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Investigations of the Reactivity of "Kick-Started" Oxetanes in Photoinitiated Cationic Polymerization

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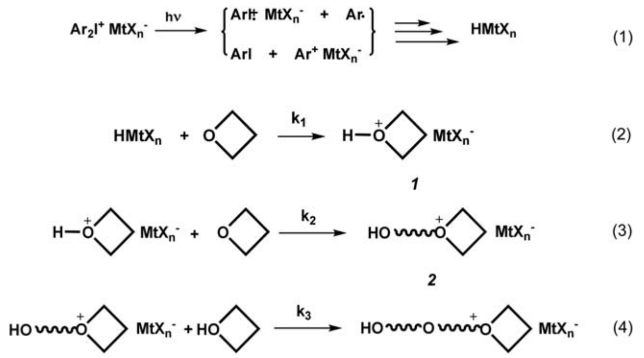
ABSTRACT: The ability of certain alkyl substituted epoxides to accelerate the photoinitiated cationic ring-opening polymerizations of oxetane monomers by substantially reducing or eliminating the induction period altogether has been termed by us "kick-starting." In this communication, the rates of photopolymerization of several model "kick-started" oxetane systems were quantified and compared with the analogous biscycloaliphatic epoxide monomer, 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL). It has been found that the "kick-started" systems undergo photopolymerization at rates that are at least two-fold faster than ERL. These results suggest that "kick-started" oxetanes could replace ERL in many applications in which high speed ultraviolet induced crosslinking photopolymerizations are carried out. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *00*, 000–000

KEYWORDS: crosslinking; cationic polymerization; kinetics; photopolymerization; epoxides

INTRODUCTION Work in this laboratory over the past two decades has been focused on the photoinitiated cationic ring-opening polymerization of epoxide monomers. These photopolymerizations have found a wide range of commercial uses in thin film applications such as coatings for metals, plastics, glass and wood, pressure sensitive adhesives, marking inks for electronic components, and in additive manufacturing [three-dimensional (3D) imaging]. However, epoxide photopolymerizations have a number of drawbacks. The most useful epoxide monomers are those that are prepared by the epoxidation of carbon–carbon double bond containing substrates with peroxides. Due to the well-known[1] hazards associated with peroxides, the commercial availability of epoxides by this method is currently restricted to only a few monomers that command rather high prices. Further, many epoxides also possess considerable toxicological issues, especially with respect to undesirable eye and skin irritation.

Oxetanes are closely related compounds to epoxides and share many of the same desirable characteristics. Moreover, the synthetic methods used for the preparation of oxetane monomers do not involve epoxidation. Instead, the preparative methods rely on simple, direct base-mediated ring-closure[2] or thermally induced carbon dioxide extrusion reactions.[3] Oxetanes are generally considerably less toxic and, consequently, more easily handled.[4] Despite their similar ring-strain, oxetanes have been reported by formulators to be considerably less reactive than epoxides in photoinitiated cationic polymerizations and this has been an impediment to the growth and use of these monomers. The fundamental reasons that underlie the sluggish reactivity of oxetane monomers in photoinitiated cationic polymerization have remained elusive and have not been fully explored until recently.

The photoinitiated acid-catalyzed cationic ring-opening polymerization of oxetane monomers proceeds by the same mechanism as epoxides[5] and is depicted in Scheme 1. For purposes of clarity, this mechanism is depicted using the unsubstituted compound oxetane (trimethylene oxide). The photolysis of a photoacid generator such as a diaryliodonium or triarylsufonium salt produces a strong Brønsted acid (eq 1) that protonates the oxygen atom of the oxetane ring (eq 2). Then, ring-opening (eq 3) occurs by a S_N2 attack of the oxygen atom of a neutral monomer on one of the carbon atoms adjacent to the protonated oxygen atom of the monomer (secondary oxonium ion), ***1***, to give tertiary oxonium ion, ***2***. This latter reaction is fast in the case of an epoxide, but considerably slower for an oxetane. Previously, Sasaki et al.[6,7] have pointed out that the oxygen ring atom of an oxetane is considerably more basic than the oxygen atom in an epoxide. This leads to a higher energy barrier for the ring-opening of the protonated oxetane. Subsequent S_N2 attack by monomer molecules on the respective tertiary oxonium ion, ***2***, (eq 4) is rapid due to relief of the ring-strain in the oxonium ion. The third step of the mechanism shown in Scheme 1 is the rate-determining step. Since each of the



SCHEME 1 Mechanism of the photoinitiated cationic polymerization of oxetanes.

propagation steps involves S_N2 reactions, substitution at the 2 and 4 positions of the oxetane ring would be expected to have a large impact on slowing the rates of those reactions. For that reason, the work described in this communication has been specifically restricted to 3-mono- and 3,3-disubstituted oxetanes.

