Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 159 (2003) 189–195

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Kinetic studies of cationic photopolymerizations of phenyl glycidyl ether: termination/trapping rate constants for iodonium photoinitiators

Vishal Sipani, Alec B. Scranton*

Department of Chemical and Biochemical Engineering, University of Iowa, 4133 Seamans Center, Iowa City, IA 52242-1527, USA

Received 14 January 2003; accepted 25 January 2003

Abstract

In this contribution, we have performed a comprehensive investigation of cationic photopolymerizations of phenyl glycidyl ether using two iodonium photoinitiators: diaryliodonium hexafluoroantimonate (IHA), and (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate (IPB). We characterized these reactions using dark-cure experiments in which the polymerization was monitored in the dark after illuminating it for a pre-determined period of time, and obtained profiles of the rate constant for termination/trapping as a function of time. Our studies reveal that though these photoinitiators result in similar reaction kinetics (reaction rate and conversion profiles that are nearly identical) for constant illumination with a Hg(Xe) arc lamp, they lead to very different results in the dark-cure experiments with the iodonium borate salt exhibiting a higher polymerization rate at a given time, and a higher limiting conversion (76%) than observed for the iodonium antimonate salt (62%). These dark-cure trends were explained by the fact that the rate constant for termination/trapping was approximately 50% higher for the iodonium antimonate photoinitiator (0.041 and 0.027 min^{-1} for the IHA and IBP photoinitiators at 50 °C, respectively). The active center concentrations and propagation rate constants were also characterized. Relative to the IPB, it was found that the IHA initiator leads to a higher active center concentration (due to the higher molar absorptivity of this initiator at the prominent emission wavelengths of the light source) but a lower propagation rate constant. Therefore, these two photoinitiators yield nearly identical kinetic profiles under constant illumination due to the fact that the IPB photoinitiator leads to a lower active center concentration, which is offset by a higher value of the propagation rate constant, and a lower value of the rate constant for termination/trapping.

Keywords: Cationic photopolymerization; Active center lifetime; Kinetic rate constants; Propagation; Termination

---

1. Introduction

Cationic photopolymerizations offer several advantages over the more commonly used free-radical photopolymerizations. Two significant advantages are: (1) cationic photopolymerizations are not inhibited by oxygen, therefore it is not necessary to blanket the reaction system to obtain rapid cure rates; and (2) cationic photopolymerizations may be used to polymerize important classes of monomers such as epoxides and vinyl ethers, which do not undergo free-radical polymerization. The cationic ring-opening polymerizations of epoxides are attractive in many emerging applications because they exhibit less shrinkage than polymerizations of unsaturated monomers such as acrylates and methacrylates. Another important difference between cationic and radical polymerizations is the rate of termination and consequently, the active center lifetime. Free radicals have very high termination rate constants (on the order of $10^5\ \text{L mol}^{-1}\ \text{s}^{-1}$) and have correspondingly short active center lifetimes (typically less than a second). In contrast, for cationic polymerizations the rate of consumption of active centers is very slow and, although it has been relatively unstudied, the average cationic active centers lifetime has been found to be on the order of tens of minutes [1].

In the past decade or so, several new cationically polymerizable monomers and photoinitiators have been reported, notably by Crivello and co-workers. Examples of these monomers include novel silicon-containing epoxy resins [2–4], epoxide monomers based on bisvinyl ethers and propenyl ethers [5,6], benzyl, allyl and propargyl acetal and ether groups [7], and hybrid monomers bearing epoxy and vinyl ether or 1-propenyl ether groups [8]. Cationic photoinitiators comprise mainly the diaryliodonium and triarylsulfonium salts [9]. These salts are thermally stable at room temperatures.

