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Investigation of the photoactivated frontal polymerization of oxetanes using optical pyrometry

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Abstract

An investigation of the photoactivated cationic ring-opening frontal polymerization of a series of 3,3-disubstituted oxetanes was carried out with the aid of a novel technique, optical pyrometry. Using this technique, the effects of various experimental parameters such as photoinitiator type and concentration, light intensity and sample configuration as well as the effects of monomer structure on the frontal behavior of these monomers were examined. Upon photoactivation with UV light, 3,3-disubstituted oxetanes display a long dormant period at room temperature as the result of the formation of metastable tertiary oxonium ions. Only small amount of thermal activation energy is required to induce the further reaction of these species with resulting exothermic autoaccelerated ring-opening polymerization. Frontal polymerization was observed for both mono- and difunctional oxetane monomers and the velocity of propagation of a given monomer was found to be related to its oxetane equivalent weight.

Keywords: Photopolymerization; Frontal polymerization; Cationic polymerization

1. Introduction

The ability of many highly exothermic chemical reactions such as combustion processes to propagate along a well-defined self-sustaining front has been long noted. Chechilo and Enikolopyan were the first to report that certain free radical polymerizations can also be made to proceed in a frontal manner [1,2]. Due to these observations, considerable interest and activity developed in this area and resulted in rapid progress [3–5] so that reviews on the topic of frontal polymerization were published first by Davtyan et al. [6] in 1984 and again in 1996 by Pojman [7]. The area of the free radical frontal polymerization of acrylates and methacrylates remains an active area of research today. Although the bulk of the work in frontal polymerizations has been focused on free radical chain reactions, it was found that many other types of addition as well as condensation polymerizations can also proceed by a frontal mechanism [8]. Prominent among these are the cationic frontal ring-opening polymerizations of oxirane (epoxide) monomers [9,10]. Free radical and cationic addition polymerization reactions are especially well suited to frontal processes since they are often highly exothermic events. Typically, such self-propagating polymerizations take place as a result of the thermal decomposition of a free radical or cationic initiator at the hot reaction front. Once such a polymerization starts, it accelerates and proliferates due to the formation of a large number of active centers that liberate more heat as the polymerization proceeds.

The usual means of starting or 'igniting' a frontal polymerization is to apply a localized heat source to a small portion of the reaction mass. Recently, it has been shown that both free radical [11] and cationic [10] frontal polymerizations can be ignited by UV irradiation in the presence of an appropriate photoinitiator. In both instances, a conventional thermal free radical initiator was also added that sustains the thermally driven frontal polymerization. In marked contrast to these previous papers, in two recent preliminary articles [12,13] from this laboratory we have reported that the self-sustained cationic frontal polymerizations of certain oxiranes and oxetanes can be achieved by a two-step process involving first, photoactivation then, in a second step, a thermally induced frontal polymerization. The mechanism of this process is shown in Scheme 1 in which oxetane is depicted for simplicity. In the first step, photolysis of the cationic photoinitiator takes place (Eq. (1)) with very fast, nearly instantaneous protonation of the monomer (Eq. (2)) by

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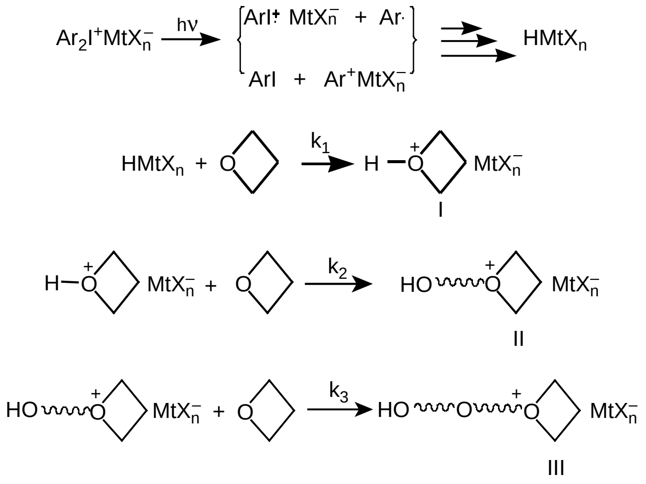


Scheme 1. Mechanistic scheme for photoactivated cationic ring-opening polymerizations.

the photogenerated Brønsted acid. Also rapid is the subsequent reaction of the initially formed protonated species, **I**, with monomer (Eq. (3)) to form the corresponding tertiary oxonium ion, **II**. The tertiary oxonium ions have previously [14] been shown to possess considerable stability and to persist in the reaction mixture for hours eventually going on to form polymer, **III** (Eq. (4)). Little visible change takes place on irradiation of an oxetane monomer in the presence of the photoinitiator both with respect to the appearance of the solution or its viscosity. Infrared spectral and NMR spectral analysis of the irradiated monomer mixture confirms that very little conversion of monomer to polymer has occurred. Such 'photoactivated' 3,3-disubstituted oxetane monomer solutions containing dormant tertiary oxonium ion species are quiescent and can be stored for hours at room temperature and for days at low temperatures without substantial change. However, when a localized heat source is applied to a previously irradiated film of the monomer, vigorous polymerization is observed to emanate outward as a front from that site to consume the entire irradiated sample. It was observed that only a modest temperature rise, well below the onset of the thermal decomposition of the photoinitiator, was required to ignite the frontal polymerization. Frontal polymerization does not extend to regions of a sample that are not activated by irradiation.

