# Chain Transfer Agents in Cationic Epoxide Polymerizations: Kinetic and Physical Effects

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## Introduction

UV/EB curing is a rapid and energy efficient method used to produce protective coatings, adhesives and sealants, templates for electronic devices, and even biomaterials such as tissue scaffolds.[1-5] A variety of chemical polymerization mechanisms are initiated via radiation curing including free radical (both chain and step polymerization), cationic, and anionic.[6-14][13-15] Free-radical polymerization is the most commonly used mechanism in UV/EB curing due to the low cost materials and high rates of polymerization. Cationic polymerization is used at lower volumes; anionic polymerization has been demonstrated to work in research laboratories, but to the author's knowledge has not yet been implemented in industry. Though cationic systems are more costly than the free-radical systems (in terms of monomers and photoinitiators), the use of cationic resins can be economically viable do to the tolerance of atmospheric oxygen.[12] Free-radical systems are inhibited by molecular oxygen in both the active center generation step (via photoinitiation) and the subsequent polymerization.[15,16] Conversely, cationic systems are unaffected by molecular oxygen in both the photoinitiation and polymerization steps.[11,17] The oxygen-tolerating capacity of cationic systems allows for good cure of thin films with hard, fully cured surfaces without the use of expensive purging equipment and inert gases ($N_2$, $CO_2$, and Ar). Other characteristics that set cationic systems apart include: monomer side reactions with other nucleophilic compounds (water and alcohols) and long-lived active centers (virtually no chemical termination occurs in many systems).[18-26]

The effects of other atmospheric factors and process contaminants that may affect the curing kinetics and the material properties of epoxy resins are important to consider. The ubiquitous contaminant that is most difficult to control is water. Alcohols may also be introduced during monomer synthesis and purification phases of manufacture. In this paper, the effects of alcohols have been studied and will be discussed, with respect to kinetic and physical effects.

## Experimental

### Materials

3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexyanecarboxylate (EEC, Aldrich) was the epoxide monomer used in this study (Figure 1). 1-Dodecanol, 1-butanol, t-butanol, 1,4-butanediol, 1,2-propanediol, and 1,6-hexanediol were purchased from Aldrich and used as chain transfer agents (CTA). The photo-acid generator was an iodonium hexaflouroantimonate salt (IHA) manufactured under the trade name PC2506 and donated by Polyset Company. All formulations were prepared to contain 0.3 wt% IHA. The CTAs were formulated such that the ratio of hydroxyl groups to epoxide ranged from 0.1 to 1.0 in the kinetic experiments and equal to 0.3 for mechanical analysis.
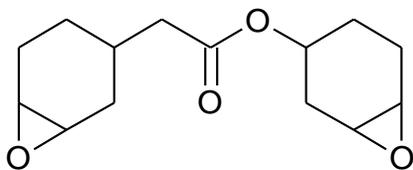
**Figure 1:** Molecular structure of epoxide monomer EEC.

## Methods

### *RT-Raman Spectroscopy*

The formulations with 1,6-hexanediol and 1,2-propanediol were analyzed kinetically using RT-Raman spectroscopy. The formulations were injected into a 1 mm ID quartz capillary tube which was placed in a thermo-stated sample holder maintained at 45ºC during UV illumination. UV light (300 nm $< \lambda <$ 450 nm) measured to deliver 50 mW/cm$^2$ from a 100 W high pressure mercury lamp (Acticure$^®$ Ultraviolet/Visible spot cure system, EXFO Photonic Solutions, Inc.) via a fiber optic light guide. Raman spectra were induced with a 785 nm NIR laser and collected every 1-1.5 seconds for 5 to 10 minutes of total illumination time.

