"Kick-Starting" Oxetane Photopolymerizations

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ABSTRACT: In the presence of small amounts of 2,2-dialkyl-, 2,2,3-trialkyl-, or 2,2,3,3-tetraalkyl substituted epoxides such as isobutylene oxide, 1,2-limonene oxide, and 2,2,3,3,-tetramethyl oxirane, the photoinitiated cationic ring-opening polymerizations of 3,3-disubstituted oxetanes are dramatically accelerated. The acceleration affect was attributed to an increase in the rate of the initiation step of these latter monomers. Both mono- and disubstituted oxetane monomers are similarly accelerated by the above-mentioned epoxides to give crosslinked network polymers. The potential for the use of such "kick-started" systems in applications such as coatings, adhesives, printing inks, dental composites and in three-dimensional imaging is discussed. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2934–2946

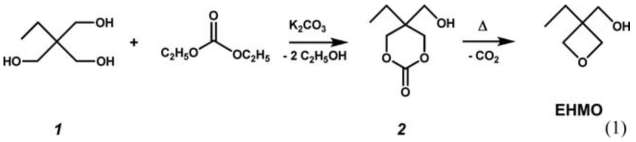
KEYWORDS: cationic polymerization; kinetics (polym.); monomers; networks; photopolymerization

INTRODUCTION Oxetanes are strained, reactive heterocyclic compounds that undergo facile cationic ring-opening polymerization and this topic has been the subject of two review articles.[1,2] Some of the seminal studies of the cationic ring-opening polymerizations of these compounds were performed by Kops et al.,[3–6] Dreyfus and Dreyfus,[7] and by Goethals.[8,9] Oxetanes possess a high degree of ring strain (107 kJ/mol) that is only slightly less than epoxides (114 kJ/mol).[10] On the other hand, oxetanes are considerably more basic ($pK_a = 2.0$) than epoxides ($pK_a = 3.7$).[11,12] These two factors offset one another and lead to the prediction that both classes of monomers should have similar reactivity in cationic ring-opening polymerizations. Despite this conclusion, until recently oxetanes have received comparatively little attention from both academic and industrial researchers while research publications on epoxide monomers, oligomers, and resins abound.

This scenario is slowly beginning to change due to several significant factors. At the present time, epoxide resins based on bisphenol-A and epichlorohydrin have received a great deal of negative press regarding ongoing health and worker safety concerns. Bisphenol-A has been reported to be an estrogen mimic,[13,14] while epichlorohydrin used in the synthesis of these resins is an orally and dermatologically active toxic agent[15] as well as a human mutagen and carcinogen.[16] The corresponding 3,3-disubstituted oxetane monomers do not have these drawbacks and, in general, have low orders of acute and chronic toxicity and are also non-mutagenic.[17] Oxetanes with substituents at the second and fourth positions undergo sluggish cationic ring-opening polymerizations, while those with substituents in the third position are considerably more reactive.

An additional factor that accounts for the relatively slow development of oxetane technology relative to the well-entrenched epoxide chemistry appears to have been the general lack of commercial availability of analogous 3,3-disubstituted oxetane monomers and oxetane functional oligomers. However, in recent years, the development of versatile and practical synthetic methods that afford mono-, di-, and multifunctional 3,3-disubstituted oxetanes in high yields has made these monomers freely available from several commercial sources.

Two of the major synthetic routes for the synthesis of 3,3-disubstituted oxetanes are based on work originating from this laboratory and they are depicted in eqs 1 to 4.[18] In 1957, Pattison[20] showed that 1,3-propane diols could be converted to oxetanes by reaction with diethylcarbonate in the presence of potassium carbonate. Applying this reaction to trimethylolpropane, ***1***, as shown in eq 1 affords the cyclic carbonate, ***2***, as an intermediate which on heating extrudes carbon dioxide to give 3-ethyl-3-hydroxymethyloxetane (EHMO). EHMO is a key intermediate for the synthesis of a wide variety of 3,3-disubstituted oxetane-containing monomers. For example, the reaction of EHMO with α,α'-dibromo-p-xylylene under basic reaction conditions in the presence of a phase transfer catalyst (PTC) gives difunctional oxetane monomer, **XDO** (eq 2).



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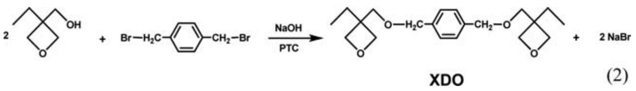
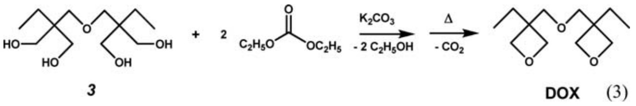


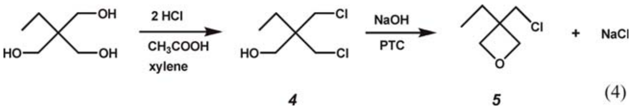
(2)

Applying the ring closure reaction shown in eq 1 to ditrimethylolpropane (*bis*[2,2-dihydroxymethyl)butyl]ether), ***3***, gives difunctional oxetane monomer **DOX** (eq 3).



(3)

A third method involving a dehydrohalogenation reaction is shown in eq. 4.[21] Trimethylolpropane is treated with gaseous HCl in a mixture of m-xylene and acetic acid to give 1,1-*bis* (chloromethyl)−1-hydroxymethylpropane, ***4***. After isolation, ***4*** is dehydrochlorinated with aqueous NaOH in the presence of a quaternary ammonium salt phase-transfer catalyst to give the desired 3-chloromethyl-3-ethyloxetane, ***5***. This latter compound also serves as an intermediate for the preparation of a number of mono- and multifunctional oxetanes. For example, 3-ethyl-3-phenoxymethyloxetane, **POX**, is prepared by an S_N2 reaction of phenol with ***5*** in the presence of a base (eq 5).



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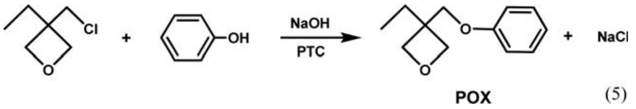
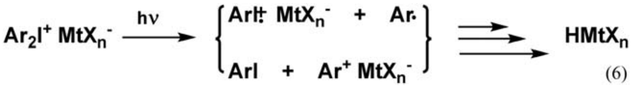


(5)

It is worth noting that the starting materials; trimethylolpropane and ditrimethylolpropane are derived by aldol chemistry from low cost readily available and biorenewable butyraldehyde and formaldehyde. This favorable environmental aspect of oxetane chemistry provides an added attractive incentive for the further development of oxetane monomers and reactive oligomers.

In addition to the oxetane monomers prepared using the three synthetic methods described above, a number of other novel oxetanes have been synthesized such as; silicon-containing oxetanes,[22–24] oxetane-functionallized novolac resins,[25] oxetane-functional polymers for use in organic light emitting diodes (OLEDs)[26] and oxetane esters.[27] These efforts exemplify the great versatility of oxetane chemistry and illustrate the ease with which the oxetane group can be introduced into different substrates to produce polymerizable monomers, polymers and functional oligomers.[28]

The major interest of this laboratory in oxetane chemistry relates to their potential use as cationically photopolymerizable monomers and reactive oligomers in such applications as coatings, adhesives and printing inks. Two especially attractive future uses for photopolymerizable oxetanes are three-dimensional imaging applications (sometimes termed "additive manufacturing") and dental composites. Presented in Scheme 1 is the mechanism that we have previously proposed for the photoinitiated cationic ring-opening polymerization of oxetanes using a diaryliodonium salt as the cationic photoinitiator.[29] A very similar mechanism can be written for the photopolymerization of these monomers using triarylsulfonium salts as photoinitaitors. When onium salt photoinitiators are irradiated with UV light, they undergo very efficient photolysis to generate a number of reactive species that include radicals, cations and cation-radicals (eq 6). Further reaction of these species with water or other protonic species present in the reaction mixture results in the generation of the acid, $HMtX_n$, corresponding to the anion that accompanies the diarylidonium cation in the starting salt. Typically, the anion is selected such that a very strong protonic acid is generated which serves as the initiator (eq 7) for the subsequent polymerization (eqs 8 and 9) of the oxetane monomer. The overall polymerization process is complex, involving three separate steps each with its own characteristic rate constant. From the results of our previous work,[30,31] we suggest that the rate determining step in this reaction sequence is eq 8 (Scheme 1).



