Electronic Supplementary Information

Elucidation of Network Structure in Cationic Photopolymerization of Cyclic Ether Comonomers

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Detailed method for monomer reactivity ratio calculations in *Experimental: Kinetic characterization of copolymerizations* section

A method was developed for calculating the reactivity ratios of two monomers using 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 two monomers have overlapping Raman reaction peaks, this method will not work. Similarly, if the polymerization reaction happens too quickly and there are little 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 monomer pair EEC (M_1) and EHOX (M_2) are used as a representative example.

A. A range of formulations was made with differing ratios of the two monomers, each containing 0.5 wt% of the cationic photoinitiator IFA. Initial trials of EEC and EHOX used 9 formulations with the following epoxide:oxetane concentrations: 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9. In these formulations of epoxides and oxetanes, several formulations were eliminated due to the error in calculating peak intensity. Trials of the 9:1 and 8:2 formulations were found to have too large an error relative to the oxetane peak heights and were eliminated. Similarly, trials of the 1:9 formulation had too large of an error relative to the epoxide peak heights and were eliminated. Subsequent experiments used 6 ratios of EEC:oxetane: 7:3, 6:4, 5:5, 4:6, 3:7, and 2:8.

B. Real-time Raman data were collected for each of the 6 formulations for four monomer sets: EEC/OXA, EEC/EHOX, EEC/POX, and EEC/DOX. Each formulation was run in triplicate. For the first round of experiments, all formulations were illuminated for 5 min at 725 mW/cm^2. Several of the formulations containing EEC and EHOX reacted too quickly, and little to no data points were collected between 0 and 10% conversion. After initial data analysis, all concentrations for these monomer pairs were re-run at lower illumination parameters: 3 min at 450 mW/cm^2.

C. Conversion (α) profiles as a function of time were calculated for the epoxide and oxetane functional group from the Raman peak intensity (peak height) using Eqn S1 (Eqn 1 in the main paper). 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 Eqn S1, *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*).

$$fractional\ conversion,\ \alpha = 1 - \frac{I(t)_{rxn}/I(t)_{ref}}{I(0)_{rxn}/I(0)_{ref}} \tag{S1}$$

D. To smooth the data, 3-point averages were used when modeling the reaction kinetics. To do this, the first time point was set to have a conversion of zero, and subsequent time points used the average of three conversions, including the conversion before and after that time point.

E. 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 (see Figure S1 for a representative example). Typically, the R^2 values of these trendlines were greater than 0.9 with the exception of some oxetane trendlines of the EEC:POX formulations at a monomer ratio of 70:30 (0.654, 0.822, and 0.705 for the three trials) and 60:40 (0.926, 0.784, 0.802). All epoxide R^2 values were at least 0.967, and the oxetane R^2 values for the remaining formulations were at least 0.897. For a few formulations/trials, the reaction happened very quickly, and instead of setting the threshold to 10.0%, only the first four data points were used, where the fourth data point could be greater than 10.0%. Table S1 is included to illustrate the full data analysis for the EEC/EHOX monomer pair.
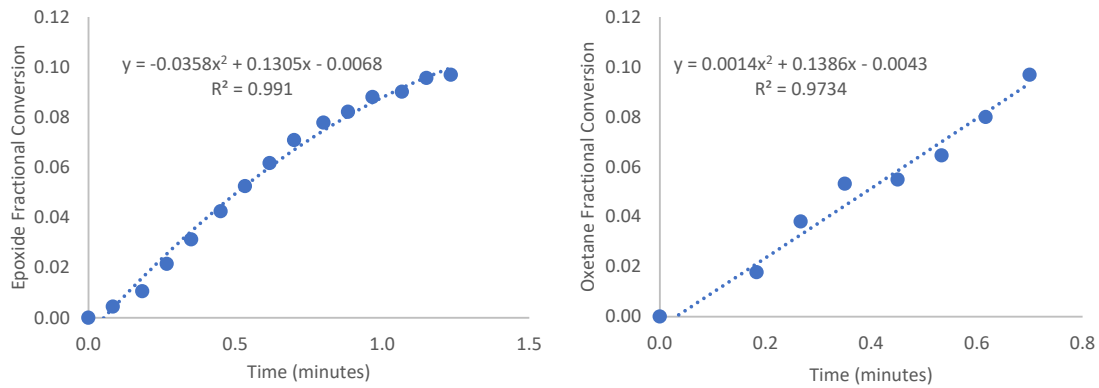