There are several consequences of the mechanistic scenario presented in Scheme 1 and they are further exemplified in the optical pyrometry (OP) plots shown in Figure 1. In the photoinitiated cationic polymerization of a simple, highly strained epoxide monomer such as 1,2-cyclohexene oxide, polymerization begins almost instantaneously at the start of the ultraviolet (UV) irradiation as the Brønsted acid is produced by photolysis of the photoinitiator. In the case of cyclohexene oxide, the photolysis of the photoinitiator is the rate-determining step. For that reason, those factors that directly affect the photolysis of the photoinitiator including the quantum yield and UV irradiation intensity have a large impact on the rate of photopolymerization. The shape of the OP curve for cyclohexene oxide given in Figure 1 is complicated in the latter stages by the vaporization of the monomer due to the highly exothermic polymerization. Under the same conditions, the oxetane monomer, 3-ethyl-3(2-ethylhexyloxymethyl)oxetane displays quite different behavior. As irradiation proceeds, the protonated secondary oxonium ion that is formed does not react further with monomer to yield polymer. Instead, the concentration of the protonated oxetane species builds up in the reaction mixture and this is manifested by an induction period. Once the onset of the oxetane polymerization takes place, a rapid, autoaccelerated exothermic ring-opening polymerization occurs producing a sharp rise in sample temperature.

The presence of the oxetane induction period is highly undesirable and makes these monomers unsuitable for many in-line, high-speed coating, printing, and bonding applications that are the major uses of current photopolymerization technology. Accordingly, it was the purpose of this investigation to explore means of eliminating the induction period in the photoinitiated cationic polymerizations of oxetane monomers and oxetane-functional oligomers.

EXPERIMENTAL

Materials

1,2,8,9-Limonene dioxide [limonene dioxide (LDO), a mixture of isomers] was provided as a sample by Arkema, Inc., Grand Rapids, MI, and purified by fractional vacuum distillation before use. 2,2,3,-Trimethyloxirane (2,3-epoxy-2-methybutane) was purchased from Acros Organics, Waltham, MA. 3,4-Epoxycyclohexylmethyl 3′,4′-cyclohexylcarboxylate (ERL-4221E, abbreviated ERL) was purchased from the Union Carbide Corporation (now Dow Chemical Corp., Midland, MI). 3-Ethyl-3(2-ethylhexyloxymethyloxetane [EHOXT]), 3-ethyl-3(2-phenoxymethyloxetane [POX]), and bis{[(1-ethyl(3-oxetanyl)]methyl} ether (DOX), were gratefully received as gifts from the Toagosei Chemical Company, Nagoya, Japan. POX and DOX were purified prior to use by fractional vacuum distillation (POX bp 117–118/0.6 mmHg). A sample of Irgacure 651 was kindly supplied by the Ciba Specialty Products Corp., Basel, Switzerland. 1,2-Cyclohexene oxide was purified by distillation from calcium hydride. Other reagents used in this work were obtained from the Aldrich Chemical Company, Milwaukee, WI, and used as received without further purification. The diaryliodonium salt[8] and triarylsulfonium[9] salt and dialkylphenacylsulfonium salt[10] photoinitiators were prepared as described previously. In this article, three of these photoinitiators were employed and we have developed shorthand designations for these compounds. For example, IOC-8 SbF_6 refers to (4-*n*-octyloxyphenyl)phenyliodonium hexafluoroantimonate, having the structure shown below in which an *n*-octyloxy 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*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate and SOC-10 PF_6 to S(4-*n*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluorophosphate with the structures indicated below. DAPSC1,C8 SbF_6 is a shorthand notation for S-*n*-octyl-S-methyl-S-phenacylsulfonium hexafluoroantimonate.

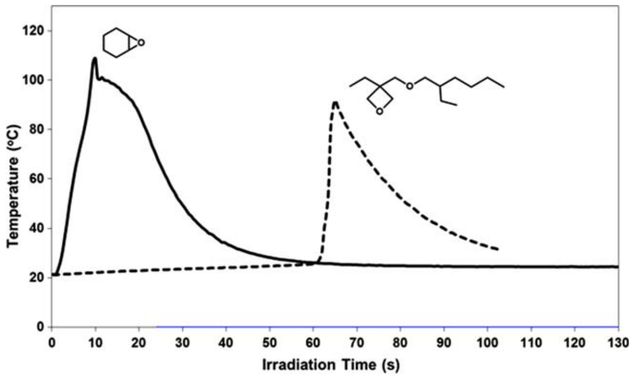
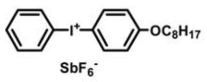
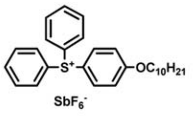


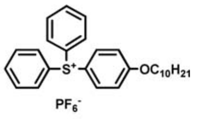
FIGURE 1 Comparisons of the photoinitiated cationic polymerizations of 1,2-cyclohexene oxide and 3-ethyl-3(2-ethylhexyloxymethyl)oxetane using 2.0 wt % (0.3 and 0.7 mol % respectively) of S(4-*n*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF_6).



