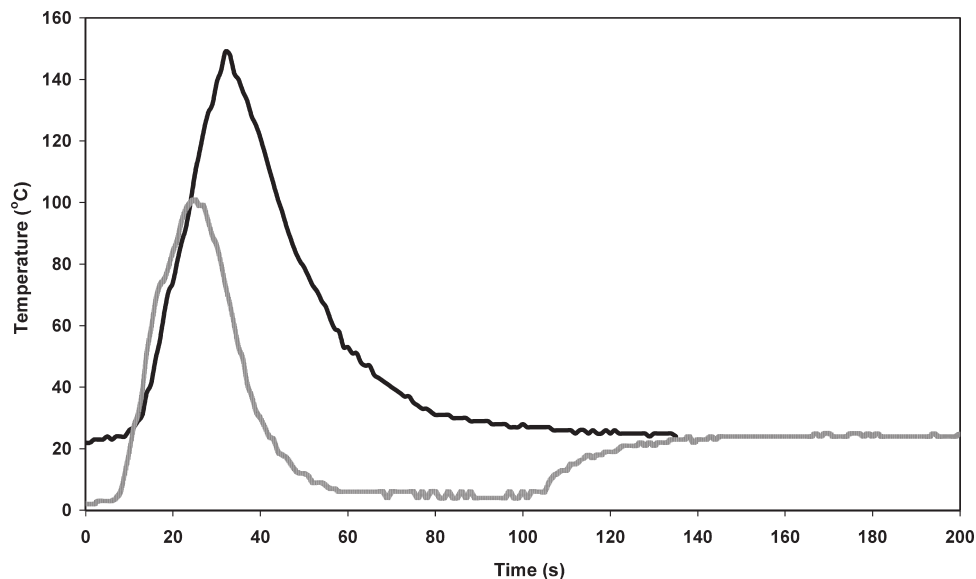
Fig. 3.   OP study of the photopolymerization of cyclohexene oxide with 1.0 mol% IOC-8 SbF$_6$ (light intensity 452 mJ/cm^2 min).

temperature of the attained by the sample is somewhat depressed due to the dynamic cooling of the sample. These results agree with previous proposed interpretation of the mechanism of polymerization of this monomer. The high reactivity of the secondary (IV) and tertiary oxonium ions together with a high ring strain energy results in a low activation energy and a high propagation rate for cyclohexene oxide and other related cycloaliphatic epoxide monomers. When IOC-8 SbF$_6$ was replaced by the less reactive (4-n-decyloxyphenyl)phenyliodonium hexafluorophosphate (IOC-10 PF$_6$) as the photoinitiator in the photopolymerization of cyclohexene oxide as shown in Figure 4, the respective polymerization curves carried out at both high and low temperature were broadened. However, the onset of both photopolymerizations appear to be independent of the temperature, again reflecting the high reactivity of the oxonium intermediates that are formed.

IV   **V**
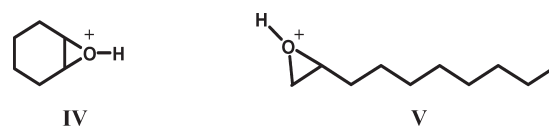
Terminal alkyl epoxides such as 1,2-epoxydecane are also highly reactive monomers in photoinitiated cationic polymerizations, although less so than the aforementioned cycloaliphatic epoxides. Displayed in Figure 5 is a study of the effects of a variation in the temperature and irradiation conditions on the photopolymerization of this monomer. As a control, the photopolymerization of 1,2-epoxydecane was carried out at ambient temperature under continuous UV irradiation conditions. Also shown in the figure is the thermal profile of a photopolymerization carried out at a starting temperature of $-6°$C. In this latter study, cooling was applied for 100 s and then the polymerization allowed to proceed further without cooling. Continuous
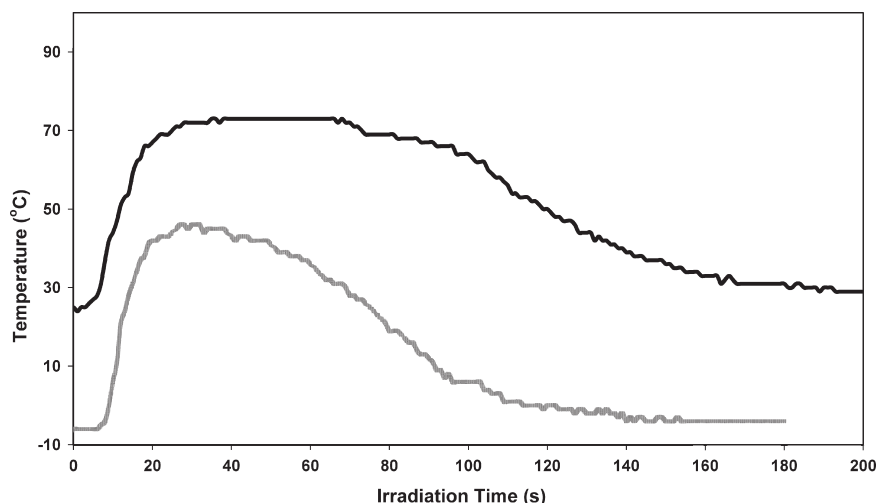