The unique ability to separate the 'photoactivation' step from the actual frontal polymerization, suggested many potential applications for these cationic oxetane polymerizations. For example, photopolymerizations cannot be employed in adhesive applications where both of the substrates to be bonded are opaque to light. However, a photosensitive epoxide or oxetane adhesive applied to one substrate surface can be first activated by exposure to light, then covered with the other substrate and thermally induced frontal polymerization conducted. This results in the effective bonding of the two opaque substrates. This and other potential applications will be explored in more detail later in this article. Highly promising monomers for such applications are 3,3-disubstituted oxetanes since they were observed to display well-behaved frontal behavior due to the high ring-strain (16–20 kcal mol^{-1}) [15] together with excellent latency in the postirradiated state. In addition, a variety of these monomers are now commercially available from several sources due to the development of efficient, low-cost methods for their synthesis. For these reasons, an in-depth study was conducted using these monomers to determine the effects of various experimentally controlled parameters on both the stability of the postirradiated monomer solutions and their reactivity in the subsequent thermally induced frontal polymerizations. The results of this study are reported in this article.

2. Experimental section

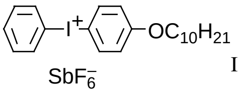
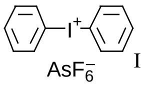
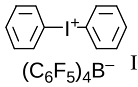
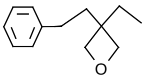
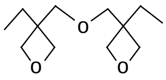
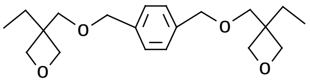
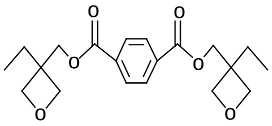
2.1. Materials

All organic starting materials and reagents employed in this investigation were reagent quality and were used as purchased unless otherwise noted. The oxetane monomers 3-ethyl-3-[(phenoxy)methyl]oxetane (POX), bis{[1-ethyl(3-oxetanyl)] methyl} ether (DOX), and 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene (XDO) used in this work were kindly provided as gifts by the Toagosei Chemical Company, Ltd, Nagoya, Japan. 1,4-Bis[(3-ethyl-3-oxetanylmethoxy) methyl]terephthalate (OXT) was donated by Ube Industries, Ltd, Tokyo, Japan. The diaryliodonium salt photoinitiators used in this work were prepared as described in an earlier publication [16] from this laboratory. The structures of all the monomers and photoinitiators used in this work are shown in Table 1 together with their abbreviations. All concentrations used in this article are given in mol% based on the oxetane content of the monomer used.

2.2. Monitoring the photoactivated cationic frontal polymerizations of 3,3-disubstituted oxetanes using optical pyrometry (OP)

The basic optical pyrometry apparatus and method employed for monitoring the photopolymerizations carried out in this investigation were recently described in an earlier communication from this laboratory [17]. A schematic drawing of the OP instrument and details of the design of the sample holders are depicted in Fig. 1. Samples for analysis were prepared by dissolving the photoinitiator in the desired monomer and placing them in the sample holders. The sample holders used for monitoring the frontal polymerizations were constructed by milling a 8 mm wide × 40 mm long channel in a 5 cm × 5 cm × 3.5 mm block of poly(tetrafluoroethylene) (PTFE). Three versions of the sample holders respectively with channel depths of 1, 2 and 3 mm were fabricated. Prior to analysis, a sample holder filled with the liquid monomer/photoinitiator mixture was placed in the OP apparatus and irradiated using a UVEX spot cure UV lamp system equipped with a liquid optic cable. Various light intensities

Table 1
Structures of monomers and photoinitiators used in frontal polymerizations

 IOC-10 SbF_6 IOC-10 SbF_6	 IOC AsF_6 IOC AsF_6	 IOC $(C_6F_5)_4B$ IOC $(C_6F_5)_4B$
 POX	 DOX	 XDO
	 OXT	

and irradiation times were employed and are noted in the figure captions. The liquid optic cable allows the passage only of light with wavelengths greater than 300 nm. Infrared radiation (heat) is also excluded by the fiber optic cable. The position of the focal point of the pyrometer was adjusted with the use of a laser sight to be at the center and at one end of the channel. The frontal polymerization was initiated at the other end of the channel by an electrically heated chromel wire formed into a sharp tip that was immersed in the monomer at a predetermined position along the channel. Unless otherwise indicated, the path length of the front was 4.0 cm. The polymerization front was detected by the optical pyrometer as it passed the focal point of the instrument in the channel. Temperature data were collected at a rate of 1 measurement per second and directly recorded and downloaded to an IBM 350-P137 personal computer for analysis. The time at which the temperature departs from the baseline is taken as the front time, t_f. The front velocity, V_f was calculated according to Eq. (5). Also recorded was the maximum temperature of the front, T_f.