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 laboratory,

---

* Corresponding author. Tel.: +1-319-335-1414; fax: +1-319-335-1415.
E-mail address: alec-scranton@uiowa.edu (A.B. Scranton).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00183-7

we are characterizing the active center lifetimes (or equivalently, the low values of the termination rate constant). Here, we define the propagation lifetime as average time during which an active center consumes monomer molecules to form a growing polymer chain before chemically terminating or becoming trapped. We characterize the propagation and termination rates using a dark-cure, or post polymerization, experiment in which active centers are produced photochemically until the initiating light is shuttered off, and then the polymerization rate is monitored in the dark. This technique has been used extensively to characterize free radical polymerizations, including determination of kinetic rate constants and studies of the termination rate constant as a function of conversion [10–12], but has seen relatively little application to cationic polymerizations. Since these dark-cure studies are based upon the measurement of the polymerization rate after the illumination is ceased, we cannot distinguish between termination of the active centers (which results in chemical consumption of the active centers) and trapping of the active centers (in which case the active centers still exist, but are no longer propagating).

In this contribution, we will present a series of dark-cure studies for photopolymerizations initiated with iodonium salts containing two different counterions: hexafluoroantimonate, and tetrakis (pentafluorophenyl) borate. These photoinitiators are known to exhibit similar photopolymerization kinetics under constant illumination conditions; however, our studies reveal that they behave very differently under dark-cure conditions. These observations will be explained by examining the relative values of the propagation and termination/trapping rate constants.

2. Experimental

2.1. Materials

Phenyl glycidyl ether, which is a monoepoxide monomer, was supplied by the Shell Chemical Company. This monomer was selected because it is a monoepoxide monomer that yields a polymer with a relatively low glass transition temperature. The purity of this monomer was verified using mass spectrometry (Voyager GC/MS Trace 2000 series by ThermoQuest), and no impurities were detected. The photoinitiators used were: diaryliodonium hexafluoroantimonate (IHA, Fig. 1), and (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate (IPB, Fig. 2). These two iodonium photoinitiators were selected because they are known to be among the most effective photoinitiators for yielding high polymerization rates. In all the experiments described here the photoinitiator concentration was 8.86 mM.

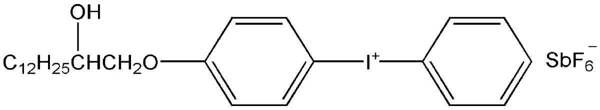

Fig. 1. Molecular structure of diaryliodonium hexafluoroantimonate (IHA).

2.2. Photo-differential scanning calorimetry (DSC)

Photo-DSC experiments were conducted using a Perkin-Elmer DSC-7 modified in-house for photo-experiments. The light source was a 200 W Oriel Hg(Xe) arc lamp. The beam was passed 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 graphite disc absorption. The intensity in the wavelength range of interest was determined to be 25 mW/cm^2 using a calibrated Ocean Optics S2000 spectrophotometer. 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.

3. Results and discussion

3.1. Cationic photopolymerization under constant illumination

Before conducting the dark-cure experiments, polymerizations were carried out under constant illumination to provide the complete profiles of reaction rate versus time, and the conversion versus time, as shown in Fig. 3. The reaction rate versus time profile has a general shape that is characteristic of cationic photopolymerizations. Immediately upon

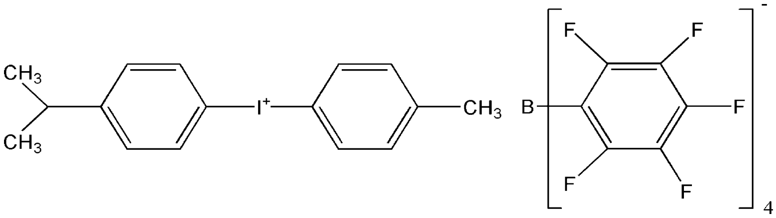

Fig. 2. Molecular structure of (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate (IPB).