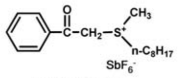
IOC-8 SbF_6



SOC-10 SbF_6



SOC-10 PF_6



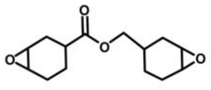
DAPSC1,C8

OP Characterization of Oxetane and Epoxide Photopolymerizations

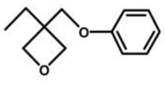
We have previously described the analytical techniques and apparatus used in this laboratory for OP.[11,12] Samples for OP kinetic analysis were prepared by sandwiching a liquid monomer containing the designated photoinitiator between two thin (12.5 μm) films of fluorinated poly(ethylene-co-propylene) (DuPont FEP thermoplastic film) using a thin, 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 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 served as a light filter passing UV light of wavelengths greater than 300 nm, but blocks both shorter wavelengths as well as wavelengths in the infrared region. UV irradiation intensities were measured using a Control Cure Radiometer (UV Process Supply, Chicago, IL). 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. Typically, the reproducibility of the kinetic data was ±5%. All kinetic studies were conducted at ambient laboratory temperature (25 °C–28 °C) unless otherwise noted. Photoinitiator concentrations are given in either or both mol % and wt % depending on the given experiment.

RESULTS AND DISCUSSION

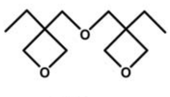
A common strategy for increasing the apparent reactivity of a monomer is to copolymerize it with a more reactive monomer. Most of the efforts directed at accelerating the photopolymerization of oxetane monomers have been undertaken using 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL).[13–16] Shown in Figure 2 are plots of the induction periods of the mono- and bisoxetane monomers; POX (3-ethyl-3(2-phenoxymethyloxetane) and DOX (bis{[(1-ethyl(3-oxetanyl)]methyl} ether) as a function of the molar content of ERL present in the mixture. From these two studies, it may be concluded that the reduction in the induction period of an oxetane monomer is directly proportional to the amount of ERL present in the mixture. Thus, substantial amounts of ERL must be added to appreciably shorten the induction period. However, in no case studied, was the induction period eliminated. Based on these results, it is understandable why oxetanes have been employed as modifiers of epoxy resins and not the other way around.



ERL



POX



DOX

In a recent article from this laboratory,[17] we have described the marked acceleration of the photoinitiated cationic ring-opening polymerization of 3-mono- and 3,3-disubstituted oxetanes by certain alkylated epoxide compounds. It was observed that, due to steric hindrance, 2,2-, 2,2,3-tri-, and 2,2,3,3-tetraalkyl substituted epoxides either undergo facile rearrangements to aldehydes or ketones or very inefficient homopolymerization in the presence of cationic initiators. In contrast, when these same epoxides were present in small concentrations in mixtures with oxetanes, they were shown to markedly accelerate the cationic ring-opening polymerizations of those monomers. Investigations showed that the acceleration of the rate of the oxetane polymerization by these specific epoxides was due to a basic change in the mechanism of the initiation step of the polymerization. Depicted in Scheme 2 is a sequence of reaction steps we have proposed to explain the experimental results. Attack by the photogenerated Brønsted acid on 2,2,3-trimethyloxirane results in ring-opening to give the tertiary carbocation, ***3***

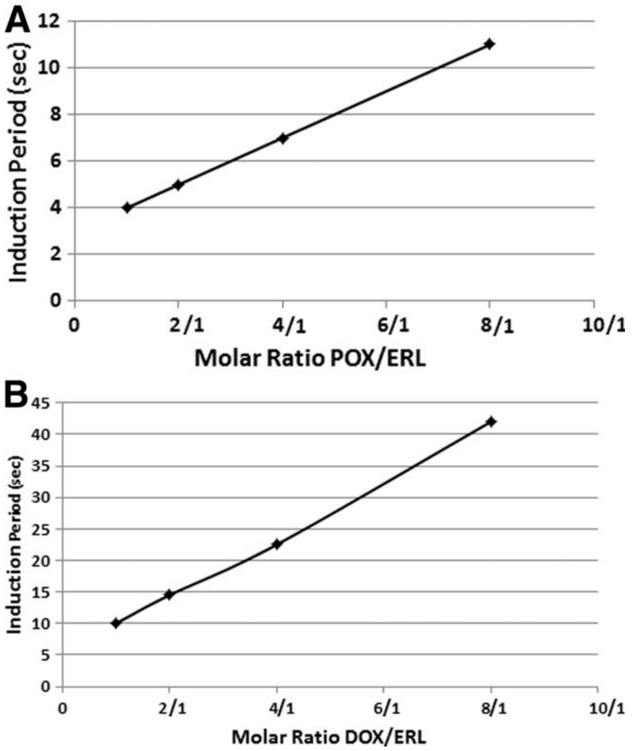
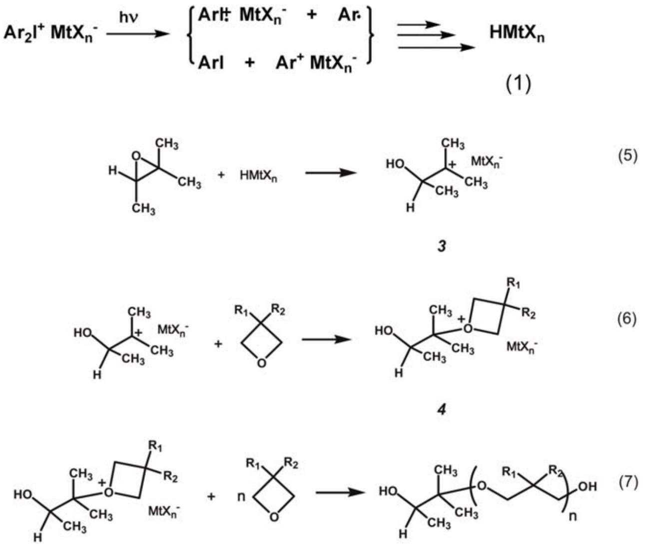


