3584 *Macromolecules* **2005,** *38,* 3584−3595

Investigation of the Reactivity of Epoxide Monomers in Photoinitiated Cationic Polymerization

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Received January 18, 2005; Revised Manuscript Received February 14, 2005

ABSTRACT: An investigation of the photoinitiated cationic ring-opening polymerizations of various epoxy monomers was conducted using real-time infrared spectroscopy and optical pyrometry. Several types of behavior were observed and interpreted on the basis of the relative stabilities of the secondary and tertiary oxonium ion intermediates that are generated during the ring-opening polymerization of these monomers. Based on the mechanistic interpretations proposed, attempts were made to accelerate the photopolymerizations of epoxy monomers that undergo overall slow reaction as a result of the presence of an induction period. Three general methods were effective for the acceleration of the photopolymerizations of these and other epoxy monomers: (1) carrying out the photopolymerizations at higher temperatures, (2) copolymerization with more reactive monomers, and (3) the use of free radical photoinitiators.

Introduction

Currently, the photoinitiated cationic ring-opening polymerizations of epoxide (oxirane) monomers are widely employed in a variety of commercial applications, among which may be mentioned coatings, adhesives, printing inks, microelectronic photoresists, and stereolithography. In such applications, the polymerizable substrate together with a photoinitiator is subjected to irradiation with light for only a fraction of a second, during which time the photopolymerization must proceed essentially to completion. Consequently, only those epoxide monomers that undergo very rapid polymerizations may be employed. It has been empirically noted by several investigators[1−3] that certain epoxide monomers display high reactivity in photoinitiated cationic polymerization and are suitable for such uses while others undergo apparently sluggish reactions and are not. Still other epoxy monomers that possess basic groups as part of their structures are not polymerizable under cationic conditions. For this reason, the range of currently available epoxide monomers that are useful in applications involving photoinitiated cationic polymerization is limited. Accordingly, most of the present and past research emphasis has been placed on developing and optimizing only those monomer−photoinitiator systems that display the highest possible reactivity. Little effort has been directed toward understanding the underlying reasons for the reactivity differences that have been observed between various epoxide monomers.

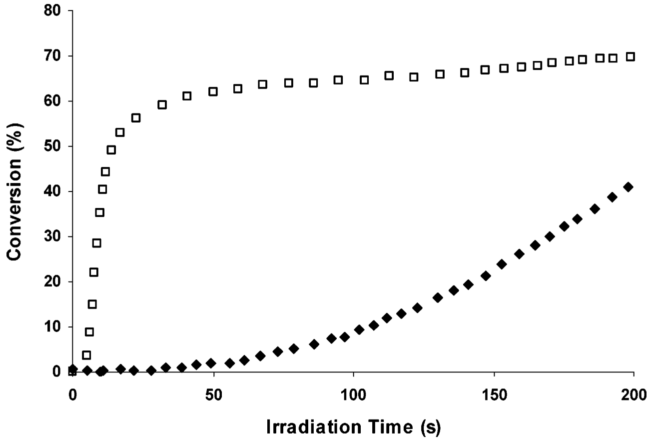

Figure 1. RTIR comparison of the photopolymerizations of cyclohexene oxide (□) and neopentylglycol diglycidyl ether (◆) and carried out respectively with UV light intensities of 170 and 473 mJ/cm^2 min using 1.0 mol % IOC-10 SbF$_6$.

Recently, we reported[4] that epoxide monomers display different characteristic types of kinetic behaviors in cationic photopolymerization that can be readily ascertained by examining their conversion vs time plots as determined by Fourier transform real-time infrared spectroscopy (FT-RTIR). For example, Figure 1 depicts the FT-RTIR plots for the photopolymerizations of the model compounds, cyclohexene oxide (7-oxabicyclo[4.1.0]-heptane) and neopentylglycol diglycidyl ether, carried out with the same diaryliodonium salt cationic photoinitiator, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10 SbF$_6$). In both cases, irradiations were conducted using "cold" UV light in which all infrared radiation and UV wavelengths shorter than 300 nm were removed. Because of the much greater reactivity of cyclohexene oxide, the polymerization of this monomer was carried out using less than one-third the light intensity (170 vs 475 mJ/(cm^2 min)) employed with neopentylglyclol diglycidyl ether. The responses of these two monomers are characteristic of two extremes in the photopolymerization behavior exhibited by epoxy monomers under cationic ring-opening polymerization conditions. Cyclohexene oxide is representative of what can be termed a "class I" monomer that undergoes very rapid polymerization on UV irradiation with very little induction period. In contrast, under the same conditions, neopentyl glycol diglycidyl ether, a typical "class II" monomer, undergoes very slow photopolymerization. In fact, as shown in Figure 1, UV irradiation of this latter monomer for periods of up to 1 min at room temperature results in only a few percent conversion of monomer to polymer. Similar sluggish photoinduced cationic polymerizations were observed with other mono- and multifunctional aliphatic glycidyl ether monomers. This

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10.1021/ma050106k CCC: $30.25

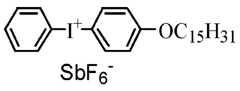
behavior could not have been predicted considering the large negative values of the enthalpies of polymerization ($\Delta H_p = 18-24$ kcal mol^{-1})[5] that have been determined for all types of oxirane monomers. The RTIR curves shown in Figure 1 suggest an explanation for the aforementioned generally well-known but empirical observation that cycloaliphatic epoxy monomers are useful in cationic photopolymerizations while glycidyl ether-type epoxide monomers are not. Specifically, these latter monomers are characterized by an extended induction period that is incompatible with many applications that require high-speed operation. As shown in Figure 1, after a long induction period during the irradiation, very rapid exothermic autoaccelerated polymerization of neopentylglycol diglycidyl ether suddenly sets in. It should also be pointed out that the behavior exhibited by class II monomers is distinct from the well-known[6−8] "postpolymerization" or "dark cure" effects often observed in the cationic ring-opening photopolymerization of epoxide and other cyclic ether monomers. These effects are attributed to the continued polymerization that proceeds after irradiation is terminated due to the presence of long-lived propagating species.

In the past, the differences observed in the induction periods of various members of the epoxide family of monomers in cationic ring-opening photopolymerization were noted and ascribed to several different causes. For example, the contributions of steric, ring-strain, and electronic effects to the general reactivity of different types of epoxide monomers in photoinitiated cationic ring-opening polymerizations were discussed in a previous publication from this laboratory.[9] In specific instances, the reason for the low rate of polymerization of a given monomer was attributed to the inhibiting or retarding effects of deliberately added or adventitious basic contaminants. However, when such monomers were exhaustively purified and handled under carefully controlled conditions that minimized contamination, their induction periods remained and were not significantly shortened. It was, therefore, concluded that the induction period is an inherent characteristic of these compounds. As a consequence, contemporary practical applications that require short irradiation periods are currently restricted to the use of only a relatively few, typically expensive, class I epoxide monomer substrates. The photopolymerizations of other, more readily available and less expensive monomers (e.g., class II monomers) are hampered by the presence of long unproductive induction periods. These factors currently seriously limit the proliferation of photoinitiated cationic polymerizations in both with respect to their technical uses as well as their academic interest.

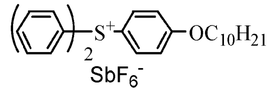
In this article, we report the results of recent investigations of the effects of monomer structure and various reaction parameters on the photoinduced cationic polymerizations of epoxide monomers. In this investigation, we have placed special emphasis on attempting to understand and characterize the origin of the different kinetic behaviors displayed by various epoxide monomers with the objective of broadening the range of substrates applicable for use in cationic photopolymerization technology.