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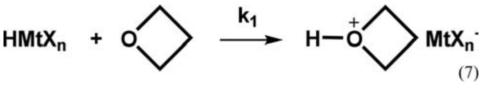

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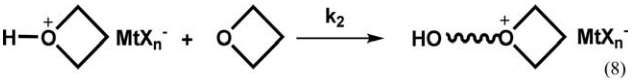

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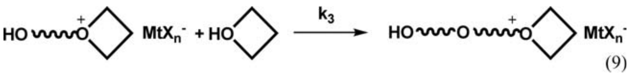


(9)

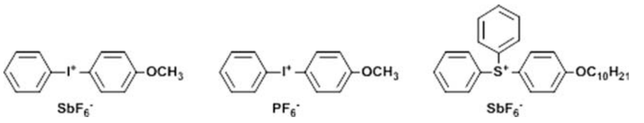
Despite the similarity of their ring-strains and steric hindrance considerations and the SN^2 mechanisms of polymerization, oxetanes display a very sluggish response to onium salt-induced cationic photopolymerizations compared to their epoxide counterparts. Investigations have shown that this apparent sluggish polymerization behavior is manifested in the characteristically long induction periods. These results have been interpreted as due to a higher energy barrier for the ring-opening of the four membered oxetane ring than for the three membered epoxide group.[32,33] During the induction period, we have shown that photolysis of the photoinitiator takes place and that the photogenerated acid that is produced very rapidly protonates the oxetane monomer.[34,35] However, no substantial amount of polymerization takes place at room temperature until the acid concentration reaches a certain threshold required to support a thermally induced autoaccelerated polymerization. Often, this can be observed as a highly exothermic polymerization front that moves rapidly from one part of the sample to another within the irradiation zone. Additionally, the polymerization can be triggered by heating the sample at almost any time within the induction period.

Most importantly, the presence of an extended induction period in the photopolymerization of oxetane monomers is totally incompatible with the rapid response required for many of the high speed applications in which photoinitiated cationic polymerizations are employed. Ideally for such applications, the rate of a photopolymerization should be determined by the rate of the generation of the active species. This implies that in Scheme 1, eq 1 should be the rate determining step. Considerable efforts have been expended in attempts to minimize the induction periods of oxetane monomers or to eliminate them entirely. Most of the investigations in this area have centered about the copolymerizations of oxetanes with epoxide monomers and especially with the commercially available cycloaliphatic diepoxide, 3,4-epoxycyclohexylmethyl 3′4′-epoxycyclohexanecarboxylate.[31,36–38] However, previous work in this laboratory,[39] demonstrated that this latter diepoxide undergoes comparatively slow cationic photopolymerizations in the presence of onium salt photoinitiators. In this communication, we report a new approach towards enhancing the reactivity of oxetane monomers and functional oligomers that is both highly effective and general in its scope.

EXPERIMENTAL

Materials

1,2,8,9-Limonene dioxide, 1,2-limonene oxide, and α-pinene oxide (mixtures of isomers) were provided as samples by Arkema, Inc., Grand Rapids, MI, and purified by fractional vacuum distillation before use. 3,3-*Bis*(chloromethyl)oxetane, isobutylene oxide, (−)-caryophyllene oxide, 2,2,3,3-tetramethyloxirane and other reagents used in this work were obtained from the Aldrich Chemical Company, Milwaukee, WI; 3-carene and camphene were kindly provided as a samples from the S.H. Kelkar & Co. LTD, Bombay, India; 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-phenoxymethyloxetane (POX), 3-ethyl-3-hydroxymethyloxetane (EHMO), *bis*{[(1-ethyl(3-oxetanyl)]methyl} ether (DOX), and 1,4-*bis*[(3-ethyl-3-oxetanylmethoxy)methyl]benzene (XDO) were gratefully received as gifts from the Toagosei Chemical Company, Nagoya, Japan. DOX was purified before use by fractional vacuum distillation (b.p. 117–118/0.6 mmHg). Unless otherwise noted, all other reagents, monomers and photoinitiators were used as received without further purification. A sample of Irgacure 651 was kindly supplied by the Ciba Specialty Products Corp., Basel, Switzerland. The diaryliodonium salt[40] and triarylsulfonium[41] salt 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-1 SbF_6 refers to (4-methoxyphenyl)phenyliodonium hexafluoroantimonate, having the structure shown below in which a methoxy group is attached to one of the phenyl groups in the 4-position, while SbF_6 denotes the hexafluoroantimonate anion. In a similar manner, IOC-1 PF_6 refers to (4-methoxyphenyl)phenyliodonium hexafluorophosphate and SOC-10 SbF_6 refers to S(4-*n*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate with the structures indicated below.



Preparation of Terpene Epoxides

The procedure employed for the epoxidiation of the terpenes described in this communication was adapted from that published by Fieser and Fieser.[42] 3-Chloroperoxybenzoic acid (MCPBA) was purified by washing the commercially supplied compound with a pH 7.5 buffer potassium hydrogen phosphate buffer followed by drying *in vaccuo*.[43] This affords 99% pure MCPBA. The epoxidation of 3-carene is exemplary of the general method employed in this work. There were placed in a 500-mL three-necked flask equipped with a magnetic stirrer, reflux condenser and a thermometer, 13.6 g (0.1 mol) of 3-carene and 120 mL dichloromethane. The reaction vessel was placed in an ice-water bath and 19.5 g (0.113 mol) MCPBA dissolved in 120 mL dichloromethane was added to the reaction vessel via a dropping funnel maintaining the temperature at or below 25 °C. When the addition was complete, stirring was continued for 20 to 30 min at 25 °C. During reaction 3-chlorobenzoic acid was observed to precipitate. The excess peracid was destroyed by the addition of 100 mL of 10% sodium sulfite and then 200 mL 5% sodium bicarbonate solution was added to neutralize the 3-chlorobenzoic acid. The reaction mixture was transferred to a separatory funnel and the layers were separated and the lower organic layer washed with an additional 100 mL 5% sodium bicarbonate solution. This was followed by washing with 100 mL deionized water. The solvent was removed on a rotary evaporator and 14.1 g of a colorless pleasant smelling liquid product were obtained. 3-Carene oxide (a mixture of *cis* and *trans* isomers) was purified by fractional vacuum distillation (b.p. 67 °C/3.30 mmHg; lit.[44] b.p. 52–52 °C/0.3 mmHg).

The same procedure was applied to the epoxidation of camphene. The yield of crude liquid product was 13.95 g. The impure product was subjected to fractional vacuum distillation and the product boiling at 69 °C/0.23 mmHg was collected. Pure camphene oxide had a tendency to crystallize during distillation and on standing and this corresponds to the behavior of this compound as reported in the literature[45] (m.p. 86–88 °C).

(−)-Caryophyllene oxide was purchased from the Sigma-Aldrich Chemical Co. and purified by recrystallization from methanol before use (lit.[46] b.p. 262–264 °C/760 mmHg).

Optical Pyrometry Characterization of Oxetane-Epoxide Photopolymerizations

We have previously described the analytical techniques and apparatus used in this laboratory for optical pyrometry (OP).[47,48] Samples for OP kinetic analysis were prepared by sandwiching a liquid oxetane monomers and mixtures of oxetane and epoxide monomers containing the designated photoinitiator between two thin (12.5 μm) films of fluorinated poly(ethylene-co-propylene) (DuPont FEP thermoplastic film) 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 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 longer 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 (25–28 °C) unless otherwise noted. All monomer concentrations unless otherwise noted are given in moles while the photoinitiator concentrations are given in weight %.

