Macromol. Symp. **2005**, *226*, 97-107

Photoactivated Cationic Frontal Polymerization

*Benjamin Falk, Michael R. Zonca, Jr., James V. Crivello**

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York, 12180, USA
E-mail: crivej@rpi.edu

Summary: Photoactivated cationic ring-opening polymerizations of certain oxirane and oxetane monomers take place in a frontal manner. The study of the frontal behavior of those monomers was conducted using a new analytical technique involving optical pyrometry that provides insight into the mechanism of these polymerizations.

Keywords: cationic photopolymerization; frontal polymerization; oxetanes; oxiranes

Introduction

In recent years, the cationic ring-opening photopolymerizations of oxirane monomers have found many commercial uses for example, in coatings, adhesives and printing inks. In such high-speed applications, one is interested in attaining the highest photopolymerization rates possible with the shortest irradiation times. It was observed that only certain oxirane monomers underwent very rapid photopolymerization and were suitable for use in the above-mentioned applications while others displayed apparent polymerization rates that were too sluggish to be useful under the same UV irradiation conditions. This was initially somewhat perplexing since this class of monomers uniformly displays quite high reaction enthalpies (18-24 k-cal mol^{-1})[1] that would suggest that they all should possess correspondingly high reactivities. Similarly, oxetanes have high enthalpies of polymerization (19-20 k-cal mol^{-1}) but display comparatively slow overall rates of polymerization. In this laboratory, we have undertaken to elucidate the underlying factors that determine the reactivity of oxirane and oxetane monomers in cationic photopolymerization. In a recent paper,[2] we have investigated the effects of structure on the reactivity of several model epoxide monomers. This article continues this investigation with a study of the contributions of kinetic and thermodynamic factors to the cationic photopolymerization rates of epoxide and oxetane monomers.

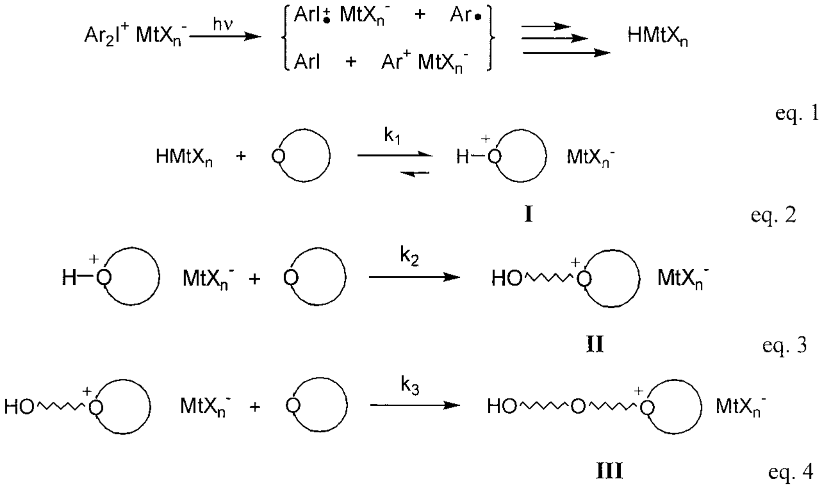
DOI: 10.1002/masy.200550810

Results and Discussion

General Observations for the Cationic Photopolymerizations of Oxiranes and Oxetanes

Recent kinetic investigations[2] of the cationic ring-opening photopolymerizations of mono- and multifunctional oxiranes and oxetanes showed that these monomers exhibit different types of behavior depending upon their structures. For example, the polymerizations of epoxyalkanes typically take place rapidly and nearly instantaneously at the onset of irradiation while the corresponding photopolymerizations of alkyl glycidyl ethers occur with an appreciable induction period. Aryl glycidyl ethers exhibit intermediate behavior; i.e. slow polymerization without an appreciable induction period. The presence of an induction period is very undesirable in practical applications since it effectively slows the overall photopolymerization process. Despite many attempts to reduce the induction period by exhaustive monomer purification and by conducting the polymerizations under rigorously controlled conditions to eliminate the possible presence of inhibiting contaminants, the induction periods remained. This led to the conclusion that the observed induction periods of these monomers were due to the inherent kinetics and mechanisms of the polymerization reactions of the monomers themselves.

