The role of water in photoinitiated cationic ring-opening photopolymerization of cyclohexane epoxides

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ABSTRACT

We characterized the role of water in cationic ring-opening photopolymerizations of the diepoxide, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (EEC) and the monoepoxide, methyl 3,4-epoxycyclohexane-1-carboxylate (MEC). Conversion and rate of polymerization were measured by Raman spectroscopy and photo-DSC and increased as water concentration was increased up to 1.5wt% for both EEC and MEC. Unusual MEC kinetic features are explained by active-center propagation lifetime at low conversions. These results may be useful for high-speed coating processes in moisture-rich environments.

INTRODUCTION

Photoinitiated polymerizations have emerged as attractive techniques for rapid production of polymer films and solvent-free coatings.[1-3] Cationic photopolymerizations of epoxides and vinyl ethers produce polymer films or coatings containing excellent adhesion, chemical resistance, low vapor pressure and excellent rheological properties in an environmentally friendly and economical manner.[4] In addition, cationic photopolymerizations are not inhibited by oxygen as compared to acrylate-based free-radical photopolymerizations, eliminating the requirement of an inert nitrogen atmosphere.[4] Unlike free-radical polymerizations, cationic photopolymerizations undergo post-polymerizations in the dark since these systems typically generate high active center concentrations, as well as exhibit long active center lifetimes.[5,6] Finally, the cationic ring-opening polymerizations of cyclic ether monomers such as oxirane and oxetane monomers exhibit excellent mechanical properties, high thermal stability, lower volume shrinkage, little odor, and lower toxicity.[7-9] These unique benefits described above have stimulated the development of monomers and initiators which are widely used for this polymerization process, as well as have increased interest in cationic polymerizations. However, fundamental characterization of cationic reaction systems has been reported only macroscopically and received less attention than free-radical reaction systems.

A number of researchers have investigated the effect of water on the cationic ring-opening photopolymerizations. The nature of these reaction systems is complex, and the role of water has been ascribed numerous characteristics. For example, it is generally reported that water acts primarily as a termination agent (or inhibitor) or chain transfer agent because cationic active centers react faster with water than with the monomer.[10-12] This reaction inhibits the polymerization kinetics and noticeably prolongs the induction time until the water has been substantially consumed.[10] In addition, when water precipitates chain transfer, heterogeneity of the polymer can be anticipated because chain transfer results

in a much broader molecular weight distribution, lower molecular weight and decrease in the T_g of the polymer product.[10,13] In contrast, water can also be involved in an active propagation step because it promotes polymerization kinetics as a co-initiator. For example, Crivello *et al.*[14,15] reported that, in the presence of alcohol, the activated monomer (AM)[16,17] mechanism is an effective means of accelerating the cationic ring-opening polymerization of many types of epoxide monomers due to the chain transfer nature of the AM mechanism.