FT-IR Spectroscopy

Fourier Transform infrared (FT-IR) spectra were recorded on a Nicolet 4700 FT-IR spectrometer. The spectra of various liquid reagents, starting materials and the synthesized oligomers were obtained using samples prepared by sandwiching between two KBr plates. Mixtures of the epoxy functional oligomers with dissolved photoinitiators were spread as thin films on a KBr salt plate and covered with a thin film of fluorinated poly(ethylene-propylene) copolymer. The samples were subsequently irradiated through the polymer film for 3 min using a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a liquid optic cable. The measured light intensity was 2200 mJ cm^{-2} min^{-1}. Thereafter, the polymer film was removed and the FT-IR spectrarecorded.

Photosensitized Polymerizations

Irradiation of the 4:1 molar POX:LDO samples in the above described optical pyrometer apparatus was carried out using a UVEX Model SCU-110 spot cure mercury arc lamp equipped with a liquid optic cable. The light beam was passed through a 25 mm dia. Melles-Grigot (Zevenaan, Neth.) MG 03FCG457 glass band pass filter to limit the UV irradiation of the sample to only wavelengths longer than 400 nm. The light intensity used in these experiments was 24 mJ cm^{-2} min^{-1}.

Photopolymerization of POX with 2-Methyl-2,3-epoxybutane for NMR Studies

Placed into a photolysis tube were 1.53 g (8 mmol) POX, 0.086 g (1 mmol) 2-methyl-2,3-epoxybutane, and 0.40 g SOC-10 SbF_6. The reaction vessel was closed with a rubber septum and placed a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co., Hamford, CN) equipped with a merry-go-round holder and 16 low pressure 2537 Å mercury arc lamps. After irradiation for 2 h, the reaction mixture was poured into 100 mL of methanol to precipitate the polymer. A colorless, viscous semi-solid separated and the methanol was removed by decantation and the polymer again extracted three times with 50 mL fresh methanol. The oil was placed in a oven at 120 °C for 2 h to remove solvent. There remained 0.70 g of a clear, colorless tacky solid polymer that was dissolved in $CDCl_3$ and the ^1H-NMR spectrum recorded on a Varian Unity 500, 500 MHz Nuclear Magnetic Resonance Spectrometer with tetramethylsilane (TMS) as the internal standard.

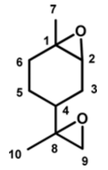
Thin Film Photopolymerization Studies

These photopolymerizations were carried out on a Fusion Systems Model MC 6R microwave-activated 300W electrodeless lamp system equipped with a UV D bulb mounted above a variable speed conveyor. Exposure intensities were measured using a Control Cure Radiometer, UV Process Supply, Chicago, IL. Line speeds were calculated using a stopwatch. The length of the conveyor belt is 120 cm. Uniform 1 mL (25 μm) liquid monomer-photoinitiator films were coated onto steel Q-panels using a drawknife and transferred to the conveyor for curing. Tack-free times were determined by immediately testing the films for tackiness on exiting from the UV cure zone. The UV cured samples were colorless, glossy and hard.

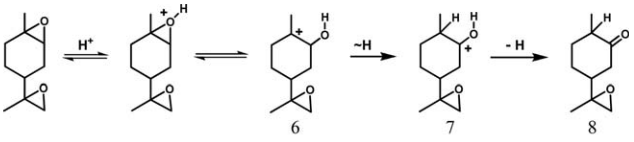
RESULTS AND DISCUSSION

Discovery and proposed mechanism of the “kick-starting” effect

Recent investigations in this laboratory have centered about the development of photopolymerizable epoxy monomers derived from biorenewable sources. Among the several classes of potentially interesting monomers are terpene epoxides. Of particular interest is the monoterpene diepoxide, limonene dioxide (LDO). LDO is prepared by the epoxidation of limonene using peracetic acid. Since limonene is obtained from the steam distillation of waste citrus peels, LDO is potentially a readily available and inexpensive diepoxide. Moreover, LDO is aliphatic and therefore, transparent at wavelengths from 200 to 700 nm making it ideal for UV induced photopolymerizations. Unfortunately, studies in this laboratory have demonstrated that while extraordinarily reactive, the photoinitiated cationic polymerization of LDO is remarkably inefficient. Although LDO is a difunctional epoxide, the cationic photopolymerization of this monomer using onium salt photoinitiators does not yield the expected cross-linked products. Work is continuing to better understand the photopolymerization behavior of LDO and the results of those investigations will be discussed in full in a forthcoming publication.

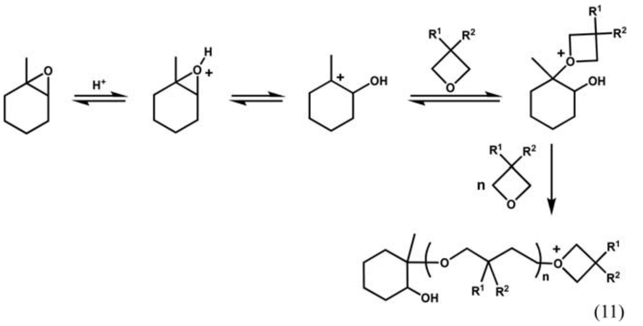


Examination of the structure of LDO reveals that each of the two epoxide groups present in the molecule are unique with respect to their reactivity due to differences in the steric and electronic environments in which they are located. The 1,2-epoxy group bears three alkyl substituents that would tend to enhance its susceptibility towards protonation, however, at the same time, these substituents greatly increase the steric hindrance at this site. Similarly, the 8,9-epoxide group bears two bulky substituents on one of the carbons of the oxirane ring and is, consequently, less sterically hindered than the 1,2-epoxide group in the same molecule. For these reasons, the cationic ring-opening homopolymerization of the 1,2-epoxy group of LDO is very inefficient, while polymerization of the 8,9-epoxide group is considerably more favorable. Further complicating this situation is the occurrence of side reactions at both sites. As shown in eq 10, protonation of the 1,2-epoxide of LDO results in ring-opening to give the tertiary carbocation, ***6***, that can rearrange via oxycarbocation ***7*** to give ketone ***8***. A similar process can take place with the 8,9-epoxide group to give an aldehyde. These rearrangements are very well known to take place with many different 2,2,3-trialkyl-substituted epoxides and 2,2-dialkyl-substituted epoxides from the work of Surya Prakash et al.[49]



(10)

Based on mechanism shown in eq 10, it was predicted that stabilized intermediates such as ***6*** generated from the protonation of 2,2,3-trialkyl epoxides and 2,2-dialkyl-substituted epoxides should exhibit appreciable carbocationic character. Indeed, this conclusion has been verified by the work of Puskas et al.[50–53] who showed that in the presence of Lewis acids, these epoxides serve as initiators for the carbocationic polymerization of isobutylene. Using similar reasoning, we predicted that in the presence of strong photogenerated acids, LDO should protonate to form species such as ***6*** and that these carbocations would be expected to rapidly alkylate the relatively sterically unhindered 3,3-disubstituted oxetanes by a SN^1 mechanism to initiate rapid ring-opening polymerizations. Equation 11 depicts this reaction in which only the 1,2-epoxide of LDO is represented for the sake of clarity.