Figure S1. Monomer conversion as a function of time for the epoxide (left) and oxetane (right) in a 70:30 formulation of EEC and EHOX. Only points less than 10% conversion were used to generate these second-order polynomial equations.

Table S1. EEC/EHOX equations and individual monomer conversions at 5% bulk conversion

Formulation (wt% EEC)	Epoxide Equation	Oxetane Equation	Epoxide α_1	Oxetane α_2
70 – Trial 1	y = -0.0358x² + 0.1305x - 0.0068 R² = 0.9910	y = 0.0014x² + 0.1386x - 0.0043 R² = 0.9734	0.04503	0.05886
70 – Trial 2	y = -0.0404x² + 0.131x - 0.0062 R² = 0.9934	y = -0.0381x² + 0.1599x - 0.0133 R² = 0.9285	0.04728	0.05455
70 – Trial 3	y = -0.2876x² + 0.411x - 0.0005 R² = 0.9989	y = 0.8193x² + 0.0821x - 0.0009 R² = 0.9965	0.05841	0.03376
60 – Trial 1	y = -0.007x² + 0.1335x - 0.0055 R² = 0.9916	y = 0.1374x² + 0.0754x - 0.008 R² = 0.9672	0.05045	0.04958
60 – Trial 2	y = 0.0053x² + 0.1358x - 0.0026 R² = 0.9943	y = 0.1554x² + 0.1057x + 0.0044 R² = 0.9724	0.04369	0.05755
60 – Trial 3	y = 0.0079x² + 0.1322x - 0.003 R² = 0.9942	y = 0.3941x² - 0.0508x - 0.0013 R² = 0.9970	0.05351	0.04607
50 – Trial 1	y = 0.1007x² + 0.1026x - 0.0008 R² = 0.9987	y = 0.2459x² + 0.0763x + 0.0041 R² = 0.9818	0.04342	0.05520

Formulation (wt% EEC)	Epoxide Equation	Oxetane Equation	Epoxide α_1	Oxetane α_2
50 – Trial 2	$y = 0.1597x^2 + 0.063x - 0.0015$ $R^2 = 0.9984$	$y = 0.5614x^2 - 0.0733x - 0.0042$ $R^2 = 0.9750$	0.04707	0.05204
50 – Trial 3	$y = 0.0969x^2 + 0.1235x - 0.0003$ $R^2 = 0.9994$	$y = 0.4248x^2 + 0.0289x - 0.0013$ $R^2 = 0.9952$	0.04886	0.05100
40 – Trial 1	$y = 0.0133x^2 + 0.1371x - 0.0022$ $R^2 = 0.9957$	$y = 0.0512x^2 + 0.1814x - 0.0012$ $R^2 = 0.9924$	0.03879	0.05588
40 – Trial 2	$y = 0.1423x^2 + 0.1104x - 0.0012$ $R^2 = 0.9975$	$y = 0.6494x^2 + 0.0608x - 0.0001$ $R^2 = 0.9992$	0.03653	0.05832
40 – Trial 3	$y = 0.2436x^2 + 0.0648x + 7E-05$ $R^2 = 0.9994$	$y = 0.2006x^2 + 0.1356x + 0.0006$ $R^2 = 0.9969$	0.03891	0.05626
30 – Trial 1	$y = 0.5465x^2 + 0.1052x + 0.0007$[a] $R^2 = 0.9968$	$y = 1.2852x^2 + 0.0259x + 0.0005$[a] $R^2 = 0.9994$ (4 points)	0.04120	0.05310
30 – Trial 2	$y = 0.4692x^2 + 0.1308x - 0.0003$[a] $R^2 = 0.9991$	$y = 0.9694x^2 + 0.1039x - 0.0005$[b] $R^2 = 0.9992$	0.04115	0.05372
30 – Trial 3	$y = 0.5546x^2 + 0.0678x + 0.0003$[a] $R^2 = 0.9994$	$y = 0.5342x^2 + 0.2216x + 0.0007$[b] $R^2 = 0.9989$	0.02979	0.05684
20 – Trial 1	$y = 0.4453x^2 + 0.0072x + 0.0009$ $R^2 = 0.9983$	$y = 1.1134x^2 - 0.0755x + 0.0007$[a] $R^2 = 0.9926$	0.03150	0.05344
20 – Trial 2	$y = 0.3358x^2 + 0.0516x - 0.0015$ $R^2 = 0.9975$	$y = 0.7041x^2 + 0.0121x - 7E-05$[a] $R^2 = 0.9999$	0.03593	0.05287
20 – Trial 3	$y = 0.4908x^2 - 0.0498x - 0.0013$ $R^2 = 0.9952$	$y = 0.4839x^2 + 0.0661x - 0.0008$ $R^2 = 0.9988$	0.02341	0.05591