Experimental Section

Materials. Cyclohexene oxide, 4-vinyl-1-cyclohexene diepoxide, benzyl glycidyl ether, neopentylglycol diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,4-cyclohexanedimethanol diglycidyl ether (mixture of cis and trans isomers), phenyl glycidyl ether, bisphenol A diglycidyl ether, and other reagents used in this work were obtained from the Aldrich Chemical Co., Milwaukee, WI. ERL-4221 (3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate) was received from the Union Carbide Corp., Bound Brook, NJ. PC-1000 (1,3-bis-2[3,4-epoxycyclohexylethyl]-1,1,3,3-tetramethyldisiloxane) was purchased from the Polyset Co., Mechnicville, NY. Cyclohexene oxide was dried over calcium hydride and distilled prior to use. Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone), 184 (1-hydroxycyclohexylphenyl ketone), and 819 (phenyl [bis-2,4,6-trimethylbenzoyl]phosphine oxide) were kindly provided as gifts from the Ciba-Geigy Corp., Basel, Switzerland. Unless otherwise noted, all other reagents, monomers, and photoinitiators were used as received without further purification. The diaryliodonium salt[10] and triarylsulfonium salt[11] photoinitiators were prepared as described previously. In this article, a variety of these photoinitiators were employed. For example, IOC-15 SbF_6 refers to (4-*n*-pentadecyloxyphenyl)phenyliodonium hexafluoroantimonate having the structure shown below in which a 15-carbon linear alkoxy group is attached to one of the phenyl groups in the 4-position while SbF_6 denotes the hexafluoroantimonate anion. In a similar manner, SOC-10 SbF_6 refers to S(4-*n*-dodecyloxyphenyl)-*S*,*S*-diphenylsulfonium hexafluoroantimonate with the following structure:



IOC-15 SbF_6



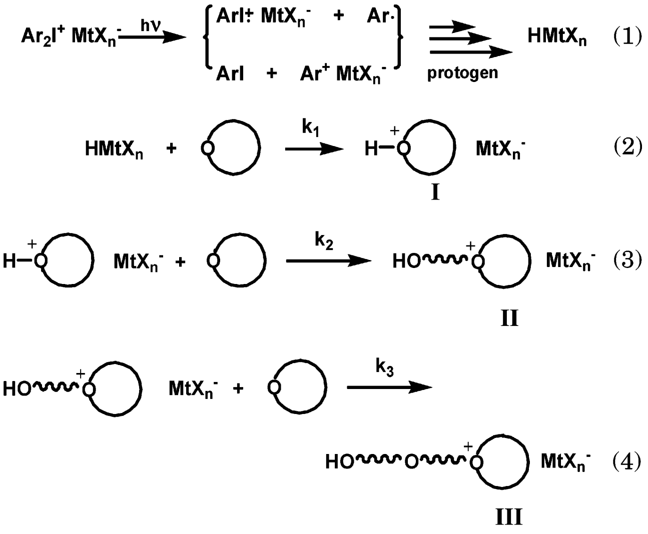
SOC-10 SbF_6

^{31}P NMR Spectra. ^{31}P NMR spectra were obtained using a Varian XL 500 MHz spectrometer at room temperature with phosphoric acid (in a sealed capillary tube) as an internal standard. To a small reaction vessel containing neopentyl glycol diglycidyl ether cooled to −5 °C hexafluoroantimonic acid (5 mol %) was added. After 1 min, tri-*n*-butylphosphine (10 mol %) was added to the monomer solution to trap the species present. The peaks at −37 and −52 ppm in the ^{31}P NMR spectrum are due to impurities present in tri-*n*-butylphosphine.

Kinetic Characterization of Epoxide Photopolymerizations. We have previously described the analytical techniques and apparatus used in this laboratory for both real-time infrared spectroscopy (RTIR)[12] and optical pyrometry (OP).[13,14] Samples for RTIR and OP kinetic analysis were prepared by sandwiching a liquid monomer containing the designated photoinitiator between two thin (10 μm) films of oriented and corona-treated poly(propylene) using an open polyester mesh as a spacer. The samples were mounted in plastic 2 cm × 2 cm slide frames and then inserted into the sample holder for analysis. The average thickness of the samples was 0.912 mm. Irradiation with "cold" UV light was accomplished using a UVEXS model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a liquid optic cable. The liquid optic cable serves as a light filter passing only UV light in the wavelength region 300−750 nm and blocking the transmission in the infrared region. Several kinetic runs were performed for each photopolymerizable system, and the results reported in this article were the average of at least three kinetic runs. All reactivity studies were conducted at ambient laboratory temperature (25−28 °C) unless otherwise noted. The infrared band at 912 cm^{-1} due to the epoxy group was monitored for the RTIR photopolymerization studies.

Thin Film Photopolymerizations. A thin film of the monomer containing the photoinitiator(s) was cast onto a glass microscope slide and then placed on a variable speed conveyor equipped with a 300 W Fusion Systems (Rockville, MD) electrodless mercury arc lamp. The speed of the conveyor was adjusted until the film emerged from under the lamp in a tack-free state. This is the maximum conveyor speed corresponding

Scheme 1



to the lowest irradiation dose that is required to cross-link the monomer.

Results and Discussion

General Mechanistic, Kinetic, and Structural Relationships in the Photoinitiated Cationic Ring-Opening Polymerization of Epoxides. Depicted in Scheme 1 is the generally accepted mechanism for the photoinitiated cationic ring-opening polymerization of heterocyclic ether monomers that includes epoxides.[15] The mechanism that is depicted in Scheme 1 is illustrated with the use of a diaryliodonium salt photoinitiator but applies generally to all cyclic ether monomers and diaryliodonium and triarylsulfonium salt cationic photoinitiators. Four discrete steps can be discerned. In the first step (eq 1), UV irradiation of the diaryliodonium salt results in excitation and then fragmentation of the photoinitiator into a variety of radical and cationic species. Further reaction of those species with monomer, solvent, or other protogenic components (e.g., traces of water or alcohols) present yields the Brønsted acid, $HMtX_n$. The photogenerated superacids ($HMtX_n$ = e.g. HBF_4, HPF_6, $HAsF_6$, $HSbF_6$) with Hammett acidities (H_0 values) of the order of -14 to -30[16] very rapidly protonate the cyclic ether (i.e., k_1 is large) as depicted in eq 2. The secondary oxonium species (**I**) that are formed undergo S_N2 attack by the nucleophilic cyclic ether monomer to yield the tertiary oxonium species (**II**) as a result of ring-opening of the heterocyclic ring (eq 3).[17] Finally, repetitive attack by a cyclic ether monomer on the tertiary oxonium ion (eq 4) leads to chain growth (**III**). The rate constants k_2 and k_3 respectively for eqs 3 and 4 are different since the species **II** and **III** have different ring strains, steric interactions, and electronic charge distributions. Generally, eq 3 is rate-limiting, and thus, k_3 is greater than k_2. However, as will be shown later in this paper, the relative magnitudes of k_2 and k_3 depend on the specific monomer undergoing polymerization.

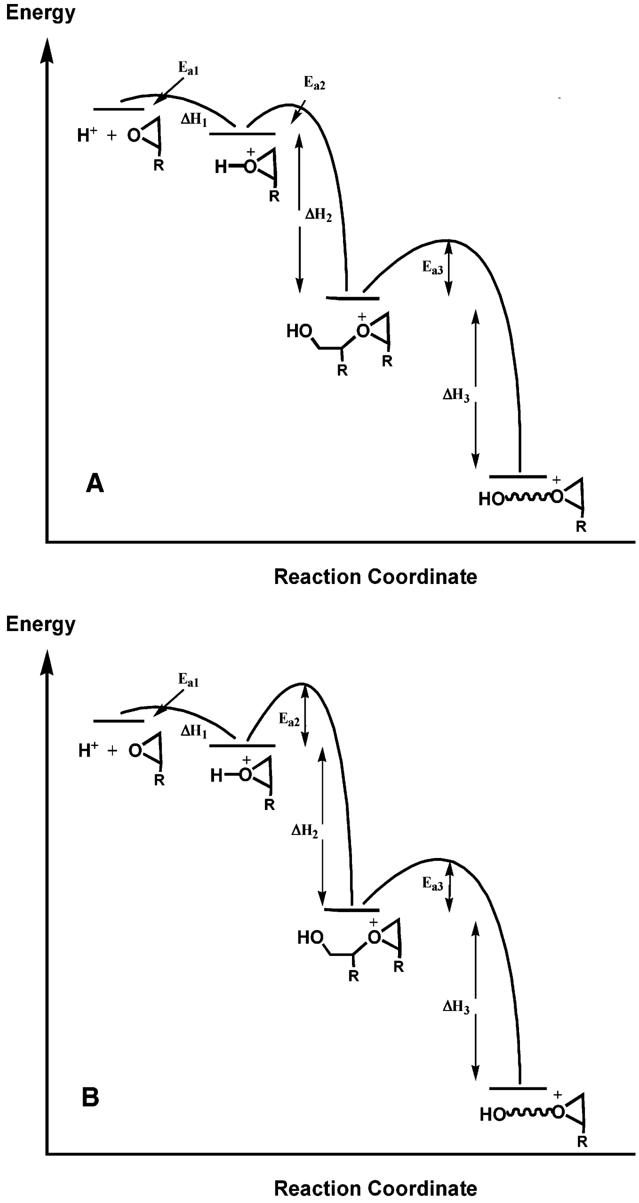


Figure 2. Proposed energy diagram for the photoinitiated cationic ring-opening polymerization of (A) 1,2-epoxycyclohexane and (B) alkyl glycidyl ethers.