Fig. 4.   OP study of the photopolymerization of cyclohexene oxide with 1.0 mol% IOC-10 PF$_6$ (light intensity 452 mJ/cm^2 min).
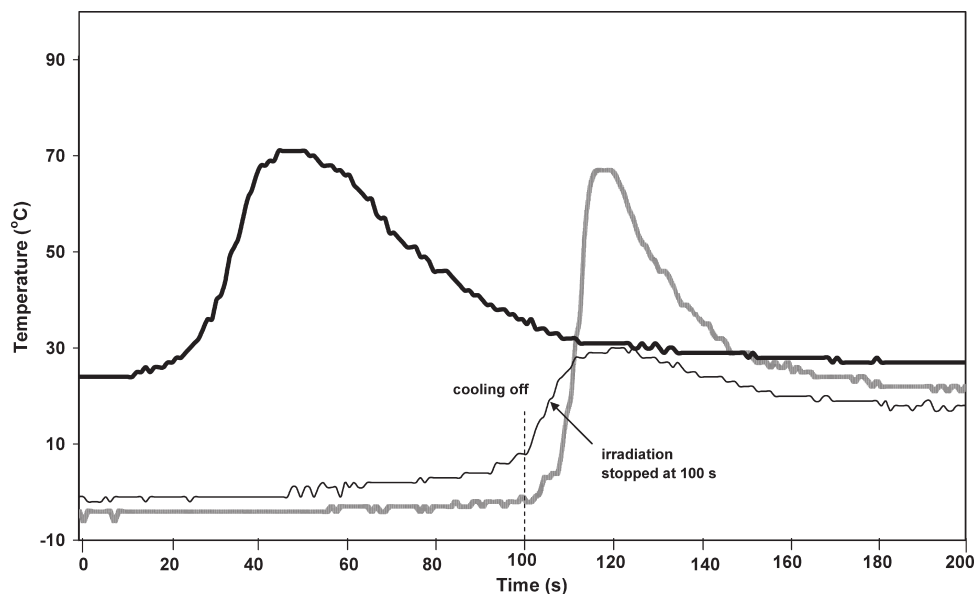
Fig. 5. Photopolymerization of 1,2-epoxydecane with 1.0 mol% IOC-8 SbF$_6$ (light intensity 452 mJ/cm^2 min).

UV irradiation was applied throughout the course of this run. During the first 100 s, polymerization is markedly slowed but not completely suppressed. This is indicated by the slow rise in temperature over the course of the 100 s irradiation period. However, once the cooling is removed, the polymerization takes place spontaneously and then proceeds exothermically. The temperature of the monomer sample rises quickly and the polymerization progresses further under autoacceleration conditions. A parallel study is also shown in Figure 5 in which both the irradiation and cooling are switched off after 100 s. In this case, the temperature of the sample rises to a few degrees above room temperature as the polymerization proceeds. The temperature of the sample never rises sufficiently high enough to induce a run-away thermally autoaccelerated polymerization. Like cyclohexene oxide, the secondary oxonium ion intermediates (V) derived from epoxides such as 1,2-epoxydecane are quite unstable and reactive. This is why reducing the temperature by approximately 20°C attenuates but does not completely suppress the polymerization. This indicates that the oxonium ion intermediates V are less reactive than IV since they possess less ring strain.

