Characterizing reactivity and network structure in photo-initiated cationic copolymerizations of cyclic ethers

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Abstract

Recent research in cationic photopolymerization demonstrates that combining epoxides and oxetanes results in improved kinetic outcomes; however, the nature of this copolymerization has not been fully examined. Here, a spectroscopic method is presented to determine the reactivity ratios for these cationic photopolymerizations. Reactivity ratios are unique for a comonomer pairing and indicate preference for propagation. The calculated reactivity ratios have confirmed copolymerization in these systems and provided classification for the resulting network structure.

Introduction

The synergy between epoxide and oxetane monomers results in improved outcomes for comonomer systems undergoing cationic ring-opening photopolymerization.[1-3] The epoxide reduces the oxetane inhibition time, and the oxetane facilitates increased epoxide polymerization rate and conversion. However, it is not entirely clear if the epoxide and oxetane monomers copolymerize or, if they do copolymerize, what type of polymer structure they form. Understanding the nature of their interaction is critical for design of polymer properties and network structure and is instrumental in controlling phase separation.

Copolymers are categorized according to the arrangement of the two monomer units along the polymer chain (Table 1).[4] When comonomers favor homopolymerization, block copolymers result. When comonomers favor copolymerization, alternating copolymers form. When comonomers do not have a preference for homopolymerization or copolymerization, random copolymers are produced.

Table 1. Polymer chain arrangement for various types of copolymers.

Monomer Arrangement	Type of Copolymer
AAAAAAAAAAAABBBBBBBBBBBBB	Block
AB**A**B**A**B**A**B**A**B**A**B**A**B**A**B**A**B**A**	Alternating
ABB**AA**B**A**B**AA**BB**AAA**B**A**BBB**AA**B**AA**	Random

The kinetics play a crucial role in determining the polymer microstructure for a comonomer system. Mayo and Lewis developed a theoretical basis for the distribution of monomers in a copolymerization.[5] Although the method was developed for copolymerization by a free-radical mechanism, it can also be used to describe the addition of cationic monomers (M_i) to an activated chain end (M_i^+). Equations 1 and 3 describe homopropagation of monomers M_1 and M_2, respectively, while Equations 2 and 4 describe the corresponding cross-propagation reactions.[6]

$$M_1^+ + M_1 \xrightarrow{k_{11}} M_1M_1^+ \qquad (1)$$

$$M_1^+ + M_2 \xrightarrow{k_{12}} M_1M_2^+ \qquad (2)$$

$$M_2^+ + M_2 \xrightarrow{k_{22}} M_2M_2^+ \qquad (3)$$

$$M_2^+ + M_1 \xrightarrow{k_{21}} M_2M_1^+ \qquad (4)$$

The relative rates at which the two monomers react and enter a copolymer are the monomer reactivity ratios (r_i). Equation 5 describes the reactivity ratio of M_1, and Equation 6 describes the reactivity ratio of M_2.[6]

$$r_1 = \frac{k_{11}}{k_{12}} \qquad (5)$$

$$r_2 = \frac{k_{22}}{k_{21}} \qquad (6)$$

Each r_i value is the rate of homopropagation (k_{ii}) over the rate of cross-propagation (k_{ij}). These reactivity ratios indicate monomer preference for propagation: when r > 1, the monomer favors homopolymerization; when r < 1, the monomer favors copolymerization (Table 2).[6]

Table 2. Reactivity ratio values for the various types of polymer networks.

Type of Polymer	**Reactivity Ratios**
Two homopolymers	r >> 1
Block copolymer	r > 1
Alternating copolymer	r ≈ 0
Random copolymer	r ≈ 1

In this work, a method was developed to calculate the reactivity ratios of epoxide and oxetane comonomers based on conversion measurements from real-time Raman spectroscopy. The only requirements are the ability to calculate the conversion of both monomers separately

and to have several data points under 10% conversion. If the comonomers have overlapping Raman reaction peaks, this method will not work. Similarly, if the polymerization reaction happens too quickly such that there are few to no data points collected between 0 and 10% conversion, this method will not accurately calculate the monomer reactivity ratios. In the description of this method, the reactivity ratios of the comonomers EEC (epoxide) and EHOX (oxetane) are used as an example.