$$V_f = \frac{\text{path length}}{t_f} \tag{5}$$

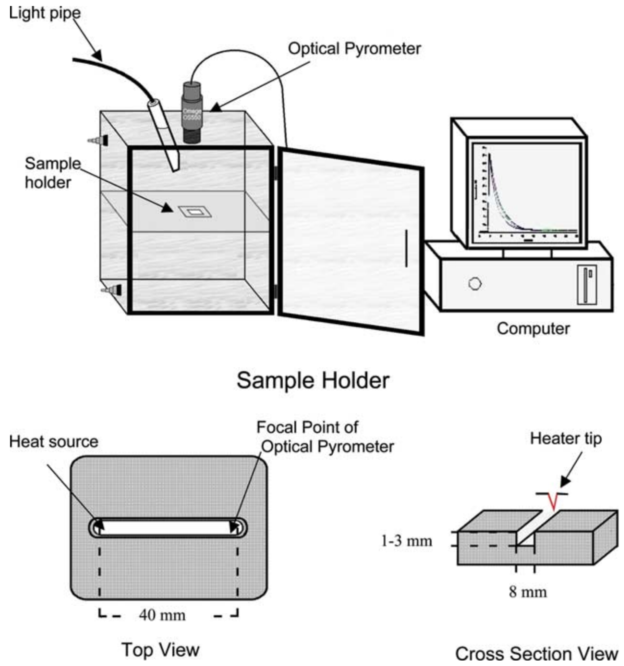


Fig. 1. Schematic diagram of the optical pyrometer apparatus employed for the monitoring of frontal polymerizations.

2.3. OP monitoring of the ignition temperature for oxetane frontal polymerizations

Samples for analysis were prepared by sandwiching a liquid monomer containing the designated photoinitiator between two thin (5 μm) films of DuPont fluorinated poly(ethylene-propylene) (FEP) 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 of the optical pyrometer instrument for analysis. The average thickness of the samples was 0.40–0.45 mm. Irradiation with ‘cold’ UV light for a specific time was accomplished as previously described using a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a liquid optic cable. After the irradiation period, a heater was turned on in the instrument and the temperature of the sample monitored as a function of time as the sample was slowly heated. The ignition temperature (T_{ig}) was taken at that point at which the temperature markedly departs from the base line due to the generation of a frontal polymerization.

3. Results and discussion

3.1. Development of optical pyrometry to monitor frontal polymerizations

Requisite for our study of the photoactivated cationic frontal ring-opening polymerizations of oxetanes is the use of a convenient, sensitive and reproducible technique for monitoring these interesting reactions. The conventional method employed for monitoring the course of thermally induced frontal polymerizations involves carrying out these reactions in standard diameter test tubes and simply measuring the displacement of the propagating front with time [7]. The polymerizations are initiated (ignited) using a localized heat source such as a soldering iron, which is applied to the outside of the reaction tube. Often, a thermocouple is placed in the test tube to record the temperature at the reaction front. The Pojman group [18–20] was the first to apply an instrumental technique called laser line deflection and shadowgraphy (LLD) for monitoring isothermal frontal polymerization (IFP) reactions. This technique makes use of the deflection of a laser beam that is due to a change in refractive index at the polymerization front. This technique works best for optically clear frontal polymerizations that remain homogeneous and do not produce light scattering due to the formation of bubbles. Further, the LLD technique has not been applied to thermally induced frontal reactions.

Recently, we have reported the development of a new method for following the progress of exothermic photopolymerization reactions during UV irradiation by monitoring the reaction temperature as a function of time using an optical pyrometer [17,21,22]. This simple, low-cost device was modified specifically for use in the study of photoinitiated and photoactivated frontal polymerizations. A schematic drawing of the apparatus used is presented in Fig. 1. The pyrometer is mounted above the sample in the irradiation cabinet and the focal point of the instrument is centered in the middle and at one end of a channel milled into the poly(tetrafluoroethylene) (PTFE) sample cell. The dimensions of the channel can be varied as desired. The channel was filled with the liquid monomer/photoinitiator sample and then subjected to UV irradiation. After irradiation, the polymerization is triggered with the hot tip of an electrically heated wire that is immersed in the monomer at the other end of the channel. Once ignited, the frontal polymerization ensues and proceeds rapidly in the monomer down the length of the channel. The passage of the reaction front past the focal point of the optical pyrometer is recorded as a sharp rise in temperature. The distance and time of passage of the front from the point of ignition to the focal point of the detector allows the straightforward calculation of the frontal velocity, V_f. Other experimentally determined parameters of interest are the time required by the front to traverse the channel, t_f, and the maximum temperature of the front, T_f.

At the outset of the study, it was important to conduct studies to validate the utility of the optical pyrometric (OP) method for monitoring frontal polymerizations. Of crucial importance are the determination of the sensitivity and reproducibility of this method. Accordingly, we have elected to conduct our initial investigations of these two parameters using the photoactivated cationic ring-opening frontal polymerization of 3-ethyl-3-phenoxymethyloxetane (POX) as a model system. In Fig. 2 is depicted two typical separate experiments of the frontal polymerization of this monomer using the photoinitiator, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10 SbF_6) as the photoinitiator. In this experiment, the monomer/photoinitiator mixture was irradiated in a standard 1 mm PTFE sample cell with UV light for 2 min and then the light extinguished. The frontal polymerization was then ignited as described previously. As can be seen in this figure, in both cases, the frontal polymerizations proceed very rapidly with a transit time, t_f, down the 40 mm channel of 3 s and a resulting frontal velocity, V_f of 1.3 cm/s. Maximum frontal temperatures, T_f observed for these two runs were, respectively, 164 and 158 °C. Considering that the frontal polymerizations were triggered manually and that the sampling rate of the instrument is one temperature data point per second, the reproducibility of these experiments is excellent. To further enhance the reliability of the results obtained in this study, all the subsequent OP data reported in this article are the averages of two to three separate runs. It is also noteworthy that the t_f, T_f and the V_f values all indicate that the cationic ring-opening polymerization of this oxetane monomer (POX) is exceptionally vigorous and exothermic.