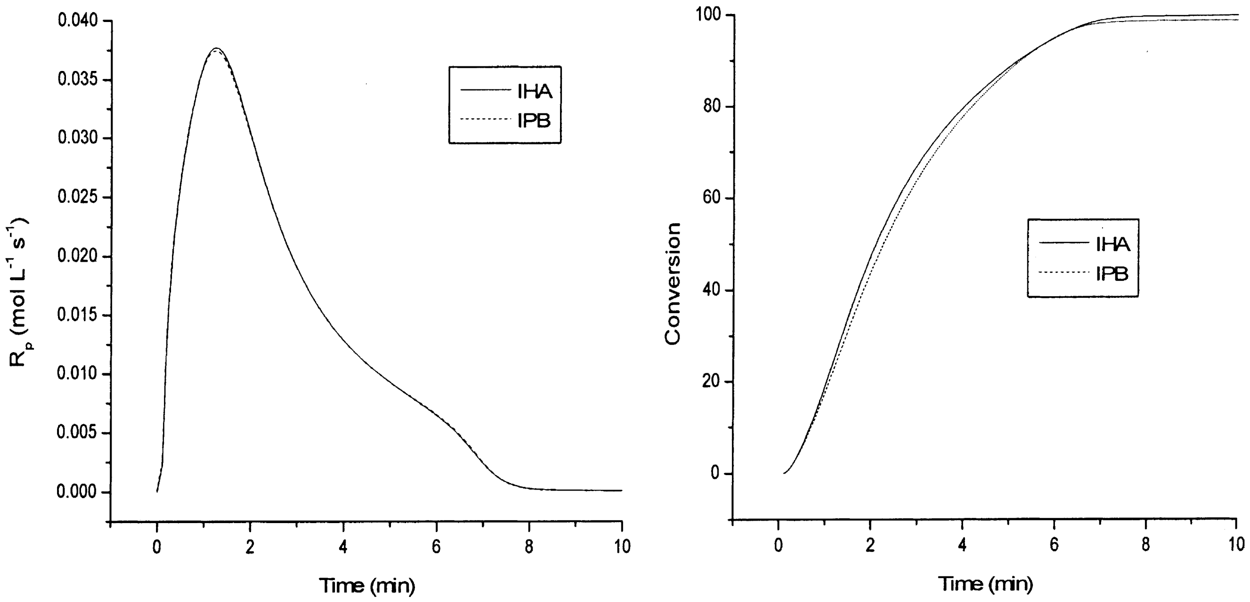

Fig. 3. Reaction rate and conversion versus time profiles for photopolymerization of phenyl glycidyl ether under full illumination with 8.86 mM concentration of IHA and IPB photoinitiators at 50 °C and light intensity of 25 mW/cm^2.

illumination, cationic active centers are formed and react with the surrounding monomer molecules to form a growing polymer chain. The reaction rate increases monotonically due to the increase in the concentration of active centers, reaches a peak, then decreases, primarily due to the decrease in the concentration of monomer.

Fig. 3 illustrates the widely known result that for a Hg(Xe) arc lamp source the two photoinitiators studied yield similar polymerization kinetics under constant illumination (both the time-resolved reaction rate and the conversion profile curves lie almost on top of each other).

3.2. *Cationic photopolymerizations in dark*

In these experiments, the system was illuminated for a pre-determined period of time, then the light was shuttered off and the reaction was monitored in the dark. 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. Therefore, the dark-cure, or post-polymerization, experiments are useful for examining the rate of termination and the average propagation lifetime of active centers.

Fig. 4 compares the conversion as a function of time for photopolymerization of phenyl glycidyl ether for an illumination of 15 s for the two photoinitiators studied. Note that although these two salts exhibit nearly identical rate profiles for continuous illumination (Fig. 3), they exhibit very different rate profiles in the dark-cure experiment (Fig. 4). Specifically, the borate salt (IPB) exhibits a higher conversion (and polymerization rate) at a given time, and a higher limiting conversion (76%) than observed for the antimonate salt (62%). These results suggest that the IPB initiator results in a lower rate constant for termination/trapping, and therefore a higher active center lifetime. To further investigate the kinetic characteristics of these photoinitiators, we characterized the kinetic constants for termination/trapping and propagation as well as the active center concentration, as described below.