One can also view the series of reactions shown in the mechanism of Scheme 1 from the perspective of the relative thermodynamic relationships between the starting monomers, reactive intermediates, and products. A proposed energy vs reaction coordinate plot for the photoinduced ring-opening polymerization of cyclohexene oxide is depicted in Figure 2A. Photolysis of diaryliodonium salt photoinitiators generates Brønsted superacids that rapidly and quantitatively protonate cyclic ether monomers at room temperature to generate the corresponding secondary oxonium ions. This reaction is exothermic and probably takes place with little or no activation energy (E_{a1}).[18] In the second step, the nucleophilic monomer attacks the secondary oxonium ion to generate the corresponding tertiary oxonium ion. Since cyclohexene oxide is a highly strained monomer and possesses no structural or electronic features that can stabilize the secondary oxonium ion, the activation energy (E_{a2}) for this reaction is relatively small and is thermally accessible at room temperature. Once ring-opening takes place, a large amount of heat (ΔH_2 = 18−24 kcal mol^{-1}) is evolved due to the relief of ring strain in this monomer. This energy is available to overcome the activation energy barrier, E_{a3}, of the next step to generate a propagating tertiary oxonium ion with the consequent liberation of additional enthalpy of polymerization (ΔH_3) to drive the reaction forward. As a result, once polymerization is initiated in this system, it proceeds smoothly through the cascade of reactions

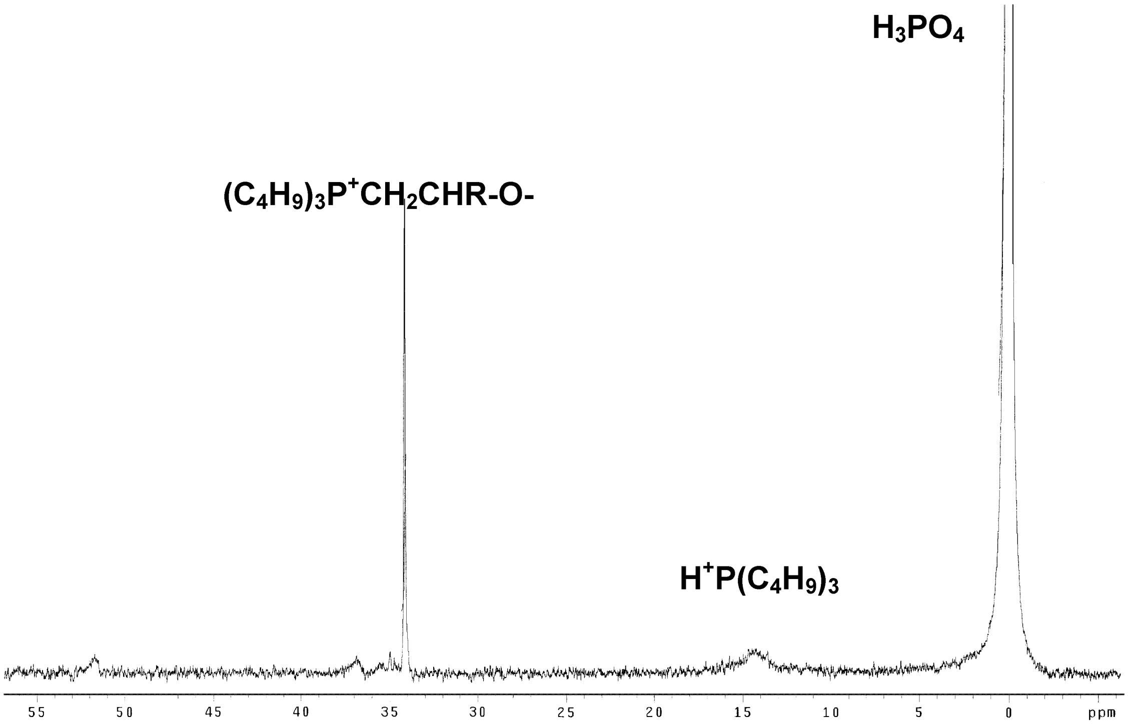
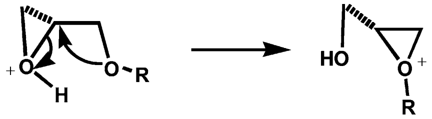


Figure 3. ^{31}P NMR spectra of neopentylglycol diglycidyl ether containing 1 mol % $HSbF_6$ and quenched after 5 min with tri-*n*-butylphosphine.

shown in Scheme 1 to give the product polymer. With such highly reactive monomers, the overall rate of the polymerization depends on the rate of the photolysis of the onium salt photoinitiator which delivers the highly reactive protonic acid initiator to the system. From a practical point of view, such monomer/photoinitiator systems are optimal for applications that require high rates of polymerization. The speed of the overall photopolymerization process may be tuned simply by adjusting the photoinitiator concentration and the light intensity used to irradiate the system. As previously noted, few monomers are known that behave in this manner. Along with cyclohexene oxide, 4-vinyl-1, 2-cyclohexene oxide, limonene dioxide, 4-epoxy-1, 2-cyclohexene oxide, and dicyclopentadiene diepoxide are additional examples of epoxide monomers that display such desirable characteristics.

In contrast to the above highly reactive class I monomers, the photopolymerization of neopentyl glycol diglydicyl ether, 1,4-butanediol diglycidyl ether, benzyl glycidyl ether, and other mono- and multifunctional alkyl glycidyl ethers (class II monomers) display an extended induction period as shown in the RTIR study of Figure 1, during which only a very slow conversion to polymer is noted. However, at a given point during UV irradiation, polymerization of this monomer takes place suddenly and rapidly and is completed within a very short time. Since diaryliodonium salt photoinitiators have high quantum yields ($\Phi = 0.5-0.8$),[19,20] in most cases, a considerable portion of the photoinitiator has already been decomposed by light to produce acid during the long induction period and before the onset of the exothermic polymerization. Since, as noted before, k_1 in Scheme 1 is generally considered to be large for onium salt photoinitiators that generate Brønsted superacids, the slowest and rate-determining step for the polymerization of such monomers ether must, therefore, be either eq 3 or 4. Sasaki[21] has attributed the analogous long induction period that is observed in the photoinitiated cationic polymerization of 3,3-disubstituted oxetane monomers to the slow, rate-determining ring-opening reaction of the secondary oxonium salt, **I** (i.e., eq 3). Earlier work by Pruckmayr and Wu[22] suggested that the rate-determining step for 3,3-bischloromethyloxetane is the ring-opening of the tertiary oxonium ion **II** (i.e., eq 4). In a forthcoming paper,[23] the mechanistic details of the photopolymerizations of these latter oxetane monomers will be discussed in detail.

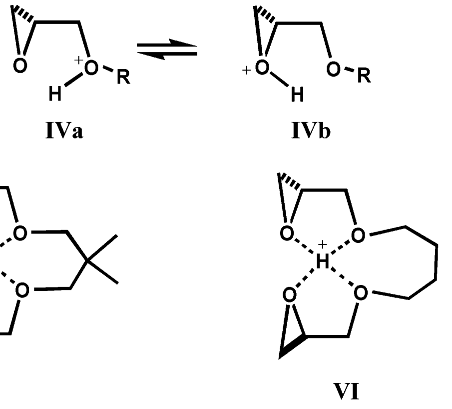
The long induction periods observed with class II epoxide monomers suggested that the reactive intermediates involved may have sufficient lifetimes for spectroscopic observation. Direct observation of the initially formed oxonium ion reactive intermediates involved in the cationic polymerizations of several different heterocyclic monomer systems by Brønsted acids has been reported using NMR spectroscopy. For example, Klages et al.[24] and Lambert and co-workers[25] have investigated the structure and stability of oxiranium ions using this technique. Secondary oxonium ions formed by the protonation of THF by fluorosulfonic acid at low temperatures have been studied by Pruckmayr and Wu,[22] while Penczek and Kubisa[26] have detected analogous species in the polymerization of 1,3-dioxolane using this same acid. Accordingly, ^{31}P NMR studies were carried out using the method developed by Penczek and Kubisa in which hexafluoroantimonic acid was added to neopentyl glycol diglycidyl ether at −5 °C. After 1 min, tri-*n*-butylphosphine was added to the monomer solution to trap the species present. Figure 3 depicts the ^{31}P NMR spectrum of the resulting solution. Three major phosphorus resonances were observed. Using model compounds and the phosphorus chemical shifts (relative to H_3PO_4) reported by Penczek and Kubisa, assignments for the unreacted phosphine (31.8 ppm), protonated phosphine (14.2 ppm), and quaternary phosphonium (35.0 and 36.9 ppm) species could be made. The spectrum indicated that the predominant species present was the protonated phosphine derived by transfer of a proton from the secondary oxiranium intermediate to the phosphine. In addition, the possibility that initially formed secondary oxiranium ions from glycidyl ethers could rapidly be converted to tertiary oxonium ions by the process shown in eq 5 can also be ruled out.