Specifically, in the initiation step, iodonium or sulfonium salts generate highly reactive radical cations upon UV irradiation. The highly reactive radical cation abstracts a hydrogen atom from hydrogen-donating species such as water, alcohol, monomer, or other impurities, leading to a superacid. The superacid initiates the cationic ring-opening polymerization by addition to the monomer. According to the AM mechanism, in the active propagation step, the oxonium ion terminus of the growing polyether chain is captured by the hydroxyl group of the alcohol, which results in rapid proton transfer from the growing chain end back to the epoxide monomer in the propagation step. This is an iterative process since the alcohol and cationic active center are regenerated in this reaction pathway as illustrated in Scheme 1. In the AM mechanism, the apparent rate acceleration is a result of chain transfer. The AM mechanism provides advantages for multifunctional epoxide monomer systems because the mechanism offers a way to mobilize the propagating cationic species that would usually be sequestered within the glassy matrix of the cross-linked polymer formed.[14]
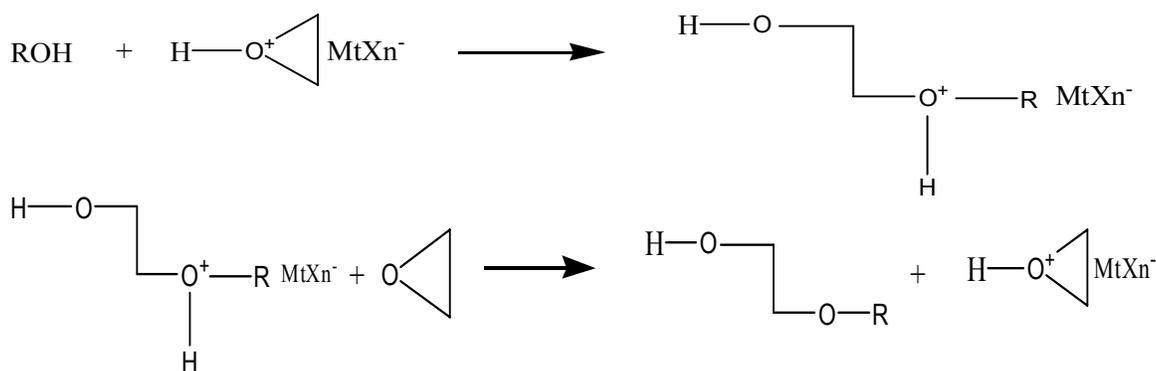
Scheme 1. Activated monomer (AM) mechanism in the propagation step for cationic ring-opening polymerization of an epoxide monomer[14].

Therefore, we have investigated the role of water on the fundamental polymerization kinetics of cationic ring-opening systems using Raman spectroscopy and photo-differential scanning calorimetry (photo-DSC). A series of experiments were performed using cycloaliphatic monoepoxide and die-epoxide as model monomer systems. The conversion profiles as a function of water concentration were obtained from analysis of Raman spectroscopy; the rate of polymerization profiles was also determined by photo-DSC. Comparison of the conversion profiles and rate of polymerization profiles as a function of water concentrations allowed fundamental information regarding the role of the water to be obtained in these cationic ring-opening photopolymerizations.

EXPERIMENTAL METHODS

Materials

To characterize the role of water in cationic ring-opening photopolymerizations, the diepoxide, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (EEC) and the monoepoxide, methyl 3,4-epoxycyclohexane-1-carboxylate (MEC) were used as model monomer systems as shown in Figure 1. The EEC, MEC and DAI were by Union Carbide Corporation, Dow Chemical Company and Sartomer Company, respectively. Diaryliodonium hexafluoroantimonate (DAI) was used for cationic photoinitiation. The range of water concentration used in this study was 0 to 1.5 wt%.
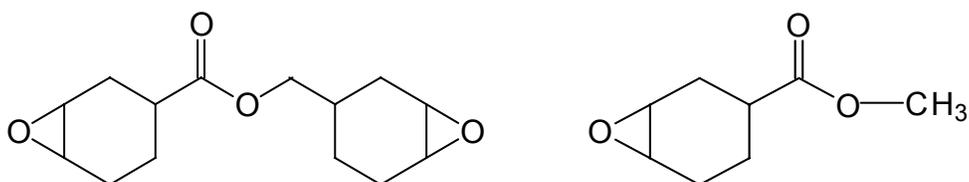
Figure 1. Molecular structure of monomers: 3, 4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (EEC, left) and methyl 3,4-epoxycyclohexane-1-carboxylate (MEC, right).