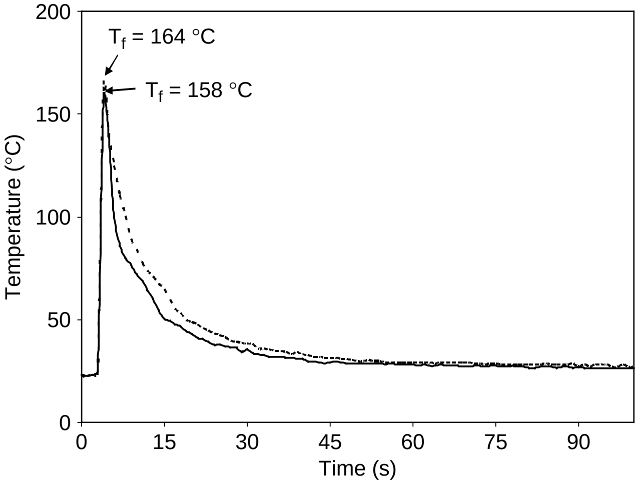


Fig. 2. Optical pyrometry study of the photopolymerization of POX using 1.0 mol% (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10 SbF_6) as the photoinitiator (light intensity: 856 mJ/cm^2 min; sample thickness 1.0 mm; path length 4 cm).

Ultimately, the sensitivity of the OP method depends on the ΔT experienced by the sample and the time period over which it occurs. Both of these parameters are directly related to the rate of conversion and to the heat of polymerization for a given monomer. From Fig. 2, the value of ΔT/s for the frontal polymerization of POX under the conditions of this experiment is 135 °C/s. Previously, we have reported that a minimum ΔT/s value of approximately 10 °C/s is required to provide adequate OP sensitivity and that the greater this value, the better the sensitivity. This requirement is greatly exceeded for POX and it will be further shown that this also applies to other oxetane monomers as well.

The mass and configuration of the sample are also important experimental parameters in a frontal polymerization. In this study, we have adopted the standard sample configuration shown in Fig. 2 in which only one dimension, the thickness (i.e. depth of the channel), was varied. This allows the mass of the sample to be varied incrementally. Displayed in Fig. 3 are the results of a study of the frontal polymerization of POX in which the sample thickness (and hence it's mass) was varied from 1 to 3 mm. All other parameters, light intensity and photoinitiator type and concentration were held constant. The OP derived temperature versus time curves obtained for the 1 and 2 mm

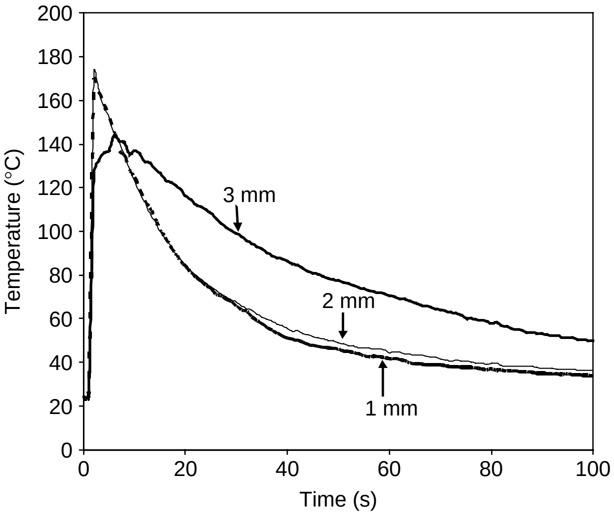


Fig. 3. Effect of sample thickness on the photopolymerization of POX (1.0 mol% IOC-10 SbF_6; light intensity: 1745 mJ/cm^2 min).

samples nearly overlap while the curve for the 3 mm sample is considerably broadened. The observed curve broadening in the latter case is likely due to a concentration gradient of active cationic centers that are set up across the thickness of the sample during the UV irradiation step. The concentration gradient arises because, although the diaryliodonium salt photoinitiators used in this study have high quantum yields ($\Phi = 0.5$–0.8) [23,24], they do not bleach during photolysis. For this reason, the bottom layers of the relatively thick samples are screened and receive less light than the top layers. Thus, photopolymerization of POX proceeds faster in the top than bottom layers resulting in a slower, broader, more diffuse reaction front. To avoid this problem, the experiments reported in this article were carried out using sample cells with channel depths of 1 and 2 mm.