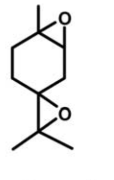
FIGURE 2 (**A**) Effect of ERL on the induction period of the photoinitiated cationic polymerization of POX (2.0 wt %, 0.3 mol % SOC-10 SbF_6 as photoinitiator, light intensity, 2910 mJ/cm^2 min). **(B)** Effect of ERL on the induction period of the photoinitiated cationic polymerization of DOX (2.0 wt %, 0.3 mol % SOC-10 SbF_6 as photoinitiator, light intensity, 1350 mJ/cm^2 min).



SCHEME 2 Proposed mechanism of the acceleration of the photoinitiated cationic ring-opening polymerization of oxetane monomers by epoxides.

(eq 5). This species subsequently adds to the oxetane to produce the tertiary oxonium ion, ***4***, (eq 6) that initiates the further polymerization of the oxetane monomer (eq 7). Comparing the mechanism shown in Scheme 1 with that depicted in Scheme 2, it can be seen that in the latter mechanism, the direct alkylation of the monomer by the carbocation, ***3***, to form the highly reactive tertiary oxonium species, ***4*** replaces the slow step of Scheme 1 (eq 3) involving the formation of a secondary oxonium ion by protonation of the oxetane monomer. Since we have previously shown[18] that the acceleration and reduction of the induction period in the photopolymerization of a "kick-started" system is not affected by rather large variations in the oxetane–oxirane molar ratio in the mixture, but, instead, are sensitive to variations in photoinitiator concentration and light intensity, we suggest that in such systems, the rate-determining step is photogeneration of the Brønsted acid (eq 1). Acceleration of the cationic photopolymerization of all 3-mono- or 3,3-disubstituted oxetanes investigated has been observed with a variety of 2,2-di-, 2,2,3-tri-, and 2,2,3,3-tetraalkyl-substituted epoxides. In all cases, these epoxides are capable of undergoing proton-induced ring-opening to generate tertiary alkyl carbocations capable of alkylating the oxetane monomer. In the special cases of diepoxides such as LDO and terpinolene diepoxide, both epoxide groups can function as reactive sites for initiation of oxetane polymerization

limonene dioxide



terpinolene dioxide

Shown in Figure 3 is a comparison of the photopolymerizations of 3-ethyl-3(2-ethylhexyloxy)methyloxetane carried out in the presence and absence of LDO. The rapid photopolymerization without a substantial induction period is characteristic of "kick-started" oxetane photopolymerizations carried out in the presence of a small amount of the diepoxide. This is in stark contrast with the results shown in Figure 2(A,B) obtained with ERL as a modifier and is indicative of a major change in the mechanism of the polymerization.

OP[12] was used to monitor the progress of the photopolymerizations shown in Figures 1 and 3 in real time. Real-time infrared spectroscopy (RTIR) was found to be insensitive for these photopolymerizations due to the lack of strong unobscured absorption bands in the IR spectra of oxetane monomers. The OP analytical method is useful for comparing the reactivity of different monomer types. Given in Figure 4(A,B) are two comparative OP studies of the respective cationic photopolymerizations of a 4:1 molar "kick-started" mixture of DOX and LDO with the photopolymerization of ERL. Both polymerizations were conducted using a light intensity of 1174 mJ/cm^2 min with 2.0 mol % of SOC-10 SbF$_6$ as the photoinitiator. A visual inspection of the OP temperature versus time profiles of the two different photopolymerizations (solid lines) led to the conclusion that the "kick-started" system was considerably more reactive than ERL.