Shown in Scheme 1 is the generally accepted mechanism for the photoinitiated cationic ring-opening polymerization of heterocyclic oxygen monomers exemplified here with the use of diaryliodonium salt photoinitiators.[3]



Scheme 1.

In the first step (eq. 1), UV irradiation of the diaryliodonium salt results in excitation, then fragmentation of the photoinitiator into a variety of radical and cationic species. Further reaction of those species with monomer, solvent or other protogenic components yields the Brønsted acid, $HMtX_n$. The photogenerated strong "super acid" (when $HMtX_n$ = e.g. HBF_4, HPF_6, $HSbF_6$) very rapidly protonates the cyclic ether (i.e. k_1 is large) as depicted in equation 2. The secondary oxonium species (**I**) that is formed undergoes attack by the nucleophilic cyclic ether to yield the tertiary oxonium species (**II**) with the resultant opening of the heterocyclic ring (eq. 3). Finally, attack by the cyclic ether monomer on the tertiary oxonium ion (eq. 4) leads to chain growth (**III**). The rate constants k_2 and k_3 respectively, for equations 3 and 4 are different since the species **II** and **III** have different ring strains, steric interactions, and electronic charge distributions. Generally, equation 4 is rate limiting and, thus, k_2 is greater than k_3. However, the respective magnitudes of k_2 and k_3 depend on the specific monomer undergoing polymerization. Factors such as ring strain, steric crowding at the reaction site and the nucleophilicity of the heteroatom of the attacking monomer all play a role. For example, in the cationic photopolymerization of highly strained cycloaliphatic epoxides both k_2 and k_3 are large and observation of the effects of the difference in rates is difficult. Such a case is the polymerization of cyclohexene oxide which displays no appreciable induction period during photopolymerization. In contrast, Sasaki[4,5] has reported that the photoinduced cationic ring-opening polymerizations of 3,3-disubstituted oxetanes display appreciable induction periods. This was confirmed in this laboratory.[6,7] For example, when the photopolymerization of 3-ethyl-3-[(phenoxy)methyl]oxetane (POX) was carried out under similar conditions to those used for the polymerization of cyclohexene oxide, only a very slow conversion (~2-5%) of monomer to polymer took place even after 2 minutes of continuous UV irradiation.[8,9] However, when polymerization did occur, it took place exothermically under autoacceleration conditions. Since diaryliodonium salt photoinitiators have high quantum yields (Φ = 0.5-0.8),[10,11] essentially all of the photoinitiator is photolytically decomposed to produce acid during the long induction period. Sasaki[12] has suggested that the presence of the prolonged induction period in the cationic polymerization of oxetane monomers is due to the slow, rate-determining ring-opening reaction of the secondary oxonium salt with monomeric oxetane (eq. 3, Scheme 1; i.e. $k_2 < k_3$). Consistent with this hypothesis, we were able to demonstrate that if the photopolymerization of POX was carried out under increasingly higher temperatures, the induction period was correspondingly reduced until it disappeared altogether. However, it should be pointed out that the results can also be explained if equation 4 is the slow, rate determining step. Similar thermal effects were observed in the photopolymerizations of alkyl glycidyl ethers.