Methods

For the kinetic studies, a HoloLab 5000R Raman spectrometer (Kaiser Optical Systems, Inc.) and a modified DSC-7 (Perkin-Elmer) were used. The conversion profiles as a function of water concentration were obtained from analysis of Raman spectra at 50°C with a light intensity of 1 W/cm^2. A 785-nm diode laser was used as the excitation source to induce the Raman scattering effect, while the Acticure® Ultraviolet/Visible Spot Cure System (EFOS) was used to induce photoinitiation. The exposure time for spectra was 1 s. From the Raman spectra, the Raman intensity at ~1730 cm^{-1}, which is the band for C=O stretching of aliphatic ketones, was chosen as a reference band because the intensity remains constant during the reaction.[18,19] In addition, the peaks at 789 cm^{-1} (ring vibration of alkyl cyclohexane) and 1262 cm^{-1} (ring breathing of oxirane or ring stretch of epoxy derivatives) were selected as reactive bands because both decrease as the reaction proceeds and exhibit high a 200-W mercury-xenon lamp (Oriel) with a light intensity of 70 mW/cm^2. The average sample size was approximately 12 mg. Dark curing experiments were also performed using photo-DSC under the same reaction conditions to determine the termination rate constant ($k_{t/t}$).

RESULTS AND DISCUSSION

Effect of water for ring-opening cationic photopolymerizations of cyclohexane monoepoxides.

To investigate the effect of water on the kinetics of ring-opening photopolymerizations in the monoepoxide MEC systems, conversion profiles from real-time Raman spectra and rate of increased up to 1.5 wt %, the ultimate conversion increased as illustrated in Figure 2. The conversion profiles exhibit a number of notable results. First, the MEC system without water has a slow induction time and an unusually sluggish conversion profile with two distinct slopes. In addition, all conversion profiles exhibit a very similar initial conversion profile within the first minute of reaction. This slow induction time may be attributed to an unusual initiation mechanism for generation of cationic active centers. Sasaki *et al.*[20] reported that 3-ethyl-3-phenoxymethyl-oxetane (PHO) exhibited an induction time for cationic active center generation. Based on real time FTIR spectroscopic results and in models using a

semi-empirical molecular orbital method, they concluded that a superacid attacks the cyclic ether and produces a dialkyl oxonium cation, which generates a trialkyl oxonium cation through the ring-opening reaction of the dialkyl oxonium cation. The trialkyl oxonium cation is the cationic active center for propagation reaction step.
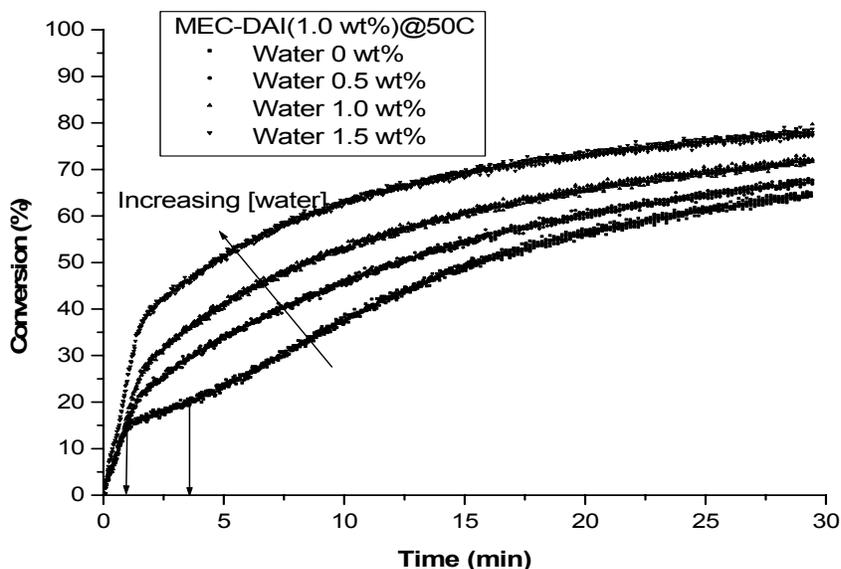
Figure 2. Effect of water on the conversion profiles of the monoepoxide MEC at 50ºC with a light intensity of 1 W/cm^2 obtained from real-time Raman spectra.