(11)

Based on this analysis, the photopolymerization of the oxetane monomer, POX, (3-ethyl-3-phenoxymethyloxetane) was carried out in the presence and absence of LDO (2:1 molar mixture of POX and LDO) and the progress of the photopolymerization followed by optical pyrometry (OP). OP has been shown to be a rapid, accurate and reproducible method for monitoring the progress of free radical and cationic photopolymerizations in real-time.[39,40] The initial slope of the time versus temperature OP plot gives a visible assessment of the rate of a photopolymerization and the maximum in the curve directly relates to the overall exothermicity of the polymerization taking place. Of particular interest in these studies is the length of the induction period before the aforementioned polymerization process sets in. The highly soluble triarylsulfonium salt, S(4-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate (abbreviated SOC-10 SbF_6), was used as the photoinitiator in most cases. As shown in Figure 1, there is a dramatic difference in the induction periods of the two photopolymerizations. The photopolymerization of POX displays a long induction period (∼125 s). In contrast, the OP trace of the 2:1 molar mixture of POX and LDO proceeds almost instantaneously when the shutter is opened. A slight, ∼1 s delay is always observed due to the configuration of the sample and results from the time required for the heat of the sample to pass through and reach the surface of the cover film. When the cover film is removed, this delay time is essentially eliminated.

We have termed the effect of LDO on the oxetane monomer "kick-starting" since it results in a very rapid, virtually induction period-free photopolymerization. "Kick-started" photopolymerizations provide systems that have inherently high light sensitivities that are essential for use in imaging applications as well as for the high speed UV cure of thin film coatings. As will be described in this communication, the "kick-starting" effect observed with LDO on oxetane monomers is a general phenomenon that may be applied to many different types of oxetane monomers using 2,2-di-, 2,2,3-tri- and 2,2,3,3-tetraalkyl substituted epoxides as accelerators.

A FT-IR spectral analysis of the photopolymerization of 2:1 molar mixture of POX and LDO is shown in Figure 2. Before UV irradiation, POX does not display a band at 1723 cm^{-1}, nor is there a band at this wavelength in the 2:1 molar

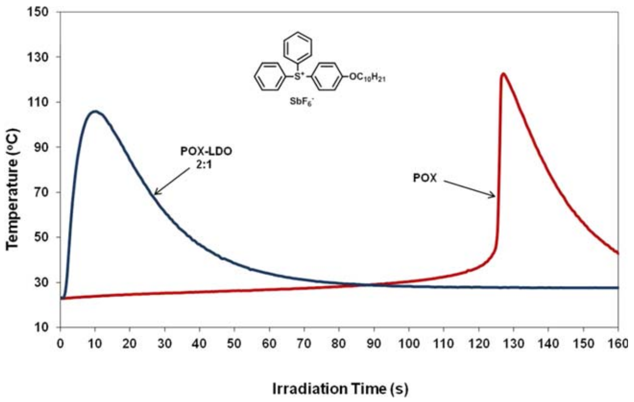


FIGURE 1 OP study of the photopolymerization of POX in the presence and absence of LDO with 4 wt % SOC-10 SbF_6 as the photoinitiator (light intensity 1610 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture of POX and LDO as may be noted in spectrum A of this figure. After photopolymerization (spectrum B), several conspicuous changes take place; including the appearance of a small OH band after polymerization and a ketone peak at 1723 cm^{-1}. The hydroxyl absorption results from the ring-opening addition of the protonic acid to the epoxide and oxetane groups while the appearance of the band at 1723 cm^{-1} indicates that ketone formation (eq 10) is not completely suppressed by the presence of the oxetane monomer. The polymer film formed after irradiation is solid, clear and colorless. It swells but does not dissolve in ethyl acetate indicating that some crosslinking has taken place.

Determination of the effects of experimental variables on "kick-starting"

A study of the effects of the LDO concentration on the photopolymerization of POX was carried out and the results are shown in Figure 3. The molar ratios of POX with LDO ranged from 2:1 to 16:1 while maintaining the SOC-10 SbF_6 concentration at 4.0 wt %. On a weight % basis, the range of LDO in the samples is from 5.2 to 30%. Surprisingly, the results show that even at the lowest concentration, LDO is highly effective in reducing the induction period of the photopolymerization of POX. All the curves are nearly superimposable and this would tend to argue for participation of LDO primarily in the initiation step rather than be simply ascribed to fast copolymerization kinetics.

The results of a study of the effects of the SOC-10 SbF_6 photoinitiator concentration on the photopolymerization of a 4:1 molar ratio of POX to LDO are given in Figure 4. It is interesting to observe that the sample containing lowest (1.3 wt %) photoinitiator concentration displayed the highest maximum temperature response as shown in the OP traces. However, it can be noted that at all three photoinitiator concentrations, the initial portions of the OP curves are very similar. These results again confirm the very high reactivity of this "kick started" monomer system.

Employing POX as a model oxetane monomer and LDO as the accelerator, the effects of the replacement of the triarylsulfonium salt photoinitiator with 2.5 mol % of the analogous (4-methoxyphenyl)phenyliodonium salt photoinitiators bearing both SbF_6^- and PF_6^- anions (respectively designated IOC-1 SbF_6 and IOC-1 PF_6) were examined. The results

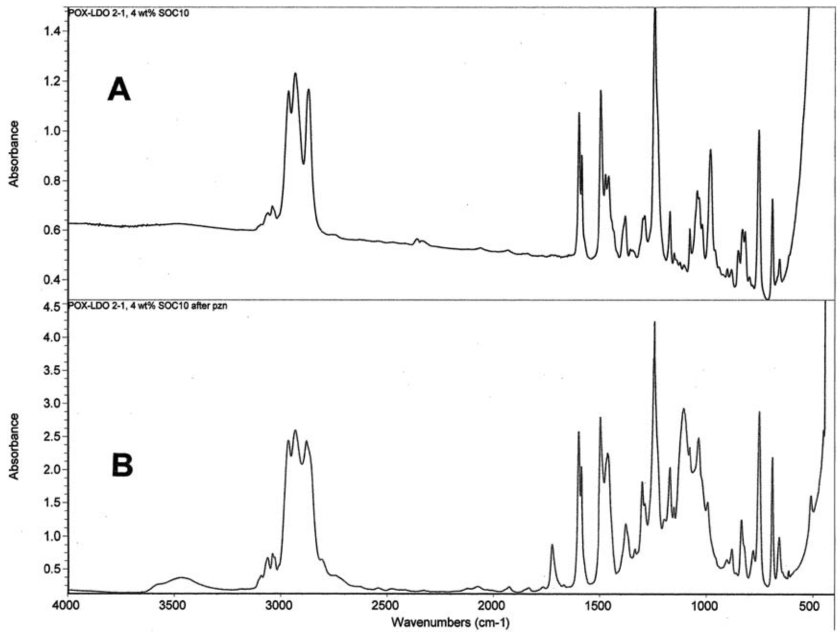


FIGURE 2 OP study of a 2:1 mixture of POX and LDO with 4 wt % SOC-10 SbF_6 before and after photopolymerization. (irradiation carried out at 1610 mJ cm^{-2} min^{-1} for 3 min).

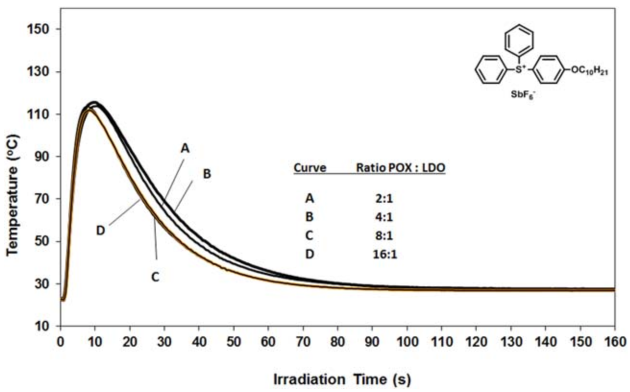


FIGURE 3 OP study of the effect of the concentration of LDO on the photopolymerization of POX in the presence 4 wt % SOC-10 SbF_6 as the photoinitiator (light intensity 1640 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the OP study are given in Figure 5. Also included in this figure for comparison is an OP curve for the photopolymerization of POX alone carried out using 2.5 mol % of IOC-1 SbF_6 as the photoinitiator.