Cationic Frontal Polymerizations

When the UV irradiation of alkyl glycidyl ethers and 3,3-disubstituted oxetanes were terminated during the induction period, no appreciable polymerization of these monomers takes place. However, if the resulting reaction mixtures were heated slightly, polymerization takes place rapidly and exothermically. A closer observation reveals that these reactions occur in a frontal manner with the polymerizations propagating through the mass of a monomer along a well-defined localized reaction zone or front. The concept of photoinduced cationic frontal polymerizations is depicted in the cartoon in Figure 1. Typically, frontal polymerizations are highly exothermic events that depend on the rapid, thermally induced decomposition of an initiator within the reaction zone to maintain and propagate the reaction front.[13,14] However, in the instances cited above, the behavior is quite different since the photoinitiator must first be activated with light before the frontal polymerization can proceed. This could be easily demonstrated as shown in Figure 2 by masking off a portion of the sample so that irradiation activates only approximately one half the sample. When the frontal polymerization is thermally initiated in the irradiated region, polymerization progresses rapidly throughout that portion of the sample, but stops abruptly at the boundary of the portion of the sample that was not irradiated.

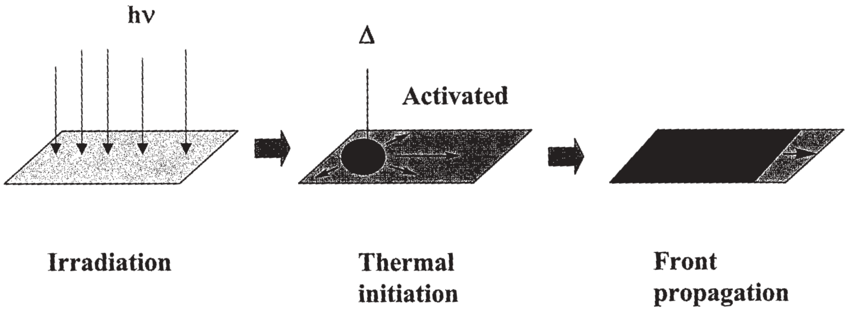


Figure 1. Front propagation in photoinduced frontal polymerizations.

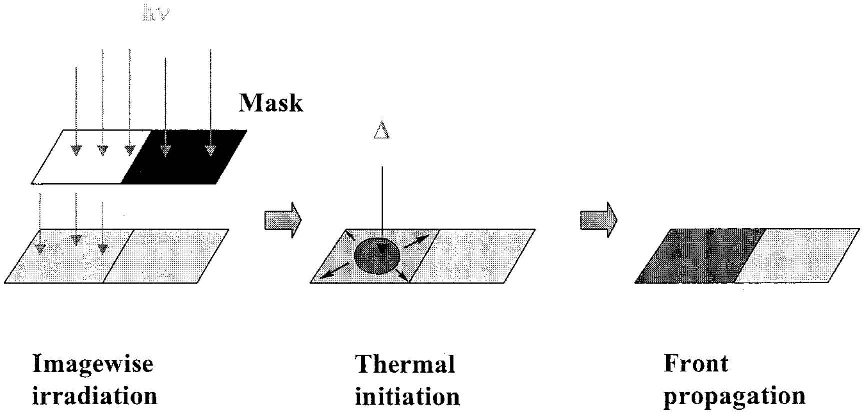


Figure 2. Demonstration of photoactivated frontal polymerization.

To facilitate our study of photoactivated frontal polymerizations, we have employed a technique called optical pyrometry that was previously used in this laboratory for monitoring the progress of photopolymerizations. Using this method, the temperature profile of a sample undergoing photopolymerization is recorded in real time. The optical pyrometry (OP) technique with slight modification can also be used for the study of photoactivated thermally induced frontal polymerizations by following the rapid temperature rise that accompanies the reaction front as it moves past the focal point of the sensor of the optical pyrometer. A schematic drawing of the OP apparatus is depicted in Figure 3. Samples of a liquid monomer together with a dissolved photoinitiator are placed in a specially designed poly(tetrafluoroethylene) holder constructed with a channel (0.8 cm wide by 0.1 cm deep, length 4.2 or 2.0 cm). The sample is first irradiated with UV light and then placed into the chamber of the OP instrument in such a manner that the focal point is positioned at one end of the channel. Then, polymerization is thermally started at the opposite end of the channel using the hot tip of an electrically heated wire. The time of the arrival and passage of the polymerization front (t_f) can be directly observed as well as the maximum temperature (T_f) attained by the front. Using this data, the frontal velocity (V_f) can be calculated.