Experimental

Materials

The comonomer system consisted of the industrially relevant difunctional epoxide 3,4-epoxycyclohexyl-methyl-3',4'-epoxycyclohexane carboxylate (EEC, Synasia) and the monofunctional oxetane 3-ethyl-3-[(2-ethylhexyloxy)methyl] oxetane (EHOX, Toagosei). The cationic photoinitiator used in all formulations was [4-[(2-hydroxytetradecyl)oxy] phenyl]phenyliodonium hexafluoroantimonate (IFA, Polyset). All materials were used as received, and chemical structures are shown in Figure 1.

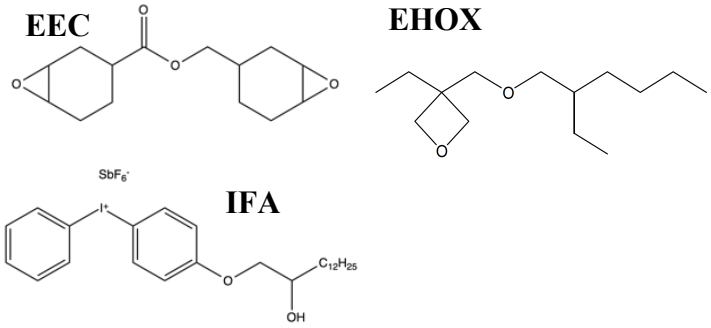

Figure 1. Chemical structures for the epoxide monomer EEC, the oxetane monomer EHOX, and the cationic photoinitiator IFA.

Methods

Sample preparation. Six EEC/EHOX formulations were prepared based on the weight fraction of the two cyclic ether monomers: 70:30, 60:40, 50:50, 40:60, 30:70, and 20:80 (epoxide:oxetane). Formulations with smaller ratios of epoxide or oxetane were not used because they resulted in large errors in calculating Raman peak intensity for the conversion measurements. All formulations contained 0.5 wt% of the cationic photoinitiator IFA.

Raman spectroscopy of photopolymerizations. Real-time Raman experiments were conducted for each of the six EEC/EHOX formulations, and each formulation was run in triplicate. Samples of the EEC/EHOX formulations were injected into 1 mm-ID quartz capillary tubes and illuminated with a mercury arc lamp fitted with a 250-450 nm filter (Acticure® Ultraviolet/Visible Spot Cure system, EXFO Photonic Solutions Inc.). For the first round of experiments, all formulations were illuminated for 5 minutes at 725 mW/cm^2. However, several of the EEC/EHOX formulations reacted too quickly, resulting in too few data points between 0 and 10% conversion. After initial data analysis, all formulations were re-run at lower

illumination parameters: 3 minutes at 450 mW/cm^2; results from these latter trials were used to calculate the reactivity ratios. Real-time Raman spectra were acquired using a holographic probe head (Mark II, Kaiser Optical Systems Inc.) with a single-mode excitation fiber delivering ~220 mW of 785-nm near-infrared laser intensity to the quartz capillary tubes. The spectra were collected with a 1-s exposure time and 3 accumulations.

Conversion (α) profiles as a function of time were calculated for the epoxide and oxetane functional groups from the Raman peak intensity (peak height) using Equation 7. The epoxide reaction peak was measured at 790 cm^{-1}, the oxetane reaction peak at 1150 cm^{-1}, and the reference peak characteristic of n-alkanes for both monomers at 1450 cm^{-1}. This stable reference peak is used to eliminate error due to baseline changes. In Equation 7, *I(t)* denotes the peak intensity at time *t*, and *I(0)* represents the initial peak intensity before polymerization begins. The subscripts denote whether the measurement is of the reaction peak intensity (*rxn*) or the reference peak intensity (*ref*).

$$\underset{\text{Conversion}}{\alpha, \text{Fractional}} = 1 - \frac{I(t)_{rxn} / I(t)_{ref}}{I(0)_{rxn} / I(0)_{ref}} \qquad (7)$$

To smooth the data, 3-point averages were used when modeling the reaction kinetics. For the first time point, the conversion was set to zero, and subsequent time points used the average of three consecutive conversions (the conversion immediately before, at, and after the corresponding time measurement).