3.3. *Determination of the rate constant for termination/trapping*

The dark-cure conversion profiles were analyzed to determine the instantaneous value of the effective termination/trapping rate constant based upon the assumption that the decrease in active center concentration is first order. It is clear that the rate for active center trapping should be first order since it (or equivalently the decrease in the propagating active center concentration) is proportional to the active center concentration. In addition, the rate of chemical termination is pseudo-first order if the concentration of the terminating agent is much higher than the concentration of the active centers. In our case, it is unclear what the nucleophilic termination agent would be since the purity of the monomer is high and the counterions are relatively inactive for termination [13]. As shown below, the analysis based upon the assumption of first-order termination/trapping fit the experimental data very well, while an analysis based upon the assumption of second-order termination did not fit the data.

If termination/trapping is first order, the following equation describes the concentration of active centers as a

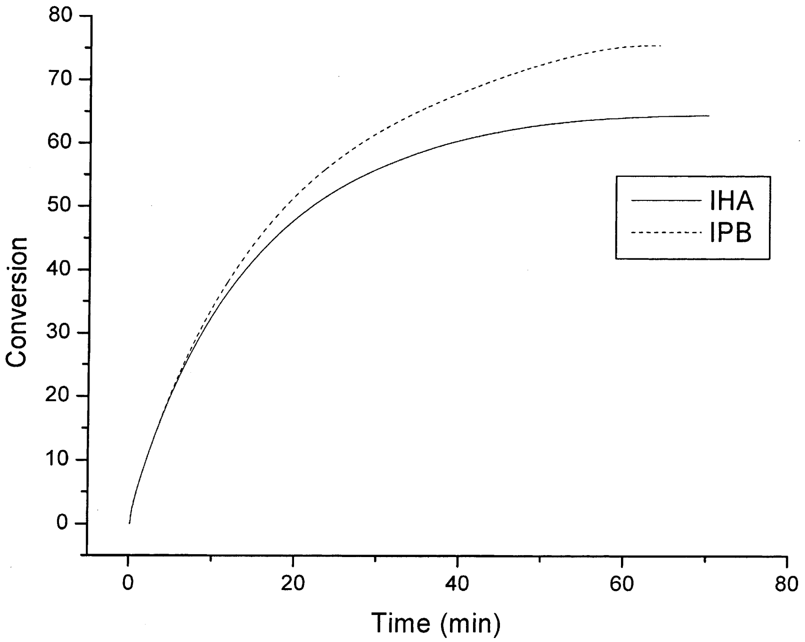

Fig. 4. Dark-cure profiles of conversion as a function of time profiles for 15 s of illumination times for photopolymerizations of phenyl glycidyl ether initiated using 8.86 mM of IHA and IPB salts at 50 °C and light intensity of 25 mW/cm^2.

function of time:

$$\frac{d[M^+]}{dt} = -k_{t/t}[M^+] \tag{1}$$

where $[M^+]$ corresponds to the concentration of propagating (untrapped) active centers, while $k_{t/t}$ represents the kinetic rate constant for termination/trapping of active centers. To determine the instantaneous value of $k_{t/t}$ during a dark-cure experiment, the following equation for the rate of polymerization is combined with Eq. (1):

$$R_p = k_p[M][M^+] \tag{2}$$

This standard equation [14] states that the rate of polymerization is proportional to the product of the monomer concentration and the active center concentration, with the proportionality constant being the effective propagation rate constant, k_p. In general, the value of k_p depends upon the distance between the cationic active center and the counterion. The reactivity of separated cation is much higher than that of an ion pair [14]. Consequently, k_p should remain constant for low to intermediate conversions, when the active center–counterion distance does not change appreciably.