[a] Equation uses only first four points, but the fourth point has a conversion less than 10%
[b] Equation uses only first four points with the fourth point at a conversion greater than 10%

F. To calculate the mole fractions f_1 and f_2 for the monomer feed, the initial concentration in mol/L was determined. These calculations used the measured grams, density, and molecular weight of each monomer in the formulation (see Table S2 for a representative example). The calculated initial concentrations of each formulation, $[M_1]_0$ and $[M_2]_0$ (see Table S3 for a representative example), correspond to the concentrations at $t = 0$ and $\alpha = 0$.

Table S2. Inputs used to calculate the initial concentration of each formulation of EEC+EHOX. Required inputs were the molecular weight and density of each monomer, along with the mass of both monomers in each formulation.

Formulation (wt% EEC)	EEC (g)	Oxetane (g)
70	0.7006	0.3027
60	0.6073	0.4049
50	0.5063	0.5073
40	0.4070	0.6111
30	0.3248	0.7654
20	0.2225	0.8914
Molecular weight (g/mol)	252.3	228.4
Density (g/mL)	1.16	0.892

Table S3. Intermediate and final calculations for obtaining the epoxide and oxetane concentration for all formulations of EEC+EHOX.

Formulation (wt% EEC)	Epoxide vol (mL)	Oxetane vol (mL)	Total volume (mL)	Moles Epoxide	Moles Oxetane	Epoxide $[M_1]_0$	Oxetane $[M_2]_0$
70	0.604	0.339	0.943	0.00278	0.00133	2.94	1.40
60	0.524	0.454	0.977	0.00241	0.00177	2.46	1.81
50	0.436	0.569	1.01	0.00201	0.00222	2.00	2.21
40	0.351	0.685	1.04	0.00161	0.00268	1.56	2.58
30	0.280	0.858	1.14	0.00129	0.00335	1.13	2.94
20	0.192	0.999	1.19	0.000882	0.00390	0.740	3.28

G. The trendlines from Step E (Table S1) were used to calculate the molar concentrations as a function of time and conversion (see Table S4, Columns 2 and 3, for a representative example). The initial molar concentrations represent $t = 0$, and conversion increases with time according to the trendlines, which were then used to determine the change in concentration for the epoxide and oxetane.

H. Mole fractions f_1 and f_2 in the monomer feed and mole fractions F_1 and F_2 in the copolymer were calculated at several times to estimate the time at which the bulk conversion would approach 5% (see Table S4). The mole fractions in the monomer feed (f_i) were calculated using Eqns S2 and S3. The mole fractions in the copolymer (F_i) depend on the change in mole fraction of the monomer feed. These F values were calculated using Eqns S4 and S5. The subscripts in Eqn S4 represent the concentration values at different times in the reaction; both the current concentration ($[M_i]_t$) and an earlier concentration ($[M_i]_{t-1}$) are required to calculate the molar composition of the copolymer.