Results and Discussion

Real-time reaction modeling was used to determine the reactivity ratios for the EEC/EHOX system. Data points corresponding to conversions less than or equal to 10.0% conversion were used to generate a second-order polynomial of conversion vs. illumination time (Figure 2). Typically, the R^2 values of these trendlines were greater than 0.9. However, for trials of a few formulations, the reaction happened very quickly. Thus, instead of setting the threshold to 10.0%, only the first four data points were used, with the fourth data point being greater than 10.0%.

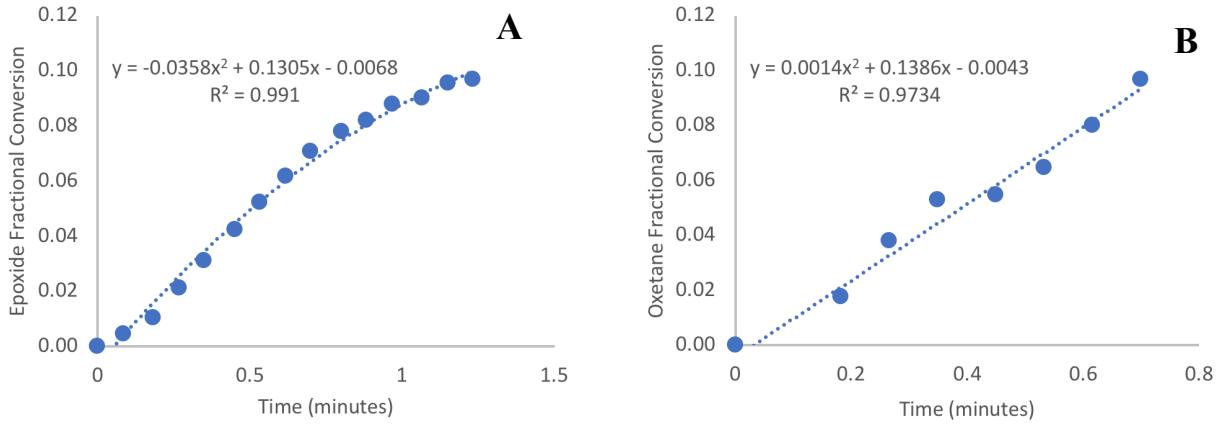

Figure 2. Monomer conversion as a function of time for the epoxide (A) and oxetane (B) functional groups in a 70:30 formulation of EEC and EHOX. Only points less than 10% conversion were used to generate these second-order polynomial equations.

Real-time Raman data provided epoxide and oxetane conversion as a function of time, allowing for calculation of mole fractions of monomer in the feed (f_1 and f_2) and in the copolymer (F_1 and F_2), where the subscript *1* indicates EEC and *2* indicates EHOX. An Excel spreadsheet was used for these calculations, and a representative example is shown in Table 3 for one trial of the 70:30 EEC/EHOX formulation.

Table 3. Calculation of f_1 and F_1: Trial 1 for the 70:30 formulation of EEC and EHOX.

Time (min)	Epoxide conversion	Oxetane Conversion	$[M_1]$	$[M_2]$	f_1	f_2	F_1	F_2
0	-0.00680	-0.00430	2.9437	1.4049	0.6769	0.3231	-	-
0.458527	0.04551	0.05955	2.8097	1.3213	0.6802	0.3198	0.6156	0.3844
0.5	0.04950	0.06535	2.7980	1.3131	0.6806	0.3194	0.5902	0.4098
0.6	0.05861	0.07936	2.7712	1.2934	0.6818	0.3182	0.5767	0.4233
0.7	0.06701	0.09341	2.7465	1.2737	0.6832	0.3168	0.5561	0.4439
	Bulk conversion	**0.050000025**						