Previously,[18] we have demonstrated that the temperature versus time plots obtained by OP can be converted by integration to curves that are very closely related to conversion versus time profiles obtained by Fourier transform RTIR (FT-RTIR). Moreover, the values of the slopes of the early portions of the integrated OP curves give values which are numerically nearly identical to $R_p/[M]$ values for the photopolymerization of the same monomer obtained by FT-RTIR. Also shown in Figure 4(A,B), respectively, are the integrated OP curves (dashed lines) for the respective photoinitiated "kick-started" DOX/LDO and ERL polymerizations. The rate

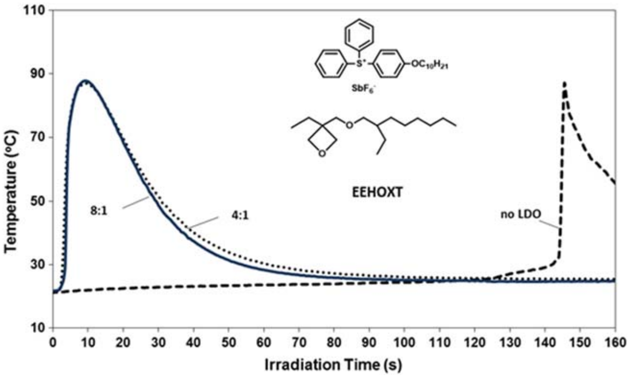


FIGURE 3 Photoinitiated cationic polymerization 3-ethyl-3(2-ethylhexyloxy)methyloxetane (EEHOXT) conducted alone and in the presence of 8:1 and 4:1 molar ratios with LDO using 2.0 wt % (0.3 mol %) of S(4-*n*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF$_6$) as a photoinitiator at a light intensity of 1400 mJ/cm^2 min.

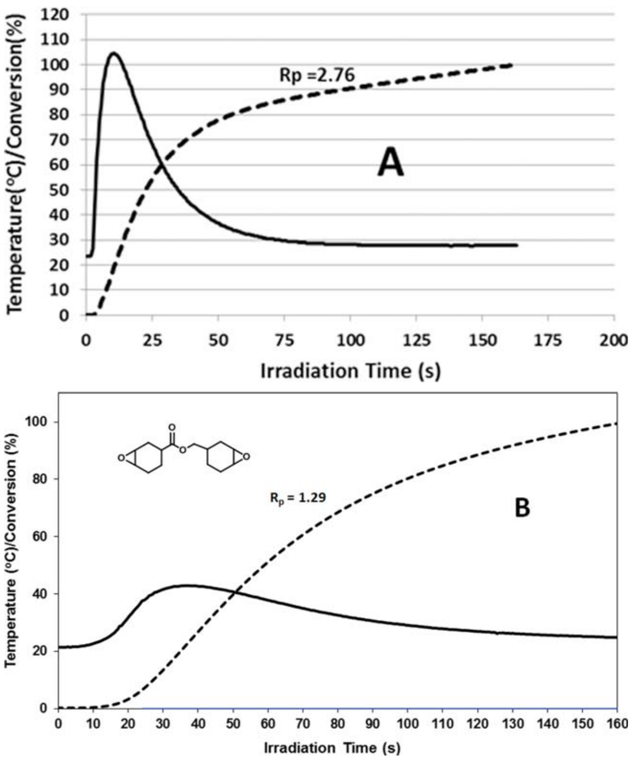
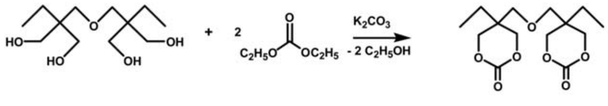


FIGURE 4 OP comparison of the cationic polymerizations of A: an 4:1 molar "kick-started" mixture of DOX and LDO with B: ERL containing 2.0 wt % (0.3 mol %) of SOC-10 SbF_6 (*solid curve*, time vs. temperature plots; *dashed line*, time vs. conversion plots).

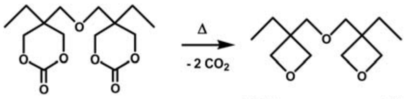
of the photopolymerization of the former "kick-started" oxetane is more than twice that of ERL. Under very similar conditions, the R_p value for the photopolymerization of an 8:1 molar mixture of DOX and LDO was found to be 3.2. It should be noted that integrated curves in both of the studies shown are based on normalized values for the conversion assuming complete conversion of either oxetane or epoxide functional curves. While this assumption appears to be valid for the oxetane system, under the conditions of these experiments, the epoxide conversion for LDO falls considerably short of 100%. Nevertheless, the R_p values taken from the slopes of the initial portions of the integrated temperature versus time OP curves are a reasonable measure of the reactivity of that system.

The bisoxetane monomer, DOX, appears to be an excellent offset for ERL. This monomer is prepared by the straightforward two-step synthesis scheme depicted in equations 8 and 9.[19] Ditrimethylolpropane obtained as a byproduct of trimethylolpropane (TMP).[20] TMP is synthesized by the base-catalyzed sequential aldol condensation and Canazzaro reaction of formaldehyde with butyraldehyde and is widely used in the production of commodity polyesters and polyurethanes. Condensation of ditrimethylolpropane with diethylcarbonate as shown in eq 8 gives the bis(cyclic carbonate), ***5***. Thermolysis of ***5*** (eq 9) in the presence of catalysts such as lithium chloride results in the extrusion of carbon dioxide and the formation of DOX3.[21] DOX is a colorless, high boiling (bp 119 °C/5 mmHg) low viscosity (12.8 mPa s) liquid compound with almost no detectable odor. DOX is also notable for its very low toxicity characteristics.[22]



ditrimethylolpropane

5 (8)



