Spectroscopic Quantification of Kinetic Rate Constants for Epoxy-Acrylate Hybrid Photopolymerization

Brian Dillman University of Iowa, Chemical and Biochemical Eng. Dept., Iowa City, USA

Julie L. P. Jessop University of Iowa, Chemical and Biochemical Eng. Dept., Iowa City, USA

Introduction

Photopolymerization has been used widely in coatings, adhesives, and inks, as well as in medical applications such as dental filling composites. This widespread use is due to the high level of spatial and temporal control inherent to photopolymerization and the associated energy and material savings.[1-3] In order to further reduce cost and broaden the applicability of photopolymerization, hybrid resin systems have been developed by combining acrylates with epoxides or other cationic monomers.[3-5] The unique curing capabilities of these systems result in a high degree of cure for acrylate in ambient atmospheric conditions. In order to optimize the use of these hybrid systems for practical applications, it is essential to obtain a quantitative understanding of and the factors that influence each component in the system. The epoxide monomers used in this research, like most cationically polymerizable monomers, are affected by atmospheric moisture. The work presented in this paper strives to clarify kinetic effects of water on these epoxide monomers.

Water has been shown to react cationic photopolymerization in several ways. Water can induce decomposition of the photoinitiator,[6] but it can also participate in propagation reactions and consequently impact the final polymer properties.{{39 Ghosh,N.N. 2005; 79 Decker, C. 2001}} In a system containing only epoxide monomers, the propagation reaction proceeds via the active chain end (ACE) mechanism, as shown in Scheme 1a. If nucleophilic species are introduced to the system a secondary reaction pathway becomes available. This pathway is referred to as the activated monomer (AM) mechanism, as shown in Scheme 1b.[7, 8] These two reaction pathways are not kinetically equivalent. The relative reactivity of the initiating molecules and the active centers with the monomer and other nucleophilic species, water, alcohols or other functional groups in the system, will factor into the prevalence of one of the two reaction mechanisms. Thus, the measured rate of epoxide consumption should be indicative of the pathway that dominates the overall cationic curing process. Additionally, polymers resulting from the respective reaction mechanisms will differ in structure and therefore in properties. For example, increasing amounts of water have been shown to reduce the average molecular weight of linear polymers and the hardness of cross-linked polymers.[9, 10]

In this study, the conversion of epoxide monomer and consumption of water were monitored by real-time mid-infrared (RT-MIR), and real-time near-infrared (RT-NIR) spectroscopy. The RT-MIR technique has been used widely in monitoring rapid photopolymerizations due to its short data acquisition time, ability to monitor multiple functional groups simultaneously, and high resolution.[3, 11-13] The use of RT-NIR spectroscopy has been limited due to less spectral information available in the NIR region and lower molar

absorptivities which then require much more sample volume to obtain reasonable signals. The advantage of RT-NIR spectroscopy in this research is the higher resolution of bands associated with water vibrations and O-H bonds of other species, such as alcohols and carboxylic acids. [14]

Scheme 1 a: ACE Mechanism
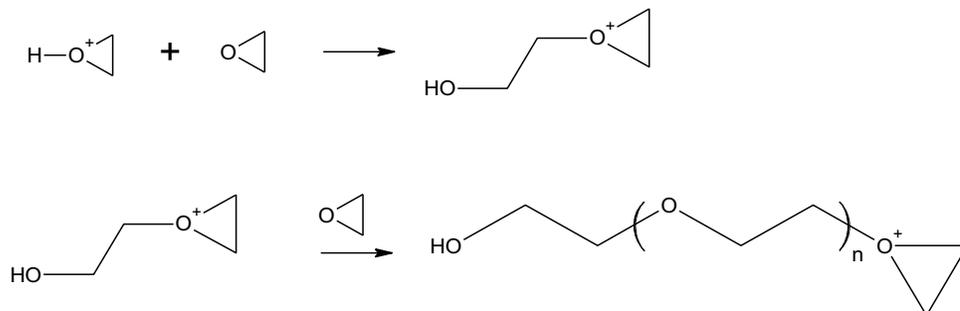
Scheme 1 b: AM Mechanism
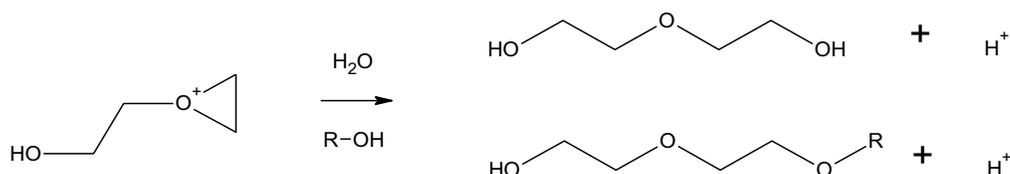
Experimental