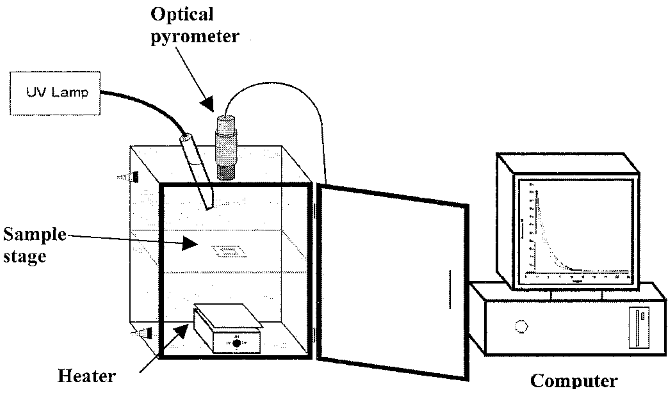


Figure 3. Optical pyrometry apparatus used for the study of photoactivated cationic frontal polymerizations.

Figure 4 shows a typical OP study of the frontal polymerization of benzyl glycidyl ether that was carried out after a UV preirradiation of 2.5 minutes. Upon thermal initiation, the polymerization front passes down the sample channel and arrives at the focal point of the sensor of the optical pyrometer at 35 s. The temperature abruptly rises and at 39 s the maximum temperature, (T_f = 180 °C), is reached by the sample. The frontal velocity is was constant over the entire length of the channel and was found to be 7.2 cm min^{-1}.

A similar study was conducted for the frontal polymerization of neopentylglycol diglycidyl ether. The results are given in Table 1. Most striking is the very high frontal temperature reached by the sample. During the frontal polymerization of neopentylglycol diglycidyl ether sufficient thermal and oxidative decomposition takes place such that there is a pronounced change from colorless to black in the sample immediately behind the front.

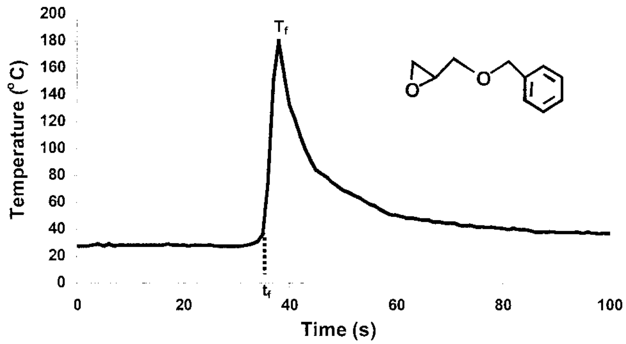
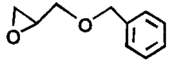
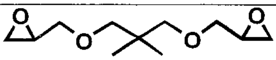
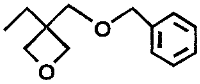
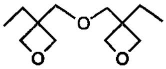


Figure 4. Frontal polymerization of benzyl glycidyl ether with 1.0 mol% (4-n-pentadecyloxyphenyl)phenyliodonium SbF_6^- after 2.5 min. UV irradiation at 439 mJ/cm^2 min.

Table 1. Frontal Polymerizations of Various Oxirane and Oxetane Monomers.*

Monomer	**Irrad. Time (min)**	**Intensity (mJ/cm^2 min)**	**T_f (°C)**	**t_f (s)**	**V_f (cm/min)**
	2.5	439	180	35	7.2
	6	413	232	22	11
	5	483	169	14	18
	8	575	203	6	20

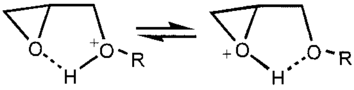
*1.0 mol% (4-pentadecyloxyphenyl)phenyl iodonium SbF_6^- as photoinitiator.