However, in the initiation stage, the generated dialkyl oxonium cation is in equilibrium with the superacid and the cyclic ether. Due to this equilibrium, the initiation step becomes the rate-determining step, which results in the induction time. Likewise, the MEC system may exhibit this equilibrium state during initiation. For this reason, the MEC system without water exhibits low conversions at initial reaction times (until 4 min), with two distinct slopes in the initial profile. In contrast, MEC systems with water addition do not show two distinct slopes in the conversion profile, and notably enhanced conversion profiles were observed as the water concentration increased. Due to effective protonation, the initiation step becomes less rate-determining as the water concentration increases.[20] In the propagation step, water addition may cause MEC to undergo a chain-transfer reaction via the AM mechanism because water reacts faster with cationic active centers than the MEC monomer.[10] Therefore, the conversion increased dramatically as water concentration was increased to 1.5 wt% since cationic active centers and hydrogen-donating species may be regenerated in the propagation step via the AM mechanism.

The rate of polymerization profiles also contain striking results as shown in Figure 3. The rate of polymerization profile of MEC system without water has two maximum peaks, and the second maximum peak decreases as the water concentration increases. These double maximum peaks are not an instrumental artifact because Raman spectroscopy (which possesses better time resolution than photo-DSC) also presents unusual conversion profiles. These kinetic results also support the existence of an equilibrium state in the initiation step because the first maximum rate of polymerization peak increases, while the second maximum rate of polymerization peak decreases in the photo-DSC traces, as the water concentration increases.
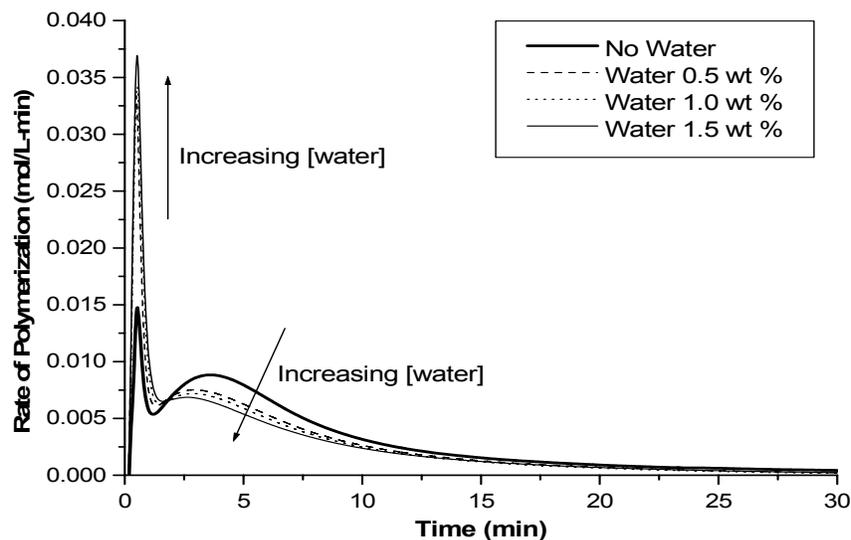
Figure 3. Effect of water on the rate of polymerizations for the monoepoxide MEC as measured by photo-DSC at 50ºC with a light intensity of 70 mW/cm^2.

Effect of water addition on the termination rate constant ($k_{t/t}$): ring-opening cationic photopolymerizations of cyclohexane monoepoxide.

As shown in the conversion profiles from the real-time Raman spectra, the conversions dramatically increased as water concentration was increased up to 1.5 wt% for MEC systems. It is still not clear why there are significant differences in the Raman conversion profiles of the MEC systems with and without water. Therefore, further investigations on the effect of water on the cationic ring-opening reaction mechanism of cyclohexane epoxide were conducted in order to explain these phenomena and to support conclusively the participation of the AM mechanism in this systems. As part of this study, termination rate constant ($k_{t/t}$) profiles[21] were characterized at low conversions (below 15% conversion) for MEC cationic photopolymerizations.