Materials

3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexyanecarboxylate (EEC, Aldrich) was the epoxide monomer used in this study (Figure 1). The water concentration in this material was determined by a standard addition method to be 0.07 mol H_2O/L. Additional distilled water was added to the formulations to reach the target concentrations. Five formulations were prepared ranging from 0.07 to 1.43 moles H_2O/ L. The cationic photoinitiator used was diaryliodonium hexafluoroantimonate (DAI, Sartomer). All materials were used as received. All formulations were prepared to contain an initiator concentration of 8 mmol/L.
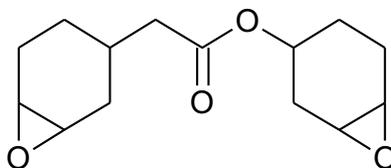
Figure 1: Molecular structure of epoxide monomer EEC.

Methods

RT-MIR Spectroscopy

RT-MIR spectra were collected using a FT-IR spectrometer (Thermo Nicolet 670 Nexus) with a KBr beam splitter and a MCT/B detector to determine epoxide conversion with respect to

time. The sample solutions were sandwiched between a pair of NaCl plates with 15 micron spacers used to ensure a constant path length for each sample. The spectra contained sample absorbance of 600-4000 cm^{-1}. The photopolymerization of the formulations was initiated using a 100 W high pressure mercury lamp (Acticure$^{®}$ Ultraviolet/Visible spot cure system, EXFO Photonic Solutions, Inc.) equipped with a fiber optic port to deliver the light dose. The full spectrum irradiance used in these experiments was measured to be 50 mW/cm^2 using a radiometer (Cole-Parmer). The conversion of epoxide was calculated using the peak height of the 750 cm^{-1} band (Figure 2) in the following equation:

$$Epoxide\ fractional\ conversion = 1 - A_{760}(t)/A_{760}(0)$$

where $A_{760}(0)$ is the peak height before polymerization and $A_{760}(t)$ is the peak height and time t during the polymerization.

Every sample formulation was illuminated for for 3 min while spectra were collected. Additionally a "long-term" experiment was performed to monitor post-exposure curing, referred to as "dark cure," as well as the persistence of different functional groups. In this experiment, spectra of the formulations were collected with illumination for 10 min and then without illumination for 110 min.
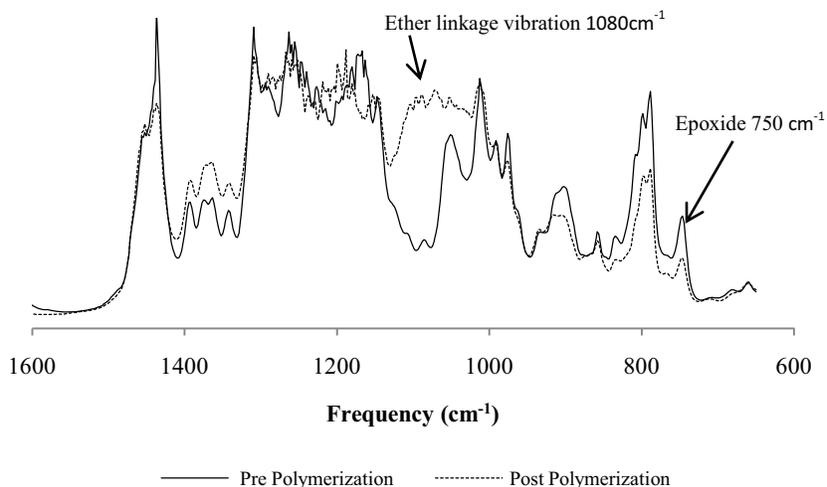
Figure 2: Characteristic MIR spectral bands of epoxide monomer EEC before and after photopolymerization. Reactive epoxide band is located at 760 cm^{-1}, and the band for ether linkages formed by polymerization are located at 1080 cm^{-1}.

