Lifetimes and Mobility of Cationic Active Centers

Beth Ficek, Amber Thiesen, and Alec B. Scranton
Department of Chemical and Biochemical Engineering
University of Iowa, Iowa City, IA, USA

Abstract

Cationic photopolymerization exhibits essentially no termination, which leads to active center lifetimes of hours or even days. In this contribution the migration of these long-lived active centers into regions that have never been illuminated is characterized. In addition, the potential for creating active centers photochemically prior to mixing with the monomer is investigated. Experimental results revealed that long-lived cationic active centers may lead to shadow cure of unilluminated regions of the sample. Increases in temperature, counter-ion size and exposure time all increased the extent of shadow cure as a function of time. All of the experimental observations are consistent with the hypothesis that the active center mobility responsible for shadow cure arises largely from reactive diffusion. A second set of studies demonstrated that cationic active centers can be produced photochemically in a monomer-free solution, and then stored up to six weeks at temperatures up to 50 ºC without losing reactivity.

Introduction

Photopolymerizations are well-established as the preferred option for a variety of films and coating applications. Most of these processes are based upon free radical photopolymerization, however cationic photopolymerizations offer unique advantages. For example, termination is extremely slow for cationic photopolymerization, leading to high active concentrations and long active center lifetimes.[1] In contrast, free radicals generally have propagating lifetimes on the order of seconds due to rapid radical-radical termination reactions or efficient oxygen quenching reactions which consume the active centers. Cationic active centers do not combine with one another, and termination occurs predominately through relatively slow processes such as combination with counter ion or active center entrapment due to polymerization of surrounding monomer.

The long cationic lifetimes allow the polymerization to proceed long after the irradiation has ceased, leading to significant dark cure in which previously generated active centers (created during the illumination) continue to polymerize surrounding monomer until they terminate or become entrapped. Several investigators have studied this dark cure or postpolymerization effect.[13] Decker and Moussa studied post-polymerization in several cationic systems and reported that dark cure can account for 80% of monomer conversion, and resulted in significant property development over time.[1,4,5] Sipani and Scranton characterized dark cure in cationic photopolymerizations of monoepoxide monomers and found that post-polymerization experiments are particularly useful for evaluating the kinetic rate constants for termination and propagation.[6,7] They found cationic that most cationic active centers ceased propagation due to depletion of the monomer rather than chemical termination reactions.

In a recent contribution, Ficek *et al*. presented a more comprehensive study of the lifetime and mobility of cationic active centers for crosslinking photopolymerizations of diepoxide monomers.[8] These investigations showed that the active centers will slowly migrate throughout the sample, leading to polymerization in regions that were never illuminated (shadow cure). A polymerization front was observed to move from the illuminated region into the shadow region at a rate proportional to the square root of time. The mobility has a temperature dependence that is well described by the Arrhenius relationship with an activation energy of 89 kJ/mol. Further studies reveal the mobility also has a dependence on the photoinitiator counterions. The photoinitiator with the larger counterion (and therefore a correspondingly higher propagation rate constant) exhibited a significantly higher effective shadow cure diffusion coefficient indicating that the active center mobility responsible for shadow cure arises largely from reactive diffusion.

In this contribution we present a further exploration of the mobility and lifetime of cationic active centers. The effects of several variables including temperature, counter-ion effect, and exposure time on the active center mobility and subsequent shadow cure are examined. A second set of studies were performed to investigate the active center lifetime in monomer-free solutions. If, as suggested by previous studies,[6,7] the active centers cease to polymerization primarily due to depletion of the monomer rather than chemical termination reactions, they should be particularly long-lived in monomer-free solutions. In these experiments, cationic active centers are produced photochemically in a monomer-free solution, and then stored for a predetermined duration and temperature before adding them to the monomer to be polymerized to test for reactivity.