3.2. OP study of the frontal ring-opening polymerization of oxetane monomers

The rate of an addition polymerization is dependent on a number of factors including the concentration of active propagating species present. In photoinitiated cationic polymerizations the concentration of active species and hence the polymerization rate is governed by such parameters as the concentration and quantum yield of the photoinitiator and the light flux delivered to the sample [25]. Another controlling parameter is the reactivity of the reactive species generated. The effects of some of these factors on the frontal polymerization of POX were examined in this investigation. It was observed that frontal polymerizations of POX with 1.0 mol% IOC-10 SbF_6 as the photoinitiator could be ignited after irradiation with doses of 2936 and 1468 mJ/cm^2, but not with a dose of 734 mJ/cm^2. Apparently, an insufficient number of active species are generated at the lowest flux that does not allow the generation of sufficient exothermic heat of polymerization to sustain a self-propagating front. The structure of the anion of the photoinitiator is critical as to whether or not frontal polymerization is observed. Although other types of onium salt photoinitiators can be used to induce frontal polymerizations, in this study, only diaryliodonium salts as photoinitiators were employed. It was found that, independent of the structure of the diaryliodonium cation, photoactivated cationic frontal polymerizations of POX were observed for diaryliodonium salts bearing the SbF_6^-, AsF_6^- and $(C_6F_5)_4B^-$ anions. An example is shown in Fig. 4 in which the photoactivated polymerization of POX was carried out using diphenyliodonium hexafluoroarsenate (IOC AsF_6) as the photoinitiator. At the same time, the frontal polymerizations of POX could not be ignited when any diaryliodonium salt bearing either the PF_6^- or BF_4^- anions were used no matter what photoinitiator concentration or irradiation dose were employed. An explanation for this behavior is as follows. As we have already indicated, the photolysis of diaryliodonium salt photoinitiators results in the generation of Brønsted acids that correspond to the anions present in those compounds. Thus, with the above-mentioned diaryliodonium salts, $HSbF_6$, $HAsF_6$, $(C_6F_5)_4BH$, HPF_6 and HBF_4 are generated photochemically. While all of these acids may be classified as ‘superacids’, they vary greatly in acid strength. Measurement of the actual strengths of such acids is problematic.

One measure of the strengths of strong acids including ‘superacids’ is the logarithmic Hammet acidity scale in which acidity constants, H_0, can be determined. In this scale, the larger and more negative the H_0 value, the stronger the acid. The H_0 values for $HSbF_6$, $HAsF_6$, HPF_6 and HBF_4 are, respectively; ~ -30, -20 to 25, -20 to 25 and -16.6 [26]. Unfortunately, the H_0 value for $(C_6F_5)_4BH$ has not been reported, however, it has been suggested on the basis of its reactivity in the polymerization of epoxide monomers that the strength of this acid may be similar to $HSbF_6$ [27]. It is interesting to note that based on the H_0 values, $HSbF_6$ is a stronger acid by a factor of at least 5–10 orders of magnitude than HPF_6 and at least 14 orders of magnitude stronger than HBF_4. Of course, the strength of an acid has a major impact on its ability to protonate the monomer in the initiation step. However, its influence does not end there. The propagating species in the ring-opening cationic polymerization of an

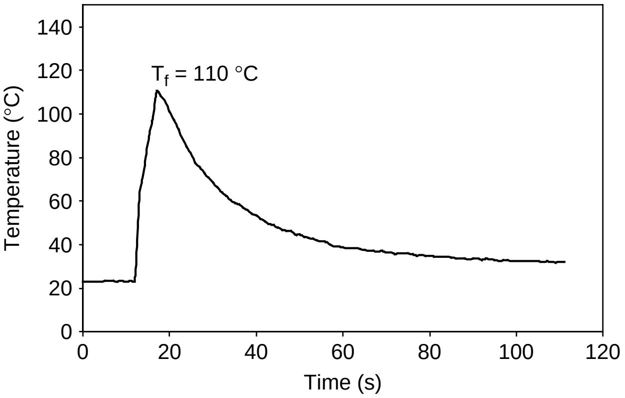


Fig. 4. Study of the frontal polymerization of POX Using 1.0 mol% diphenyliodonium hexafluoroarsenate as the photoinitiator (irradiation for 1 min at a light intensity of 1334 mJ/cm^2 min).

oxygen heterocyclic monomer consists of an oxonium cation-anion pair whose reactivity depends on its ‘ionicity’ or degree of association. The strength of a Brønsted acid (i.e. its protonating ability) is an indicator of the corresponding nucleophilicity of the anion: the stronger the acid, the lower the nucleophilicity of the anion. It also follows that the lower the nucleophilicity of the anion, the lower the degree of association and higher the reactivity of the ion pair in the propagation step(s) of the polymerization. In the case of diaryliodonium salts containing the PF_6^- and BF_4^- anions, apparently both the protonating ability of the photogenerated acid and the reactivity of the ion pair formed are not sufficiently high enough to support a self-sustaining frontal polymerization. On the other hand, while the H_0 values are listed as being similar, the ability of photogenerated $HAsF_6$ to induce frontal polymerization indicates that its acidity is actually higher than HPF_6. These results are in good agreement with previous results [23] that showed a marked difference in the rates of the photoinitiated cationic polymerization of simple epoxide monomers when diaryliodonium and triarylsulfonium salt photoinitiators bearing the same types of non-nucleophilic anions were used.

