

Characterization of the Kinetic Rate Constants for the Cationic Photopolymerizations of Epoxide Monomers

by Vishal Sipani and Alec B. Scranton, Department of Chemical and Biochemical Engineering, University of Iowa, 4133 Seamans Center, Iowa City, IA 52242-1527

Abstract

We have characterized the effective rate constants for termination and propagation for solvent-free cationic photopolymerizations of epoxide monomers. We performed post-polymerization studies in which the active centers are produced photochemically for a specified period of time until the initiating light is shuttered off, then the polymerization rate is monitored in the dark. This method is especially well suited for characterizing cationic polymerizations due to the long lifetimes of the active centers.

Introduction

When compared with free radical photopolymerizations, cationic photopolymerizations offer many advantages, such as high active center concentrations, practically non-terminating polymerization, and no oxygen inhibition effect. Cationic polymerizations may also be used to polymerize important classes of monomers including epoxides, vinyl ethers, and propenyl ethers¹⁻⁵ and the resulting polymer films exhibit excellent adhesion, abrasion resistance, and chemical resistance. Furthermore, the cationic ring-opening polymerizations of epoxides exhibit less shrinkage than polymerizations of unsaturated monomers such as acrylates and methacrylates. These features make cationic photopolymerizations very attractive; however, these reactions are not well understood, especially compared to their free radical counterparts.

A breakthrough in cationic photopolymerization was achieved by the development of diaryliodonium and triarylsulfonium salts⁶ as initiators. Unlike previous initiators, these salts are remarkably stable in the absence of light, and they are thermally stable at room temperature. A key feature of cationic photoinitiators is the use of acids possessing anions of very low nucleophilicity. Therefore, most cationic photoinitiators are based on salts of non-nucleophilic anions⁷ such as BF_4^- , PF_6^- , AsF_6^- , or SbF_6^- . In the past decade, several new cationically-polymerizable monomers have also been developed, most notably by Crivello and collaborators. Examples of these monomers include novel silicon-containing epoxy resins,⁸⁻¹⁰ epoxide monomers based on bisvinyl ethers and propenyl ethers,^{1,5} benzyl, allyl and propargyl acetal and ether groups¹¹ and hybrid monomers bearing epoxy and vinyl ether or 1-propenyl ether groups.¹² The selection of cationically polymerizable monomers and cationic photoinitiators is now reasonably broad; however, the fundamental characterization of these reaction systems has received relatively little attention.

In our recent research¹³⁻¹⁴ we have addressed the need for a better understanding of cationic photopolymerizations by characterizing the termination and propagation rate constants of these reactions. In this paper, we will present the effects of a number of factors on the rate constants for termination and propagation. Our analysis of the data for the dark cure polymerization rate provides profiles of the instantaneous kinetic rate constants as functions of time (or conversion) without the assumption that they do not change as the reaction progresses. Therefore, this analysis provides insight in how the effective rate constants change with conversion as the sample transforms from a liquid monomer to a solid polymer.

Furthermore, we will present the propagation lifetime of the active center, which is defined as the average time during which an active center consumes monomer molecules to form a growing polymer chain before chemically terminating (which results in chemical consumption of the active centers) or becoming trapped (in which case the active centers still exist, but are no longer propagating since the surrounding monomer molecules have polymerized and the active centers are unable to access unreacted monomer).

Experimental

Materials. The monomer phenyl glycidyl ether was supplied by the Shell Chemical Company and was stored over molecular sieves to remove any trace water impurities. This monomer was selected because it is a monoepoxide monomer that yields a polymer with relatively low glass transition temperature. The following two photoinitiators were used in this study: (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate (IPB) supplied by Rhodia, Inc., and diaryliodonium hexafluoroantimonate (IHA) supplied by the Sartomer Company. These two iodonium photoinitiators were selected because they are known to be among the most effective photoinitiators for yielding high polymerization rates, and because their counterions are vastly different in size. In all the experiments described here the concentration of the photoinitiator used was 8.86×10^{-3} M.

Photo-differential scanning calorimetry. As in previous studies¹⁵ photo-differential scanning calorimetry (photo-DSC) experiments were conducted using a Perkin-Elmer DSC-7 modified in-house for light-induced experiments. The light source was a 200 W Oriel Hg(Xe) arc lamp which was directed through a water filter outfitted with a thermostatted recirculating jacket to reduce infrared radiation and limit sample heating. A quartz cover on the DSC sample block was used to seal the reaction chamber, which was purged with nitrogen. The total radiant power incident on the sample was 75 mW/cm^2 , as measured by the graphite disc absorption. The intensity in the wavelength range of interest, where the photoinitiators absorb but the monomer does not (290 – 340 nm), was determined to be 25 mW/cm^2 using a calibrated Ocean Optics S2000 spectrophotometer. DSC has become a standard technique for studying the kinetics of polymerization reactions.¹⁶⁻¹⁸ Since the polymerization reactions are exothermic, the reaction rate can be calculated by measuring the heat released during the reaction. Conversion profiles can be obtained by integrating the area under the curve for the heat profiles and dividing by the heat of polymerization, ΔH_p .