As mentioned previously, aromatic glycidyl ethers, such as phenyl glycidyl ether, display different behavior than that described above for alkyl glycidyl ethers. The pure monomers do not display a prolonged induction period, but undergo immediate but slow polymerization when irradiated with UV light in the presence of an onium salt photointiator. In contrast, cycloaliphatic epoxides possessing considerable ring strain such as cyclohexene oxide, undergo rapid polymerization without an appreciable induction period. An oxetane monomer that shows well-behaved cationic frontal polymerization behavior is POX (3-ethyl-3-[(phenoxy)methyl]oxetane). An OP study of this polymerization was conducted and the results are included in Table 1. This monomer displays well behaved frontal behavior that is characterized by a long induction period. After thermal initiation, frontal polymerization proceeds with a fast frontal speed. An even more reactive monomer is the difunctional oxetane monomer bis[1-ethyl(3-oxetanyl)methyl] ether (DOX). Due to its low mass to oxetane functional group ratio, the frontal polymerization proceeds with a high frontal velocity and temperature.

Mechanistic Considerations

From the data provided thus far, it is clear that the different behaviors observed in the response of various oxirane and oxetane monomers to photoinitiated cationic polymerization can be ascribed to differences in the relative kinetic rates of the individual steps of their ring-opening polymerizations as depicted in Scheme 1. Those monomers that display a substantial induction period prior to polymerization undergo a slow ring-opening reaction of monomer with the initially formed secondary or tertiary oxonium ions. It is also these same polymerizations that proceed by a photoactivated frontal mechanism. In contrast, monomers that undergo rapid reaction of their oxonium ions with monomer do not exhibit an appreciable induction period and also do not display frontal behavior. The thermodynamic relationships of these two extremes are depicted in the proposed reaction coordinate versus energy diagrams shown in Figure 5. In both cases, there are three maxima and two minima in the reaction pathway. One scenario leading to frontal behavior is portrayed by the thermodynamic relationship shown in diagram A that appears to be characteristic of alkyl glycidyl ether monomers. In this case, protonation takes place with little or no activation energy to generate a secondary oxonium ion that lies in a relatively deep energy well. For polymerization to occur, sufficient energy must be input into the system to overcome the activation energy (E_a2) of the second step. However, once this happens, the energy released provides a rapid rise in temperature that results in overcoming the activation energy barrier (E_a3) for the next step (Scheme 1, step 4) as well. If no thermal energy is supplied, the secondary oxonium ion is relatively stable and can persist for a considerable length of time at room temperature. Frontal behavior occurs when a localized heat source is applied and the resulting autoacceleration propels further polymerization along a reaction front. The second case shown in diagram B of Figure 5 describes the behavior of monomers that require a low activation energies to undergo conversion from the secondary or tertiary oxonium ions to propagating oxonium ions. When this occurs, sufficient activation energy is available at room temperature for the reaction to enter an autoacceleration regime. As a result, these polymerizations exhibit no appreciable induction period and thermally induced frontal polymerization is not possible.

While the above discussion explains the general kinetic and thermodynamic behavior of the ring-opening polymerization of heterocyclic oxygen monomers, it does not give a rationalé for distinguishing why specific monomers do or do not exhibit frontal characteristics. An understanding of this point can be reached by considering those structural parameters that contribute to the stability of the oxonium salt intermediates that are critical to the observation of frontal polymerization behavior. In the case of alkyl glycidyl ethers, the ether oxygen is situated in such a fashion that it can stabilize the protonated epoxide group by hydrogen bonding through a pseudo five membered ring as depicted in structure **IV.** The ether and epoxide oxygens are of similar basicity and hydrogen bonding to both oxygen atoms should result in stabilization of **IV**. Monomers such as epoxy alkanes or cycloaliphatic epoxides that do not possess such stabilization polymerize without an induction period and do not display frontal characteristics. For aryl glycidyl ethers (R = aryl), the resonance interaction of the lone pairs on oxygen with the benzene ring results in a greatly reduced basicity of this oxygen and consequently, its diminished ability to participate in hydrogen bonding.