(5)

As an additional indication of the specific formation of secondary oxiranium species, the following set of experiments was carried out. As described previously, when neopentylglycol diglycidyl ether is first photolyzed in the presence of a diaryliodonium salt photoinitiator, a latent monomer mixture is formed that displays little evidence of polymer formation. When this mixture is heated in the absence of light, rapid polymerization ensues. In contrast, when 2,6-di-*tert*-butylpyridine was added after UV irradiation, polymerization is completely suppressed. Since 2,6-di-*tert*-butylpyridine is well-known[27,28] to react with protons or protonated species but not with trialkyloxonium ions, it can be used to distinguish between these two species. These results support the presence of long-lived secondary oxiranium ion species in the polymerization of this monomer.

Class I and II monomers possess characteristic structural features that allow them to be readily distinguished from one another with respect to their behavior in photoinduced cationic polymerization. For example, cyclohexene oxide is a highly strained epoxide monomer that on protonation possesses no means by which the intermediate secondary oxonium ion may be stabilized. Therefore, this monomer undergoes rapid, efficient transformation to the tertiary oxonium ion with subsequent polymerization. On the other hand, neopentylglycol diglycidyl ether and other alkyl glycidyl ethers possess a neighboring ether oxygen atom that has a similar basicity and proton affinity to the oxirane oxygen.[29−32] In addition, this ether oxygen is located such that it can stabilize the secondary oxonium ion species by hydrogen bonding through a pseudo-five-membered ring as depicted in tautomeric structures **IVa** and **IVb** (see eq 6). Molecular modeling using MOPAC-type calculations show that these two protonated cyclic structures represent local minimum-energy conformations, implying considerable stabilization. MOPAC calculations have been used by many investigators to probe the stabilities of both the intra- and intermolecular structures of compounds and molecular assemblies; only a few references are provided here.[33−36] Stabilization due to hydrogen bonding effectively raises the activation energy (E_{a2}), necessary for nucleophilic attack by the monomer reaction to proceed to give the tertiary oxonium ion, and this effectively retards the formation of polymer. Factors that decrease the stabilization of the protonated species also decrease the activation energy barrier, E_{a2}. For example, enhanced stabilization should be afforded by the multiply hydrogen-bonded structures **V** and **VI** respectively for neopentylglycol diglycidyl ether and 1,4-butanediol diglycidyl ether. In contrast, phenyl glycidyl ether (**IVa** and **IVb**, R = phenyl), and aryl glycidyl ethers in general, in which the basicity of the lone pairs of electrons on the ether oxygen is decreased by resonance interaction with the phenyl group, undergo slow (i.e., retarded) polymerization without an appreciable induction period (see Figure 1 in Supporting Information). We include these latter epoxide monomers in "class III". Class III epoxides are not generally useful by themselves in cationic photopolymerizations designed for high-speed applications.



IVa **IVb** **V** **VI**

(6)

Further insight into the reactivity of these latter class II monomers can be gained by once again considering the proposed energy vs reaction coordinate diagram shown in Figure 2B and comparing it to cyclohexene oxide in Figure 2A. On the basis of this diagram, we suggest the following explanation for the observed behavior of class II monomers during photoinitiated cationic polymerization. As noted before, the activation energy (E_{a1}) for the first step of the polymerization involving the protonation of the monomer is either nonexistent or very small, but overall, the reaction is expected to be exothermic.[18] However, in this case, there is a lowering of the energy of the secondary oxonium ion **IVa**−**IVb** due to hydrogen-bond stabilization as well as an elevation of the activation energy (E_{a2}) necessary for attack by a neutral epoxide monomer on these species to give the corresponding tertiary oxonium ion. With such monomers, E_{a2} is too high to be readily accessible by thermal activation at room temperature. Under such conditions, the protonated monomer intermediate, **IVa**−**IVb**, is comparatively stable and persists in the reaction mixture for considerable lengths of time before it reacts further. We propose that this is the origin of the observed induction period. Eventually, the thermal energy necessary to overcome the activation energy, E_{a2}, must come either from the exothermic monomer protonation step or from the very slow polymerization of the monomer. The UV irradiation as a significant source of heat can be ruled out. Only a very small temperature increase (1−2 °C over 10 min at 100 mJ/cm^2 min) was noted when the sample is irradiated in the absence of a photoinitiator. Figure 4 shows the diaryliodonium salt induced photopolymerization of benzyl glycidyl ether carried out under similar reaction conditions as those employed in the RTIR experiment shown in Figure 1. However, in this case, the sample temperature was monitored using optical pyrometry. Optical pyrometry (OP) is a technique developed in this laboratory[13,14] in which the course of a photopolymerization is monitored by following the progress of the temperature of the sample as a function of the irradiation time using an infrared camera (optical pyrometer). In Figure 4 it can be seen that the temperature of the sample slowly rises with the UV irradiation time during

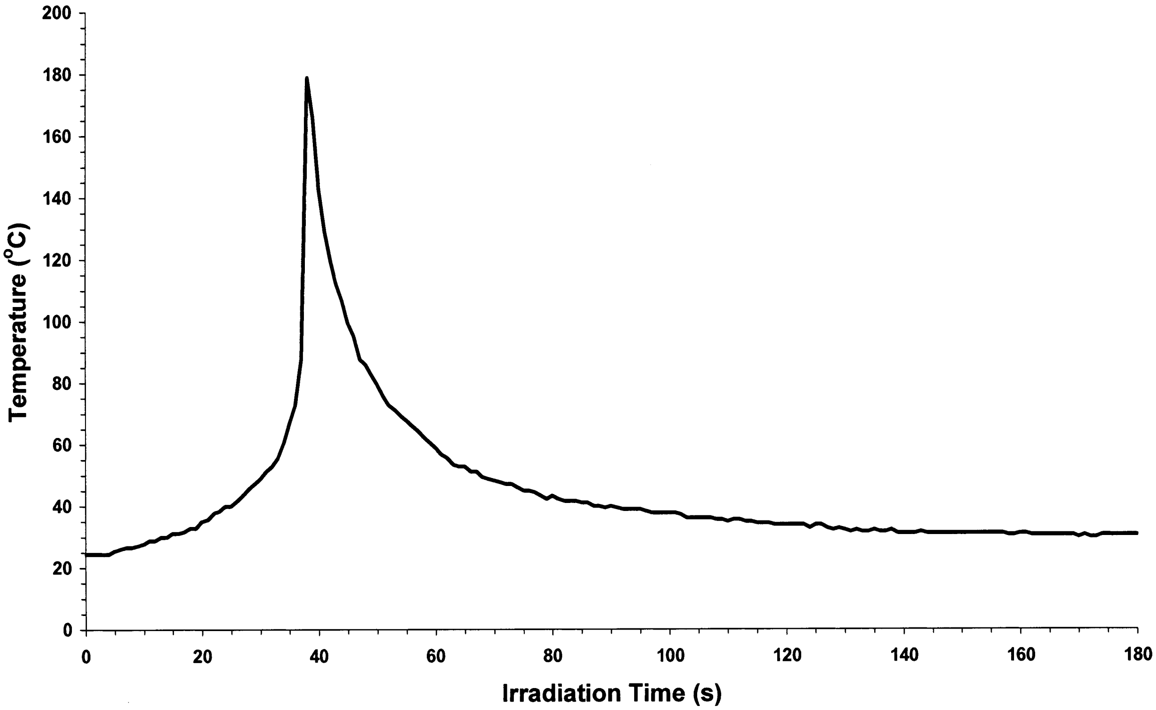


Figure 4. OP study of the photopolymerization of benzyl glycidyl ether using 1.0 mol % IOC-10 SbF_6 as photoinitiator (light intensity 1030 mJ/(cm^2 min)).

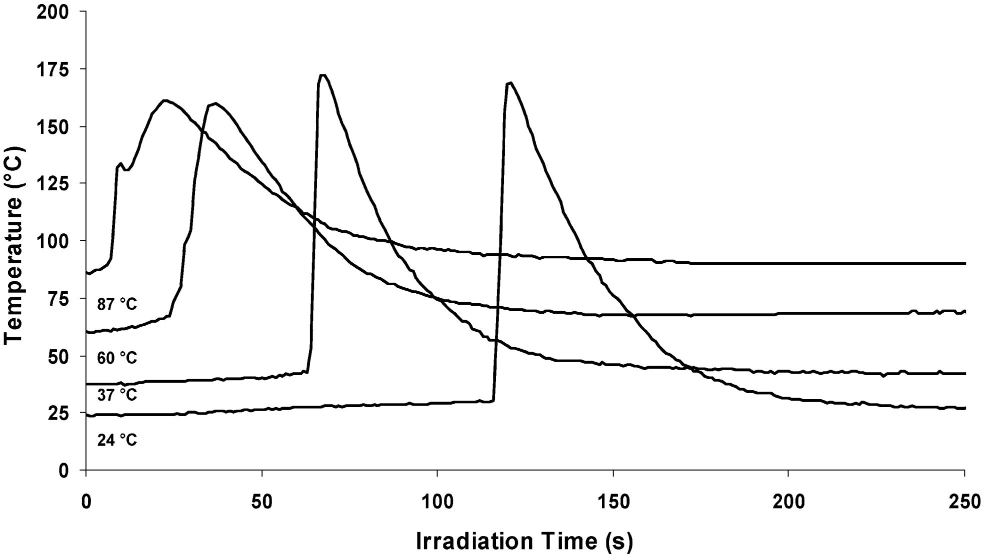
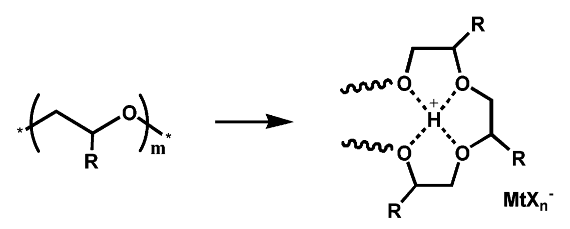