Results and Discussion

The effects of temperature and photoinitiator counterion on the active center propagation lifetime were studied by performing dark-cure experiments in which active centers are produced photochemically for a specified length of time until the initiating light is shuttered off, then the polymerization rate was monitored in the dark. During the time in which the system is illuminated, active centers are formed, and the reaction rate increases monotonically. When the light is shuttered off, no new active centers are formed, and the rate of polymerization decreases monotonically due to both the decrease in monomer concentration associated with propagation, and the decrease in active center concentration associated with termination or trapping. Monitoring the rate of polymerization during this dark cure allows the effective active center propagation lifetime to be determined (the average time during which an active center propagates before being trapped or terminated).

Representative results for the dark cure studies of phenyl glycidyl ether monomer at 8.86×10^{-3} M concentration of the IHA photoinitiator at 60°C are shown in Figure 1. The figure contains profiles of the conversion as a function of time for five identical reaction systems illuminated for different periods of time ranging from 15 seconds to the duration of the experiment (full illumination). Figure 1 illustrates that, as expected, each of the curves traces the profile obtained for full illumination up until the light is shuttered off. In addition, the figure shows that the reaction proceeds long after the illumination has ceased, often consuming all of the monomer. For example, the sample that was illuminated for only 15 seconds continues to react for more than 50 minutes in the dark. It is also interesting to observe that same final limiting conversion for the illumination times of 90, 60, and 30 seconds is obtained as that for the system under full illumination.

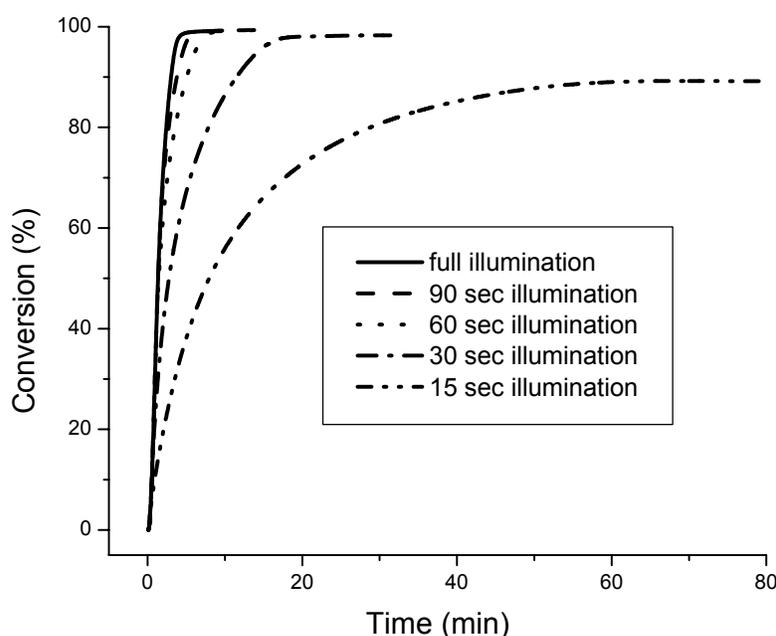


Figure 1. Conversion vs. time profile for photopolymerizations of phenyl glycidyl ether initiated using 8.86 mM concentration of the iodonium antimonate salt at 60°C and light intensity of 25 mW/cm^2 at different illumination times.

Calculation of the Kinetic Rate Constants at Low to Intermediate Conversions. The dark cure conversion profiles for the low to intermediate conversions were analyzed to determine the instantaneous value of the effective termination rate constant using the procedure we described in detail previously.^{13,14} It is easier to calculate the kinetic rate constants in this conversion range because the instantaneous propagation rate constant, k_p , is largely invariant. Figure 2 shows the representative profiles for k_t and k_p as functions of time for the photopolymerization of phenyl glycidyl ether monomer using this procedure. This figure illustrates that both the termination and trapping rate constants are flat within an order of magnitude for the reaction time shown (which corresponds to a conversion of 50%), although they are allowed to change freely as functions of time.

