# Simple and Accurate Determination of Reactivity Ratios Using a Nonterminal Model of Chain Copolymerization

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## Additional $^1$H NMR Spectra for the Copolymerization of Allyl Glycidyl Ether and Phenyl Glycidyl Ether

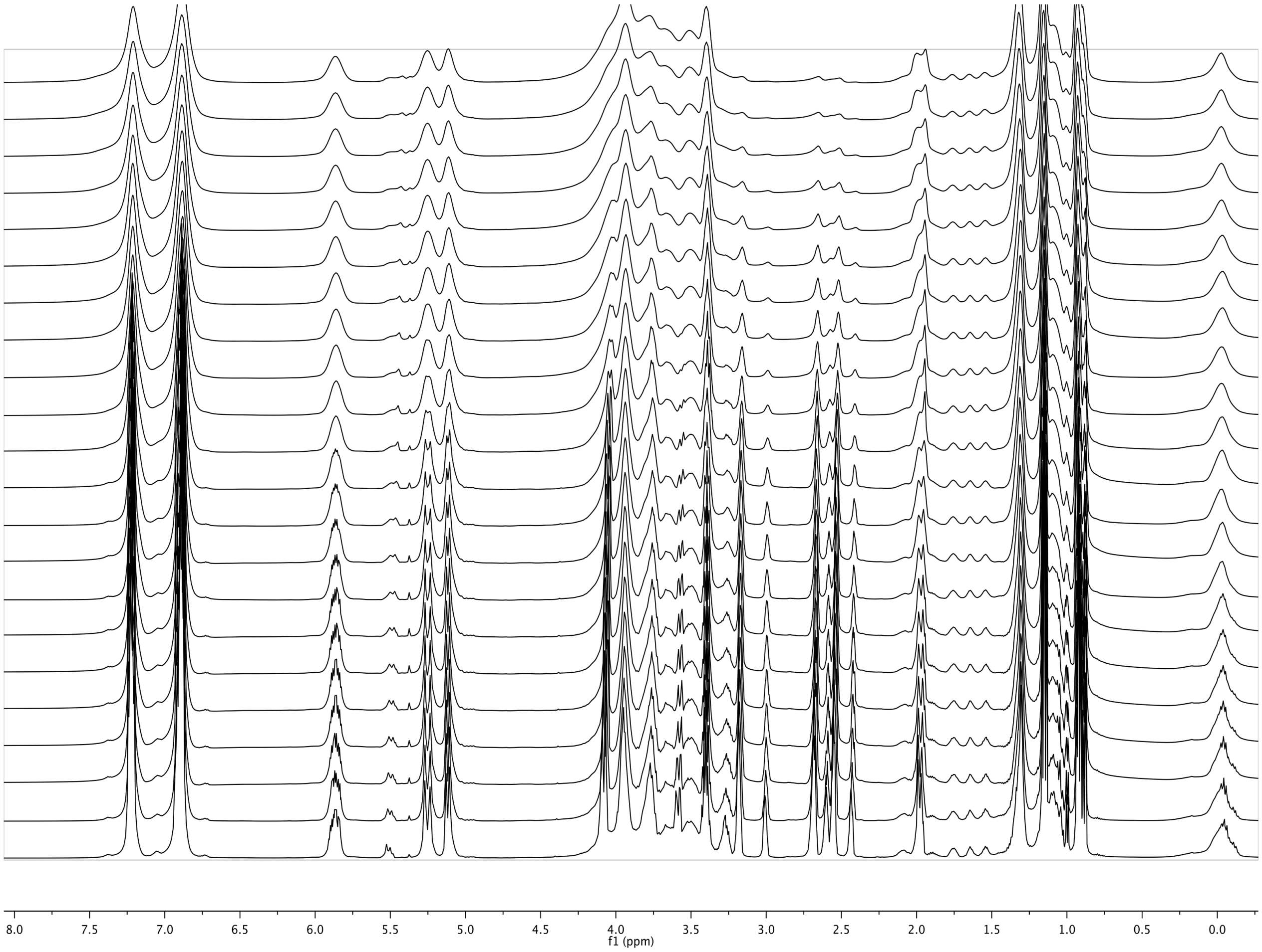

**Figure S1.** Time resolved $^1$H NMR spectra of a Vandenberg-catalyzed copolymerization of allyl glycidyl ether and phenyl glycidyl ether. Bottom spectra represents t = 0 with spectra of increasing time from bottom to top.

## Forcing Ideal Behavior for Determined Reactivity Ratios

As noted in the discussion, the reactivity ratios for L-LAC and ε-CL obtained from the non-terminal model give a better fit to the observed compositional drift than was found using Kelen-Tudos (a terminal model). Yet, the product of the obtained reactivity ratios differs slightly from unity. However, as this was a fit achieved through error minimization we can alter the parameters of our fit and examine how well the non-terminal model can fit the data when ideal behavior is prescribed. As the smaller reactivity ratio (that of ε-CL) is the most sensitive qualitatively to changes in value we re-fit the compositional drift and continue to fit to 0-100% conversion but do not include the data points beyond the initial 100% conversion point. This refines the fit to the data points at lower conversions and rebalances the error regression away from its 100% conversion bias. The result is the fit below in Figure X. Note, this fit gives an accurate representation of the compositional drift (indeed much better again than Kelen-Tudos) while constraining the copolymerization to perfectly ideal behavior.