Figure 5. OP study of the effect of the temperature on the photopolymerization of benzyl glycidyl ether with 1.0 mol % IOC-15 SbF_6 as photoinitiator (light intensity 403 mJ/(cm^2 min)).

the induction period until it reaches approximately 45–47 °C. At this point, runaway polymerization takes place essentially under autoacceleration conditions. The temperature spontaneously reaches 179 °C and then falls rapidly as the monomer is exhausted. This behavior is consistent with the thermodynamic scenario shown in Figure 2B. Several additional experiments were conducted to demonstrate that the slow initial temperature rise takes place primarily as a result of the exothermic protonation of the monomer by the Brønsted superacid. When photolysis is conducted using “cold” UV light at low light intensities, there is little or no temperature increase due to the irradiation. In this case, the protonated species that are formed can remain stable for several hours without undergoing appreciable further polymerization. Similarly, it is possible to conduct a photolysis of the onium salt photoinitiator in an inert solvent such as dichloromethane. If this solution containing the Brønsted acid is very slowly added to the monomer to avoid heat buildup, a mixture is obtained that is stable for several minutes before polymerization sets in. However, when the same photolyzed onium salt solution is added rapidly, highly exothermic polymerization takes place without an appreciable induction period.

Stabilization due to hydrogen bonding of the secondary oxonium ion intermediates in class II epoxides affords an explanation for their behavior in cationic photopolymerizations. It should also be pointed out that hydrogen bonding with the polymer that is formed may also be an important contributing factor to the overall rate of polymerization. All epoxides undergo polymerization to give polymers containing repeating ethyleneoxy groups disposed along the backbone of the chain.

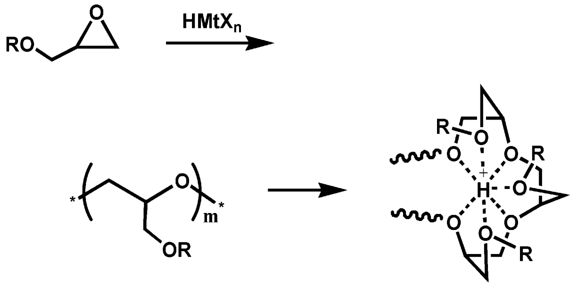
Such repeating units can work alone or in combination with each other analogous to crown ethers[37,38] to bind acidic protons as depicted in **VII** in eq 7. In the presence of strong protonic acids such as HCl, HBr, or HBF_4, crown ethers have been observed to form stable, isolable hydronium ion complexes.[39−41] Further, Entelis et al.[42] have observed retardation of the cationic polymerizations of epoxide monomers on the addition of poly(ethylene oxide). It is also worth noting that the energy associated with hydrogen bonding is generally quite small (3−6 kcal/mol[43]) and that it is likely to be only effective as a stabilization/retardation factor in these systems at low temperatures. However, we suggest that this may be sufficient to contribute significantly toward the extended induction period in photopolymerizations such as those described in this article which are carried out at room temperature using “cold” UV irradiation. Under these conditions, Brønsted acids released by slow photolysis of the photoinitiator may be captured as shown in eq 7 by polymer segments.



(7)

VII

The effect shown in eq 7 applies only to those monomers that produce polymer chains with sufficient conformational freedom to adopt a planar pseudo-five-membered ring hydrogen-bonded species. The situation is different for cycloaliphatic epoxides. The cationic ring-opening polymerization of these epoxides take place by a *trans*-nucleophilic (i.e., S_N2) attack of the monomer on the propagating tertiary oxonium ion and results in the formation of poly(cyclohexene oxide) with a *trans*-1,2-enchainment of the repeating ether groups. Because of the rigidity and steric bulk of the cycloaliphatic ring, such polymer segments cannot easily adopt a planar cyclic conformation necessary for the formation of hydrogen-bonded structures such as **V**. This may additionally contribute to the high reactivity exhibited by cycloaliphatic epoxides in cationic ring-opening polymerizations conducted at room and lower temperatures. In contrast, the cationic polymerization of alkyl glycidyl ethers proceeds as shown in eq 8 to give highly conformational flexible polymer chains with one additional ether coordination site per repeat unit that can provide further stabilization, possibly of the type shown in structure **VIII**. Again, such hydrogen-bonded species may contribute to the observed sluggish behavior of cationic polymerizations of alkyl glycidyl ethers carried out at low temperatures.



(8)

VIII

There are several consequences and observations that follow directly from the above-described mechanistic and thermodynamic interpretations of the behavior of the class II epoxy monomers. When neopentylglycol diglycidyl ether containing 1.0 mol % IOC-15 SbF_6 is irradiated for a time (e.g., 1−2 min at 500 mJ/(cm^2 s)) within the induction period, there is little evidence of polymerization and the monomer remains liquid and free-flowing. Heating this sample slightly (10−20 °C) in the absence of light produces a very rapid exothermic polymerization to give a cross-linked, insoluble network polymer. This result confirms that the reaction shown in Scheme 1, eq 3, for alkyl glycidyl ethers requires the input of an appreciable amount of thermal energy to overcome the activation energy (E_{a2}, Figure 2B) for the reaction to proceed. Figure 5 shows a study of the effect of the temperature on the photopolymerization of benzyl glycidyl ether using optical pyrometry (OP) to follow the course of the reaction. As the starting temperature is progressively increased, the induction period is progressively reduced until at 87 °C the polymerization proceeds without an induction period. Previously, it was generally known and observed in this laboratory[44] as well as by other workers[45] that the rates of cationic ring-opening polymerizations of epoxides are strongly affected by temperature. Further, we have reported in a recent article[46] that as a result of their long induction periods and high exothermicities the photoactivated thermally induced cationic polymerizations of alkyl glycidyl ether monomers take place along a well-defined propagating reaction front. Such frontal polymerizations have many potential applications.

Modification of the Reactivity of Epoxy Monomers. It was a major objective of this work to seek ways to accelerate the cationic ring-opening photopolymerizations of class II and class III monomers. In this article, it has already been demonstrated that one effective means of increasing the overall speed of the photopolymerization of an epoxy monomer is simply to reduce the problematic induction period by increasing the reaction temperature. However, this approach is not always acceptable in practice due to the sensitivity of certain substrates to heat, limitations in equipment, and fire and safety constraints. It is nevertheless worth noting that conventional UV arc lamps systems generate appreciable infrared energy. In many cases, beneficial increases in photopolymerization rate can be achieved by simply avoiding the use of infrared filters or other cooling systems.

Experiments were carried out to determine whether the induction period of a class II epoxy monomer can be appreciably shortened through the copolymerization of an alkyl glycidyl ether monomer with a more reactive, class I epoxy monomer. An example is shown in Figure 6 in which the photopolymerization of neopentylglycol diglycidyl ether was carried out in the presence of increasing amounts of the highly reactive 4-vinyl-1-cyclohexene diepoxide. As may be noted, the long induction period is progressively and proportionally reduced as the amount of the diepoxide in the reaction mixture is increased. Similar effects were observed when the photopolymerization of neopentyl glycol diglycidyl ether is carried out in the presence of different