DOX (9)

Replacement of LDO with 2,2,3-trimethyloxirane in a 1:4 molar mixture with DOX gave complimentary results as shown in Figure 5. We have observed that trisubstituted, open-chain epoxides such as 2,2,3-trimethyloxirane display excellent ability to accelerate the overall rates of oxetane monomers. Similarly, a number of terpene epoxides (e.g., 1,2-limonene oxide, alpha-pinene oxide and carene oxide) that possess 2,2,3-trialkylepoxy groups also function well as photopolymerization rate accelerators.[17] The compositions reported in this manuscript have not been optimized with respect to the amounts of oxetane and epoxide modifiers. We have definitively shown that that a 16:1 molar ratio of DOX to epoxide accelerator both increases the rate of oxetane polymerization and also eliminates the induction period. On a weight basis, the inclusion of as little as 3% of LDO is sufficient to "kick-start" oxetane photopolymerizations.

As previously mentioned, the high reactivity of "kick-started" oxetane systems was achieved by a change in mechanism that eliminates the slow, rate-determining step in their ring-opening polymerizations. This results in a shift of the kinetic rate-determining step from equation 3 in Scheme 1 to equation 1 in Scheme 2, that is, the photolysis of the onium salt photoinitiator. Consequently, factors that directly

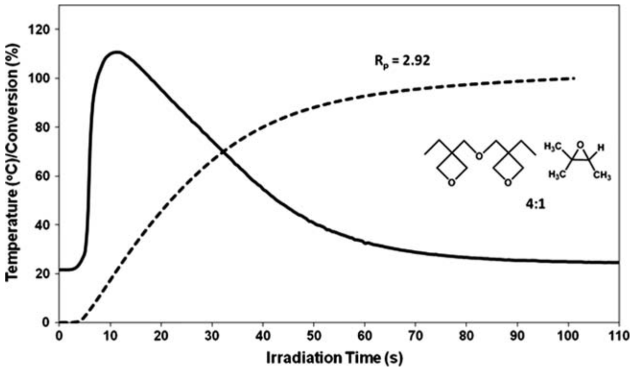


FIGURE 5 Photopolymerization study of a 4:1 mixture DOX and 2,2,3-trimethyloxetane in the presence of 2.0 wt % (0.3 mol %) SOC-10 SbF_6 at a light intensity of 1430 mJ cm^2 min (*solid curve*, time vs. temperature plot; *dashed line*, time vs. conversion plot).

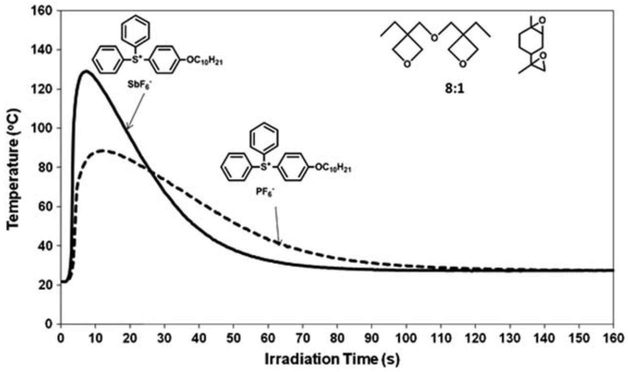


FIGURE 6 OP comparative study of the photopolymerization of an 8:1 molar mixture of DOX and LDO with 0.3 mol % SOC-10 SbF_6 and with 0.3 mol % SOC-10 PF_6 (light intensity 2560 mJ/cm^2 min).

influence the rate of photolysis of the photoinitiator such as photoinitiator concentration, UV absorption characteristics, quantum yields and acidity of the Brønsted acid generated are expected to have a marked impact the overall rate and also the induction period. In general, for a given photoinitiator and "kick-started" oxetane monomer composition, those factors that result in the highest rate of photoacid production are the most beneficial in achieving the highest overall rates. Several further studies were conducted to confirm these conclusions.