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \tag{S2}$$

$$f_2 = 1 - f_1 \tag{S3}$$

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = \frac{[M_1]_{t-1} - [M_1]_t}{([M_1]_{t-1} - [M_1]_t) + ([M_2]_{t-1} - [M_2]_t)} \tag{S4}$$

$$F_2 = 1 - F_1 \tag{S5}$$

I. Reactivity ratio calculations are only valid at early points in reactions, before outside effects like increasing viscosity and trapping start affecting the polymerization. Thus, the point at which all compositions were calculated was set to a bulk conversion of 5%. This bulk conversion was calculated using Eqn S6 (Eqn 2 in the main paper), where f_i is the mole fraction of the cyclic ether functional group in the monomer feed and a_i is the fractional conversion of the cyclic ether functional group. The time at which this occurs for every trial was determined using Goal Seek in Excel (see Table S4). The bulk conversion cell, containing Eqn S6 written as a function of illumination time, was set to 0.05000 by changing the cell highlighted in black in Column 1. Using this illumination time, monomer concentrations were calculated with the trendlines from Step E and used to calculate f_1 and F_1 values, which were then used to determine the monomer reactivity ratios.

$$\text{Bulk conversion} = f_1\alpha_1 + f_2\alpha_2 \tag{S6}$$

Note: Table S4 contains 9 columns. Values in the Time column are arbitrary except for the necessary initial time point. The epoxide conversion (Column 2) is a function of time and is calculated using the second-order polynomial trendline equation for the corresponding trial from Step E. Similarly, the oxetane conversion (Column 3) is calculated using the trendline equation for the oxetane reaction. Columns 4 and 5 are monomer concentrations ($[M_i]_t$) with the first value corresponding to the initial concentration calculated in Step F. The concentrations at $t > 0$ are calculated using Eqn S7, where a_i is the fractional conversion of the cyclic ether functional group.

$$[M_i]_t = [M_i]_0 - a_{i,t}[M_i]_0 \tag{S7}$$

Column 6 (f_1) is calculated using Eqn S2 and the $[M_i]$ values from the same row. Column 8 (F_1) uses Eqn S4, and since F_1 requires two sequential $[M_1]$ values, there are no F values for the initial time point. Columns 7 and 9 are the difference between 1 and the f_1 and F_1 values, respectively (Eqns S3 and S5).

The values in orange boxes ($[M_i]_0$) are inputs from Step F used to calculate the subsequent $[M_i]_t$ values. The bulk conversion in bold in the last row of the table is the value converged upon through Goal Seek by changing the second box in the time column (black box with white font). The epoxide and oxetane conversions associated with this new calculated time value result in the f_1 and F_1 values highlighted in grey.

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**Table S4.** Calculation of f_1 and F_1 for Trial 1 of the 70:30 formulation of EEC+EHOX.

Time (min)	Epoxide α_1	Oxetane α_2	[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**							

J. All calculations in Table S4 were performed for each trial for all six formulations of each monomer pair (i.e., all rows of Table S1). The average values of three trials were reported for each formulation (see Table S5 for a representative example).

Table S5. Calculation of the average f_1 and F_1 values for the three trials of the 70:30 formulation of EEC+EHOX.

	Average value	+/-	St Dev	Max	Min
f1	0.677	0.005	0.004764955	0.680155862	0.671244616
F1	0.682	0.103	0.09033006	0.784528366	0.615590781