### *Mechanical Analysis*

Polymer specimens were prepared by injecting the formulation resin between two silanized (Rain-X treated) microscope slides. The slides were separated by two 150 micron thick glass coverslips resulting in a nominal resin thickness of 300 microns. The resin containing assembly was illuminated by a black light (about 2-5 mW/cm$^2$) for 5 min per side then passed twice, once per side, through a belt-driven Fusion curing system fitted with a H-bulb at 3 ft/min. The specimens were stored for 2 weeks, after which they were either immediately removed from the mold for analysis or heated in a convection oven at 125ºC for 1 hour, 175°C for 1 hour, allowed to cool to room temperature, and then removed from the mold for analysis. The specimens were analyzed by dynamic mechanical analysis (DMA) in a TA instruments Q800 dynamic mechanical analyzer. Specimens of approximate dimensions (15 x 5 x 0.3 mm) were tested in a film tension clamp with a sinusoidal strain of 0.05% applied at a frequency of 1 Hz over a broad temperature range (-100 $<$ T $<$ 300°C). The glass transition ($T_g$) of the materials produced was taken to be the temperature corresponding to the maximum tan δ value.

## Results and Discussion

### Kinetic Analysis

Epoxides polymerize by two distinct mechanisms. One mechanism, called the active chain end (ACE) mechanism, is analogous to radical chain polymerization in that the active center is attached to the end of the growing polymer chain and neutral monomers react with the cationic active center to effect polymer chain growth. A second mechanism, called the activated monomer (AM) mechanism, is a chain transfer reaction in which a nucleophilic compound like water or organic alcohols react with a cationic active center that opens the epoxide ring, regenerates a hydroxyl group, and ejects a proton.[27, 28] The ejected proton then bonds with other nucleophilic species, including neutral monomers that can then react with the hydroxyl group,
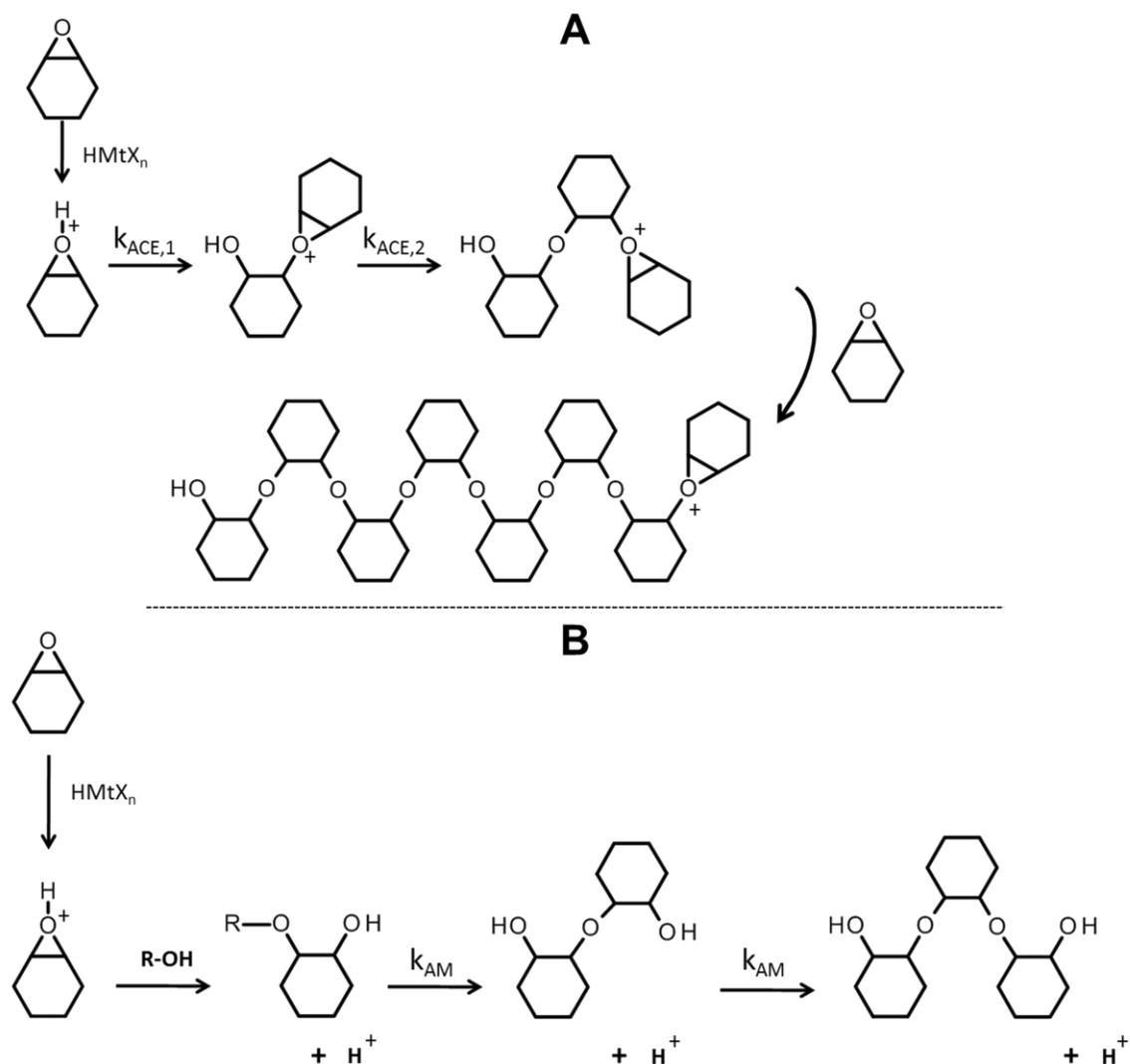
**Scheme 1:** The ACE (A) and AM (B) propagation mechanisms. ACE displays typical polymer chain growth while AM is a chain transfer reaction.