RT-NIR Spectroscopy

RT-NIR spectra were collected using the same FT-IR spectrometer to determine water consumption over time. The spectra contained absorbance values for 4000-6200 cm^{-1}. The sample volume required for strong absorbance signals was much greater for the NIR samples. Therefore, a custom glass sample holder was crafted in house and consisted of a 2.5 cm inner diameter cap with a well depth of about 1.5mm. The sample holder was filled with a sample volume of 1.0 cm^3 for each experiment. The peak height of 5226 cm^{-1} (Figure 3) was used to calculate the fractional consumption of water in the following equation:

$$Water\ fractional\ consumption = 1 - A_{5226}(t)/A_{5226}(0)$$

where $A_{5226}(0)$ is the peak height before polymerization and $A_{5226}(t)$ is the peak height at time t during the polymerization.

The "long-term" experiment was performed to investigate the persistence of the hydroxyl functional groups. In this experiment, spectra of the formulations were collected with illumination for 10 min and then without illumination for 110 min.
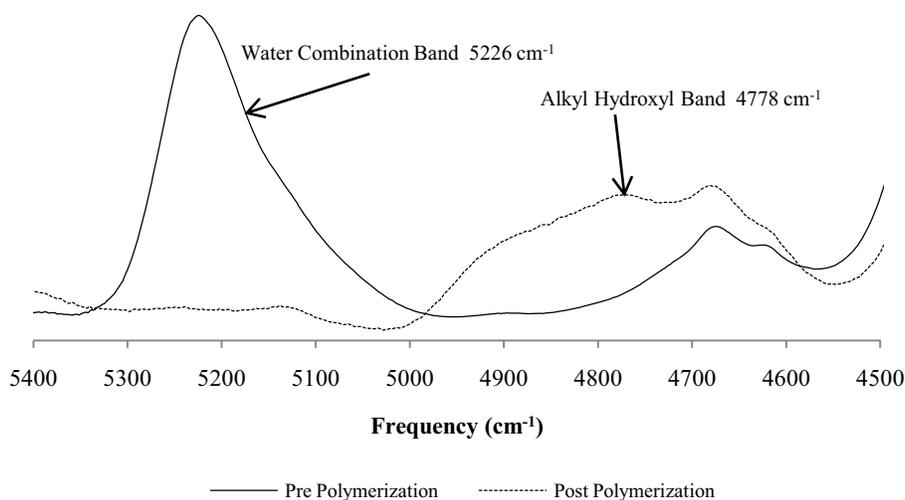

Figure 3: Characteristic NIR spectral bands of water and alkyl hydroxyl groups changing during the cationic ring-opening photopolymerization of EEC.   The peak frequency of water is located at 5226 cm^{-1} and of the alkyl hydroxyl groups at 4778 cm^{-1}.

Results and Discussion

EEC produces highly cross-linked polymer networks upon photopolymerization. Often the conversion of EEC is limited due to the early onset of gelation, resulting in trapped active centers that cannot react further due to diffusion limitations. As shown in Figure 4, the epoxide conversion is indeed affected by increased water concentration. The slowest rate of polymerization and lowest ultimate conversion was observed in the formulation with no added water (i.e., [H_2O] = 0.07 mol/L). As the water concentration increased, a more pronounced induction period was observed. Additionally, with increasing water content, there was an enhanced final conversion.