A study of the effects of changes in the type of anion present in the photoinitiator on an 8:1 molar DOX/LDO mixture is depicted in Figure 6. The triarylsulfonium salt photoinitiators, SOC-10 SbF_6 and SOC-10 PF_6 were compared at the same molar concentrations in this study. It has been observed that the quantum yields of photolysis of onium salts is dependent on the structures of the organic cation and not on the anion.[1] For that reason, identical amounts of the corresponding Brønsted acids, $HSbF_6$ and HPF_6 are produced per unit time at the irradiation intensity used in the experiment shown in Figure 6. In both cases, the photopolymerizations take place essentially without an induction period and the initial portions of the OP curves are nearly identical. This is a reflection of the high reactivity of the "kick-started" oxetane monomer system. However, thereafter, the overall temperature versus time profiles of the two photopolymerizations are different. As expected, SOC-10 SbF_6 was a more reactive photoinitiator than SOC-10 PF_6 producing a sharper and a higher exotherm. This is due to the fact that $HSbF_6$ generated on photolysis of SOC-10 SbF_6 is a considerably stronger acid and a more efficient polymerization initiator than HPF_6 produced by the photolysis of the corresponding SOC-10 PF_6 photoinitiator. When the integrated curves were constructed from the two OP plots shown in Figure 6, and the R_p values calculated from the slopes of the initial portions of those curves, the rates are rather similar (R_p SOC-10 SbF_6 = 2.7; R_p SOC-10 PF_6 = 2.0). It should be pointed out that these results have considerable practical consequences. Photoinitiators bearing the PF_6^- anion are less expensive than their counterparts bearing the SbF_6^- anion so there is an appreciable economic advantage for the use of a photoinitiator containing the PF_6^- anion.

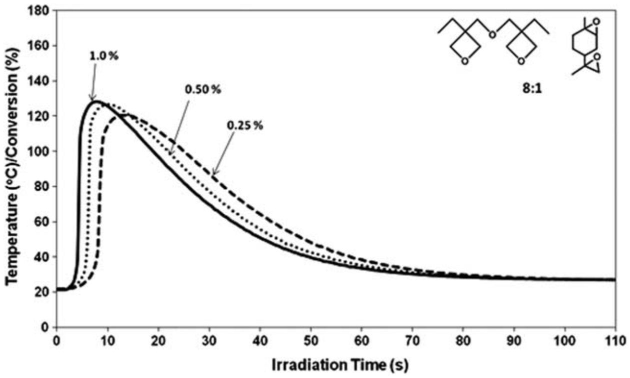


FIGURE 7 Effect of variations in the SOC-10 SbF_6 photoinitiator concentration on the photopolymerization of an 8:1 molar mixture of DOX and LDO (photoinitiator concentrations in wt %, light intensity 1860 mJ/cm^2 min)

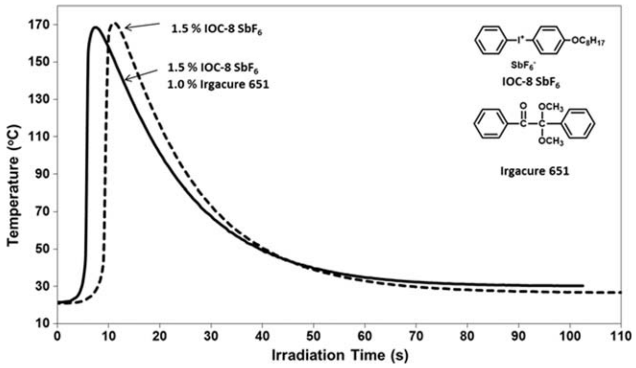


FIGURE 8 Reduction in the induction period of an 4:1 molar mixture of DOX and LDO by the addition of a free radical photoinitiator (Irgacure 651; light intensity 2320 mJ/cm^2 min; photoinitiator concentrations given in wt %).

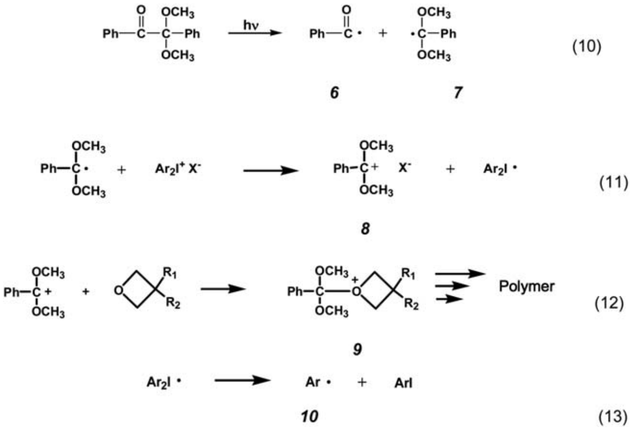
Figure 7 shows the effect of variations in the SOC-10 SbF_6 photoinitiator concentration on the photopolymerization of an 8:1 molar mixture of DOX and LDO. Reducing the photoinitiator concentration from 1.0 to 0.25 wt %, produces only a slight shift in the onset of the polymerization. Even at the lowest photoinitiator concentration (0.25 wt %), the photopolymerization of the "kick-started mixture proceeds rapidly and with nearly the same rapid exothermic behavior as when a four-fold higher photoinitiator concentration was employed.

As an alternative to optimizing the photoinitiator concentration in a given "kick-started" system to achieve the shortest induction period and highest rate of polymerization, means by which the effective quantum yield of the photoinitiator decomposition can be increased were also explored. For example, in Figure 8 is shown a comparative OP study in which a free radical photoinitiator (Irgacure 651, 2,2-

dimethoxy-2-phenylacetophenone) was used to induce the decomposition of the diaryliodonium salt cationic photoinitiator. This effect is well understood.[23–26] The photolysis of both photoinitiators in this system proceed simultaneously under broadband UV irradiation conditions. However, the two photoinitiators possess different absorption characteristics; the diaryliodonium salt has a band at 246 nm and Irgacure 651 has a long wavelength band at 340 nm. Combined, the two photoinitiators absorb a larger portion of the available emission from the broad band mercury arc light source and channel that energy into photolysis of the photoinitiators.