Experimental

Materials:

The photoinitiators used for the active center mobility studies were (tolycumyl)iodonium tetrakis (pentafluorophenyl) borate (IPB, Secant Chemicals, Figure 1) and diaryliodonium hexafluoroantimonate (IHA, Sartomer, Figure 2). Triarylsulfonium hexafluoroantimonate salts 50 wt% in propylene carbonate (THA, Aldrich, Figure 3) was used for the studies of active center lifetimes in monomer-free solutions. The monomer 3,4-epoxycyclohexylmethanyl 3,4-epoxycyclohexanecarboxylate (CDE, Dow Chemical Co, Figure 4) was used in the active center mobility experiments. A second cationically polymerizable monomer methyl 3,4-epoxycyclohexanecarboxylate (ECH, Dow Chemical Co., Figure 5) was used in the active center lifetimes experiments.

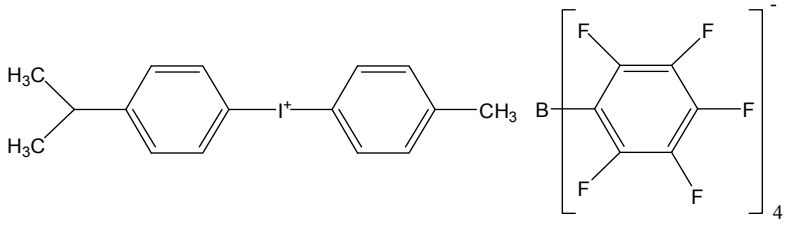

Figure 1. Molecular structure of (tolycumyl) iodonium tetrakis (pentafluorophenyl) borate.

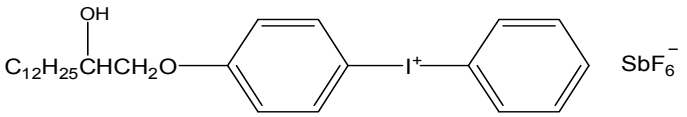

Figure 2. Molecular structure of diaryliodonium hexafluoroantimonate.

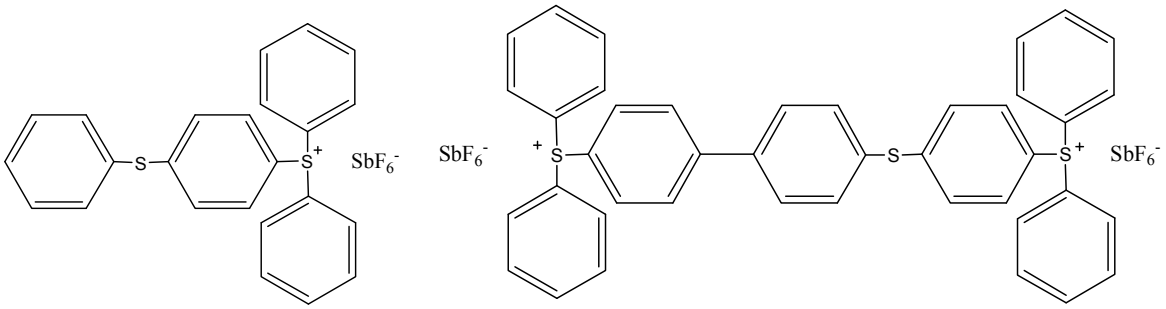

Figure 3. Molecular structure of photoinitiator: triarylsulfonium hexafluoroantimonate salts (THA)

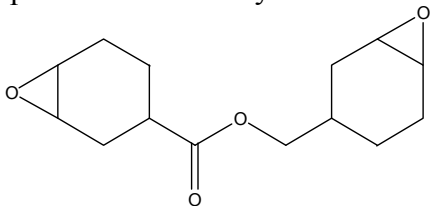

Figure 4. Molecular structure of 3,4-epoxycyclohexylmethanyl 3,4-epoxycyclohexanecarboxylate.