When plotted as a function of the proportion of EEC in the formulation, the f_1 values resulted in a linear function, and the F_1 values resulted in an exponential function (see Figure S2 as a representative example). Inspection of these plots for each monomer pair highlights if any errors were made in the calculations of f_1 and F_1 values. Outliers to the trendline indicate data treatment errors that must be corrected.
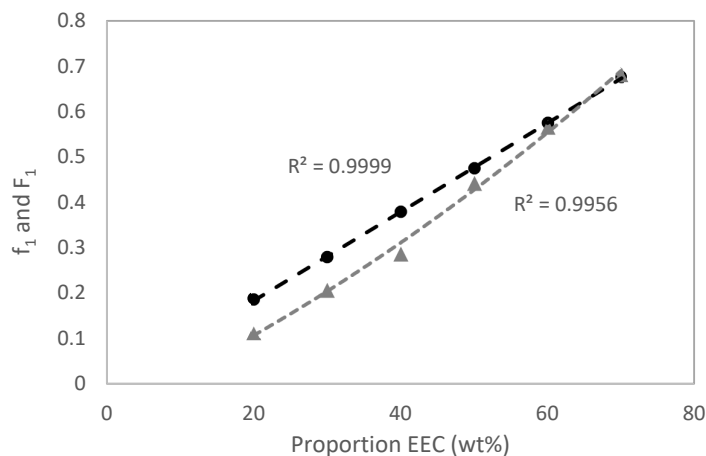
Figure S2. Calculated f_1 (black circles) and F_1 (grey triangles) as a function of wt% EEC in each EEC+EHOX formulation.

K. 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 each f_1/F_1 pair are from, since only the mole fractions are used in calculations.

Table S6. 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)	f1	f2	F1	F2
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

L. The set of values for the six formulations was used to calculate the reactivity ratios according to both the Mayo-Lewis and Fineman-Ross methods. The Mayo-Lewis method results in an interval in which the reactivity ratios lie and uses the copolymerization equation (Eqn S8 [Eqn 5 in the main paper]) to relate the reactivity ratio for the first monomer (EEC, r_1) to the reactivity of a second monomer (the oxetane, r_2) using Eqn S9 (Eqn 6 in the main paper). For each formulation, a straight line is generated relating r_1 to r_2 using a range of r_1 values. All six of these lines were plotted on the same graph, and the area in which the most lines intersect was determined to be the interval for the reactivity ratio values (see Figure S3 for a representative example). From Figure S3, the reactivity ratios for EEC and EHOX would lie around 1.6 for EEC and 2.1 for EHOX.

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{S8}$$

$$r_2 = \frac{f_1}{f_2}\left[\frac{F_2}{F_1}\left(1 + \frac{f_1 r_1}{f_2}\right) - 1\right] \tag{S9}$$
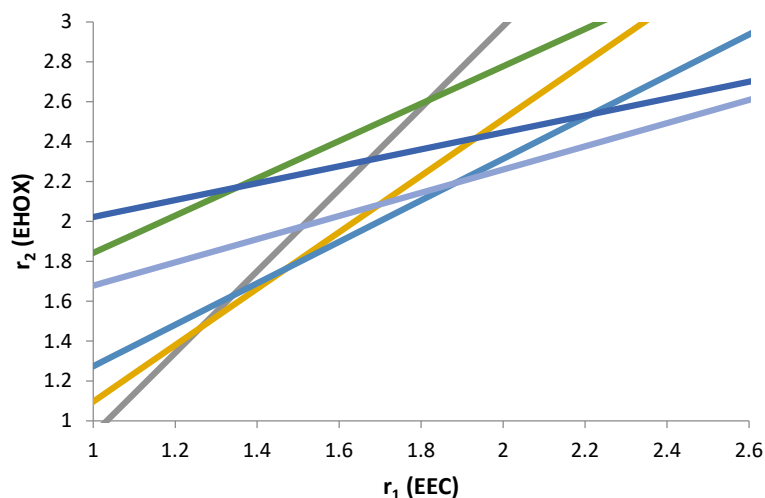

Figure S3. Mayo-Lewis method of determining reactivity ratios of EEC and EHOX according to Eqn S9. Each of the six formulations result in a straight line, and the reactivity ratios of EEC and EHOX lie in the area in which the most lines intersect.