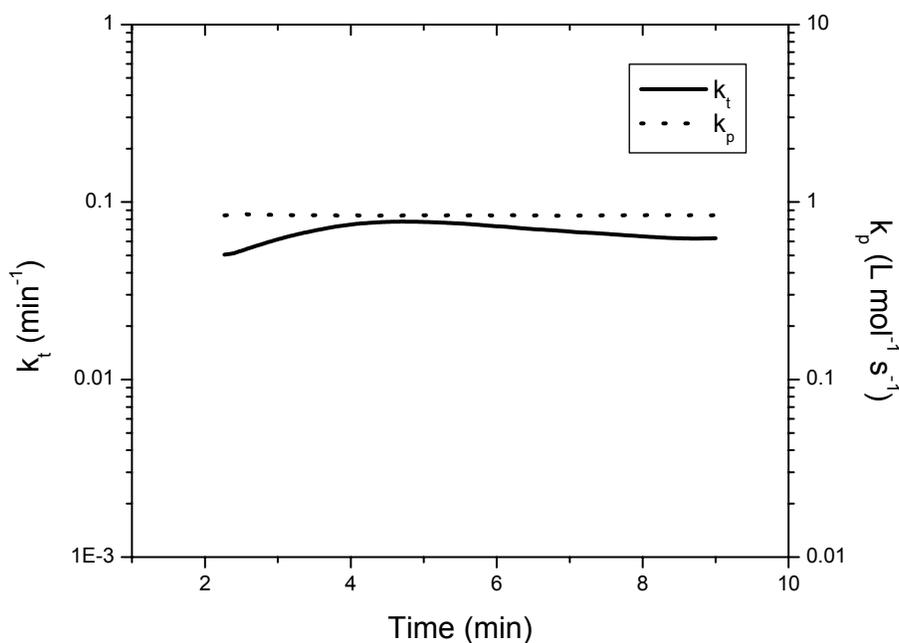


Figure 2. Profiles of k_t and k_p vs. time for photopolymerizations of phenyl glycidyl ether initiated using 8.86 mM concentration of the iodonium antimonate salt at 60°C and light intensity of 25 mW/cm².

For the photoinitiator (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate (IPB) the values of k_t at 50°C and 60°C were found to be 0.027 and 0.033 min⁻¹, respectively. The corresponding values of k_t for diaryliodonium hexafluoroantimonate (IHA) were found to be 0.041 and 0.068 min⁻¹. These results reveal that at 50°C the propagation lifetimes for the cationic active centers for the IPB and IHA photoinitiators are 37 minutes and 24 minutes, respectively. The average values of the termination rate constants as a function of temperature and the photoinitiator counterion are shown in Figure 3, which illustrates that k_t increases with increase in temperature and with increase in size of the photoinitiator counterion. The values of the effective propagation rate constants at 50°C for IPB and IHA were found to be 0.6 and 0.4 L mol⁻¹ s⁻¹, respectively. The fact that the observed propagation rate constant for the IPB photoinitiator is approximately 50% higher than that of the IHA photoinitiator likely arises from the difference in the size of the counterion. Since borate counterion is much bulkier than the antimonate, it will form a weaker ion pair with the propagating cation, resulting in higher propagation rate constant. For low to medium conversion, based on these k_p values, the activation energy for the IHA photoinitiator is 70 kJ/mol and that for the IPB photoinitiator is 85 kJ/mol.

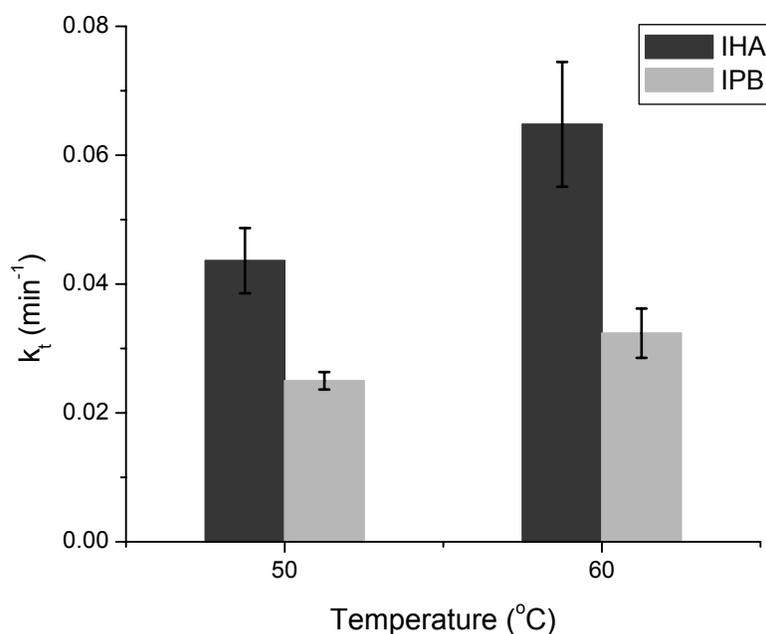


Figure 3. Effect of temperature and photoinitiator counterion on the termination rate constant for the photopolymerization of phenyl glycidyl ether at 25 mW/cm² of light intensity. Average rate constant values are shown, and the error bars denote one standard deviation.