The POX sample with IOC-1 SbF_6^- displays the usual extended induction period, while the two samples containing LDO show extraordinarily high rates of photopolymerization with essentially no induction period. Both of these samples were nearly equal in their photoresponse and independent of the anion present in the iodonium salt. Again, this is the consequence of the very high reactivity of this mixed oxetane-epoxide monomer system.

Oxetane/Epoxide systems that undergo "kick-starting"

Earlier in this communication, the rapid acceleration of the photopolymerization of POX by LDO was attributed to alkylation of the oxetane monomer by carbocations generated by the protonation of the 1,2- and possibly also the 8,9-epoxy groups of LDO by photogenerated Brönsted acids. This suggested that 1,2-limonene oxide (LMO) and α-pinene oxide (PO) should also exhibit similar accelerating effects.

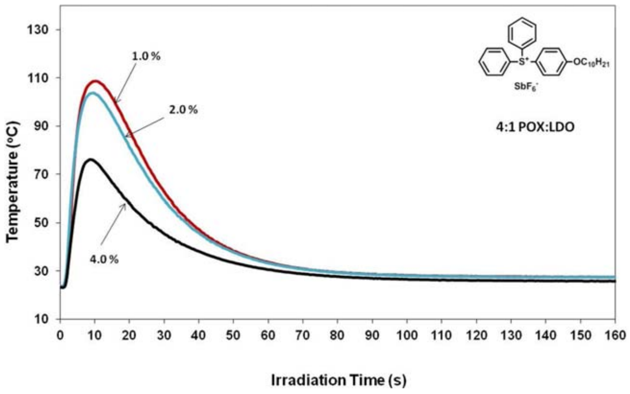


FIGURE 4 Effect of the concentration of SOC-10 SbF_6 on the photopolymerization of a 4:1 molar mixture of POX and LDO (light intensity 1640 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

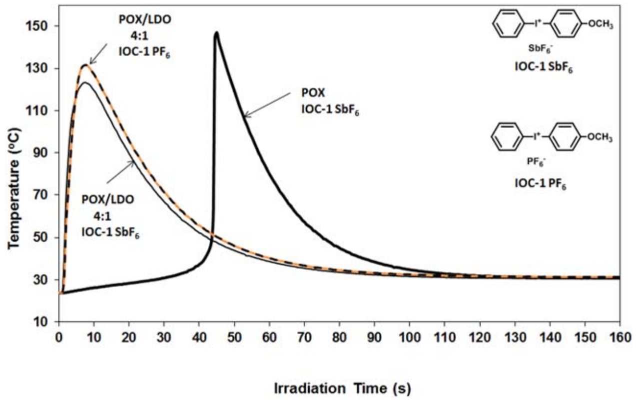
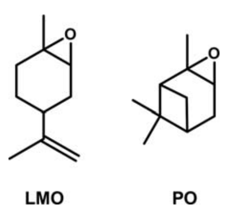


FIGURE 5 Study of the photopolymerization of a 4:1 molar mixture of POX and LDO using (2.5 mol %) IOC-1 SbF_6^-or 0.028 g IOC-1 PF_6^- as photoinitiators. (light intensity 1515 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Accordingly, photopolymerizations were conducted using 8:1 molar mixtures of POX with either LMO and PO and the results are depicted in Figure 6. Included in this figure is a baseline curve for the photopolymerization of POX omitting the epoxide accelerator. The results clearly show that at 9 wt %, both of these two isomeric epoxides are very effective accelerators for the photoinitiated cationic polymerization of POX. LMO appears to be a slightly better accelerator than PO, probably due to less steric hindrance about the reaction site. Previously,[54] we had reported that 30 wt % of PO can be used to accelerate the photopolymerization of DOX, but failed to recognize the significance, scope and magnitude of the acceleration effect.

PO is readily derived by the epoxidation of α-pinene which is one of the main constituents of turpentine. For this reason, like LDO and LMO, PO can be regarded as a sustainable biosourced, monomer. Further, PO is colorless, high boiling (102–103 °C/50 mmHg) and has a very low viscosity which makes it highly attractive as both an accelerator and a reactive diluent.

Pursuing the concept that on protonation, 2,2,3-trialkylepoxides and 2,2-dialkylepoxides generate reactive cationic species, three additional model compound studies were carried out. Accordingly, the ability of 2-methyl-2,3-epoxybutane, **9**,

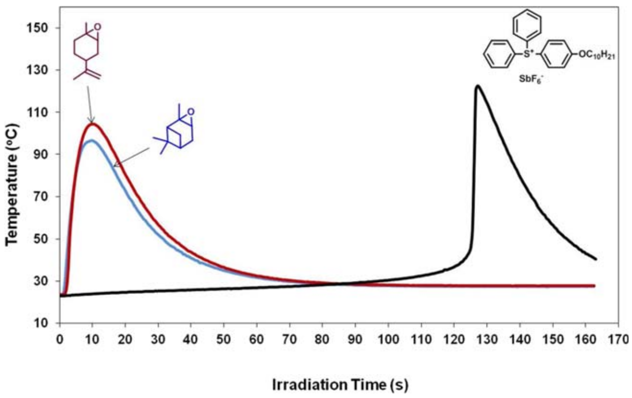
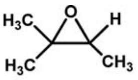


FIGURE 6 Photopolymerization of an 8:1 molar ratio of POX and LMO with 4.0 wt % SOC-10 SbF_6 as the photoinitiator at a light intensity of 1515 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2-methyl-2,3-epoxypropane, **10**, and 2,3-dimethyl-2,3-epoxybutane (2,2,3,3-tetramethyloxirane), **11**, to accelerate the photoinitiated cationic polymerization of POX was evaluated and the results are shown in Figure 7. Both **9** and **10** are close analogues, respectively, of the 1,2- and 8,9-epoxy groups of LDO while it is expected that **11** would undergo facile protonation that would lead to the same tertiary carbocation as formed from epoxides **9** and **10**. Moreover, there appears to be no published report of either the cationic ring-opening homopolymerization of **11** or its copolymerization. In all three instances, 4:1 molar mixtures of POX with the three epoxide model compounds were polymerized using 4.0 wt % of SOC-10 SbF_6. A baseline OP curve for POX alone is included in Figure 7 for comparison. As expected, epoxides **9**-**11** are all excellent accelerators for the photopolymerization of POX. Based on these results, it may be further concluded that both 1,2- and 8,9-epoxy groups of LDO participate in the fast initiation of the ring-opening polymerization of POX providing a unique dual acceleration of the photopolymerizations of oxetane monomers



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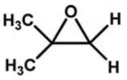

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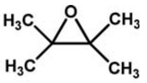

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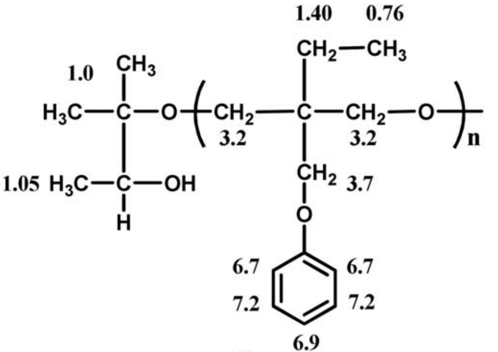
To obtain some structural information concerning the polymers formed using the "kick-starting" approach, a model polymerization was carried out using a neat 8:1 molar mixture of POX and 2-methyl-2,3-epoxybutane with 2.0 wt % SOC-10 SbF_6 as the photoinitiator. The sample was subjected to 2 hr of UV irradiation in a Rayonet Photochemical Reactor, then the polymer was dissolved in chloroform and isolated by precipitation into methanol. After extensive washing, the ^{1}H-NMR of the dried polymer was recorded. The chemical shift assignments for the various protons within the spectrum are given in structure **12**.



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As expected, the dominant peaks in the spectrum are due to the POX repeat units of the poly(oxetane). There is no evidence in the spectrum for the incorporation in the main chain of the oxirane monomer. Relatively small absorption bands at δ1.0 to 1.05 ppm correspond to the methyl protons of the end groups derived from 2-methyl-2,3-epoxybutane. Recently Schulte et al.[55] have published ^{1}H-NMR spectra as well as SEC and MALDI-TOF studies of the cationic ring-opening polymerizations of oxetane monomers. They have shown that in addition to linear polymers, considerable amounts of cyclic oligomers are formed.