In Fig. 5 are shown the results of a study of the effects of the concentration of the photoinitiator, IOC-10 SbF_6 on the frontal polymerization of POX. In this case, a standard sample cell with a 1 mm thickness was used. With this very reactive monofunctional monomer, the polymerization front propagates very rapidly requiring only 1–3 s to traverse the 40 mm length of the sample channel. The velocity of the polymerization front in this case is nearly independent of the photoinitiator concentration in the range of 0.5–2.0 mol%. At photoinitiator concentrations below 0.5 mol%, the ignition of the front became erratic. In accord with this observation, it may also be noted that the T_f for the frontal polymerization carried out using 0.5 mol% photoinitiator is significantly lower than for the experiments carried out with 1.0 and 2.0 mol% photoinitiator.

A contrasting situation is shown in Fig. 6 for the frontal polymerization of the difunctional oxetane monomer bis{[1-ethyl(3-oxetanyl)]methyl} ether (DOX). The cationic ring-opening photopolymerization of this monomer results in the formation of a crosslinked network polymer. As a result, the polymer chains rapidly become immobilized during the frontal polymerization resulting in a reduction of the frontal velocity. In this case, there is a marked effect of the photoinitiator concentration on the frontal velocity. For photoinitiator concentrations of 0.5, 1.0 and 2.0 mol%, the respective t_f values are 5, 17 and 38 s and the V_f values are 6.3, 14 and 48 cm/min. These values establish a correlation between the reactivity of the frontal system (i.e. V_f values) and the number of active centers produced on photolysis of the photoinitiator. It is also interesting to note that solid, clear bars of polymer are produced by the frontal polymerization of DOX that can be removed intact from the sample cells.

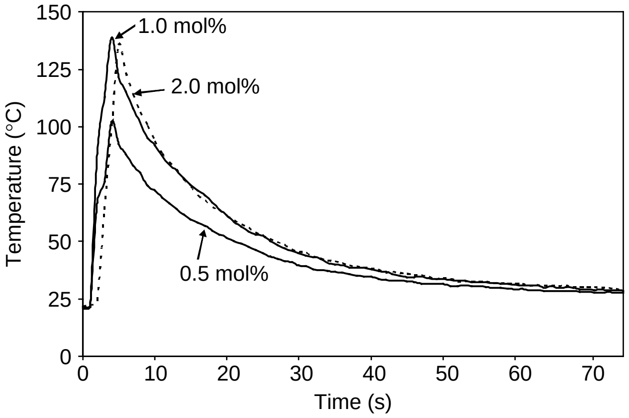


Fig. 5. Study of the effect of concentration of IOC-10 SbF_6 on the frontal polymerization of POX (irradiation for 1 min at a light intensity of 1548 mJ/cm^2 min).

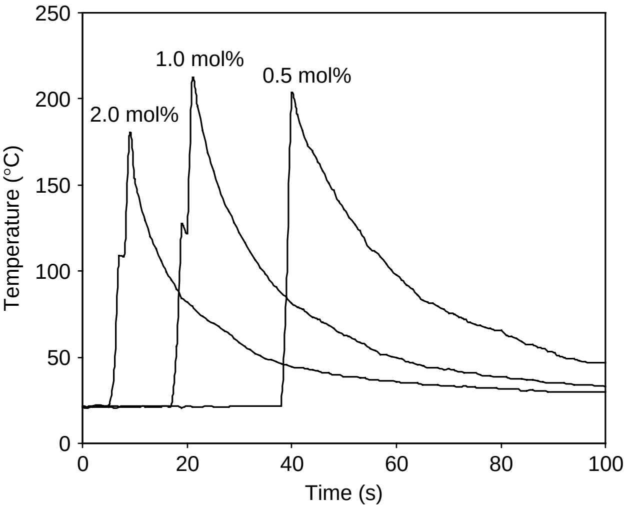


Fig. 6. Effect of concentration of IOC-10 SbF_6 on the photoactivated cationic frontal polymerization of DOX (irradiation for 2 min. at a light intensity of 1462 mJ/cm^2 min).

The structure of a monomer also plays an important role in its ability to undergo photoactivated cationic frontal polymerization. Fig. 7 depicts a comparison between the frontal

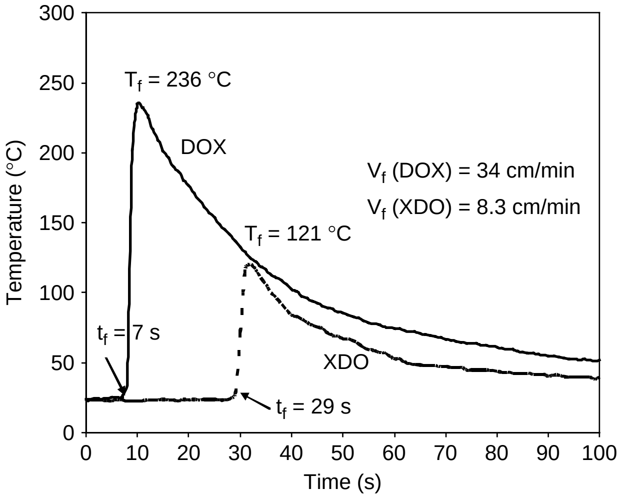


Fig. 7. Comparison of the frontal polymerizations of DOX and XDO using 1.0 mol% (IOC-10 SbF_6) as the photoinitiator. The sample was irradiated for 5 min at 1470 mJ/cm^2 min prior to ignition.