formed at the terminus of the growing polymer chain, to continue polymer propagation. Representations of the ACE and AM mechanisms are shown in Scheme 1. The effect of including alcohols or moisture in a formulation leads to promotion of the AM mechanism. When the AM mechanism is the dominant propagation mechanism, the kinetics and the network structure will be different.[29] Our group has studied a variety of alcohols formulated in epoxy resins and observed increasing rates of polymerization, increasing final conversion levels, decreasing glass transition temperatures, and decreasing gel fractions with increasing amounts of CTAs.

Conversion profiles for varying amounts of 1,2-propanediol and 1,6-hexanediol in EEC are shown in Figure 2. The general trend for both CTAs is increased conversion with increased hydroxyl concentration. The data show clear kinetic differences between the 1,2-propanediol and 1,6-hexanediol. At similar loadings, both CTAs achieve similar ultimate conversions, but 1,2-propanediol reaches high conversions much faster. The difference between these two CTAs is
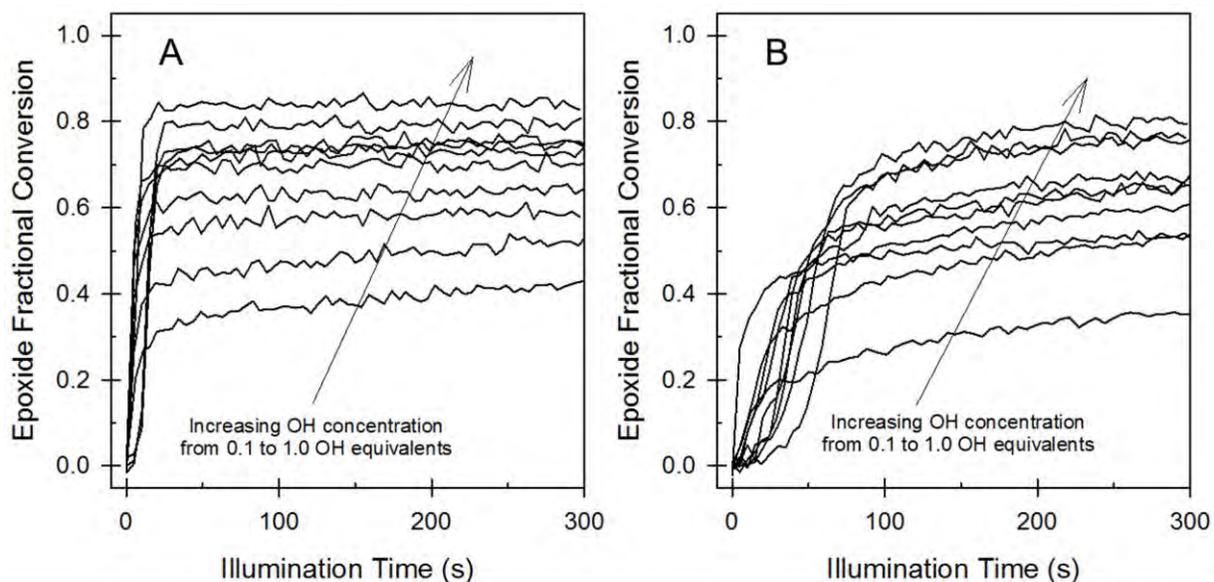
**Figure 2:** Epoxide conversion profiles obtained via RT-Raman spectroscopy. CTA concentrations ranged from 1/10 the epoxide concentration two a 1/1 ratio. All formulations contained IHA as photoinitiator, [IHA] = 0.3 wt%.