Unimolecular free radical photoinitiators such as 2,2-dimethoxy-2-phenylacetophenone undergo efficient photolysis by an alpha-cleavage reaction as shown in eq 10 of Scheme 3 to afford the benzoyl, ***6***, and dimethoxyphenylmethyl, ***7***, radicals. The reduction of a diaryliodonium salt (eq 11) by ***7*** generates the dimethoxyphenylmethyl carbocation ***8***. Thereafter, ***8*** initiates cationic ring-opening polymerization as shown in eq 12 by direct electrophilic attack on the heterocyclic monomer to given tertiary oxonium ion ***9***. The diphenyliodine free radical, ***10***, irreversibly fragments to give a phenyl radical and iodobenzene (eq 13). Scheme 3 constitutes an independent parallel photochemical process by which the diaryliodonium salt can be caused to generate acid. This process, operating in tandem with the direct photolysis, results in an incremental increase in the amount of strong acid formed during UV irradiation. This results, as shown in Figure 8, in the observed decrease in the induction period. Significant economic trade-offs can be achieved in such "kick-started" oxetane systems through the replacement of a portion of the relatively expensive diaryliodonium salt photoinitiator with an inexpensive free radical photoinitiator.

Dialkylphenacylsulfonium salts, bearing anions derived from strong Brønsted acids undergo photolysis by a different mechanism than their diaryliodonium and triarylsulfonium salt counterparts.[27] As shown in eq 14, photolysis of these former compounds proceeds by a reversible process to yield a sulfonium ylid, ***11***, along with the Brønsted acid corresponding to the anion of the starting sulfonium salt. It was of interest to determine whether such sulfonium salts would be efficient photoinitiators for use in "kick-started" oxetane systems. As the results depicted in Figure 9 show, the answer to this question is a definitive, yes. Employing 3.0 wt % of S-*n*-octyl-S-methyl-S-phenacylsulfonium hexafluoroantimonate (DAPSC1,C8 SbF_6) as the photoinitiator, the usual long induction period (∼33 sec) is observed for pure DOX. However, when an 8:1 molar mixture of DOX and LDO were used, the photopolymerization starts essentially without an induction period. The photopolymerization of this latter mixture is highly exothermic and the films obtained after UV irradiation are colorless, clear and flexible. DAPSC1,C8 SbF_6 is very soluble in the mixture of monomers.



SCHEME 3 Proposed mechanism of the photoinduced free radical decomposition of a diaryliodonium salt by 2,2-dimethoxy-2-phenylacetophenone.

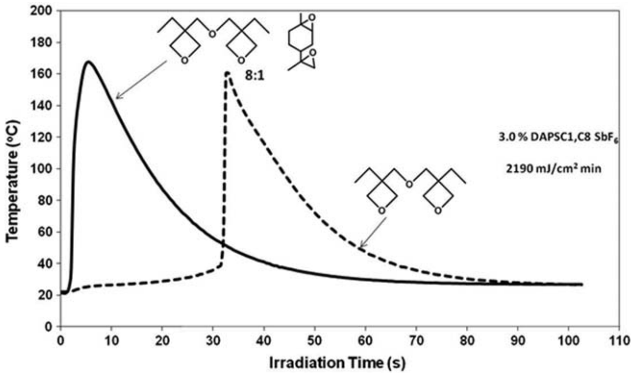
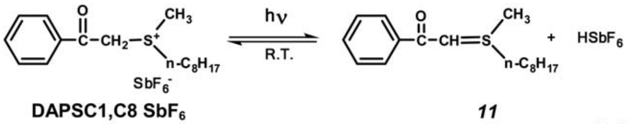


FIGURE 9 Photopolymerization of DOX and an 8:1 molar mixture of DOX and LDO in the presence of 3.0 wt % (0.55 mol %) DAPSC1,C8 SbF_6 as a photoinitiator.



DAPSC1,C8 SbF₆ ***11***

(14)

CONCLUSIONS

Kinetic comparisons of the reactivity of "kick-started" oxetanes with ERL as well as several other types of epoxide monomers in cationic photopolymerizations have shown that the former oxetane systems are considerably more reactive than the latter epoxide ones. The results of the kinetic studies also indicate that in the photopolymerization of these "kick-started" oxetane systems, an extremely favorable situation may be reached in which the rate of the photopolymerization is dependent on the rate of the photolytic generation of the strong Brønsted acid from the photoinitiator. Based on these results, it may be concluded that "kick-started" oxetane systems may find uses in high speed curing of coatings, printing inks, pressure sensitive adhesives, and in 3D printing applications. They could replace epoxide monomers in these as well as in many other commercial photocurable applications.

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