RT-NIR experiments of the same EEC formulations produced similar results as observed with the RT-MIR experiments. As shown in Figure 5, the higher the water content, the greater the induction time; however, all formulations ultimately resulted in complete consumption of the water present. The induction time for water consumption was approximately half of that observed with the respective epoxide conversion profiles. Each formulation with added water (i.e., [H_2O] > 0.07 mol/L) showed a pronounced acceleration in reaction after the induction period, both in water consumption and in epoxide conversion. The rate acceleration for water consumption appears consistently after the epoxide conversion reaches 3-5%.
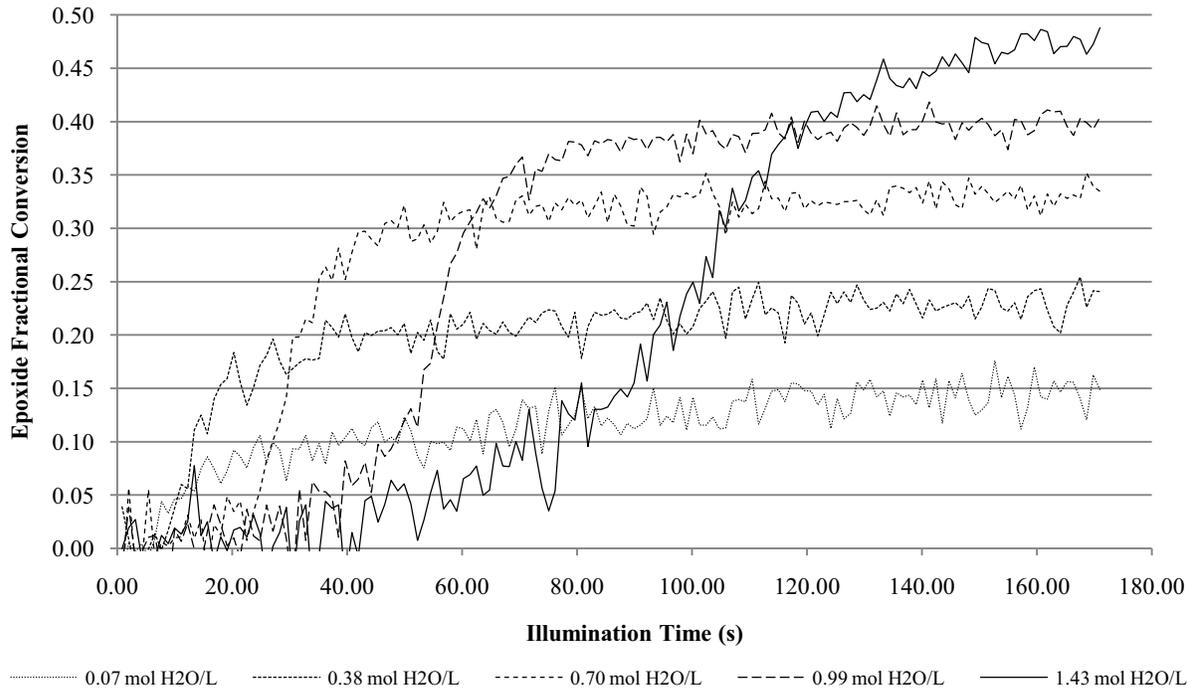
Figure 4: Epoxide conversion profiles obtained from RT-MIR spectra for the cationic ring-opening photopolymerization of EEC formulations containing varying concentrations of water.
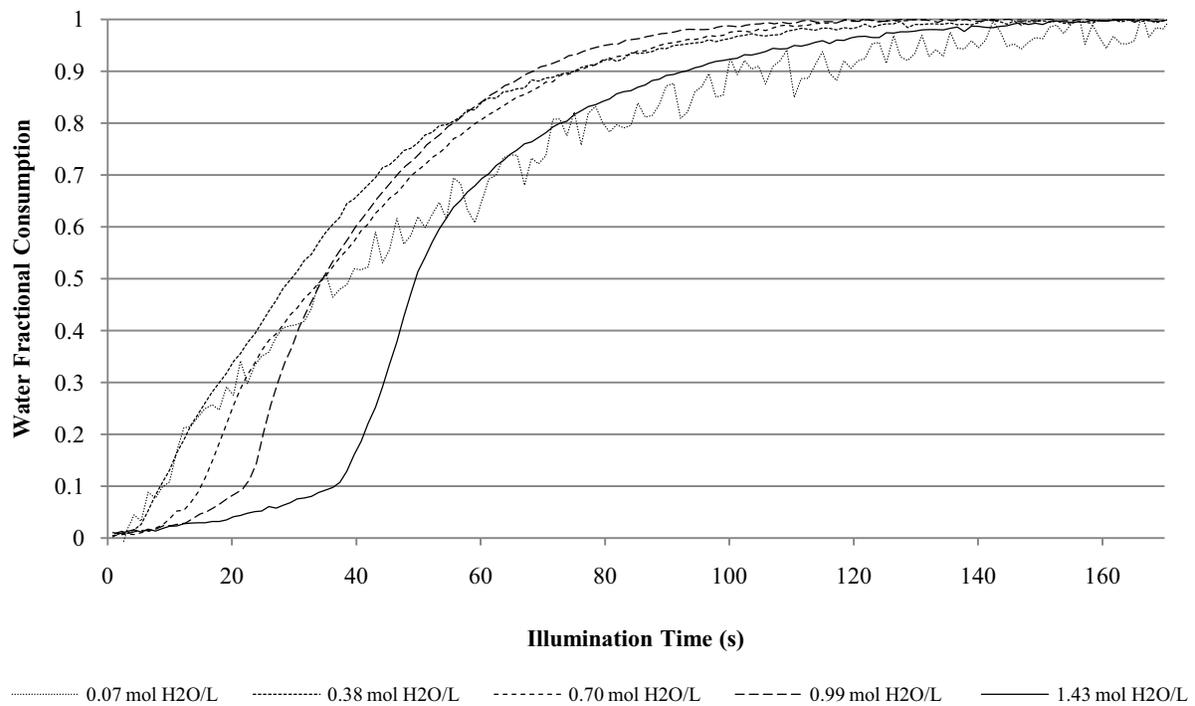
Figure 5: Water consumption profiles obtained from RT-NIR spectra for the cationic ring-opening photopolymerization of EEC formulations containing varying concentrations of water.