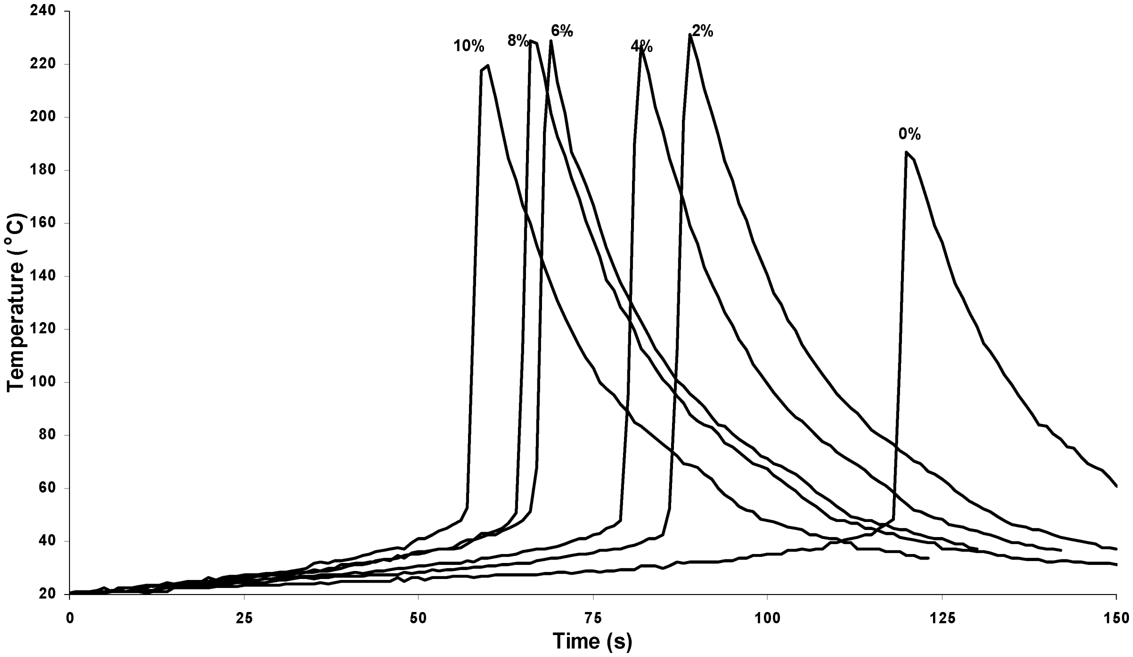


Figure 6. Effect of the addition of 4-vinylcyclohexene diepoxide to the photopolymerization of neopentylglycol diglycidyl ether. (1.0 mol % IOC-15 SbF_6; light intensity 860 mJ/(cm^2 min)).

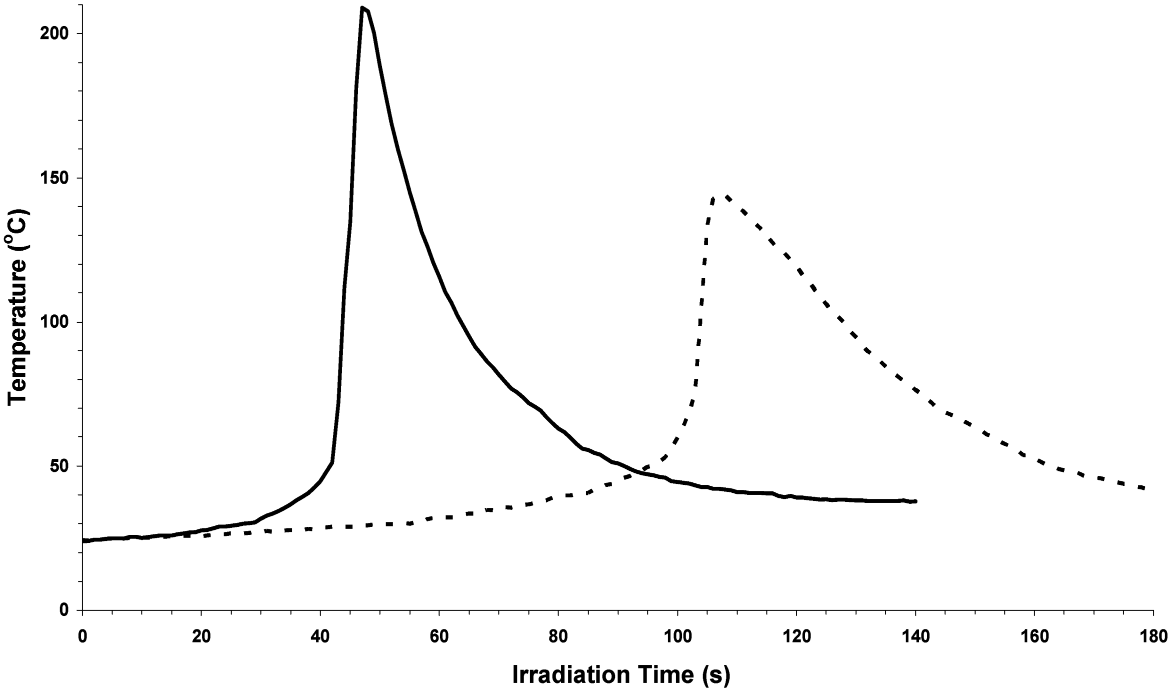
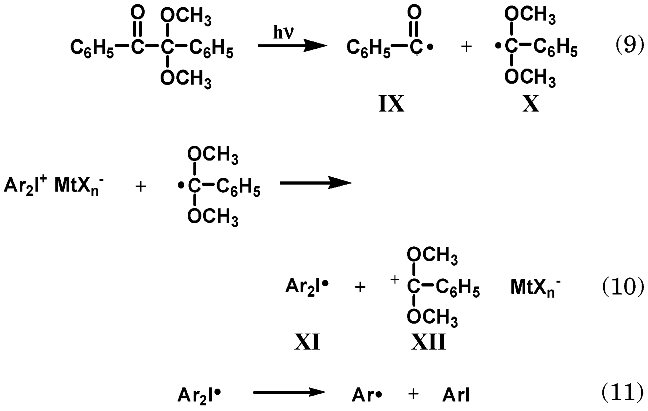


Figure 7. Comparison of the photopolymerization of neopentylglycol diglycidyl ether with 1.0 mol % IOC-15 SbF_6 conducted alone (- - -) and in the presence of 20% trimethylolpropane triacrylate and 1.0 mol % Irgacure 651 (—).

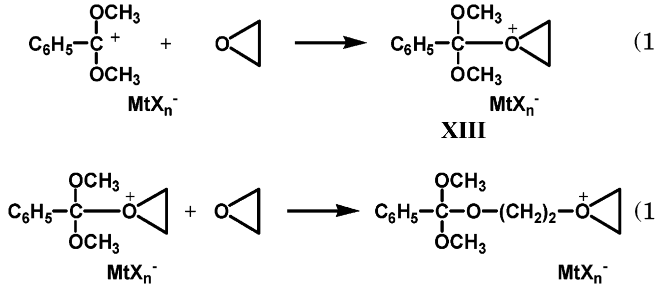
amounts of vinyl ether monomers such as trimethylolpropane trivinyl ether (Figure 2 of Supporting Information), 1,4-cyclohexanedimethanol divinyl ether, and diethylene glycol divinyl ether. The induction period of the diglycidyl ether monomer is shortened by the presence of 20% of the trivinyl ether monomer. However, the evidence for copolymerization between epoxide and vinyl ether monomers is tenuous, and it appears that these two different types of monomers mainly undergo independent homopolymerizations.[47] For this reason, acceleration due to copolymerization alone was questionable. An additional OP study is depicted in Figure 7 in which the photoinitiated cationic polymerization of neopentylglycol diglycidyl ether was conducted in the presence of 20% trimethylolpropane triacrylate and a free radical photoinitiator. In this case, the acrylate and epoxide monomers cannot undergo copolymerization. As can be noted, there is a marked reduction in the length of the induction period in the presence of the acrylate monomer.

It appears that the effects described above and shown in Figures 6 and 7 cannot be ascribed as due solely to copolymerization with a more reactive monomer. Additional experimental evidence confirms that this is the case. When a film sample of neopentylglycol diglycidyl ether is irradiated for several minutes with "cold" UV light in the presence of IOC-15 SbF_6 as a photoinitiator, a colorless transparent photoactivated mixture is ob-

Scheme 2



Scheme 3



tained that contains relatively long-lived secondary oxonium ions. The dormancy of this system can be broken as previously observed through the application of heat. However, it can also be broken by the local addition of cyclohexene oxide. If a drop of this monomer is added to only one portion of the irradiated film sample, it is observed that proliferation of the polymerization begins in that locale but rapidly also propagates to all parts of the sample. In this latter case, copolymerization cannot occur in areas remote from the application area of the cyclohexene oxide. Rather, the heat liberated from the rapid, highly exothermic polymerization of this latter monomer must induce a frontal polymerization of the neopentylglycol diglycidyl ether. On the basis of this observation, we suggest that compatible systems containing mixtures of "high and low" reactivity monomers may undergo rapid photopolymerization due to a combination of both thermal and copolymerization effects depending on the specific system under study. Further, the simultaneous polymerizations of an epoxy monomer and monomers that do not interact chemically can also result in a considerable reduction in the induction period of the alkyl glycidyl ether due only to thermal effects.