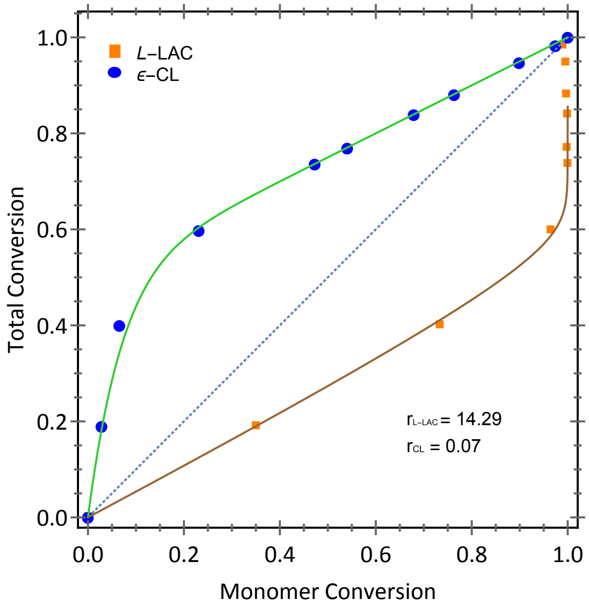

**Figure S2.** Total polymerization conversion plotted against monomer conversion, (■) L-LAC and (●) ε-CL. Solid green (—) and brown lines (—) represent fits to the experimental data using the non-terminal model, Equations 12 and 13, the initial compositions: $n_{L-LAC} = n_{\varepsilon-CL} = 0.5$. The dotted blue line (····) represents the random copolymerization case; $r_{L-LAC} = r_{\varepsilon-CL} = 1$.

## Reactivity Ratios Determination for the Copolymerization of Styrene and Isoprene

Here is an enlarged Figure for the compositional drift for styrene and isoprene where the non-terminal model values are compared to those of Worsfold[1] and of Quinebèche *et al.*[2]. Fitting the compositional drift data for isoprene up to ~60% total conversion where 100% I conversion is reached yields the dotted black line.

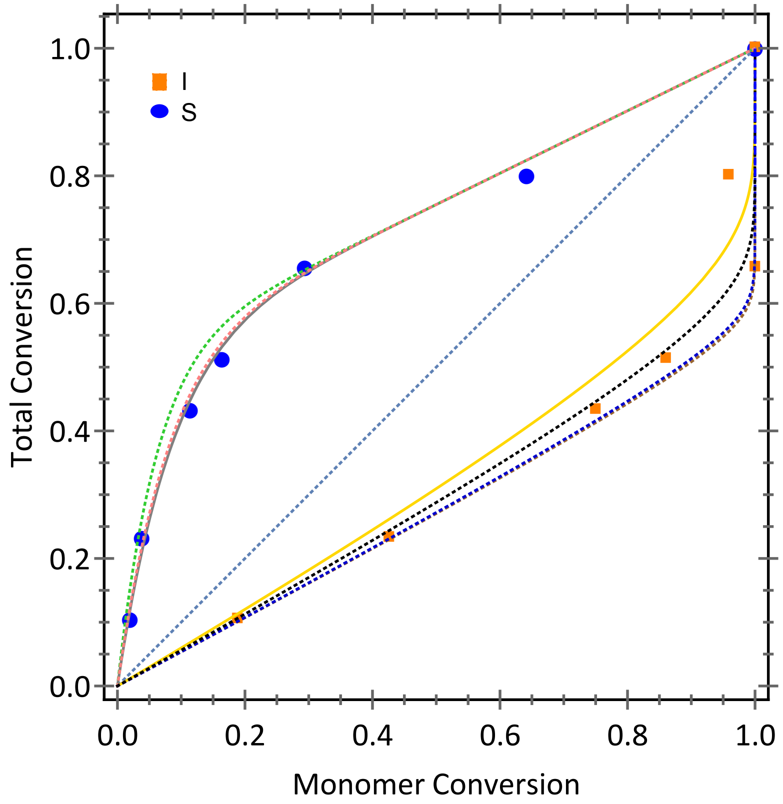

**Figure S3.** Compositional drift data taken from the literature for the copolymerization (■) isoprene (I) and (●) styrene (S)[3]. (····) Dotted blue lines represent the hypothetical random copolymerization case; $r_A = r_B = 1$. (—) Solid yellow and (—) grey lines represent fits to the experimental data using Equations 12 and 13. Dotted lines represent compositional drifts obtained using previously reported reactivity ratios. Dotted green (····) and dark brown (····) for the values of Worsfold[1] and dotted pink (····) and dark blue (····) for those of Quinebèche et al.[2] Dotted black (····) represents fit using the non-terminal model using the compositional drift data for isoprene up to ~60% total conversion where 100% I conversion is reached.

## References

(1) Worsfold, D. J. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1967**, *5*, 2783–2789.
(2) Quinebèche, S.; Navarro, C.; Gnanou, Y.; Fontanille, M. *Polymer* **2009**, *50*, 1351–1357.
(3) Beckingham, B. S.; Register, R. A. *Macromolecules* **2011**, *44*, 4313–4319.