It is generally accepted that active-center propagation lifetime (τ) mainly depends upon chemical consumption of active centers and trapping of active centers at low to intermediate conversions.[21] Because the termination rate constant ($k_{t/t}$) is inversely proportional to the active-center propagation lifetime, both chemical consumption due to combination with counterions and trapping of active centers due to polymerization of surrounding monomer molecules primarily influence the termination rate constant ($k_{t/t}$). If the AM mechanism is involved the propagation step, the addition of water to the MEC system may result in a constant termination rate constant profile with respect to time (or conversion) for low to intermediate conversions because of cationic active center regeneration in the propagation step. However, in the absence of water, the termination rate constant profile would not be constant with respect to time (or conversion) for low to intermediate conversions, and the active-center propagation lifetime should be lower than MEC systems with water added because cationic active centers cannot be regenerated in the propagation step via the AM mechanism.

To test this hypothesis, the MEC conversion profiles during dark-cure study measured by photo-DSC as a function of illumination time were obtained as shown in Figure 4. Because active centers are produced photochemically until the light is shuttered off and the polymerization rate is monitored in the absence of light, the dark-cure experiment does not lead to any more initiation events. The amount of active centers is proportional to the illumination time of the light source. The conversion profiles were analyzed to characterize the instantaneous value of the termination rate constant ($k_{t/t}$). For this analysis, it was also assumed that the decrease in the cationic active center concentration was first order and directly proportional to the chemical termination and trapping as shown in Equation 1.

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

For the determination of the instantaneous value of the termination rate constant ($k_{t/t}$) during a dark-cure experiment, Equation 2, an expression for the rate of polymerization (R_p), was combined with Equation 1.

$$R_p = k_p[M][M^+]$$ (2)

Profiles of the instantaneous value of R_p and monomer concentration [M] were obtained directly from the photo-DSC experiments. For conversions below 50%, k_p may be assumed to remain constant, and the termination rate constant ($k_{t/t}$) profile was obtained using Equation 3 (for a detailed calculation procedure, see Ref. 21).

$$\frac{d(k_p[M^+])}{dt} = k_{t/t}k_p[M^+]$$ (3)
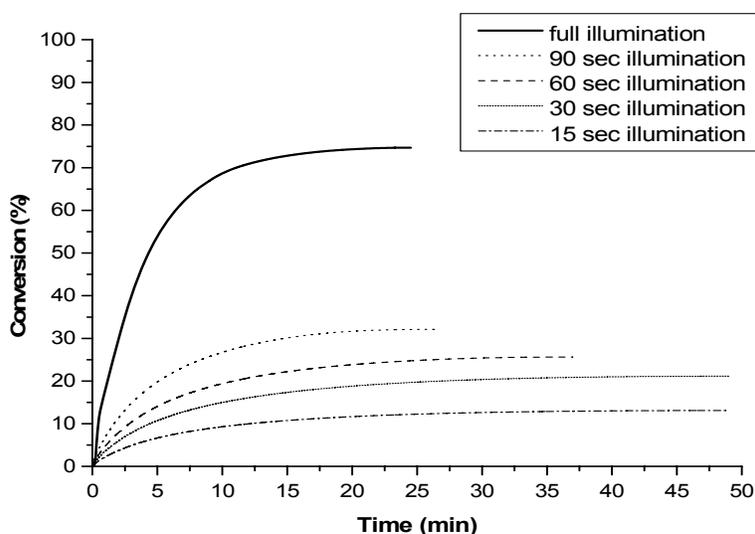
Figure 4. Conversion profiles of MEC dark curing study as a function of illumination time by photo-DSC exothermic traces at 50ºC with a light intensity of 70 mW/cm^2.
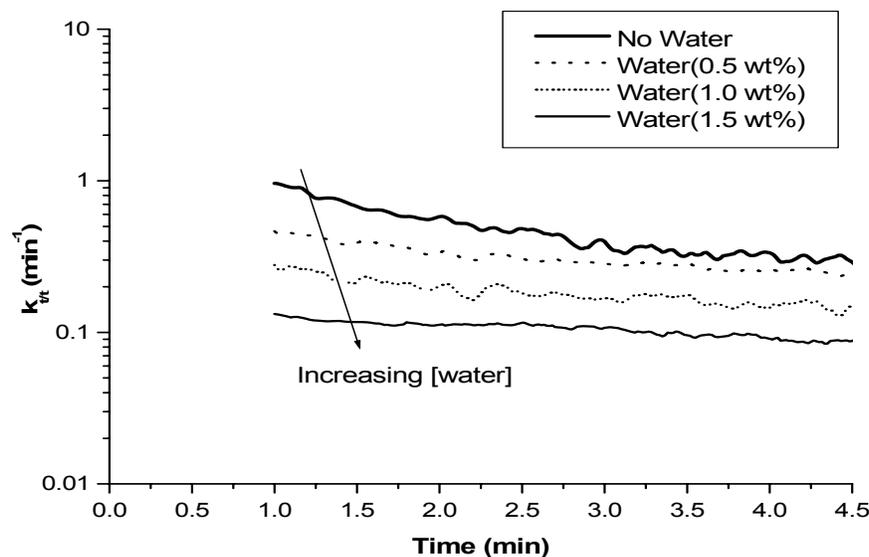
Figure 5. Effect of water on the termination rate constant profile of MEC system at 50°C with a light intensity of 70 mW/cm^2.