M. The Fineman-Ross method rearranges the copolymer equation (Eqn S8) into linear form and results in a single value for each reactivity ratio (Eqn S10 [Eqn 7 in the main paper], see Figure S4 for a representative example).

$$G = Hr_1 - r_2$$

(S10)

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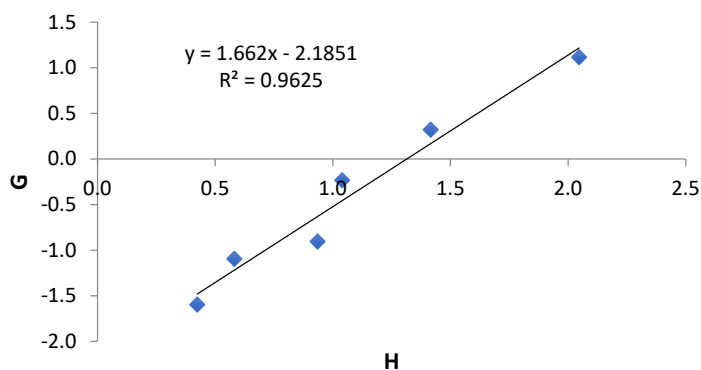

Figure S4. Fineman-Ross method of calculating reactivity ratios of EEC and EHOX. The slope of the line gives r_1 for EEC, and the negative y-intercept gives r_2 for EHOX.

N. The reactivity ratio results for the EEC/EHOX pairing are shown in Table S7, and the two methods are in agreement.

Table S7. Reactivity ratios for the copolymerization of EEC (r_1) with EHOX (r_2).

Method	r₁ (EEC)	r₂ (EHOX)
Mayo-Lewis	$1.4 < r_1 < 2.2$	$1.5 < r_2 < 2.6$
Fineman-Ross	1.7	2.2

Program link for monomer reactivity ratio calculations in *Experimental: Kinetic characterization of copolymerizations* section

The Kelen-Tüdös method improves upon the Fineman-Ross linearization method by introducing constants that give equal weight to the plotted points. A program has been written to quickly calculate r_1 and r_2 from f_1 and F_1 input values.

https://github.com/msoumounthong/ReactivityRatios

Additional kinetic profiles for comonomer formulations in *Results and discussion: Kinetic characterization of copolymerizations: Reactivity ratios of high-purity EEC with oxetanes* section
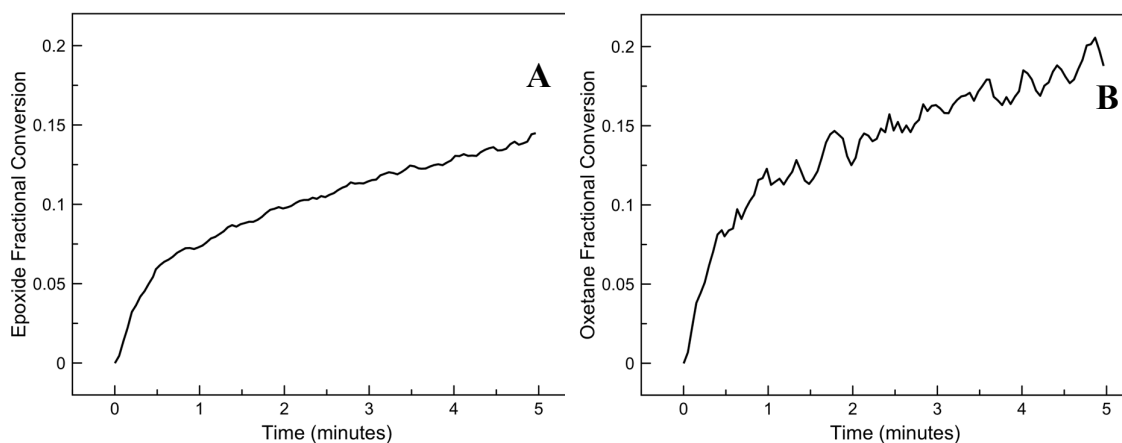
Figure S5. Kinetic profiles for the epoxide (A) and oxetane (B) for the 70:30 formulation of EEC and OXA. The EEC/OXA pair had r_1 (EEC) values much smaller than the r_2 (oxetane) values (Table 3 in the main paper).
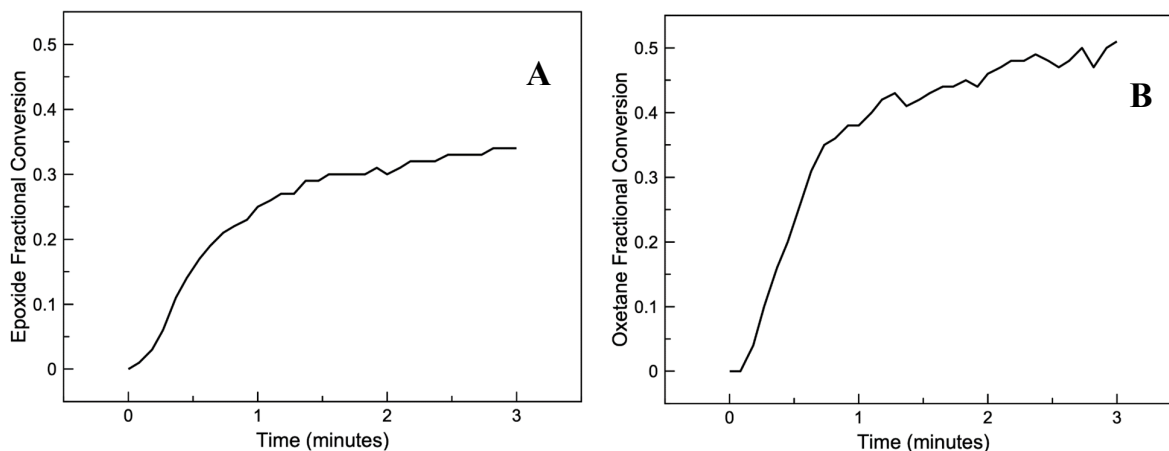