A wide variety of naturally occurring terpenes contain double bonds that undergo facile stoichiometric or catalytic epoxidation to afford 2,2,3,3-tetraalkyl, 2,2,3-trialkyl- or 2,2-dialkyl-substituted epoxides. A review article that thoroughly summarizes progress in this area in period from 1988–2008 has been published by Bakhvalov et al.[56] In addition to limonene and α-pinene, some other readily available terpenes are: 3-carene, camphene and caryophyllene. Epoxidation of these three terpenes yields the corresponding terpene epoxides **13**, **14** and **15**. Monoterpene epoxides, **13** and **14**

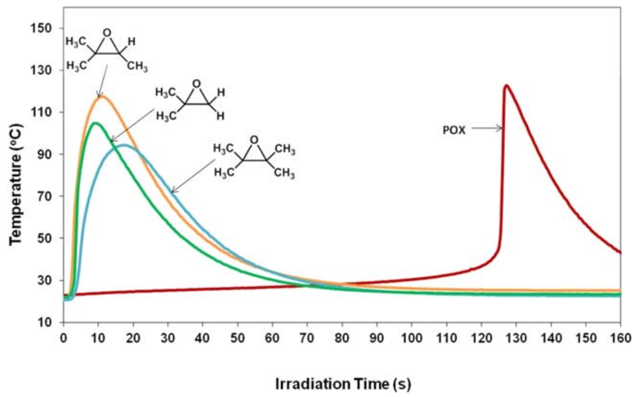


FIGURE 7 Comparison of the photopolymerizations of POX and 4:1 molar mixtures of POX with 2,3-dimethyl-2,3-epoxybutane, 2,-methyl-2,3-epoxybutane and with 2-methyl-2,3-epoxypropane using 4.0 wt % SOC-10 SbF_6 at a light intensity of 1370 mJ/cm^2min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

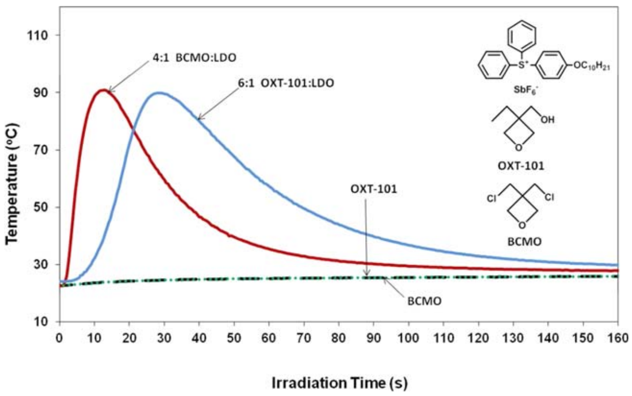
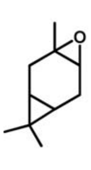


FIGURE 8 OP study of the photopolymerizations of 3,3-bis(chloromethyloxetane) (BCMO) and 3-ethyl-3-hydroxymethyloxetane (EHMO) alone and as mixtures with LDO (4.0 wt % SOC-10 SbF_6, light intensity 1640 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(mixtures of isomers) were observed to be potent accelerators for the photoinitiated cationic ring-opening polymerization of oxetane monomers. For example, the photoinitiated polymerizations of 8:1 molar mixtures of POX with **13** or **14** together with 4.0 wt % of SOC-10 SbF_6 as the photoinitiator take place very rapidly, are highly exothermic and occur without an induction period. This is especially, impressive in view of the fact that these two compounds possess high levels of steric hinderance about the epoxide reaction site. Under the same conditions, the sesquiterpene epoxide, caryophyllene oxide, **15**, does not display the same ability to markedly reduce the induction period in the photopolymerization of POX as epoxides **13** and **14**. The specific reason(s) for this anomalous behavior is unknown at this time. However, molecular modeling showed that due to the fused four-membered ring, the exocyclic double bond, the *trans*-epoxide group, and the nine-membered ring, **15** is a conformationally very rigid cyclic molecule in which access to the epoxide group is severely restricted. We suggest that a combination of these factors results in the observed poor reactivity of caryophyllene oxide as an accelerator for oxetane photopolymerizations.



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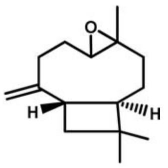

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In a direct analogy to the results described above, other terpene epoxides such as those derived from β-pinene, myrcene, farnesene, squalene, γ-terpinene, and natural rubber are expected to behave as photopolymerization accelerators for oxetanes. Like limonene, some of these terpenes, such as terpinolene,[57] contain multiple alkene sites that can be epoxidized. These terpene epoxides should provide interesting ways to both accelerate the photopolymerizations of oxetanes as well as modify the nature of the resulting crosslinked networks.

It was of some interest to examine the scope of the accelerating effects of LDO and the other related epoxides on the photopolymerizations of monomers with different oxetane structures. Figure 8 displays the results obtained when 3,3-*bis*(chloromethyl)oxetane (BCMO) and 3-ethyl-3-hydroxymethyloxetane (EHMO) are photopolymerized alone and mixtures with LDO. In both cases, 4 wt % SOC-10 SbF_6 was used as the photoinitiator The polymerizations of both these monomers occurs very slowly in the absence of LDO. However, a dramatic and very rapid polymerization of BCMO takes place with no induction period when LDO is added. The results are very comparable to those previously obtained with POX. Although the reactivity of EHMO is somewhat lower than either BCMO or POX, the addition of LDO profoundly accelerates the polymerization.

It was of special interest to determine whether the acceleration with LDO and the other related epoxide accelerators could also be applied to the photopolymerizations of difunctional oxetane monomers since those monomers are of most importance for use in many practical applications. Shown in Figure 9 is a side-by-side comparison of the reactivity of 3-ethyl-3-{[(3-ethyloxetane-3-yl)methoxy]methyl}oxetane (DOX) and a 2:1 molar mixture of DOX with LDO carried out in both cases using 4.0 wt % SOC-10 SbF_6.

The DOX reference sample shows the typical, very long induction period (longer than 3 min) during which little polymerization takes place under continuous UV irradiation. At the same time, irradiation produces almost an instantaneous polymerization response in the 2:1 molar mixture of DOX and LDO. The difference is dramatic. After photopolymerization, a clear, colorless, tack-free film of the DOX-LDO sample was obtained. The film was somewhat brittle when creased. The polymer was insoluble in chloroform, ethyl acetate and acetone.

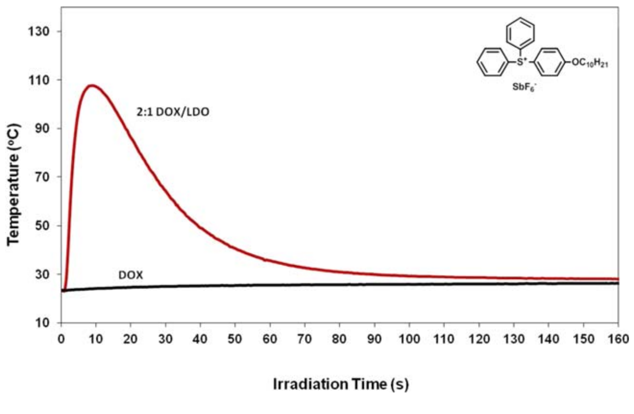


FIGURE 9 Acceleration of the photopolymerization of DOX by LDO (2:1 molar mixture) in the presence of 4.0 wt % SOC-10 SbF_6 compared to DOX without LDO. (light intensity 1640 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