During the "long-term" experiments (Figure 6) the alkyl hydroxyl peak increased in intensity as the water peak disappeared during the reaction. Also, there was measureable "dark cure" of the epoxide during the last 110 min. For example, the conversion for the formulation with the highest concentration of water (i.e., $[H_2O]$ = 1.43 mol/L) was about 49% just as the lamp was shuttered and approximately 54% at the end of the 2-h experiment. These results alsoalso demonstrated the persistence of hydroxyl content throughout the reaction.
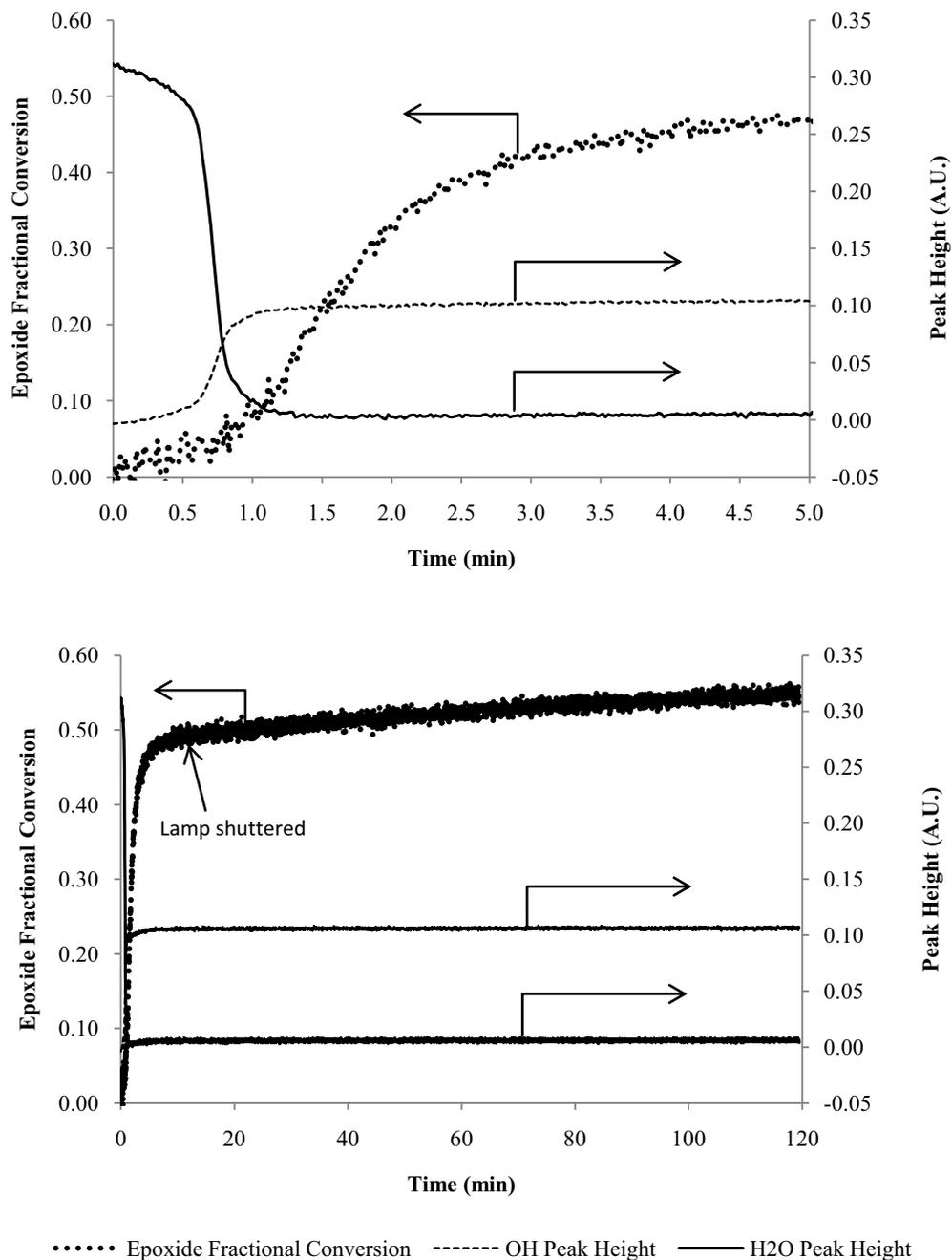
Figure 7 "Long-term" study of the cationic ring-opening photopolymerization of EEC formulation containing 1.43 mol H_2O/L: illumination started at t = 0 and stopped at t = 10 min. Water consumption and hydroxyl production obtained from RT-NIR experiments, and epoxide conversion obtained from RT-MIR experiments.