For our analysis, the instantaneous rate of polymerization, R_p, as a function of time was obtained directly from the DSC experiments, while the monomer concentration was readily obtained from the initial monomer concentration and the time-resolved conversion profiles. Dividing the instantaneous rate of polymerization by the instantaneous monomer concentration yielded the instantaneous value of the product $k_p[M^+]$. For conversions below about 50%, the effective propagation rate constant, k_p, may be assumed to remain constant, therefore the decrease in the product $k_p[M^+]$ results from a decrease in the propagating active center concentration due to termination and trapping. The resulting profile of $k_p[M^+]$ versus time was, in turn, differentiated using the numerical differentiation feature provided by the Origin (Microcal, Inc., Boston, MA) software package. Finally, to obtain a profile of $k_{t/t}$ as a function of time, the following equation, which follows from Eq. (1), was used:

$$\frac{d(k_p[M^+])}{dt} = k_{t/t}k_p[M^+] \tag{3}$$

Fig. 5 shows the profile for $k_{t/t}$ as a function of time obtained by applying the procedure described above to the data obtained for the dark-cure experiment with 15 s of illumination (the data from zero to 20 min after the shutter was closed was used, corresponding to a maximum conversion of 50%). This figure illustrates that $k_{t/t}$ has an average value of 0.041 min^{-1} for IHA salt and 0.027 min^{-1} for IPB salt, and remains essentially constant with respect to time. This supports the assumption that termination for the reaction system studied here is first order, and therefore the active centers concentration can be described by an exponential decay. Based upon this value for the termination/trapping rate constant, the average value of the propagation lifetime (which is the inverse of $k_{t/t}$) is approximately 24 min for IHA and the corresponding value for IPB salt is 37 min. This relatively high value of the active center lifetime explains why a sample illuminated for only 15 s can continue to react for nearly an hour. In addition, the relative values of the active center propagating lifetime (37 and 24 min for IPB and IHA, respectively) explain the observed trend in final limiting conversion for low illumination time.

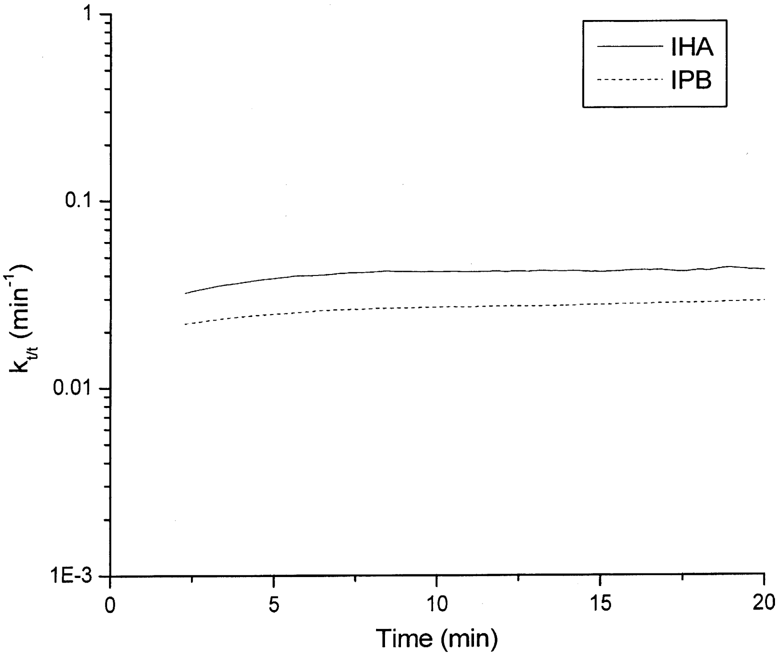

Fig. 5. Plot of $k_{t/t}$ as a function of time for photopolymerization of phenyl glycidyl ether monomer initiated using 8.86 mM concentration of IHA and IPB salts at 50 °C. The samples were illuminated for 15 s at a light intensity of 25 mW/cm^2.