Based on the analysis method, the termination rate constant ($k_{t/t}$) profiles were characterized as a function of water concentration for the MEC system as shown in Figure 5. As expected, the active-center propagation lifetime of the MEC system without water addition changes almost an order of magnitude between 1 min and 3 min. However, the value of the termination rate constant for the MEC system containing water (1.5 wt %) is manifestly lower than without water, and the termination rate constant profile approaches a horizontal plateau. These results provide convincing evidence for the AM mechanism, in which the addition of water results in cationic active center regeneration.

Effect of water for cationic ring-opening photopolymerizations of cyclohexane diepoxides

To investigate the effect of functionality on the kinetics of ring-opening photopolymerizations, the diepoxide EEC was used, and its kinetics were compared with the monoepoxide MEC (both monomers are structurally similar). The conversion profiles and rates of polymerization as a function of water concentration on the EEC system are shown in Figure 6 and 7, respectively. As water concentration increased up to 1.5 wt %, the conversion dramatically increased due to the chain-transfer reaction via the AM mechanism (Figure 6). Specifically, increasing the water concentration resulted in about a ~50% increase in conversion for the EEC monomer system (from 40% to 61%), while the conversion of MEC was only enhanced ~20% (from 64 % to 78 %). This result indicates water plays a greater role as a plasticizing agent for the EEC system. Because the diepoxide monomers can form a cross-linked structure, some of the epoxide rings become inaccessible to the propagating active centers, and the overall conversion for the diepoxide monomer is lower than that of monoepoxide. However, water can facilitate diffusion of the propagating cationic active centers in EEC system since the AM mechanism enables mobilization of the propagating cationic specis in multifunctional epoxide monomer systems.[14]

Figure 7 demonstrates the effect of water on the rate of polymerizations for the EEC system as measured by photo-DSC. For example, the rate of polymerization increases as the water concentration increases up to 1.0 wt%, and then the rate of polymerization decreases when the water concentration is