Figure S6. Kinetic profiles for the epoxide (A) and oxetane (B) for the 70:30 formulation of EEC and EHOX. The EEC/EHOX pair had r_1 (EEC) values much smaller than the r_2 (oxetane) values (Table 3 in the main paper).

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DMA profiles for comonomer formulations in *Results and discussion: Kinetic characterization of copolymerizations: Reactivity ratios of high-purity EEC with oxetanes* section
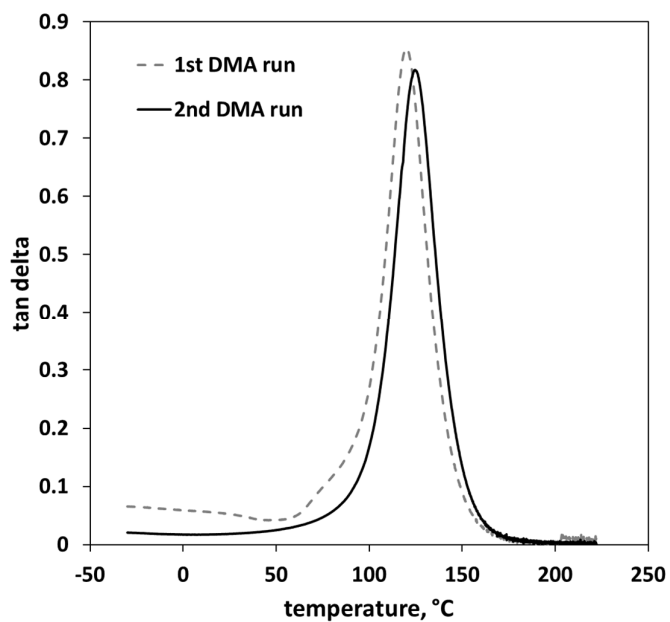
Figure S7. Representative tan δ trace for an 80:20 formulation of EEC and POX. Only one peak is present at ~124°C after the second DMA run.
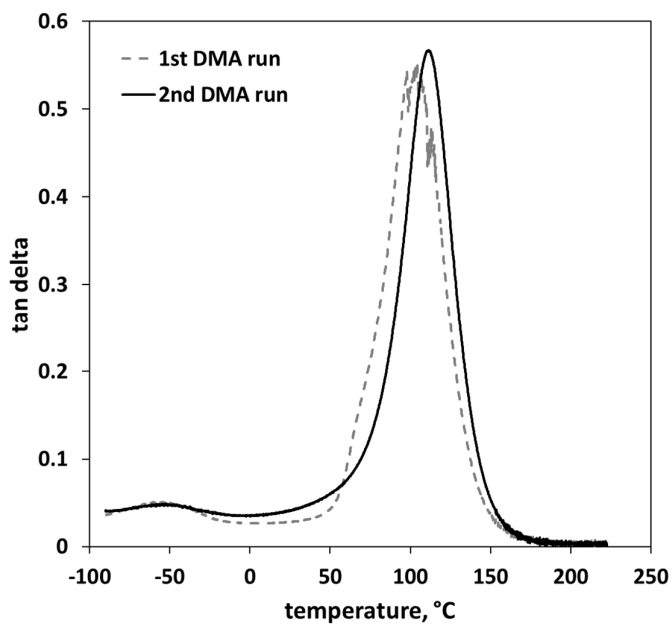