the size, or molecular weight, and the distance between the two hydroxyl groups. We have shown that size for mono-alcohols such as ethanol, butanol, or octanol has very little impact on the conversion or the rate of polymerization. It is therefore proposed that the great difference in reactivity between the diols studied here may be accounted for by the distance between the two hydroxyl groups. According to the AM mechanism, a proton is ejected after the epoxide ring is opened by a nucleophilic hydroxyl group. The ejected proton will then bind to a neutral epoxide monomer, which allows for the epoxide ring to be activated and subsequently opened. It is logical that a CTA with a second hydroxyl group in close proximity to the last ring-opening event will display greater reactivity than a CTA with the second hydroxyl group farther removed from the last reaction site. In order for a hydroxyl group to react with an active center, it must first be in close proximity to an active center. 1,2-Propanediol displays higher reactivity than 1,6-hexanediol and has a second hydroxyl group only two carbons removed from the last reaction site. The relative distance between hydroxyl groups is likely a key factor in the relative reactivities of various diol CTAs.

**Mechanical Analysis**

The cured resins formulated with CTAs yielded a range of glass transition temperatures depending on the CTA type, relative concentration, and curing protocol. We have limited the results reported here to four CTAs, all formulated at 0.3 hydroxyl equivalents (i.e., the ratio of hydroxyl to epoxide is equal to 0.3). The polymers were synthesized via photopolymerization; half of the specimens were analyzed via DMA, while the other half were annealed and then analyzed via DMA. In handling and preparing the specimens for mechanical analysis, it was observed that the specimens that were not annealed (i.e., photocured only) were more prone to fracture and premature failure. The authors do not have a working hypothesis that explains this behavior. More interesting is the mechanical analysis for the photocured-only specimens. DMA
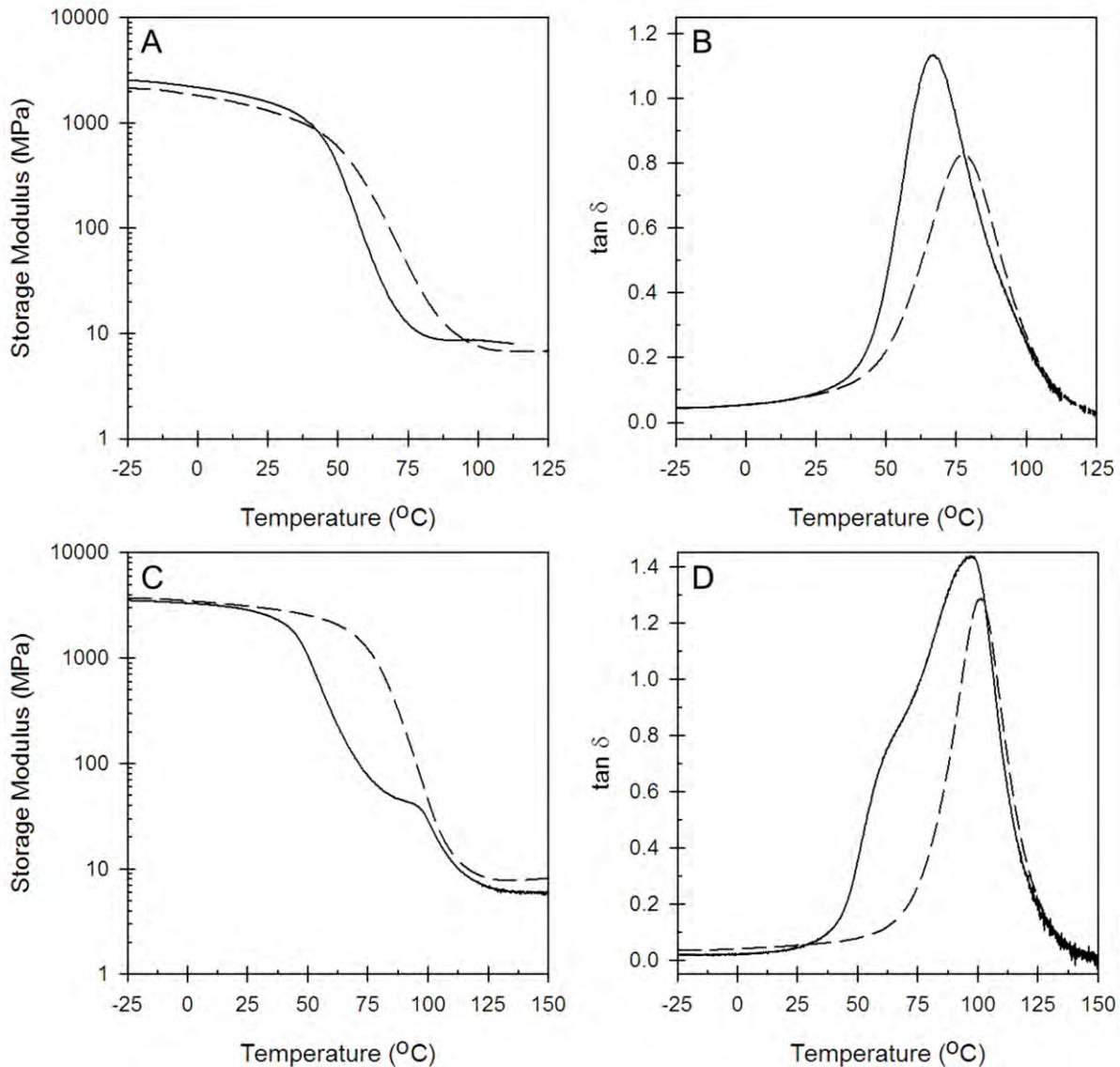
**Figure 3:** Storage modulus and tan δ profiles obtained from EEC formulations with dodecanol (A,B), and n-butanol (C,D) as CTAs. Solid lines represent data collected from specimens that were photocured and the dotted lines were obtained from specimens that were photocured and annealed above the glass transition temperature.