1.5 wt%. As described above, small amounts of water act as a co-initiator, thereby promoting the EEC cationic polymerizations. The role of water as a plasticizer also may be involved since EEC monomer is diepoxide monomer of high viscosity (380 cps at 25°C).[22] In contrast, large amounts of water (1.5 wt%) limited the rate of polymerization. In the presence of excessive water, inactivation of the proton or active center species by solvation may inhibit polymerization because the preferred reaction for the initiating proton is reaction with water to form a hydronium ion.[23]
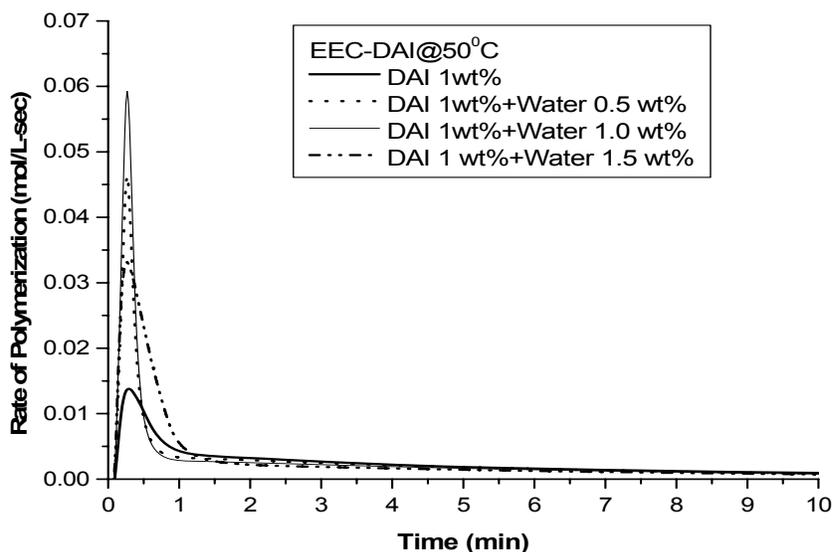
Figure 6. Effect of water on the conversions profiles of the diepoxide EEC at 50°C with a light intensity of 1 W/cm^2 obtained from real-time Raman spectra.
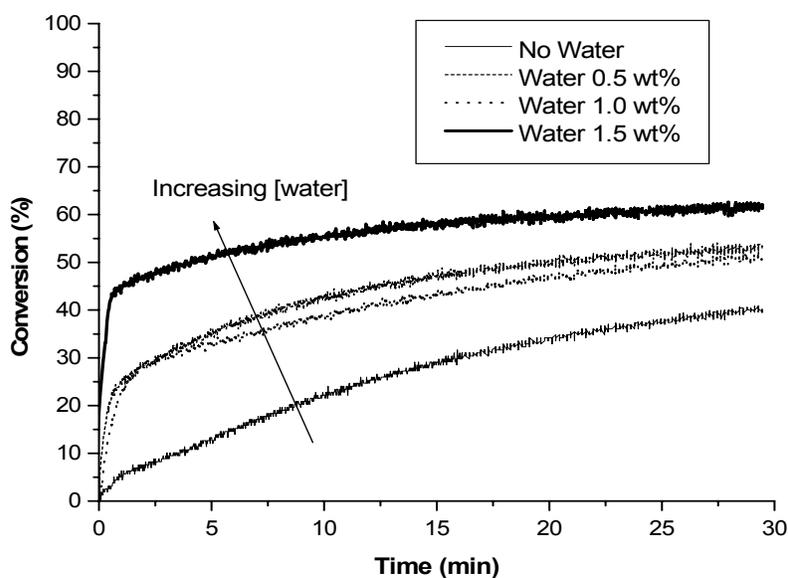
Figure 7. Effect of water on the rate of polymerizations for the diepoxide EEC as measured by photo-DSC at 50°C with a light intensity of 70 mW/cm^2.