behaviors of the monomers DOX and 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene (XDO). The study was conducted by irradiating the samples containing 1.0 mol% IOC-10 SbF_6 for 5 min at a light intensity of 1470 mJ/cm^2 min. As indicated in Fig. 7, the frontal polymerization of DOX takes place with a higher frontal velocity ($V_f = 34$ cm/min) than XDO ($V_f = 8.3$ cm/min) and also the DOX polymerization is more exothermic than XDO as indicated by the respective maximum front temperatures ($T_f = 236$ versus 121 °C). Attempts to conduct the photoactivated frontal polymerization of 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]terephthalate (OXT) under the same experimental conditions failed. It should be noted that with this latter monomer, evidence of small amount of thermal ignition in the vicinity of the hot wire was observed, but significant propagation away from that site did not take place. This suggests that it may be possible to find conditions under which a photoactivated frontal polymerization can be carried out. These results can be rationalized by first noting that the oxetane equivalent weights for DOX, XDO and OXT are, respectively, 107, 177 and 189 g/mol. Since those difunctional monomers with the highest energy content i.e. (the lowest oxetane equivalent weight) would be expected to display the greatest frontal activity, these results are in the expected order. A second factor is the observation that OXT contains ester groups while the other monomers contain ether groups. We [28] have previously shown that epoxy monomers bearing inherently basic ester groups exhibit considerable retardation of their photoinitiated cationic polymerizations. This factor may also be responsible for the sluggish frontal polymerization behavior of OXT.

It was of special interest to attempt to determine the minimum temperature at which the frontal polymerization in 3, 3-disubstituted oxetane monomers can be ignited after photoactivation. Again, OP was used for this purpose and the sampling, instrumental and experimental techniques employed are described in detail in the Experimental section of this article. A thin film sample of monomer was first activated by irradiating with UV light at room temperature and then the sample was monitored by OP as it was slowly heated. Shown in Fig. 8 is the frontal polymerization of POX carried out in this manner. Starting out at 40 °C, (T_s), the front is ignited as the temperature reaches 51 °C (T_{ig}) resulting in a rapid, auto-accelerated polymerization with the sample temperature (T_f) rising to 144 °C. Thus, a temperature rise of only eleven degrees over the ambient sample temperature (T_s) was required to ignite this frontal polymerization. Another example is given in Fig. 9. In this case, a film of POX containing the photoinitiator, diphenyliodonium tetrakis(pentafluorphenyl)-borate was irradiated and then the temperature of the sample monitored by OP as it was heated starting at 23 °C. In this case, ignition took place at 31 °C with the temperature rapidly rising to 135 °C indicating that this is an especially highly reactive system. A further example is shown in Fig. 10 in which the ignition temperature of DOX was found to be 40 °C. Thus, the ignition temperature of this crosslinking monomer is higher, probably due to reduced molecular mobility in this network forming system. Conversely, the tertiary oxonium ion intermediates in DOX display greater stability than in POX. This also accounts for the previously observed lower frontal velocities for DOX. Overall, the results obtained with both oxetane monomers indicate that an input of only a few ~(10–40) kilojoules per mole of activation energy is required to break the dormancy of these systems and to ignite their frontal polymerizations. Once ignited, the frontal polymerizations proceed driven by the rapid, large exothermic release of ring strain energy contained within the four-membered oxetane rings.

3.3. Applications of photoactivated cationic frontal polymerizations

The major technical importance of multifunctional epoxides and oxetane monomers (usually termed ‘resins’) is in applications such as adhesives, coatings, potting compounds and composites in which their crosslinking polymerizations or ‘cure’ reactions are used to provide thermosets with good mechanical properties and chemical and thermal resistance. In a large measure, the conditions of time and temperature under which the ‘cure’ of these monomers is conducted determines

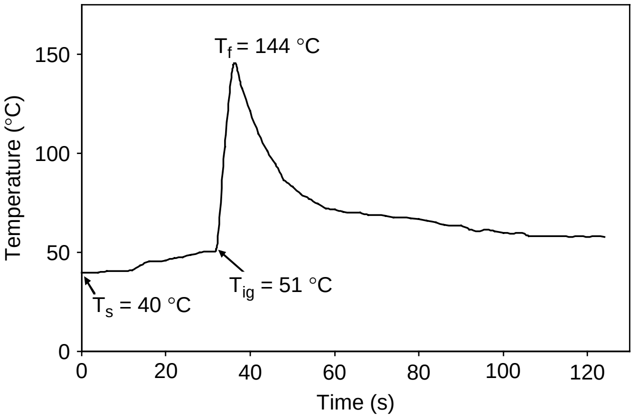


Fig. 8. Study of the thermally ignited polymerization of POX containing 1.0 mol% (IOC-10 SbF_6) as the photoinitiator. The sample was irradiated for 1 min at 1468 mJ/cm^2 min and then temperature programmed.