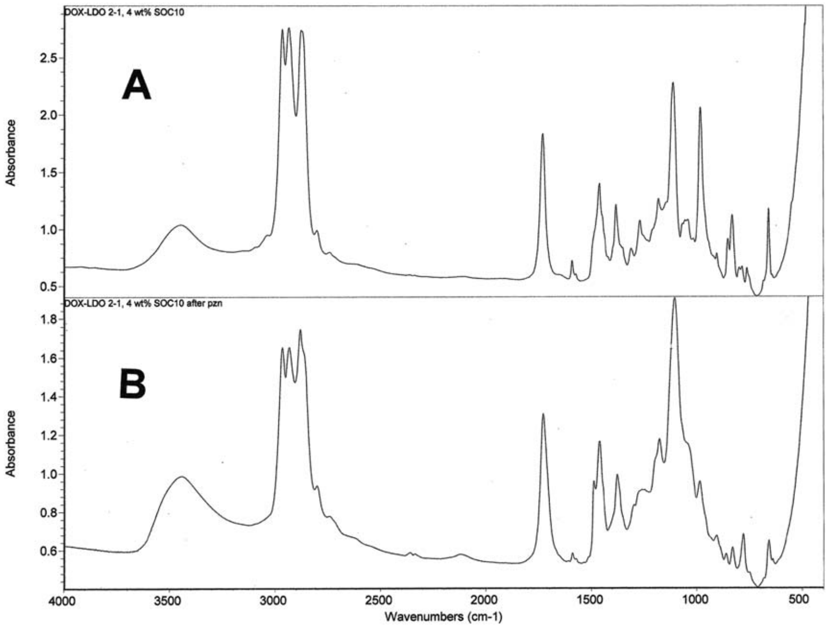


FIGURE 10 FT-IR of a 2:1 molar mixture of DOX and LDO containing 4.0 wt % SOC-10 SbF_6, A, before photopolymerization and B, after polymerization. (UV irradiation carried out at 1640 mJ cm^{-2} min^{-1} for 3 min).

The course of the photopolymerization was also followed by FT-IR with the DOX/LDO mixture deposited on a KBr disc and the results are presented in Figure 10. The DOX monomer used in this study possesses a strong carbonyl peak at 1728.5 cm^{-1} probably due to residual cyclic carbonate linkages remaining from incomplete monomer synthesis. Before photopolymerization, the IR also shows the presence of a small OH peak. Commercially supplied DOX contains a number of volatile and nonvolatile impurities. Even after attempted purification by vacuum fractional distillation, the above-mentioned peaks are reduced in intensity but remain and it appears that some impurities may co-distill with DOX. After photopolymerization, the 3038 cm^{-1} peak associated with the 8,9-epoxide of LDO disappears. A band at 980.8 cm^{-1} that is unique to DOX also vanishes. A ketone band from rearrangement of the 1,2-epoxy group of LDO usually appearing at 1722 cm^{-1} could not be detected.

A similar OP photopolymerization study was carried out with 1,4-*bis*{[(3-ethyloxetan-3-yl)methoxy]methyl}benzene (XDO) and is shown in Figure 11. As can be observed in the OP trace, pure XDO undergoes very sluggish photopolymerization that may be partially due to the high viscosity of this monomer. On the other hand, the inclusion of LDO greatly accelerates the photopolymerization of XDO, although even this accelerated photopolymerization may still be partially impeded by viscosity effects.

As mentioned previously in this communication, the use of epoxides such as 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL) to accelerate the cationic ring-opening polymerization has been reported by several investigators.[19,33,34] It seemed worthwhile to compare the accelerating behaviors of both LDO and ERL on the same oxetane monomer. The results of this study are displayed in Figure 12 and they show that on a molar basis, LDO is a much better accelerator for the photopolymerization of DOX than ERL. A 2:1 molar mixture of DOX and ERL has nearly the same OP profile as that of a 4:1 molar mixture of DOX with LDO. The effect is even more dramatic if the two mixtures are compared on a weight basis. Decreasing the amount of ERL in the mixture to give a 4:1 molar mixture with DOX results in an appreciably longer induction period. Very similar results were observed when the highly reactive diepoxide monomer 4-vinyl-1,2-cyclohexene dioxide was compared to LDO in the photopolymerization of POX. LDO was a much

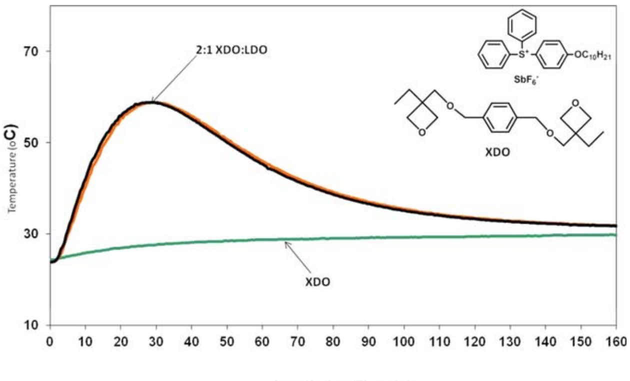


FIGURE 11 Acceleration of the photopolymerization of XDO by LDO (2:1 molar mixture) in the presence of 4.0 wt % SOC-10 SbF_6 (duplicate runs shown) compared to XDO without LDO. (light intensity 1640 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

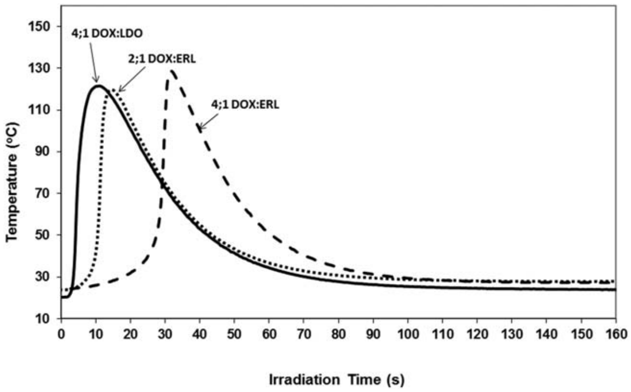
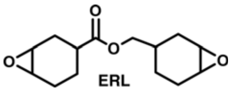


FIGURE 12 Comparison of the photoresponse of various mixtures of DOX with LDO and ERL. All photopolymerizations were conducted at 1600 mJ cm^{-2} min^{-1} with 2 wt % SOC-10 SbF_6 as the photoinitiator.

more effective accelerator for POX than 4-vinyl-1,2-cyclohexene dioxide.



Comparison of "kick-started" oxetanes with acrylate systems

Shown in Figure 13 is an interesting comparison of the photopolymerizations of a 4:1 molar mixture of DOX and LDO containing 2 wt % SOC-10 SbF_6 as the photoinitiator with 1,6-hexanediol diacrylate (HDODA) and 2% 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) as the free radical photoinitiator. While the diacrylate is clearly displays almost no induction period and a very high exotherm, the cationic oxetane system accelerated by LDO compares very favorably.

Photosensitized Polymerization

Photosensitization is an effective strategy for broadening the spectral response of cationically polymerizable monomer systems. The ability to "tailor" the spectral response of a given system is essential to their implementation in applications such as imaging, additive manufacturing, medical adhesives and dental composites that employ long wavelength UV or visible light. Considering the high sensitivity of the current "kick-started" oxetane systems, it was of interest to demonstrate that these materials can be photosensitized to long wavelength UV and visible radiation. Recently, phenothiazines and benzoxazines were reported to be efficient photosensitizers for the photolysis of triarylsulfonium salts.[58] Accordingly, two sample 4:1 molar mixtures of POX and LDO containing 1 mol % SOC-10 were prepared. To one of the samples there were added 0.5 mol % benzo[b]phenothiazine as a photosensitizer. The OP apparatus was modified to interpose a band pass filter in the light beam to allow the passage of only of wavelengths greater than 400 nm. The results of the study are presented in Figure 14.