3.3 Low Temperature Photopolymerization Behavior of Alkyl and Aryl Glycidyl Ethers

Under the same irradiation conditions as described above, alkyl glycidyl ethers do not display a pronounced exotherm immediately at the onset of irradiation at room temperature indicative of a rapid photopolymerization. Instead, for example when n-butyl glycidyl ether was irradiated with UV light in the presence of 1 mol% IOC-8 SbF$_6$, the sample temperature rose only 4–5°C over the course of 200 s. When the sample was cooled to −3°C during the irradiation and then allowed to warm to room temperature, the sample appears to be stable

and no exotherm is noted on standing. When, however, the latter irradiated liquid film was briefly heated at one end, a frontal polymerization is observed progressing from that end and consuming the entire irradiated portion of the film. As has previously reported (9), this behavior is common to alkyl glycidyl ethers and is ascribed to formation of a stabilized secondary oxonium intermediate, VI, by the formation of a cyclic oxonium ion in which there is bidentate coordination of the two oxygen atoms with the proton. The stabilization of VI is quite strong since the ether and the epoxide oxygen atoms are similar with respect to their basicity and are also optimally situated in such a manner as to form a pseudo-five membered ring by coordination with the proton.

VIIa, X = H; VIIb, X = CH$_3$; VIIc, X = CH$_3$O

Figure 6 depicts a study of the cationic photopolymerization of glycidyl phenyl ether (PGE). When the polymerization was conducted at 26°C, reaction proceeded slowly, requiring approximately 160–180 s for completion. In contrast, when the monomer sample was irradiated at −6°C, polymerization was completely suppressed. However, during that period, the photolysis of the photoinitiator, 4(1-octyloxyphenyl)phenyliodonium hexafluoroantmonate (IOC-8 SbF$_6$) continues independently. After 100 s irradiation, cooling was removed and as the sample warms rapidly to room temperature, the polymerization of the monomer takes place spontaneously and exothermically with the temperature rising to a maximum of 162°C. Then, the temperature quickly declines as the monomer is exhausted. UV irradiation of the sample was continuous during the entire time (200 s) that the
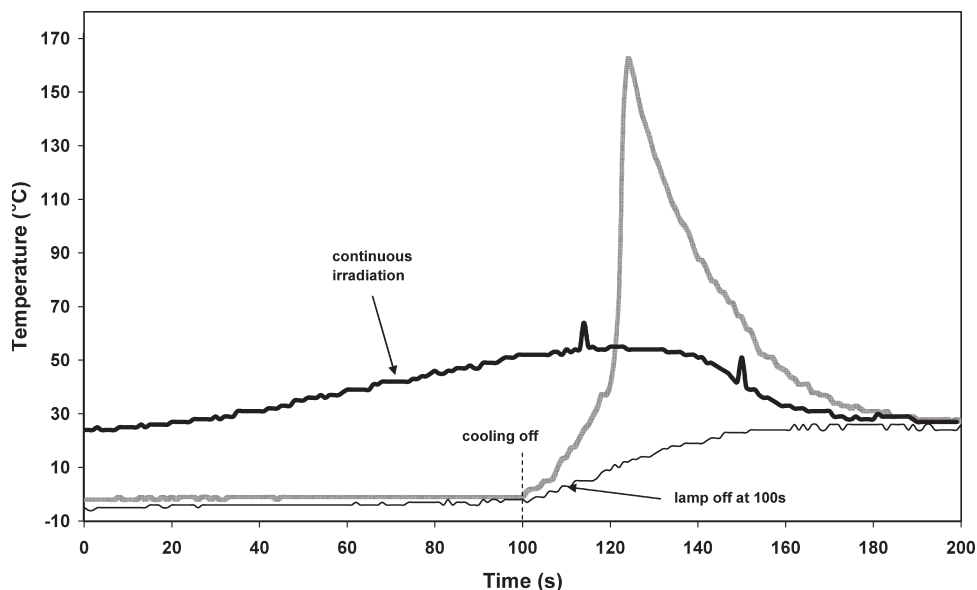
Fig. 6.   Photopolymerization of glycidyl phenyl ether with 1.0 mol% IOC-8 SbF$_6$ (light intensity 452 mJ/cm^2 min).

sample was under investigation. The profile of the OP curve for the polymerization that takes place is typical for a thermally-driven autoaccelerated process. It is interesting to note that the profile of the polymerization of this monomer that takes place after cooling is removed (i.e. 100 s) closely resembles the autoaccelerated polymerizations of the more reactive monomer cyclohexene oxide. It is markedly different than the gradual photopolymerization of this monomer carried out at room temperature. The difference can be attributed to the buildup in the concentration of active cationic centers during the cold irradiation period. When cooling is withdrawn, continued photolysis of the photoinitiator and the subsequent reaction of the photogenerated acid with monomer provides sufficient heat to induce a run-away autoaccelerated polymerization of the monomer. The third thermal profile curve shown in Figure 6 depicts the course of photopolymerization of glycidyl phenyl ether when both the cooling and UV irradiation were discontinued at 100 s after the start of the photopolymerization. Essentially, the sample warms to room temperature but does not undergo appreciable polymerization under these conditions. This sample is in a metastable condition and when it is briefly heated at one end, polymerization proceeds rapidly via a frontal propagation mechanism. If the sample is allowed to stand for some time (1 h), the frontal polymerization is not observed. This indicates that slow polymerization of the monomer in the sample continues at room temperature.