Calculation of the Kinetic Rate Constants at High Conversions. The propagation and termination rate constants at high conversions were also characterized. The value of termination rate constant, k_t is same as that obtained for the low to intermediate conversions. Based upon this value of k_t the instantaneous active center concentration may be calculated. Since the value of $k_p [M^+]$ profile is already known (by dividing the instantaneous reaction rate by the instantaneous monomer concentration), the propagation rate constant profile may be obtained. Figure 4 shows the profiles for the effective propagation rate constant, k_p , as a function of conversion obtained in this manner to the data collected for the dark cure experiment for the photopolymerization of phenyl glycidyl ether with the iodonium antimonate photoinitiator. This figure illustrates that the effective value of the propagation rate constant, k_p , remains remarkably constant up to a conversion of 60% (this result helps to validate the computational scheme because the value is allowed to float freely, but remains constant up to a threshold value of conversion). Note that the value of the propagation rate constant depends upon temperature as well as the photoinitiator counterion.

The observed increase in the effective propagation rate constant at high conversion arises from changes in the interaction between the cationic active center and the counterion as the system undergoes a transition from a liquid monomer to a solid polymer. This hypothesis is based upon the generally-accepted observation that the value of the propagation rate constant in cationic polymerizations depends strongly upon the proximity of the counterion to the active center. If the counterion remains close to the active center, the value of the propagation rate constant may be an order of magnitude lower than if the two ions are completely separated. As suggested previously by Nelson and coworkers^{16,19} for cationic

photopolymerizations of vinyl ethers, as high conversions are achieved in a polymerization process, the diffusional mobility of the photoinitiator counterion is reduced while the mobility of the cationic active center remains high due to reactive diffusion, therefore a shift from ion pairs to separated ions may occur which, in turn, may lead to an increase in the value of the effective propagation rate constant.

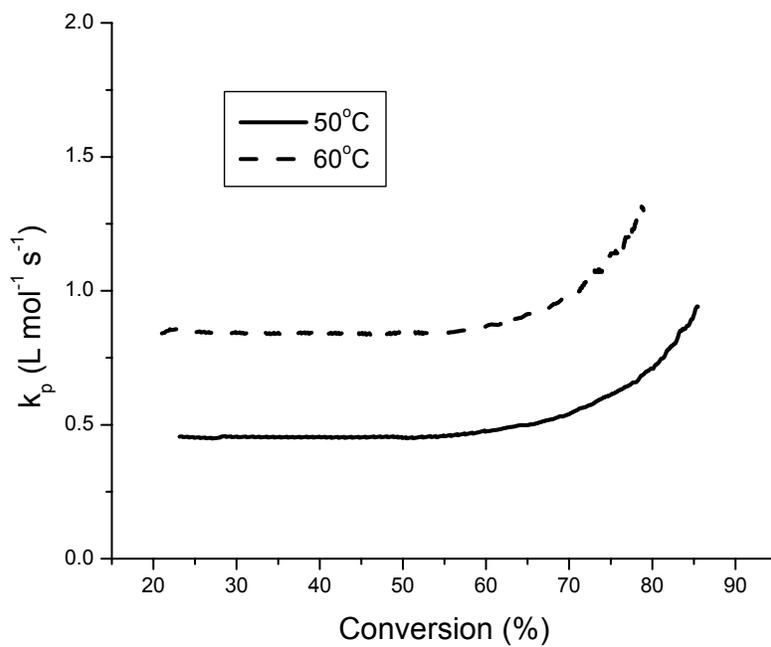


Figure 4. Propagation rate constant profiles for the photopolymerizations of phenyl glycidyl ether monomer initiated using 8.86 mM of iodonium antimonate at 25 mW/cm² of light intensity.