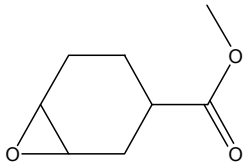

Figure 5. Molecular structure of monomer: methyl 3,4-epoxycyclohexanecarboxylate

Method for Active Center Mobility Studies

The extent of shadow cure as a function of time was characterized for a variety of temperatures, and initiators. These experiments were performed using disposable 4.5 ml polystyrene cuvettes, which were chosen because they are transparent to the wavelengths of interest and will readily dissolve in a number of solvents, therefore allowing the extent of polymerization to be easily determined. Each monomer-filled cuvette (filled to a level of ~3 cm) was illuminated from below with the light from the 200 W Hg/Xe lamp for a prescribed duration (the exposure time, typically five minutes). Since the density of the polymer is higher than that of monomer, illumination from below avoids polymerization-induced convection or mixing. After exposure, the system was maintained at the prescribed temperature for the predetermined shadow cure time. In every cuvette, the polymerization was observed to begin at

the bottom of the sample (due to the illumination from below with a penetration depth no more than ~0.7 millimeter) and moved as a polymerization front toward the top of the sample (into the unilluminated shadow region).

At the prescribed shadow cure time, the sample was placed in tetrahydrofuran (THF) to dissolve the cuvette and monomer from the uncured region of the sample. In this highly-crosslinked system, monomer becomes incorporated into the polymer matrix as it reacts with an active center, so essentially no soluble polymer fraction exists. The insoluble crosslinked polymer matrix was washed with acetone to remove any remaining THF and excess monomer. The polymer sample was dried thoroughly and its weight was recorded. The polymerized thickness was determined by dividing the weight of the polymer sample by the product of the polymer density and the area of illuminated surface (the cross-sectional area of the cuvette, 1 cm^2). At each temperature and shadow cure time, an unilluminated control sample was prepared to verify that thermally-induced polymerization did not occur. In addition, the temperature for each sample was monitor to ensure no change in the storage temperature due to heat generated from the polymerization.

Methods for Active Center Lifetimes Studies

The monomer free photoinitiator solution was illuminated, using a 200 W Oriel Hg(Xe) arc lamp, for 10 minutes to ensure complete photolysis of the photoinitiator. The irradiance of the lamp was measured to be 50.0 $^{mW}/_{cm^2}$. The photopolymerization were carried out under atmospheric conditions and at room temperature. After exposure, the system was maintained at the prescribed temperature for the predetermined storage time in a humidity free environment. At the prescribed storage time, a 5 µL aliquot of the preactivated photoinitiation solution was taken and added to ~15 mg of monomer. The resulting polymerization occurring upon contact between the active center and monomer was monitored using a differential scanning calorimeter. Each polymerization was done in triplicate to ensure the reliability of the results.

Results and Discussion

Active Center Mobility

Cationic active centers' long lifetimes have allowed them to be mobile over time, giving them the ability to not only polymerize the surrounding monomer in the illuminated region but to travel polymerizing regions that have never been illuminated, a process known as shadow cure. Using the method described above the shadow cure for a cyclo-aliphatic diepoxide was characterized for sample stored at 50°C. As shown in Table 1, active centers are generated to a depth of ~0.7 mm from the illuminated surfaces (verified both experimentally and theoretically) and quickly polymerize any surrounding monomer during illumination. Since chemical termination is practically nonexistent in cationic photopolymerization, the previously photo-generated active centers continue to move throughout the sample once the illumination has ceased, increasing the sample height and the shadow cure distance (distance from the initial depth of 0.7mm that the active center have progressed). This active center mobility creates a polymerization front with a square root of time dependence which is typical of a diffusional process. This diffusional mobility likely depends upon contributions from both monomer diffusion and reactive diffusion (which depends upon the rate of propagation). Even though the active centers are covalently linked to an immobile highly crosslinked matrix, they retain mobility

through "reactive diffusion" in which the active centers migrate by propagating with unreacted monomers (or with pendent epoxide groups). Reactive diffusion has been shown to provide an important mode for active center mobility in free radical polymerizations of multifunctional acrylates[9,10] and cationic polymerizations of divinyl ethers.[11,12] Since the shadow cure progresses in a frontal manner, a second diffusional process that may effect that shadow cure distance at a given time is the diffusion of monomer into the polymer matrix at the leading edge of the front. Since the active center must be able to access unreacted monomer for reactive diffusion to occur, it is difficult to isolate the contribution of monomer diffusion.