3.4. Determination of active center concentration and propagation rate constants

The analysis of the termination/trapping rate constant described above explains the trends observed in the dark-cure experiments. To understand why the IPB and IHA salts exhibit similar kinetic results in the constant illumination experiments, it is useful to determine the active center concentrations produced by photolysis of the iodonium initiators. The concentration of cationic active centers produced by the photolysis of the iodonium photoinitiator as a function of the illumination time, *t*, can be calculated using the following equation:

$$[M^+] = \varphi I_0(1 - e^{-k_{abs}t}) \qquad (4)$$

where φ is the quantum yield of active centers (the number of active centers formed per photon absorbed), I_0 the photoinitiator concentration at time $t = 0$, and k_{abs} the absorption rate constant, defined as the product of the incident photon flux and the photoinitiator absorption cross-section summed over all incident wavelengths. The quantum yield for the iodonium salts has been reported [15] to be between 0.7 and 0.9 and a value of 0.7 was used for our calculations. For the given system and the reaction parameters, k_{abs} for the IHA salt was found to be 0.027 s^{-1} and the corresponding value for the IPB salt was found to be 0.016 s^{-1}. These values were determined by summing the product of the photoinitiator absorption cross-section and the photon flux of the Hg(Xe) lamp for each wavelength between 297 and 335 nm. With these parameters, Eq. (4) was used to determine the active center concentrations under constant illumination for these two photoinitiators and the corresponding profiles as a function of time are shown in Fig. 6.

Fig. 6 illustrates that, in the initial stage of the polymerization, more active centers are formed for the IHA salt due to the higher molar absorptivity of this initiator at the prominent emission wavelengths of the light source used. Note that the final active center concentration is determined by the initial initiator concentration, which is same for both the cases (because the photoinitiator is completely consumed), although the time to achieve that concentration is different. After the light is shuttered off, the active center concentration decreases in accordance with Eq. (1).

Once the absolute value of the active center concentration is determined, propagation rate constant profile can be characterized using Eq. (2). As described in a previous section, time-resolved profiles of the quantity $k_p[M^+]$ were obtained by dividing the instantaneous rate of polymerization by the instantaneous monomer concentration. The active center concentration at the beginning of the dark-cure experiment was calculated using Eq. (4). Subsequently, the instantaneous active center concentration was calculated using Eq. (1), using the instantaneous $k_{t/t}$ profile obtained previously. Finally, the instantaneous k_p values were obtained by dividing the instantaneous $k_p[M^+]$ value by the instantaneous value of $[M^+]$. This was done for both the photoinitiators and the ratio of k_p is plotted as a function of time in Fig. 7.

Fig. 7 illustrates that the ratio of the propagation rate constants remains constant up to a conversion of 50% verifying our hypothesis that propagation rate constant is constant

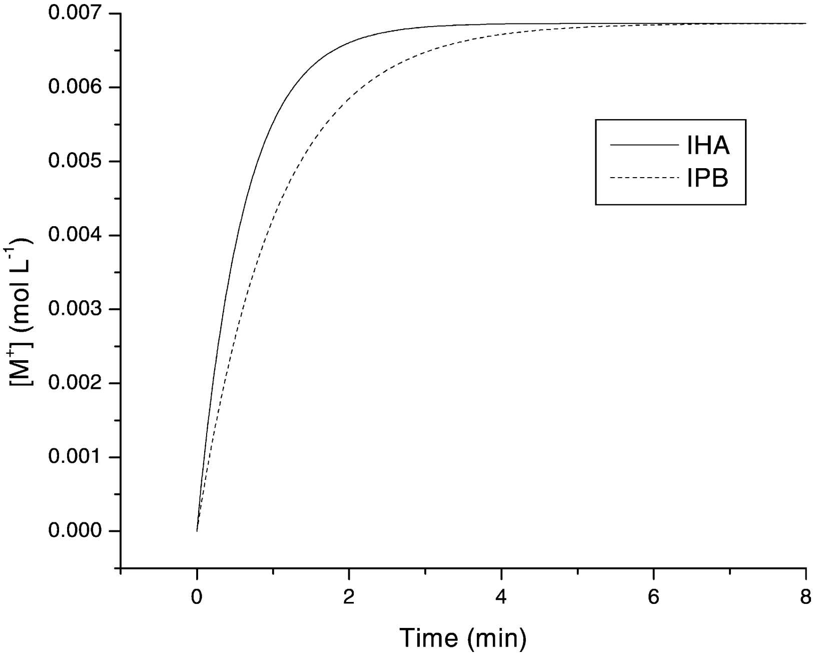

Fig. 6. Plot of the active centers concentration as a function of time for phenyl glycidyl ether monomer during illumination at 25 mW/cm^2 light intensity and a temperature of 50 °C and at 8.86 mM concentration of the photoinitiators.