The difference in the photopolymerization behavior of PGE as compared to alkyl glycidyl ethers such as n-butyl glycidyl ether can be attributed two factors. Alkyl glycidyl ethers are essentially transparent in the short wavelength region where IOC-8 SbF$_6$ absorbs whereas PGE has considerable absorption. Therefore, the rate of photolysis of the photoinitiator is significantly slowed in the presence of PGE due to the competitive UV absorption. However, the most important factor for the observed difference is the inherent lower stability of the oxonium intermediate VIIa (X = H) as compared to VI. This is due to a corresponding lower basicity of the oxygen of the aryl ether group, which cannot participate as strongly as the alkyl ether oxygen of VI in the stabilization of VIIa.

A study similar to the one described above for PGE was conducted as shown in Figure 7 with glycidyl 4-methylphenyl ether (p-cresyl glycidyl ether, CGE). Continuous UV irradiation of CGE at low UV light intensity leads to an initially slow photoinduced polymerization that autoaccelerates after approximately 100 s with the temperature rising to a maximum of 146°C. Cooling the sample prior and during irradiation to −8°C entirely suppresses the polymerization. However, after an irradiation period of 160 s when the cooling was switched off, the temperature sample rose spontaneously to room temperature and then polymerization rapidly autoaccelerated as was observed previously with PGE. When both the irradiation and the cooling are simultaneously switched off, polymerization of CGE appears to either stop or to proceed very slowly (temperature rises to 29°C). The methyl group in oxonium ion VIIb (X = CH$_3$) would be expected to inductively increase the basicity of the aryl ether oxygen and, thus, to enhance the stability of this oxonium ion. Consequently, CGE appears to be slightly less reactive at room temperature as a monomer than PGE.

The replacement of substituent X in oxonium salt VII with a methoxy group should enhance the basicity of the glycidyl ether oxygen by both inductive and resonance interaction effects. Thus, glycidyl 4-methoxyphenyl ether was predicted to undergo slower cationic photopolymerization than PGE at room temperature. A study of the effects of temperature on the photopolymerization of this monomer is shown in Figure 8. Glycidyl 4-methoxyphenyl ether is a low melting
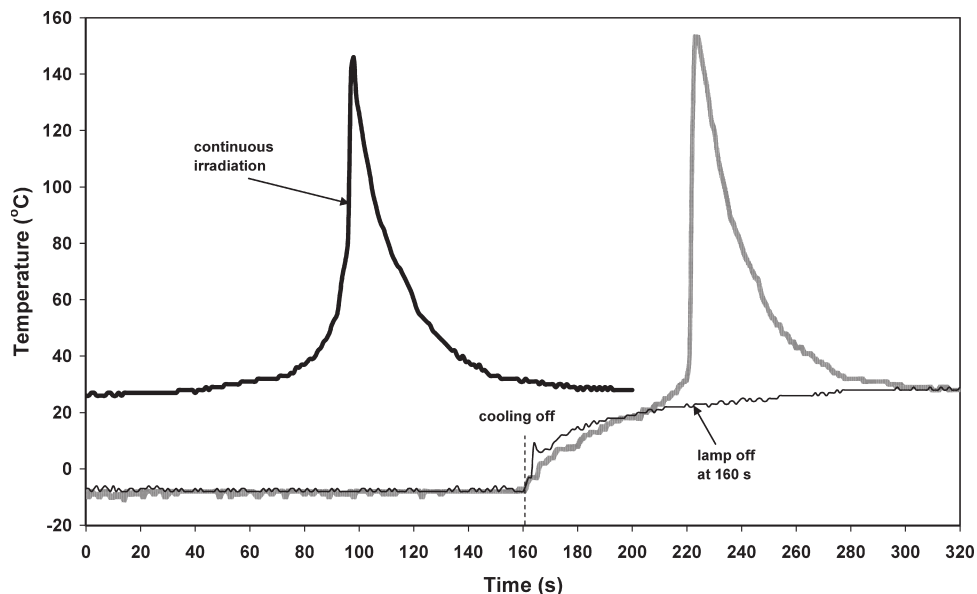
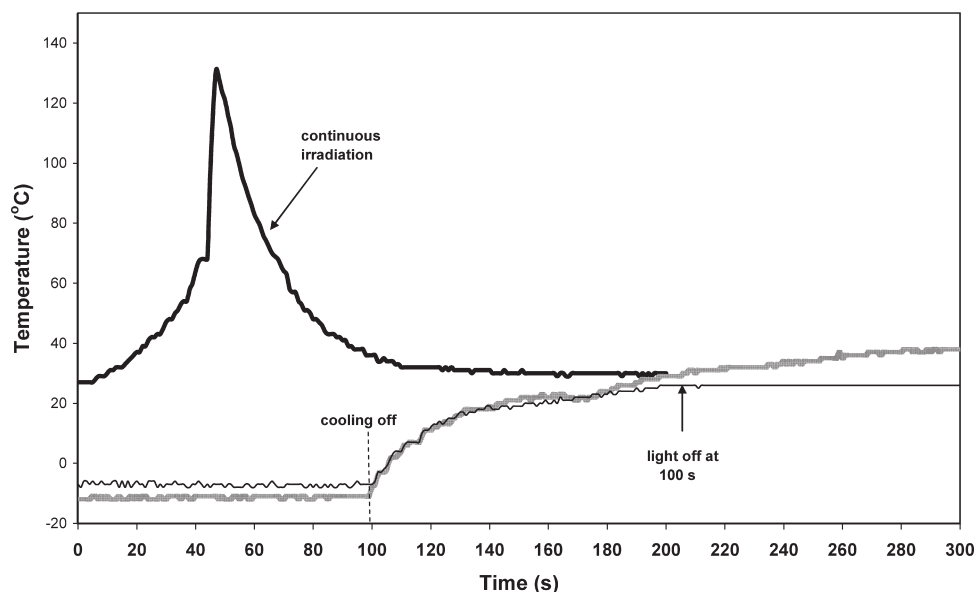**Fig. 7.** Study of the photopolymerization of CGE with 1.0 mol% IOC-8 SbF$_6$ (light intensity 380 mJ/cm^2 min).