CONCLUSIONS

In this study, a series of experiments was performed to investigate the role of water in the cationic ring-opening photopolymerizations of the cycloaliphatic monoepoxide MEC and diepoxide EEC. As water concentration increased up to 1.5 wt%, the conversion of both MEC and EEC system increased. For the MEC system, the conversion profiles and rate of polymerization profiles indicate that the initiation step becomes less rate determining as the water concentration is increased, most likely due to protonation effects. The characterization of the termination rate constant ($k_{t/t}$) in the MEC systems provides confirmation that water addition in these systems may also result in chain transfer reactions via the AM mechanism, leading to higher conversions with higher water concentrations. For the EEC system, the increased conversions with increased water concentration also point toward chain transfer reactions due to the AM mechanism, which would enhance the mobility of the propagating cationic species in such multifunctional monomers. Further investigations of these systems are ongoing and promise to yield a more fundamental understanding of the role of water in these cationic ring-opening systems.

REFERENCES

1. Crivello, J.V.; Sasaki, H., *J. Macromol. Sci. Pure,* 1993, A30 (2-3): 189-206.

2. Clark, S.C.; Hoyle, C.E.; Jonsson, S.; Morel, F.; Decker, C., *Polymer,* 1999, 40(18), 5063-5072.

3. Ward, J.H.; Shahar, A.; Peppas, N.A., *Polymer,* 2002, 43(6), 4243-4250.

4. Crivello, J.V.; Lam, J.H.W., *J. Poly. Sci.: Part A Polym. Chem.,* 1979, 17(3), 977-999.

5. Sipani, V.; Scranton, A.B., *J. Photochem. and Photobio. A: Chemistry,* 2003, 159, 189-195.

6. Sipani, V.; Scranton, A.B., *J. Poly. Sci.: Part A Polym. Chem.,* 2003, 41, 2064-2072.

7. Sasaki, H.; Crivello, J.V., *J. Macromol. Sci. Pure,* 1992, A29 (10): 915-930.

8. Crivello, J.V.; Liu, S., *J. Poly. Sci.: Part A Polym. Chem.,* 2000, 38(3), 389-401.

9. Hua, Y.; Crivello, J.V., *J. Poly. Sci.: Part A Polym. Chem.,* 2000, 38(19), 3697-3709.

10. Lin, Y.; Stansbury, J. W., *J. Poly. Sci.: Part A Polym. Chem.,* 2004, 42, 1985-1998.

11. Crivello, J. V. and Dietliker, K., *Photoinitiators for Free Radical Cationic & Anionic Photopolymerization,* 2nd Edition Volume 3, 1998, pp331.

12. Fouassier, J. P., *Photoinitiation, Photopolymerization, and Photocuring,* Hanser-Garden, Cincinnati, 1995, pp278.

13. Sangermano, M.; Malucelli, G.; Morel, F.; Decker, C.; Priola, A., *European Polymer Journal,* 1999, 35, 639-645.

14. Crivello, J. V.; Oritz, R.A., *J. Poly. Sci.: Part A Polym. Chem.,* 2002, 40, 2298-2309.

15. Crivello, J. V.; Oritz, R.A., *J. Poly. Sci.: Part A Polym. Chem.,* 2001, 39, 3578-3592.

16. Penczek, S.; Kubisa, P.; Matyjaszewski, K.; Szmanski, R., *Pure Appl. Chem.*, 1984, 140.

17. Kubia, P.; *Macromol. Symp.* 1988, 13/14, 203

18. Ingle, J.D.Jr.; Crouch, S.R., *Spectrochemical Analysis,* Prentice Hall, New Jersey, 1988.

19. Lin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G., *The Handbook of Infrared Raman Characteristic Frequeccies of Organic Molecules,* Academic Press, New York, 1991.

20. Sasaki, H.; Rudzinski, J.M.; Kakuchi, Y., *J. Poly. Sci.: Part A Polym. Chem.,* 1995, 33, 1807-1816.

21. Sipani, V.; Scranton, A. B., *J. Poly. Sci.: Part A Polym. Chem.,* 2003, 41, 2064-2072.

22. Sasaki, H., *Rad-Tech, 2000* Technifical Conference, Baltimore, MD, April 9-12, 2000, pp61.

23. Odian, G., *Principles of Polymerization*, 3rd Edition, 1991, pp373.