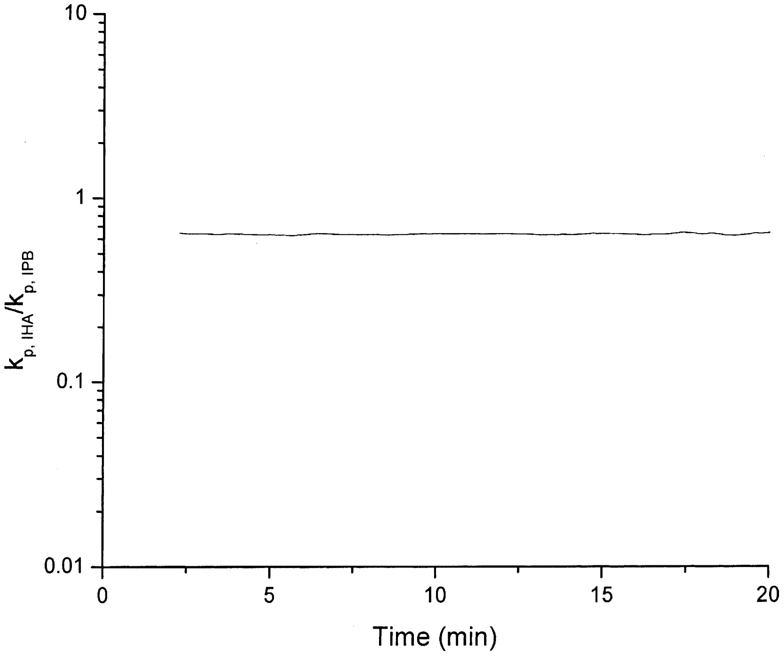

Fig. 7. Ratio of the propagation rate constants as a function of time for photopolymerization of phenyl glycidyl ether monomer initiated using 8.86 mM concentration of IHA and IPB salts at 50 °C.

up to this conversion and its value is approx. 0.6. This also suggests that the IPB photoinitiator results in a higher propagation rate constant than the IHA photoinitiator, likely due to the larger volume of the counterion. Together, these results explain why the two photoinitiators lead to nearly identical reaction profiles under constant illumination. The IPB photoinitiator leads to a lower active center concentration due to its lower molar absorptivity, which is offset by a higher value of the propagation rate constant, and a lower value of the rate constant for termination/trapping.

4. Conclusions

In this contribution, we have performed a comprehensive investigation of cationic photopolymerizations of phenyl glycidyl ether using two iodonium photoinitiators that have been reported to yield high photopolymerization rates: diaryliodonium hexafluoroantimonate, and (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate. We characterized these reactions using dark-cure experiments in which the polymerization was monitored in the dark after illuminating it for a pre-determined period of time, and we analyzed the results to obtain profiles for the rate constant for termination/trapping as a function of time. Since these dark-cure studies are based upon the measurement of the polymerization rate after the illumination is ceased, we cannot distinguish between termination of the active centers (which results in chemical consumption of the active centers) and trapping of the active centers (in which case the active centers still exist, but are no longer propagating). Therefore, we define the propagation lifetime as average time during which an active center consumes monomer molecules to form a growing polymer chain before chemically terminating or becoming trapped (and the termination/trapping rate constant is the inverse of this lifetime).