Previously,[48] we have demonstrated that diaryliodonium salts, in addition to functioning as photoacid generators, may be considered to be oxidizing agents. These compounds readily oxidize certain carbon-centered free radicals to their corresponding carbocations. For example, Scheme 2 depicts the mechanism proposed by Ledwith[49] for the photoinitiated generation of carbocations by the UV irradiation of 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) in the presence of a diaryliodonium salt. In the first step (eq 9), Irgacure 651 undergoes photolysis to generate two free radical species: the acyl radical, **IX**, and the dimethoxybenzyl radical, **X**. The latter radical is readily oxidized (eq 10) by the diaryliodonium salt to give the dimethoxybenzylcarbenium ion, **XII**. Simultaneously, the diaryliodonium salt is reduced to the diaryliodine free radical, **XI**. This latter free radical species is unstable and undergoes further fragmentation to form an aryl radical and an aryl iodide (eq 11). The irreversibility of this latter step of the mechanism prevents the possibility of back reactions. As shown in Scheme 3, carbocation **XII** would be expected to attack at the epoxide oxygen (oxirane is shown here for simplicity) to directly generate the tertiary oxonium ion, **XIII**, that is more reactive than the secondary oxonium ions formed by oxirane homopolymerization. This reaction, in analogy with the corresponding protonation reaction (eq 2, Scheme 1), is exothermic. It was hoped that reaction of the resulting increased quantity of initiating species (i.e., combined protons and carbocations) with the monomer would release sufficient energy to overcome the activation barrier E_{a3}, resulting in a reduction of the induction period.

Figure 8 shows the effect of different concentrations of Irgacure 651 on the photoinitiated cationic polymerization of neopentylglycol diglycidyl ether. In the absence of this free radical photoinitiator, the photopolymerization of neopentylglycol diglycidyl ether displays the typically observed long induction period followed by rapid, autoaccelerated polymerization. However, when Irgacure 651 is added, highly exothermic photopolymerization takes place together with a dramatically shortened induction period. The length of the induction period is inversely proportional to the amount of Irgacure 651 added. It is also worth noting that there is an appreciable sharpening of the temperature vs time peak in the thermogram and that the temperature of this sample exceeds 200 °C during polymerization. Similarly, it was found that the induction periods of all mono- and multifunctional alkyl glycidyl ethers examined were substantially reduced by the incorporation of Irgacure 651. Figures 3−5 of the Supporting Information show respectively the impact of Irgacure 651 on the photopolymerizations of 1,4-cyclohexanedimethanol digylcidyl ether with IOC-10 SbF_6 and neopentylglycol digylcidyl ether in the presence of IOC10 PF_6 and IOC10 $(C_6F_5)_4B$. To further test whether the mechanism shown in Scheme 2 is valid, the diaryliodonium salt photoinitiator (IOC-15 SbF_6) was replaced with a triarylsulfonium salt (*S*-(4-*n*-decyloxyphenyl)-*S*,*S*-diphenylsulfonium hexafluoroantimonate, SOC-10 SbF_6) that also functions as a photoacid generator. As with IOC-15 SbF_6, the polymerization in the presence of SOC-10 SbF_6 displayed a long induction period; however, this induction period was not altered when Irgacure 651 was added. Triarylsulfonium salts possess a considerably higher reduction potential than diaryliodonium salts, and for that reason, they are not readily reduced by free radicals.[50]

The reduction in the induction period of the photopolymerizations of class II monomers in the presence of Irgacure 651 can be explained by a photosensitization effect. Since the diaryliodonium salt photoinitiators that are used in these studies have their main UV absorption maxima at 247−250 nm, they are poorly photosensitive at the long (>300 nm) wavelengths emitted by the light delivery system that was used in this work. On the other hand, Irgacure 651 has long wavelength absorption bands together with a high quantum yield of photolysis (0.52 at 350 nm; 0.61 at 360 nm[51]) at those wavelengths that efficiently produce free radical species. These latter species are rapidly oxidized to carbenium ions (Scheme 2, eq 10) that undergo exothermic reaction with mono-

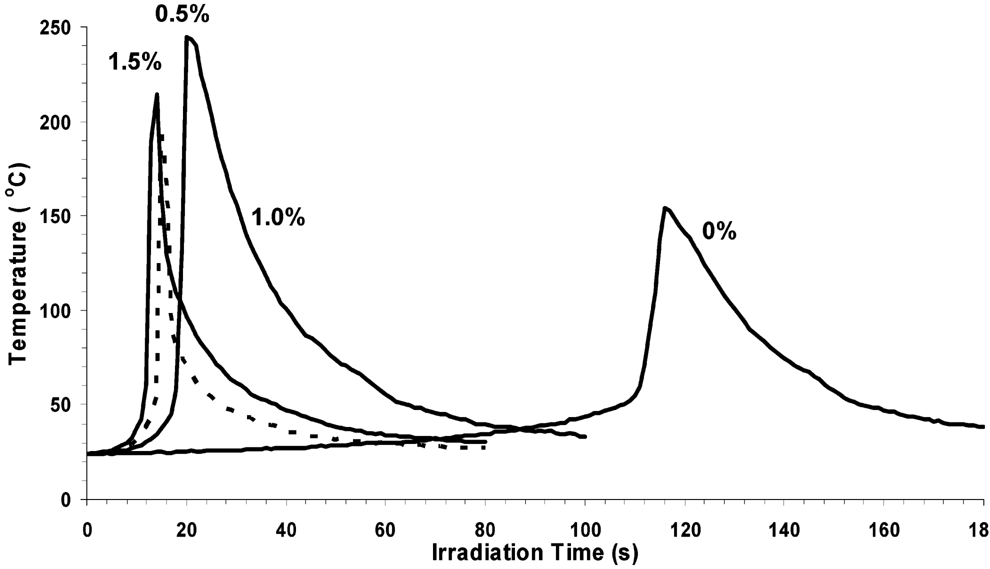


Figure 8. OP study of the photopolymerization of neopentylglycol diglycidyl ether carried out with 1.0 mol % IOC-15 SbF_6 and in the presence of various amounts of Irgacure 651 (light intensity 1030 mJ/(cm^2 min)).

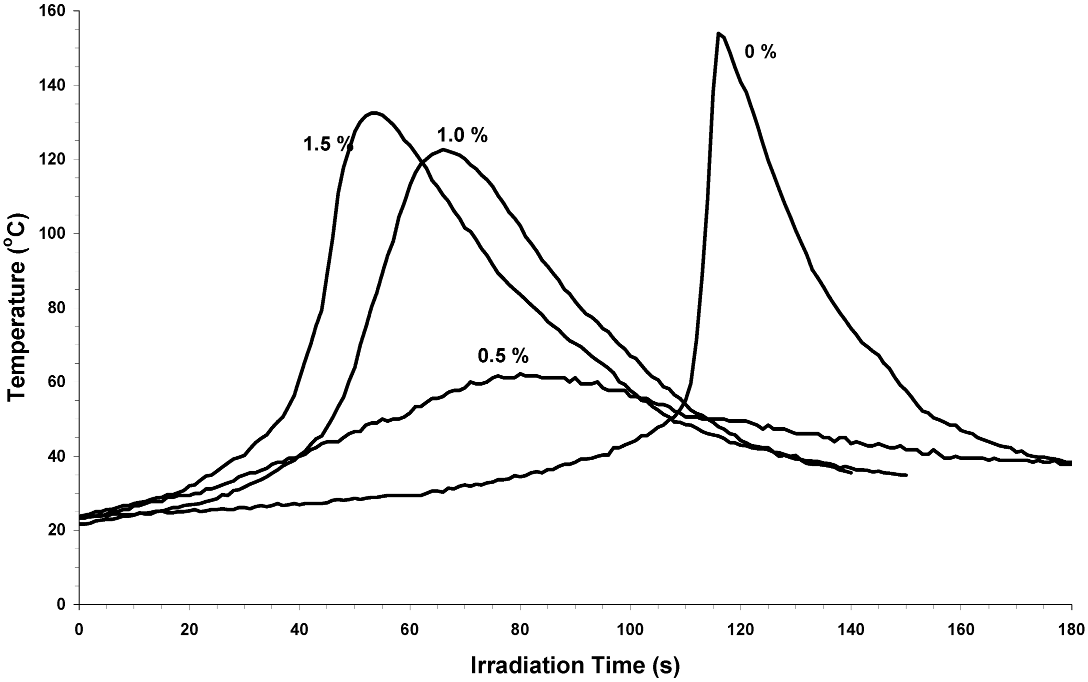
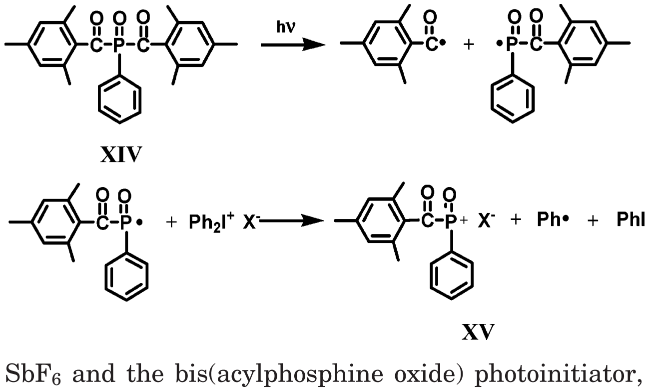


Figure 9. Influence of the addition of Irgacure 819 on the photoinitiated cationic polymerization of neopentylglycol diglycidyl ether in the presence of 1.0 mol % IOC-15 SbF_6 (light intensity 1030 mJ/(cm^2 min)).

mer (Scheme 3, eq 12), resulting in a rapid rise in the sample temperature that induces the autoaccelerated polymerization of the monomer. Other types of photosensitizers also display this same type of activity on the photopolymerizations of epoxy monomers.