Table 3 contains 9 columns. Time values (Column 1) were arbitrarily chosen within the timeframe of the 10% conversion window, except for the $t = 0$ point, which is necessary for all subsequent calculations. This spread of time values was used to approximate the time at which bulk conversion reached 5% (this procedure is discussed in more detail below). The epoxide conversion (Column 2) is a function of time and was calculated using the equation of the second-order polynomial trendline for the epoxide (Figure 2A) in the corresponding trial. Similarly, the oxetane conversion (Column 3) was calculated using the equation of the trendline for the oxetane reaction (Figure 2B). Columns 4 and 5 are monomer concentrations ($[M_i]$) in mol/L. The calculated initial concentrations of each formulation ($[M_i]_0$, shaded peach in Columns 4 and 5) correspond to the concentrations at $t = 0$ and $\alpha_i = 0$. These concentration calculations used the measured mass of each monomer in the formulation, as well as the density and molecular weight of each monomer. The concentrations at $t > 0$ ($[M_i]_t$) were calculated using Equation 8, where $\alpha_{i,t}$ is the fractional conversion of the cyclic ether functional group at time t.

$$[M_i]_t = [M_i]_0\left(1 - a_{i,t}\right) \quad (8)$$

The instantaneous mole fractions for the epoxide in the monomer feed (f_1, Column 6) and in the copolymer (F_1, Column 8) were calculated using the following equations:[5,6]

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (9)$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d([M_1] + [M_2])} = \frac{[M_1]_{t-1} - [M_1]_t}{([M_1]_{t-1} - [M_1]_t) + ([M_2]_{t-1} - [M_2]_t)} \quad (10)$$

where $[M_i]_{t-1}$ is the previous molar concentration and $[M_i]_t$ is the current molar concentration. Since F_1 requires two sequential $[M_1]$ values, there are no F_1 values for the initial time point. The corresponding oxetane values (Columns 7 and 9) are the difference between 1 and the f_1 and F_1 values, respectively (as shown in Equations 9 and 10).

Since reactivity ratio calculations are only valid at early points in the reactions (before outside effects like increasing viscosity and trapping start affecting the polymerization), the time at which the bulk conversion approaches 5% was estimated. This bulk conversion was calculated using Equation 10, using the calculated initial mole fractions of the cyclic ether functional groups in the formulation, where α_i is the fractional conversion of the cyclic ether functional group.

$$\text{Bulk conversion} = f_{1,0}\alpha_{epoxide} + f_{2,0}\alpha_{oxetane} \quad (10)$$

Using Goal Seek in Excel, the bulk conversion cell was set to a value of 0.05000, and the cell representing the illumination time (shaded black in Column 1) was varied until the bulk conversion criterion was met. This iterative process resulted in the calculated f_1 and F_1 values (shaded grey in Columns 6 and 8) used to determine the monomer reactivity ratios. Calculations in Table 3 were performed for each trial for all six EEC/EHOX formulations. The average values of the three trials are reported for the 70:30 formulation in Table 4.

Table 4. Calculation of the average f_1 and F_1 values: three trials of the 70:30 formulation of EEC and EHOX.

	Average value	+/-	St Dev	Max	Min
f_1	0.677	0.005	0.005	0.680	0.671
F_1	0.682	0.103	0.090	0.785	0.616

The mole fractions of epoxide in the feed and in the copolymer were plotted for all six EEC/EHOX formulations (Figure 3). The f_1 values varied linearly as a function of the proportion of EEC in the formulation, while the F_1 values varied exponentially. This graph facilitates detection of errors in the f_1 and F_1 calculations. Any outliers from the trendline would indicate that data treatment issues need be addressed.

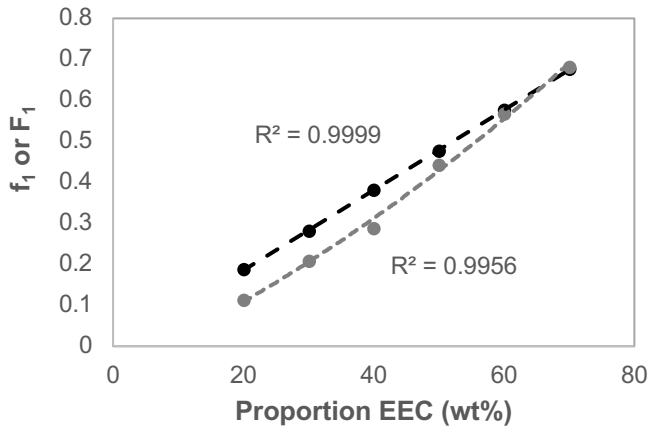

Figure 3. Calculated f_1 and F_1 values as a function of wt% EEC in each EEC/EHOX formulation. The f_1 values are black, and the F_1 values are grey.