IV

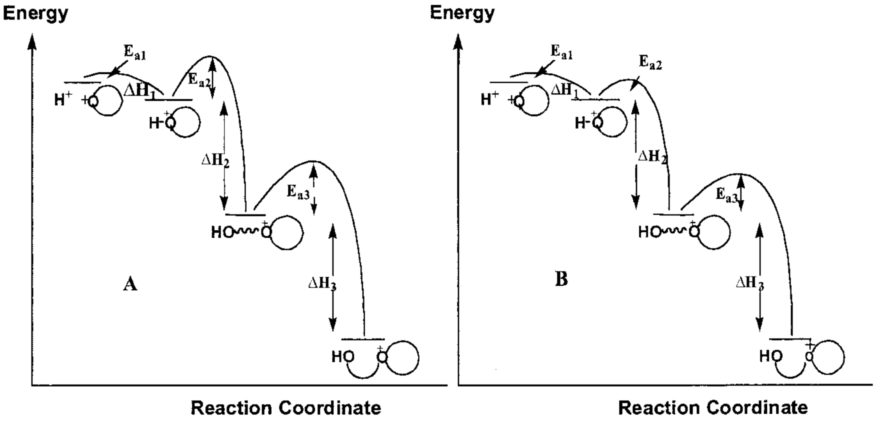


Figure 5. Energy vs reaction coordinate diagrams: **A**. for systems that display frontal behavior and **B**. monomers that do not possess frontal characteristics.

Conclusions

The UV irradiation of certain oxirane and oxetane monomers in the presence of onium salt cationic photoinitiators produces quiescent, metastable oxonium ion species. The local application of a small amount of heat provides sufficient energy to induce the polymerization of the monomer that proceeds as a front moving rapidly through the sample. The consumption of the monomer in such photoactivated frontal polymerizations is constrained to take place only within the irradiated zone. This communication reports on the development of a new technique, optical pyrometry, to monitor the course of these cationic ring-opening frontal photopolymerizations. Thermodynamic and kinetic explanations for the frontal behavior of the monomers studied were presented.

Acknowledgment

The authors would like to thank the Petroleum Research Fund administered by the American Chemical Society and Albany Molecular Research for their sponsorship of this work.

[1] K.J. Ivin, in: "*Polymer Handbook*" J. Bandrup, E.H. Immergut, Eds., Interscience, New York, **1966**, p. II/374.

[2] J.V. Crivello, V. Linzer, *Polimery* **1998**, *68(11/12)*, 661. *Chem. Abstr.* **1999**, *130*, 182793u.

[3] M. Jang, J.V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3056.

[4] H. Sasaki,. *Proc. RadTech 2000 Technical Conference*, Baltimore, MD., April 9-12, **2000**, p. 61.

[5] H. Sasaki, J.M. Rudzinski, T. Kakuchi, *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1807.

[6] J.V. Crivello, B. Falk, M.R. Zonca, Jr., *J. Appl. Poly. Sci.* manuscript submitted.

[7] J.V. Crivello, H. Sasaki, *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30(2/3)*, 189.

[8] C. Decker, K. Moussa, *Makromol. Chem.* **1990**, *191*, 963.

[9] D.B. Yang, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 199.

[10] J.V. Crivello, in: "*Ring Opening Polymerization*," D.J. Brunelle, Ed., **1993**, Hanser Pub, Munich, p.157.

[11] C. Selvaraju, A. Sivakumar, P. Ramamurthy, *J. Photochem. Photobiol. A: Chem.*, **2001**, *138*, 213.

[12] H. Kato, H. Sasaki, *Photoinitiated Polymerization*, ACS Symp. Ser. No. 847, Am. Chem. Soc., Washington, D.C. **2003**, p.285.

[13] S.P. Davtyan,P.V. Zhirkov, S.A. Vol'fson, *Russ. Chem. Rev.* **1984**, *53*, 150.

[14] J.A. Pojman, V.M. Ilyashenko, A.M. Khan, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2825.