data for four different CTAs in EEC, both for photocured-only and annealed specimens are shown in Figures 3 and 4. With every CTA, excepting dodecanol, the photocured-only specimens show multimodal behavior in the tan δ plots and have abnormal storage modulus profiles that show two distinct transitions. The DMA profiles for n-butanol suggest a degree of phase segregation in the material that is removed via the annealing process. The optical clarity of the samples and the increased symmetry of the tan δ peaks after annealing imply another mechanism must explain the apparent multimodal behavior.

The DMA data for 1,4-butanediol and t-butanol also show a disparity between the two curing protocols, but offer a second more likely mechanism for the apparent multi-modal mechanical behavior. In the storage modulus plots (see Figure 4a and c), the modulus increases after passing through the first apparent transition. The only reason that the modulus should rise
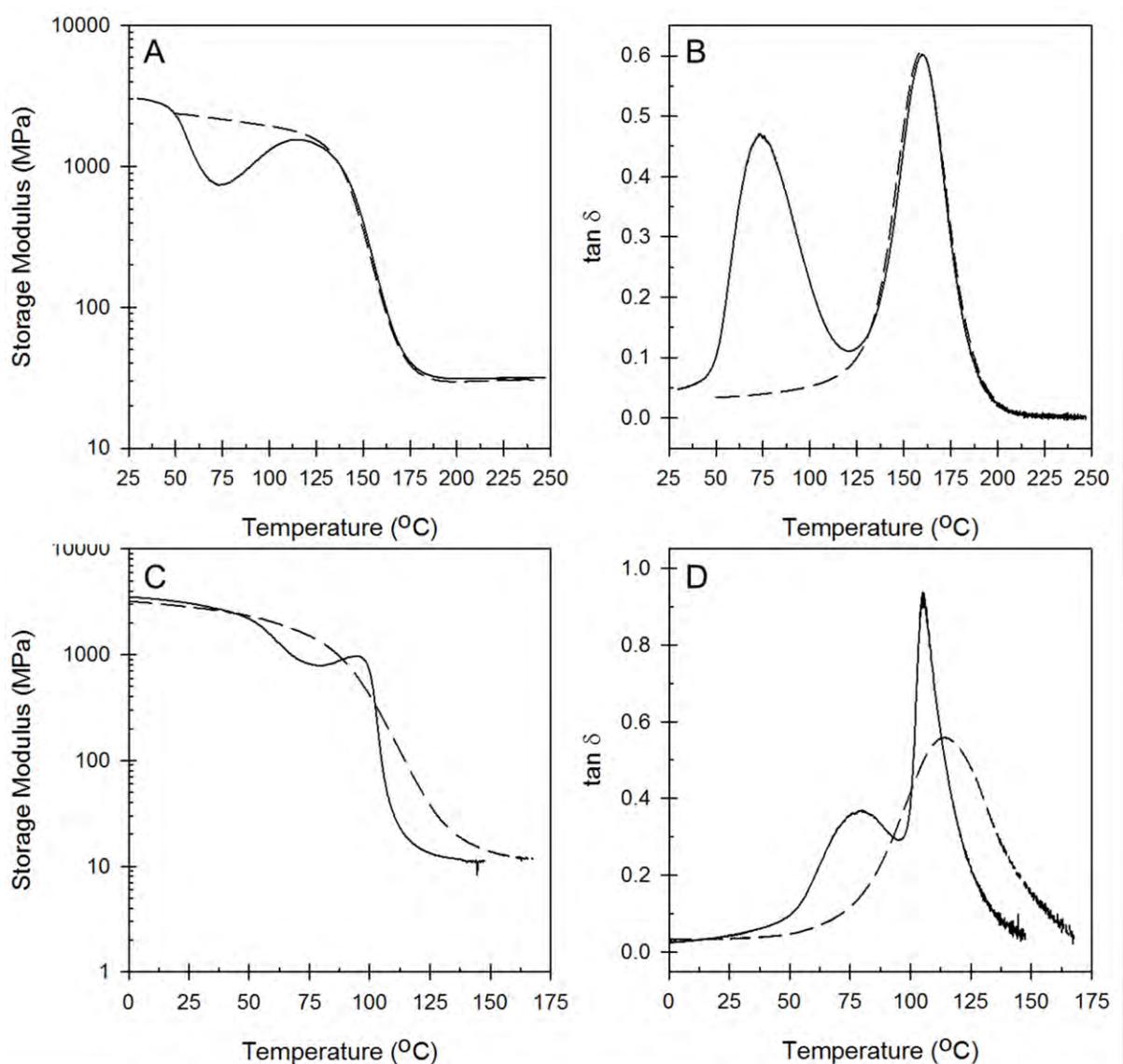
**Figure 4:** Storage modulus and tan δ profiles obtained from EEC formulations with 1,4-butanediol (A,B), and t-butanol (C,D) as CTAs. Solid lines represent data collected from specimens that were photocured and the dotted lines were obtained from specimens that were photocured and annealed above the glass transition temperature.

so dramatically at increasing temperatures is if the network is changing via increased conversion through thermally-activated dark polymerization. All of the photocured-only specimens show a tan δ maximum or shoulder centered near 70°C. The maximum glass transition for resins of this type cured at room temperature appears to be approximately 70°C.[30] The cationic systems studied here have very long-lived active centers. Once the DMA increases the sample temperature above the initial glass transition temperature, developed via photocuring, the active centers are effectively released from the once glassy matrix and will continue to react with unreacted monomer. The reaction will continue to proceed until the monomer is consumed or the network develops to a vitrified state that traps the active centers and prevents further crosslinking and polymerization reactions. In the case that the maximum glass transition temperature for a

given formulation is exceeded, the monomer will be consumed and stable physical properties will be achieved despite the "living" characteristics of the active centers.

## Conclusions

In this study the utility of CTAs are demonstrated as kinetic enhancers and transition temperature modulators. It is also shown that, despite the good air-curing qualities of cationic systems, other complications must be understood and controlled through processing. Although this research used very long times to thermally anneal, or cure, the specimens post-illumination, it is likely that shorter annealing times may result in similar properties. Further work in process optimization is required to quantify the minimum annealing time for materials with stable physical properties and good, non-brittle mechanical properties.

## Acknowledgements

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