Scheme 4



Several other free radical photoinitiators that undergo photoinduced fragmentation by a Norrish type I bond cleavage process (e.g., 1-hydroxycyclohexylphenyl ketone, Irgacure 184) were substituted for Irgacure 651. As expected, these photoinitiators are somewhat less effective in reducing the induction period for the photoinitiated cationic polymerization of simple alkyl glycidyl ethers. This is because these photoinitiators yield free radicals on photolysis that are less easily oxidized than the dimethoxybenzyl radical derived from Irgacure 651. An example is depicted in Figure 9 for the polymerization of neopentylglycol diglycidyl ether using IOC-15 SbF_6 and the bis(acylphosphine oxide) photoinitiator, Irgacure 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, **XIV**). In this figure, one can clearly observe

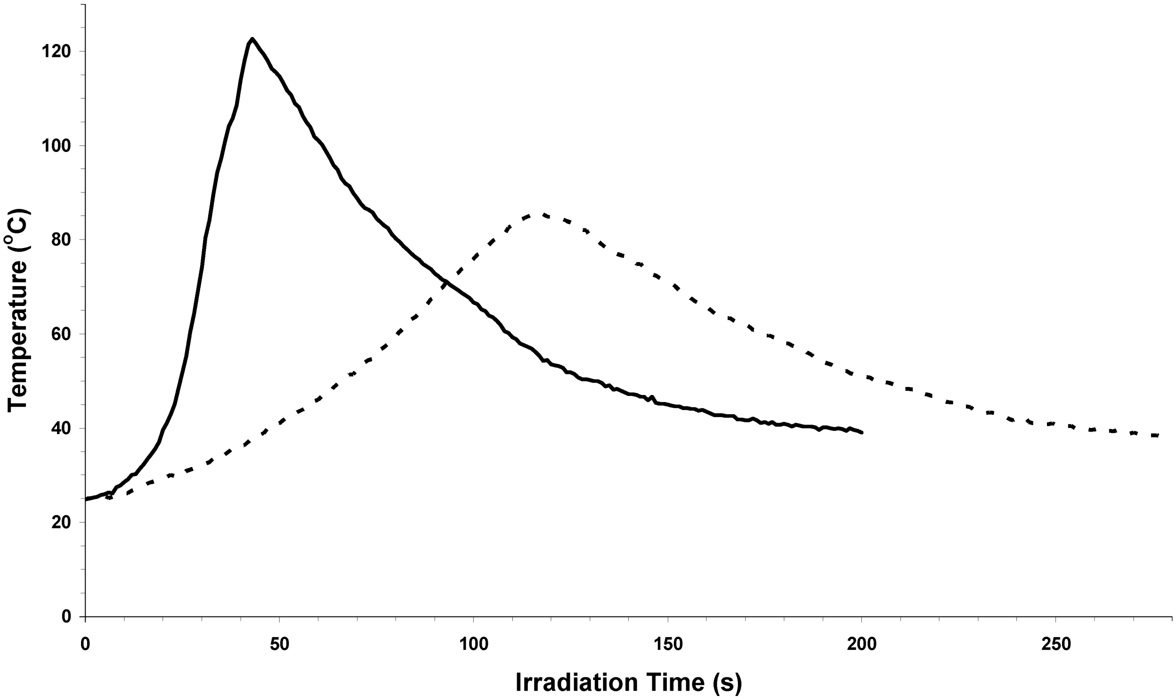


Figure 10. OP study of the photopolymerization of bisphenol A diglycidyl ether carried out with 1.0 mol % IOC-8 SbF_6 in the presence (—) and absence (- - -) of 1.0 mol % Irgacure 651 (light intensity 1060 mJ/(cm^2 min)).

a progressive shift in the position of the maximum temperature toward shorter times in as the concentration of Irgacure 819 is increased. It is evident that there is also an increase in the maximum sample temperature as the concentration of Irgacure 819 is increased. Irgacure 819 possesses strong absorption bands in the 360 nm region.[52] In addition, Yagci[53] has reported that bis(acylphosphine oxide) photoinitiators can be used to photosensitize the decomposition of diaryliodonium salts. As shown in Scheme 4, Yagci attributes this to the oxidation of the phosphinoxy radical by diaryliodonium salts to generate a phosphorus-centered cation (**XV**) that can initiate the ring-opening polymerization of epoxide monomers. The presence of aromatic proton resonances derived from the bis(acylphosphine oxide) in the ^{1}H NMR spectra of polymers obtained using these systems was taken as supportive of the proposed mechanism.

The acceleration of the photopolymerization of a wide variety of other epoxide monomers can be achieved using a diaryliodonium salt in combination with a free radical photoinitiator/photosensitizer. Among the most widely used and least expensive epoxide monomers is bisphenol A diglycidyl ether. This monomer is typically employed in condensation network polymerizations with amines, amides, and anhydrides. However, the photoinitiated cationic polymerization of this bisaryl glycidyl ether, as mentioned previously, is very sluggish. Consequently, this monomer finds little use in applications involving photoinitiated cationic polymerization. Figure 10 shows that the rate of this monomer can be markedly accelerated simply by the use of dual cationic and free radical photoinitiators. As may be seen in this figure, the slope of the temperature rise is much greater in the sample that contains Irgacure 651 as compared to when it is absent. In addition, the peak in the thermogram is markedly sharpened, and the maximum temperature attained by the sample is much higher as compared to when Irgacure 651 is absent.

The effect of Irgacure 651 on the photopolymerization of neopentylglycol diglycidyl ether was also demonstrated in a more practical way by carrying out this photopolymerization as a thin film on glass substrates using a conveyorized lamp system and determining the minimum irradiation time (highest conveyor speed) that can be used to produce a tack-free film. No photopolymerization of the monomer containing 1.0 mol % IOC15 was observed even at the minimum conveyor speed possible, whereas when 1.0 mol % Irgacure 651 was added, a tack-free film was obtained at a conveyor speed of 4.8 m/min.

Conclusions

Studies of the photoinitiated cationic ring-opening polymerizations of epoxy monomers conducted and described in this article show that these monomers display a variety of behaviors that can be related to their structures. The photopolymerizations of class I epoxides such as cyclohexene oxide that bear no means of stabilizing the intermediate protonated species (secondary oxonium ions) or tertiary oxonium intermediates proceed rapidly and exothermically on UV irradiation. In contrast, monomers (class II epoxides) that bear neighboring oxygen atoms in the molecule that are located such that they can stabilize the secondary oxonium ion intermediates undergo photopolymerizations that are characterized by an extended induction period. These induction periods are followed by rapid, exothermic autoaccelerated polymerization. Typical of monomers that exhibit this behavior are alkyl glycidyl ethers. Epoxides that possess oxygen atoms that are less effective in stabilizing the intermediates comprise a third (class III) general class of monomers. Included in this class are aryl glycidyl ethers. These latter monomers undergo slow, retarded photoinitiated cationic polymerization without a pronounced induction period. Most practical applications for photoinitiated cationic polymerization are currently limited to monomers found in class I.

In this article, we have outlined three major means by which epoxy monomers in classes II and III may be effectively accelerated so that they are also useful in a variety of practical applications. The cationic ring-opening polymerizations of all epoxide monomers can be thermally accelerated, and this method is particularly advantageous for monomers in class II. The induction period of alkyl glycidyl ethers (class II monomers) can be significantly reduced by even a modest increase in temperature making these low-cost monomers attractive for use in many applications. It has also been demonstrated here that conducting the polymerization of class II monomers in the presence of more reactive monomers from class I is effective in reducing the induction period of these latter monomers. A third method is also described that is effective for the acceleration of all three classes of epoxide monomers. This method consists of generating reactive carbocations by the photoinduced redox reaction of a free radical photoinitiator with a diaryliodonium salt. Using this approach, dramatic acceleration of the polymerizations of even the most reactive monomers derived from class I was observed.

Acknowledgment. The authors thank Dr. Herbert Schwartz for kindly assisting with acquisition of the ^{31}P NMR data.

Supporting Information Available: Five figures depicting the temperature profile of the photopolymerization of aryl glycidyl ethers and the acceleration the photopolymerizations of various epoxide monomers by free radical initiators. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA050106K