Our studies reveal that though these photoinitiators result in similar reaction kinetics (reaction rate and conversion profiles that are nearly identical) for constant illumination with a Hg(Xe) arc lamp, they lead to very different results in the dark-cure experiments. Specifically, the iodonium borate salt (IPB) exhibits a higher conversion (and polymerization rate) at a given time, and a higher limiting conversion (76%) than observed for the iodonium antimonate salt (62%). These dark-cure trends were explained through a detailed characterization of the active center termination/trapping rate constant, $k_{t/t}$, which revealed that the $k_{t/t}$ values were 0.041 and 0.027 min^{-1} for the IHA and IBP photoinitiators, respectively (8.86 mM of the photoinitiator at 50 °C and 25 $\mathrm{mW/cm^2}$ of light intensity). These values correspond to active center propagation lifetimes of 24 and 37 min, respectively.

To understand why the IPB and IHA salts exhibit similar kinetic results in the constant illumination experiments, the active center concentrations produced by photolysis of the iodonium initiators and the relative values of the propagation rate constants were characterized. Relative to the IPB, it was found that the IHA initiator leads to a higher active center concentration (due to the higher molar absorptivity of this initiator at the prominent emission wavelengths of the light source) but a lower propagation rate constant. Therefore, these two photoinitiators yield nearly identical kinetic profiles under constant illumination due to the fact that the IPB photoinitiator leads to a lower active center concentration, which is offset by a higher value of the propagation rate constant, and a lower value of the rate constant for termination/trapping.

Acknowledgements

The authors would like to acknowledge the NSF Industry/University Co-operative Research Center for Photopolymerizations at the University of Iowa for providing the financial support for this research.

References

[1] E.W. Nelson, J.L. Jacobs, A.B. Scranton, K.S. Anseth, C.N. Bowman, Polymer 36 (24) (1995) 4651–4656.

[2] J.V. Crivello, J.L. Lee, in: C.E. Hoyle, J.F. Kinstle (Eds.), Radiation Curing of Polymeric Materials, ACS Symposium Series, vol. 417, American Chemical Society, Washington, DC, 1990, pp. 398–411.

[3] J.V. Crivello, J.L. Lee, J. Polym. Sci. 28 (3) (1990) 479–503.

[4] R.P. Eckberg, K.D. Riding, in: C.E. Hoyle, J.F. Kinstle (Eds.), Radiation Curing of Polymeric Materials, ACS Symposium Series, vol. 417, American Chemical Society, Washington, DC, 1990, pp. 382–397.

[5] S.P. Lapin, in: C.E. Hoyle, J.F. Kinstle (Eds.), Radiation Curing of Polymeric Materials, ACS Symposium Series, vol. 417, American Chemical Society, Washington, DC, 1990, pp. 363–381.

[6] J.V. Crivello, D.A. Conlon, J. Polym. Sci. Polym., Chem. Ed. 21 (6) (1983) 1785–1799.

[7] J.V. Crivello, R.A. Ortiz, J. Polym. Sci. 39 (14) (2001) 2385–2395.

[8] J.V. Crivello, S. Liu, Chem. Mater. 10 (11) (1998) 3724–3731.

[9] F. Lohse, H. Zweifel, Adv. Polym. Sci. 78 (1986) 61–81.

[10] D.L. Kurdikar, N.A. Peppas, Polymer 35 (5) (1994) 1004–1011.

[11] P. Bosch, J. Serrano, J.L. Mateo, J. Guzman, P. Calle, C. Sieiro, J. Polym. Sci. 36 (15) (1998) 2785–2791.

[12] M. Wen, A.V. Mccormick, Macromolecules 33 (25) (2000) 9247–9254.

[13] J.V. Crivello, K. Dietliker, in: G. Bradley (Ed.), Photoinitiators for Free Radical Cationic and Anionic Photopolymerisation, vol. III, 2nd ed., Wiley, New York, 1998, p. 351.

[14] G. Odian, Principles of Photopolymerization, 3rd ed., Wiley, New York, 1991.

[15] J.V. Crivello, J. Polym. Sci. 37 (23) (1999) 4241–4254.