Top: zoomed view, Bottom: full view

Conclusions

This work demonstrates that RT-NIR spectroscopy can be used to determine the moisture content of monomers accurately, as well as the rate of water consumption during the polymerization. Together, the RT-MIR and RT-NIR experiments show a distinct kinetic dependence of epoxide reaction on the amount of water present. These results indicate that the AM mechanism dominates in the presence of water. The amount of alkyl hydroxyls produced has a direct relationship to the amount of water present in the system. Additionally, the "long-term" study shows that the hydroxyl content is constant once the water in the system is consumed. This persistent hydroxyl concentration further confirms the AM mechanism as shown in Scheme 1b. For every water molecule reacting with an activated monomer, one or two alkyl hydroxyl groups are produced, depending on whether the oxygen of the activated monomer is bound to a carbon or hydrogen, respectively. For every alkyl hydroxyl reacting with an activated monomer bound to hydrogen, there is no net change in the amount of hydroxyls present.

Acknowledgements

References

(1) Fouassier, J. In *Photoinitiation, Photopolymerization, and Photocuring;* Hanser/Gardner Publications, Inc.: Cincinnati, OH, 1995; , pp 375.

(2) Koleske, J. V. In *Radiation Curing of Coatings;* ASTM International: West Conshohocken, PA, 2002; Vol. 1, pp 244.

(3) Decker, C. Photoinitiated crosslinking polymerization.*Prog.Polym.Sci.; Progress in Polymer Science* **1996**, *21*, 593-650.

(4) Cai, Y.; Jessop, J. L. P. Decreased oxygen inhibition in photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy.*Polymer* **2006**, *47*, 6560-6566.

(5) Lin, Y.; Stansbury, J. W. The impact of water on photopolymerization kinetics of methacrylate/vinyl ether hybrid systems*Polym. Adv. Technol.* **2005**, *16*, 195-199.

(6) Hartwig, A.; Harder, A.; Lühring, A.; Schröder, H. (9-Oxo-9H-fluoren-2-yl)-phenyl-iodonium hexafluoroantimonate(V) – a photoinitiator for the cationic polymerisation of epoxides*European Polymer Journal* **2001**, *37*, 1449-1455.

(7) Cai, Y.; Jessop, J. L. P. Effect of water concentration on photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy*Polymer* **2009**.

(8) Lin, Y.; Stansbury, J. W. Near-infrared spectroscopy investigation of water effects on the cationic photopolymerization of vinyl ether systems*Journal of Polymer Science Part A Polymer Chemistry* **2004**, *42*, 1985-1998.

(9)   Ghosh, N. N.; Palmese, G. R. Electron-beam curing of epoxy resins: Effect of alcohols on cationic polymerization.*Bull. Mater. Sci.* **2005**, *28*, 603-607.

(10) Decker, C. Photoinitiated cationic polymerization of epoxides*Polym. Int.* **2001**, *50*, 986-997.

(11) Cramer, N. B.; Bowman, C. N. Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time Fourier transform infrared.*Journal of Polymer Science Part A Polymer Chemistry* **2001**, *39*, 3311-3319.

(12) Crivello, J. V.; Varlemann, U. Mechanistic study of the reactivity of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate in photoinitiated cationic polymerizations.*J. Polym. Sci. Part A* **1995**, *33*, 2473-2486.

(13)   Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Kudyakov, I.; Viswanathan, K.; Nason, C.; Guymon, C. A.; Hoyle, C. E. The kinetics of vinyl acrylate photopolymerization.*Polymer* **2003**, *44*, 2859-2865.

(14) Crandall, E. W. Spectroscopic analysis using the near-infrared region of the electromagnetic spectrum.*J. Chem. Educ.* **1987**, *64*, 466.