Storage/Shadow Cure Time (hours)	Sample Height (mm)	Shadow Cure Distance (mm)	Standard Deviation
0	0.7	0	
0.5	2.8	2.1	±0.3
1	3.4	2.7	±0.5
2	4.1	3.4	±0.1
4	4.9	4.2	±0.7
8	6.7	6.0	±0.5

Effect of Temperature

Temperature has a large effect on the active center mobility. As can be seen in the Figure 6, when the temperature increased from 30 to 60°C at ten degree intervals, the extent of shadow cure also increases. One hour after the illumination has ceased, the active centers at 30°C have barely progress while their mobility when stored at 60°C is very evident (around 4 mm in 1 hour). After eight hours of shadow cure time, the shadow cure is very apparent. The temperature dependence of the effective shadow cure diffusion coefficient is consistent with the hypothesis that the active center mobility is facilitated by reaction diffusion.

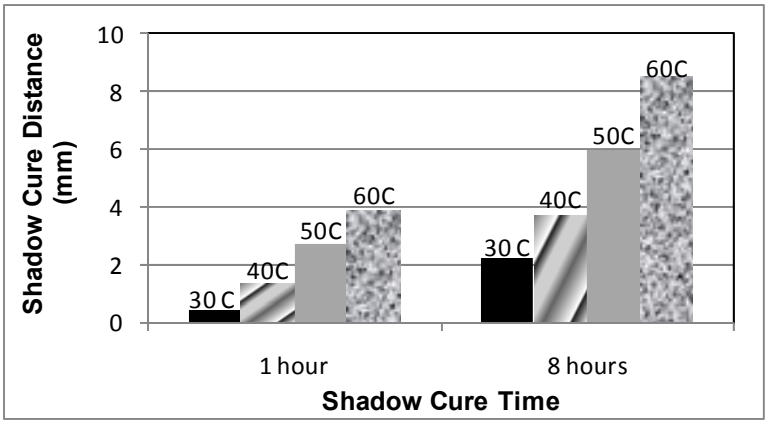

Figure 6. Effect of temperature on shadow cure at 1 and 8 hours of shadow cure time. Monomer: CDE, Initiator: 0.5 mol% IPB, Intensity: 50 mW/cm^2, Exposure time: 5 min, Exposure Temp.: 25°C

Effect of Counter-ion

The photoinitiatior's counter ion plays an important role in determining the propagation kinetic constant, with higher values arising from larger counter-ions.[7] Therefore, investigating the photoinitiator's counter-ion effect the shadow cure will indicate how important the kinetic constant for propagation is for the active center's mobility. Two different iodonium salt photoinitiators, IHA (with a hexafluoroantimonate counter-ion) and IPB (with a larger, pentafluorophenyl borate counter-ion) counter-ion, were investigated at 50°C using the method described above. As shown in Figure 7 below, the IPB with its larger counter-ion and therefore better propagation rates had a lot more shadow cure. The fact that the system with the higher propagation rate constant (all other variables held constant) also exhibits a higher shadow cure progression rate is consistent with the conclusion that the active center mobility arises largely from reactive diffusion.