The averages of the mole fractions f_1 and F_1 were imported into a separate Excel file to perform reactivity ratio calculations. It is not necessary to keep track of which formulation from which each f_1/F_1 pair originate, since only the mole fractions are used in calculations; the initial weight percent is not plotted against any data or used in any reactivity ratio calculations. The results of the EEC/EHOX formulations are shown in Table 5.

Table 5. Calculated molar compositions of the monomer feed (f_1 and f_2) and copolymer (F_1 and F_2) for the EEC/EHOX monomer pair. All values represent an average of three trials.

Formulation (wt% EEC)	f_1	f_2	F_1	F_2
70	0.677	0.323	0.681	0.319
60	0.576	0.424	0.567	0.433
50	0.476	0.524	0.443	0.557
40	0.381	0.619	0.288	0.712
30	0.281	0.719	0.208	0.792
20	0.188	0.812	0.112	0.888

The set of f_i and F_i values for the six formulations was used to calculate the reactivity ratios according to the Fineman-Ross method,[7] which rearranges the instantaneous copolymer equation (Equation 12) into a linear form and results in a single value for each reactivity ratio (Equation 13, Figure 4).

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{12}$$

$$G = H r_1 - r_2 \tag{13}$$

where $G = \frac{f_1(2F_1-1)}{(1-f_1)F_1}$ and $H = \left[\frac{f_1^2(1-F_1)}{(1-f_1)^2F_1}\right]$

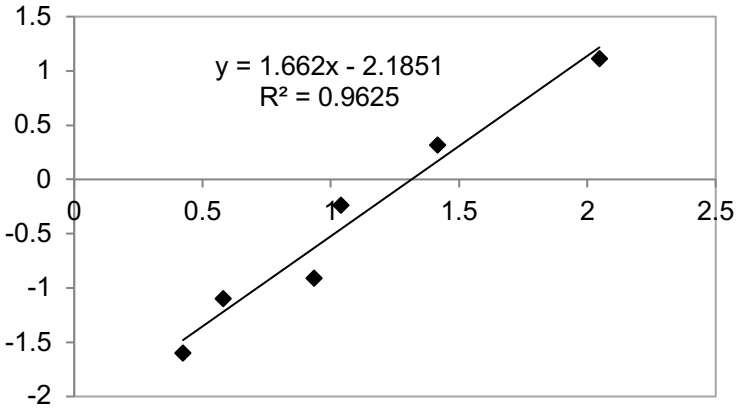

Figure 4. Reactivity ratios for EEC and EHOX calculated from the Fineman-Ross method. The slope of the line gives r_1 for EEC, and the negative y-intercept gives r_2 for EHOX.

For the EEC/EHOX formulations, the slope of the line in Figure 4 yields r_1 = 1.66 for EEC, and the y-intercept yields r_2 = 2.16 for EHOX. Based on these results, EEC and EHOX do copolymerize; however, they have a greater tendency to form a block copolymer (Table 2). In addition to the separate reactivity ratios, the product of reactivity ratios (r_1r_2) can be used to summarize the type of copolymer formed.[6] When r_1r_2 approaches 1, a random copolymer is formed. Additionally, when r_1r_2 is greater than one, blocky structures are promoted, containing larger amounts of one or the other monomeric subunit. Alternating copolymers are formed when both r_1 and r_2 approach zero, with r_1r_2 being near zero. The product of the EEC/EHOX reactivity ratios is 3.64. This result confirms that formulations of EEC and EHOX lead to homopolymer blocks within the copolymer network, though these blocks are still relatively small (3-4 monomeric units).

Conclusions

Although the benefits of epoxide and oxetane comonomer formulations have been demonstrated, copolymerization of these systems had not been confirmed. A method was developed to determine the reactivity ratios of the comonomers using formulations with six different EEC:oxetane ratios and the corresponding kinetic data obtained from real-time Raman spectroscopy. The method was successfully demonstrated with EEC and EHOX, and the resulting reactivity ratios indicate that EEC copolymerizes with EHOX such that small homopolymer blocks are formed within the copolymer network.

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