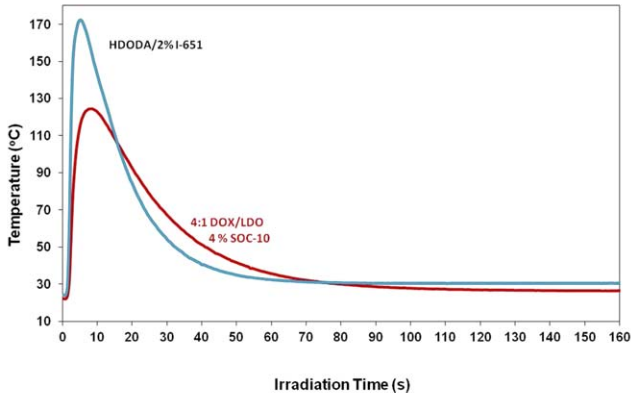


FIGURE 13 Comparison of the photopolymerizations of a 4:1 DOX-LDO mixture containing 2 wt % SOC-10 SbF_6 as the photoinitiator with the 1,6-hexanediol diacrylate (HDODA) with 2 wt % Iragcure 651. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The presence of the band pass filter greatly attenuates the incident light that reaches the sample plane. Despite the extremely low light flux levels (24 mJ cm^{-2} min^{-1}), the photopolymerization response of the 4:1 mixture of POX and LDO is excellent (curves for duplicate runs are depicted). No appreciable induction period is evident. In contrast, the sample containing no photosensitizer is completely unresponsive during the entire 3 min of continuous irradiation period of this study.

Thin Film UV Cure Studies

The results obtained from the OP studies described above strongly suggested that oxetane monomers accelerated by LDO, LMO, and PO possess rapid photopolymerization rates that that may be compatible with those required for thin film applications such as decorative and protective coatings for metals, plastics and glass, as well as for printing inks and adhesives. To provide confirmation of this conclusion, thin

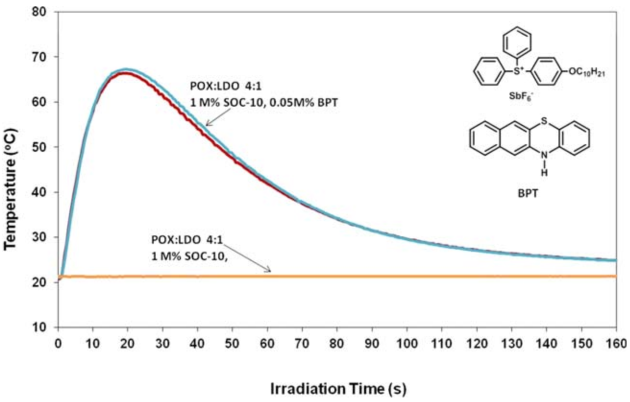


FIGURE 14 Photosensitized polymerization of a 4:1 molar mixture of POX and LDO with 1.0 mol % SOC-10 SbF_6 alone and in the presence of 0.5 mol % benzo[b]phenothiazine (light intensity 24 mJ cm^{-2} min^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

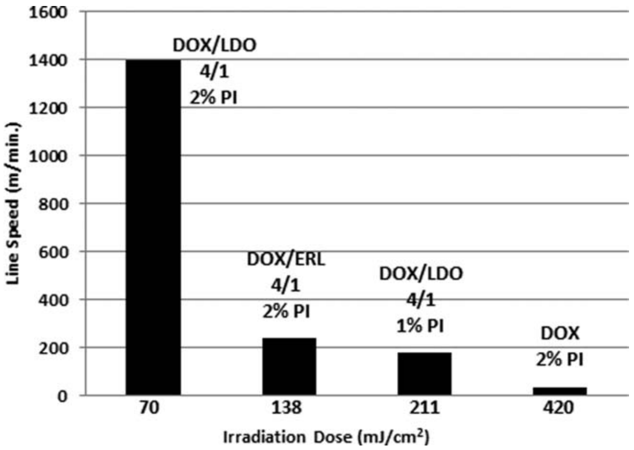


FIGURE 15 Thin film UV cure studies (PI = SOC-10 SbF_6).

film UV cure studies were conducted using a conveyorized Fusion Systems UV cure apparatus equipped with a 300 W microwave-activated mercury arc lamp. Films were drawn onto steel test panels using a drawknife with a 1 mL (25 μm) gap and placed on the moving conveyor for UV irradiation. The films were tested for tackiness immediately on exiting from the irradiation zone. The maximum conveyor speed and irradiation dose required to reach the tack-free state were recorded and the results are included in bar graph shown in Figure 15. Four different oxetane and oxetane-epoxide mixtures were tested using the above protocol: (1) a 4:1 molar mixture of DOX and LDO with 1.0 wt % SOC-10 SbF_6; (2) a 4:1 molar mixture of DOX and LDO with 2.0 wt % SOC-10 SbF_6; (3) a 4:1 molar mixture of DOX and ERL with 2.0 wt % SOC-10 SbF_6; and (4) DOX with 2 wt % SOC-10 SbF_6. All the fully UV cured samples were colorless, glossy and hard.

The thin film UV cure results confirm the conclusions made on the basis of the OP observations. Using 1.0 wt % SOC-10 SbF_6, the maximum conveyor speed that was measured was 80 m/min with a 4:1 mixture of DOX and LDO. With 2.0 wt % of photoinitiator, it was possible to attain cure speeds of at least 1200 m/min with the same mixture of DOX and LDO. At these high speeds, it was only possible to determine approximate values for both the line speed and dose and the actual values may be considerably higher. In contrast, when LDO was omitted, cure was not observed with POX alone even at the slowest speed (80 m/min) and highest dose of UV radiation (420 mJ cm^{-2}) used. The maximum cure speed for the 4:1 molar DOX/ERL mixture lies between 180 and 240 m/min., indicating that ERL is considerably less efficient than LDO in accelerating DOX photopolymerization.

CONCLUSIONS

In this communication, the acceleration of the cationic ring-opening photopolymerizations of a number of mono- and difunctional oxetanes by coreaction with limonene dioxide as well as a number of other 2,2-di-, 2,2,3-trialkyl and 2,2,3,3-tetraalkyl-substituted epoxides was demonstrated. In all but one case (caryophyllene oxide), these epoxides were highly effective in accelerating the photopolymerization of 3,3-disubstituted oxetanes by markedly reducing the induction periods. We have termed this acceleration effect as “kick-starting” and have proposed that the protonation of the epoxide generates a carbocationic species that rapidly and efficiently alkylates the oxetane monomer thereby initiating polymerization. While these same epoxides also provide appreciable acceleration effects for the photoinitiated cationic ring-opening polymerization of other epoxides such as alkyl glycidyl ethers, the effects are much less. Therefore, the results reported here appear to be unique for 3,3-disubstituted oxetane monomers.

The aforementioned epoxides are effective oxetane photopolymerization accelerators at low concentrations. This discovery makes oxetane-based monomer systems potentially interesting for a wide variety of applications such as in coatings, adhesives, printing inks, composites, and three-dimensional imaging where high rates of photopolymerization are required. An especially interesting potential application lies in the use of the “kick-started” oxetane systems described in this article in photocurable dental composites. The main attractive feature of these systems in this specific application lies in their inherent low volume shrinkage during photopolymerization.[27,59] The volume shrinkage for oxetanes (e.g. XDO 3.9%) is substantially lower than for comparable epoxides and is much lower than for acrylate or methacrylate monomers.[60] Cure shrinkage is one of the main contributors to failure of dental composites and the reoccurrence of dental caries. Accordingly, oxetane monomers have been targeted for use in dental composite applications.[61] Similarly, low volume shrinkage is also a major factor in the selection of photopolymer systems for additive manufacturing applications where a high degree of image fidelity and lack of distortion are required.

Preliminary studies have also shown that the thermally induced and redox initiated cationic polymerizations of oxetane-limonene dioxide mixtures display very similar “kick-started” behavior. Work in this area is continuing and the results will be reported in a forthcoming publication.

REFERENCES AND NOTES

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