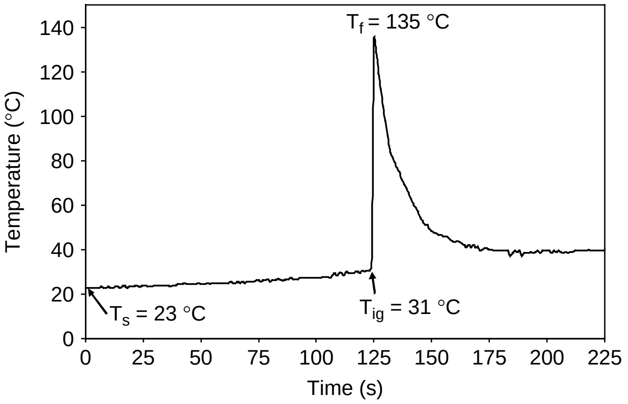


Fig. 9. Study of the thermally ignited polymerization of POX containing 1.0 mol% diphenyliodonium tetrakis(pentafluorphenyl)borate as the photoinitiator. The sample was irradiated for 1 min at 1334 mJ/cm^2 min and then temperature programmed.

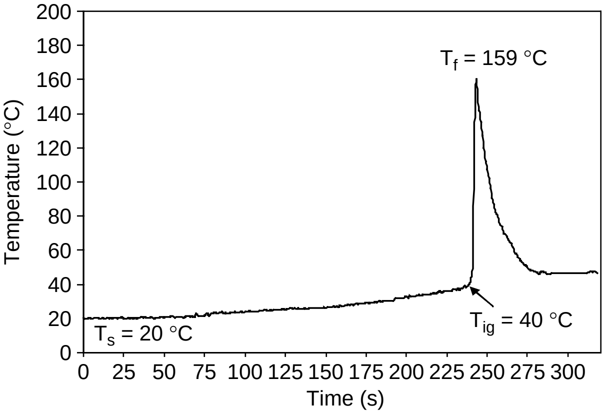


Fig. 10. Determination of the ignition temperature for DOX containing 1.0 mol% (IOC-10 SbF_6) as the photoinitiator. The sample was irradiated for 1 min at 1274 mJ/cm^2 min and then temperature programmed.

the utility of these resins as is their handling or processing characteristics. Typically, it is desirable to conduct a curing reaction as rapidly as possible at as low a temperature as is feasible. Over the span of more than six decades, many attempts have been made to design one-component (i.e. single package) systems containing the monomer(s) and a latent thermal polymerization catalyst that will meet this requirement. A very informative paper by Pappas and Feng [29] critically examines the thermodynamic and kinetic factors that impact on the construction of a one-component epoxy-based system incorporating a latent catalyst that not only undergoes rapid polymerization at low temperatures but also satisfies the critical need for long-term (e.g. minimum 6 months at 30 °C) shelf-life storage. It may be noted that the requirements for rapid cure at low temperature and long shelf life are diametrically opposed to one another. It is also not surprising that despite the many attempts to strike a compromise between these two sets of requirements, not one workable system is currently in use. For this reason, the industry has instead employed two-component systems consisting of the epoxy or oxetane resin and a hardener that are either mixed just prior to use or systems that are mixed and quickly frozen to provide pseudo one-component systems. Green and Wittcoff [30] have recently pointed out that the failure to develop workable, rapid curing, shelf-stable, one-component cure systems has precluded their use in automated assembly processes. This has resulted in stagnation in the growth of epoxy thermoset chemistry and the departure of several traditional epoxy resin manufacturers from this area.

The present article presents the possibility of a new strategy for the development of shelf stable, one component, low temperature, rapidly curing thermoset systems by decoupling the two seemingly opposed requirements. One-component systems with very long shelf stability at room as well as at elevated temperatures can be constructed consisting of an oxetane resin(s) and a cationic photoinitiator. Such systems can be applied and manipulated using various techniques then 'activated' when desired by light. UV irradiation of these systems results in photolysis of the photoinitiator and the consequent formation of a latent species, the tertiary oxonium ion derived from the monomer, which has a very low thermal threshold for polymerization. Cure takes place rapidly and exothermically by a frontal mechanism. In future articles from this laboratory, we will report on the use of this novel chemistry in several practical applications.

4. Conclusions

3,3-Disubstituted oxetanes exhibit well-behaved frontal polymerization characteristics when first activated by irradiation with UV light in the presence of a diaryliodonium salt cationic photoinitiator and then thermally ignited. Using optical pyrometry, the effects of photoinitiator concentration and structure were studied and it was found that the frontal polymerizations were critically dependant on those factors. In addition, it was observed that the frontal velocities were considerably faster for monofunctional oxetane monomers than for difunctional monomers. Using optical pyrometry, it was also possible to determine the minimum ignition temperature required to start the frontal polymerization of oxetane monomers. The results indicate that an input of only a few kilojoules per mole is required to overcome the activation energy barrier for conversion of the intermediate tertiary oxonium to polymer.

These observations suggest that such oxetane systems may have considerable potential for several types of commercial applications such as adhesives, coatings, composites and electronic encapsulants. The unique chemistry described here provides one-component mixtures of oxetane monomers and photoinitiators that are infinitely stable when stored in the dark. After 'activation' with UV light, these systems remain fluid and can be handled in this state for several hours at room temperature. Such 'activated' systems can be thermally induced to undergo frontal polymerization by raising the temperature of the reaction mixture by 10–30 °C.

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