Conclusions

In this contribution we have characterized the termination and effective propagation rate constants for cationic photopolymerizations of phenyl glycidyl ether monomer. These polymerizations were characterized using dark-cure experiments in which active centers are produced photochemically for a specified period of time until the initiating light is shuttered off, and then the polymerization rate is monitored in the dark using photo-DSC. This dark-cure technique, which has been applied much more extensively to free radical photopolymerizations, is especially well suited for characterizing cationic polymerizations due to the long active center lifetimes. Our analysis of the data for the dark cure polymerization rate as a function of time provides profiles of the instantaneous kinetic rate constants as functions of time (or conversion) without the assumption that they do not change. Therefore, this analysis could provide insight in how the rate constants change with conversion as the sample transforms from a liquid monomer to a solid polymer.

For low to intermediate conversion, the effective propagation rate constant is essentially invariant. Our analysis indicates that the cationic active center exhibits a first order decay and the termination rate constant is invariant within an order of magnitude. The propagation rate constant remains same up to a conversion of 50% because there is relatively no change in the ion pair formed between the cationic active center and the photoinitiator counterion. As the conversion increases the diffusional mobility of the photoinitiator counterion is reduced while the mobility of the cationic active center remains high due to reactive diffusion. Therefore a shift from ion pairs to separated ions occurs, resulting in an increase in the propagation rate constant.

This technique can be used to study effect of a variety of reaction parameters such as temperature, photoinitiator counterion, monomer functionality, addition of other reaction constituents like water and alcohol on the kinetic rate constants. In this contribution we have shown the effect of temperature and photoinitiator counterion on the rate constants. We found that as the temperature and the size of the counterion is increased both the termination rate constant and the effective propagation rate constant increase.

References

1. Lapin, S.P. In Radiation Curing of Polymeric Materials; Hoyle, C.E.; Kinstle, J.F., Ed.; ACS Symposium Series, vol. 417, American Chemical Society: Washington D.C.; 1990, pp 363-381.
2. Crivello, J.V.; Lam, J.H.W. In Epoxy Resin Chemistry; Bauer, R.S., Ed.; ACS Symposium Series, vol. 114, American Chemical Society: Washington D.C.; 1979, pp 1-16.
3. Watt, W.R. In Epoxy Resin Chemistry; Bauer, R.S., Ed.; ACS Symposium Series, vol. 114, American Chemical Society: Washington D.C.; 1979, pp 17-46.
4. Lohse, F.; Zweifel, H. *Adv Polym Sci* 1986, 78, 61-81.
5. Crivello, J.V.; Conlon, D.A. *J Polym Sci, Polym Chem Ed* 1983, 21, 1785-1799.
6. Crivello, J.V.; Lee, J.L. *J Polym Sci, Part A: Polym Chem* 1989, 27, 3951-3968.
7. Crivello, J.V.; Dietliker, K. In Photoinitiators for Free Radical Cationic & Anionic Photopolymerisation Volume III; Bradley, G. Ed.; John Wiley & Sons: New York, 1998.
8. Crivello, J.V.; Lee, J.L. In Radiation Curing of Polymeric Materials; Hoyle, C.E.; Kinstle, J.F., Ed.; ACS Symposium Series, vol. 417, American Chemical Society: Washington D.C. 1990, pp 398-411.
9. Crivello, J.V.; Lee, J.L. *J Polym Sci, Part A: Polym Chem* 1990, 28, 479-503.
10. Eckberg, R.P.; Riding, K.D. In Radiation Curing of Polymeric Materials; Hoyle, C.E.; Kinstle, J.F., Ed.; ACS Symposium Series, vol. 417, American Chemical Society: Washington D.C., 1990, pp 382-397.

11. Crivello, J.V.; Ortiz, R. A. *J Polym Sci, Part A: Polym Chem* 2001, 39, 2385-2395.
12. Crivello, J.V.; Liu, S. *Chem Mater* 1998, 10, 3724-3731.
13. Sipani, V.; Scranton, A.B. *J Polym Sci, Part A: Polym Chem* 2003, 41, 2064-2072.
14. Sipani, V.; Scranton, A.B. *J Photochem Photobiol, A*: 2003, 159, 189-195.
15. Padon, K.S.; Scranton, A.B. *J Polym Sci, Part A: Polym Chem* 2000, 38, 2057-2066.
16. Nelson, E.W.; Jacobs, J.L.; Scranton, A.B.; Anseth, K.S.; Bowman, C.N. *Polymer* 1995, 36, 4651-4656.
17. Barton, J.M. *Adv Polym Sci* 1985, 72, 111-154.
18. Becker, C.; Zahnhausen, H.; Krug, H.; Schmidt, H. *Ceram Trans* 1995, 55, 299-306.
19. Nelson, E.W.; Scranton, A.B. *J Polym Sci, Part A: Polym Chem* 1996, 34, 403-411.