Fig. 8. Photopolymerization of glycidyl 4-methoxyphenyl ether with 1.0 mol% IOC-8 SbF$_6$ (light intensity 444 mJ/cm^2 min).

solid that on supercooling forms a liquid at room temperature. The photopolymerization of this monomer at room temperature displays a rapid autoacceleration process. Polymerization was not observed when the monomer is subjected to UV irradiation for 100 s at −14 to −10°C. When the cooling is switched off but the irradiation is continued, a relatively slow polymerization takes place with the temperature gradually rising to 34°C. Apparently, photolysis of the photoinitiator together with the subsequent reaction of the photogenerated acid with the monomer generates sufficient heat to promote a low grade polymerization to take place. In contrast, when both cooling and irradiation are suspended after 100 s, the polymerization does not proceed when the

sample reaches room temperature. When this sample is briefly heated, an exothermic frontal polymerization takes place. The observed results are consistent with the formation of an oxonium ion intermediate VIIc, that possesses relatively greater stability than either VIIa or VIIb. Overall, as predicted, this monomer exhibits photopolymerization behavior more like that of an alkyl glycidyl ether than either PGE or CGE.

4 Conclusions

The low temperature photopolymerization studies conducted during the course of this investigation confirm the currently

held principle that the rates of the cationic ring-opening polymerizations of epoxide monomers are strongly influenced by temperature. However, this general statement needs to be further qualified by noting that the effects of temperature on the rates also show a marked dependence on the structure of the monomer. The photopolymerizations of those highly strained monomers in which the secondary oxonium ions are not stabilized by the presence of other functional groups in the molecule exhibit the highest rates and the least effects of temperature. The photopolymerizations of such monomers proceed rapidly even at temperatures below 0°C. On the other hand, monomers such as alkyl and aryl glycidyl ethers that possess less strained epoxy groups and, in addition, bear ether groups that able to stabilize the secondary oxonium ion intermediates invariably display substantially lower reaction rates and a marked dependence on temperature.

Since the photoinitiated cationic ring-opening polymerization of epoxides has become increasingly important in commercial applications, the consequences of this study are significant because they provide an insight into the basic structure-reactivity relationships of these monomers. Not only does this understanding provide a rationalé for the reactivity of currently available epoxide monomers in cationic photopolymerizations, but it also suggests means, by which novel monomers with tailored reactivity can be constructed. In future communications from this laboratory, we will present our progress in this latter area.

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