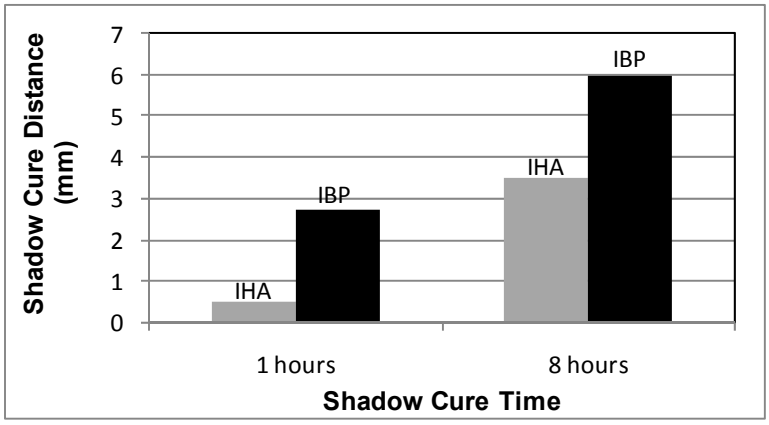

Figure 7. The effect of the photoinitiators' counterion on the extent of shadow cure at 1 and 8 hours of shadow cure time; Monomer: CDE, Exposure time: 5 minutes, Exposure temp.: 25°C, Intensity: 50mW/cm^2, Shadow Cure Temperature: 50°C..

Effect of Exposure Time

The effect of the illumination time on shadow cure was investigated and the results are shown in Figure 8. As the exposure time is increased from 2 to 6 minutes, the total number of active centers produced in the sample increases, and the depth at which active centers are create is enhanced. Since the shadow cure distance is measure from the initial depth, the increase in shadow cure does not arise directly from light penetration, but rather from the mobility of the active centers that were produced. At longer illumination times, the total number of active centers is increased, leading to an enhanced driving force for diffusion, as illustrated in the figure.

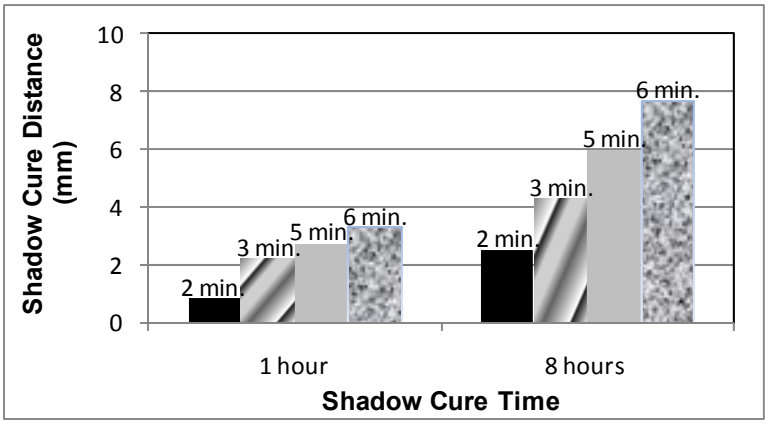

Figure 8. The effect of the exposure time on shadow cure at 1 and 8 hours of shadow cure time; Monomer: CDE, Initiator: 0.5 mol% IPB, Exposure temp.: 25°C, Intensity: 50mW/cm^2, Shadow Cure Temperature: 50°C.

Active Center Lifetimes

Figure 9 illustrates the extended active center lifetime in monomer-free solutions. It contains a plot of the maximum polymerization rate observed upon addition the active center solutions to the monomer (normalized by the rate immediately after illumination) as a function of the storage time (which ranged from 1 to 6 weeks). Figure 9 illustrates that the observed polymerization rate is essentially independent of the storage time, indicating that the active centers do not lose reactivity during storage. In addition, comparing the data for the two different storage temperatures (25ºC and 50 ºC) reveals that the active center lifetime is not degraded by temperatures up to 50 ºC.