Figure S8. Representative tan δ trace for an 80:20 formulation of EEC and EHOX. Two peaks are present after the second DMA run: one at ~-53°C and the other at ~111°C.
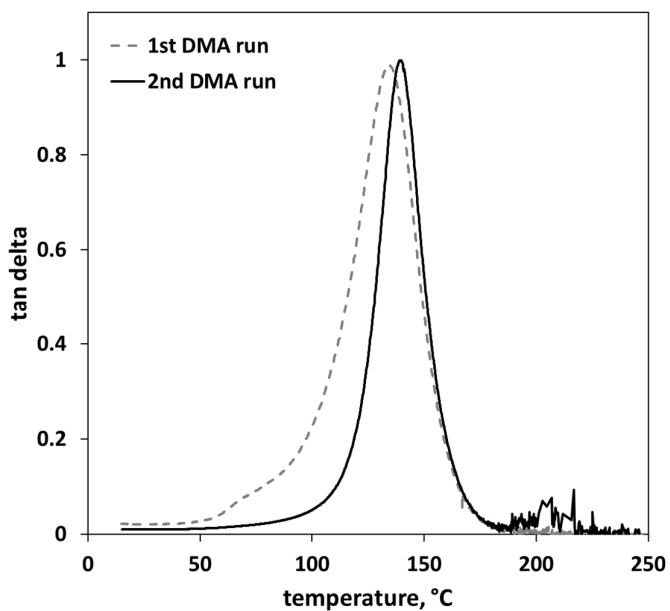
Figure S9. Representative tan δ trace for an 80:20 formulation of EEC and OXA. Only one tan δ peak is present at ~140°C after the second DMA run.
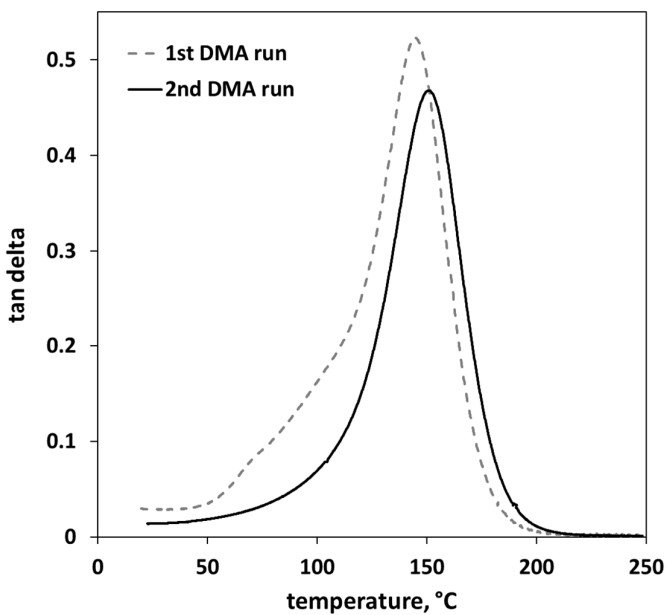

Figure S10. Representative tan δ trace for a 60:40 formulation of EEC and DOX. Only one tan δ peak is present at ~151°C after the second DMA run.