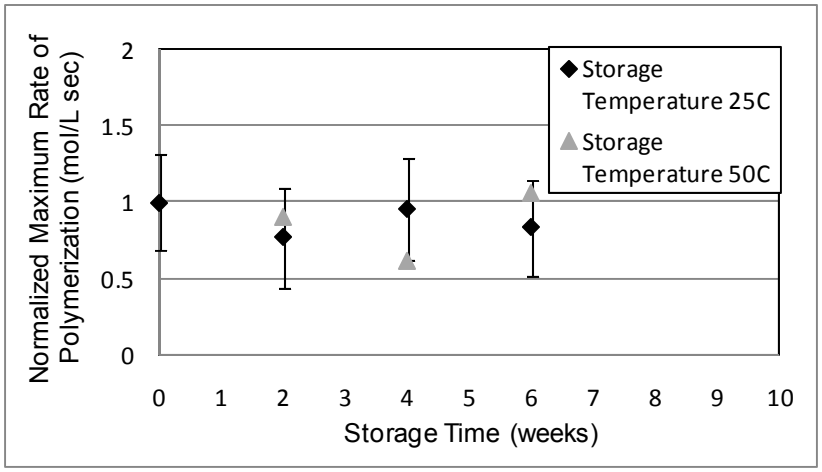

Figure 9. Maximum rate of polymerization by previously generate cationic active centers dependence on storage time for two different temperatures.

Conclusions

Cationic active centers exhibit little or no termination in the absence of strong nucleophiles, leading to active center lifetimes as long as days or weeks. These long-lived cationic active centers can migrate into unilluminated regions of the sample shadow curing the unreacted monomer. Increases in temperature, counter-ion size and exposure time all increased the extent of shadow cure as a function of time. These experimental observations demonstrate that the active center mobility responsible for shadow cure arises largely from reactive diffusion. Cationic active centers produced photochemically in a monomer-free solution, and then stored for a predetermined duration and temperature were found to be reactive upon addition the monomer independent of the storage time. This indicates that the active centers do not lose reactivity during storage and can have lifetimes up to 6 weeks. In addition, it was found that the active center reactivity is not degraded even when stored in temperatures up to 50 ºC.

---

[1]. Decker C, Moussa K. Real-time kinetic study of laser-induced polymerization. Macromolecules 1989; 22:4455-4462.

[2]. Decker C. Photoinitiated Crosslinking Polymerisation. Pro. Poly. Sci. 1996; 21:593-650.

[3]. Wicks ZW, Jones FN, Pappas SP. Organic Coatings. New York, NY: John Wiley & Son Inc., 1994.

[4] Decker C, Moussa K. Kinetic study of the cationic photopolymerization of epoxy monomers. J. Poly. Sci. A: Polymer Chemistry 1990; 28:3429-3443.

[5] Decker C. Fundamental of Photopolymerizations Conference Proceedings. 2005

[6] Sipani V, Scranton AB. Kinetic studies of cationic photopolymerizations of phenyl glyccidyl ether: termination/trapping rate constants for iodonium photoinitiators. J. Photochemistry Photobiology A: Chemistry 2003; 159:189-195.

[7] Sipani V, Scranton AB. Dark-cure studies of cationic photopolymerizations of epoxides: characterization of the active center lifetime and kinetic rate constants. J. Poly Sci: A: Polymer Chemistry 2003; 41:2064-2072.

[8] Ficek B, Thiesen A, Scranton A.B. Cationic Photopolymerizations of Thick Polymer Systems: Active Center Lifetime and Mobility. European Polymer Journal 2007; In press

[9] Anseth KS, Kline LM, Walker TA, Anderson KJ, Bowman CN. Reaction Kinetics and Volume Relaxation during Polymerizations of Multiethylene Glycol Dimethacrylates. Macromolecules 1995 28**(7)**:2491-2499.

[10] Anseth KS, Wang CM, Bowman CN. Kinetic evidence of reaction diffusion during the polymerization of multi(meth)acrylate monomers. Macromolecules 1994; 27(3):650-655.

[11] Nelson EW, Jacobs JL, Scranton AB, Anseth KS, Bowman CN. Photo-differential scanning calorimetry studies of cationic polymerizations of divinyl ethers. Polymer 1995; 36(24):4651-4656.

[12] Nelson EW, Scranton AB. Kinetics of cationic photopolymerizations of divinyl ethers characterized using *in situ* Raman spectroscopy. J. Poly Sci: A: Polymer Chemistry 1996; 34(3):403-411.