

Supporting Information

Phosphazene-catalyzed Regioselective Ring-opening Polymerization of *rac*-1-Methyl Trimethylene Carbonate: Colder and Less is Better

Geng Hua,^a Johan Franzén^b and Karin Odelius^{a}*

a. Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

b. Department of Organic Chemistry, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

This SI contains 7 figures in 8 pages.

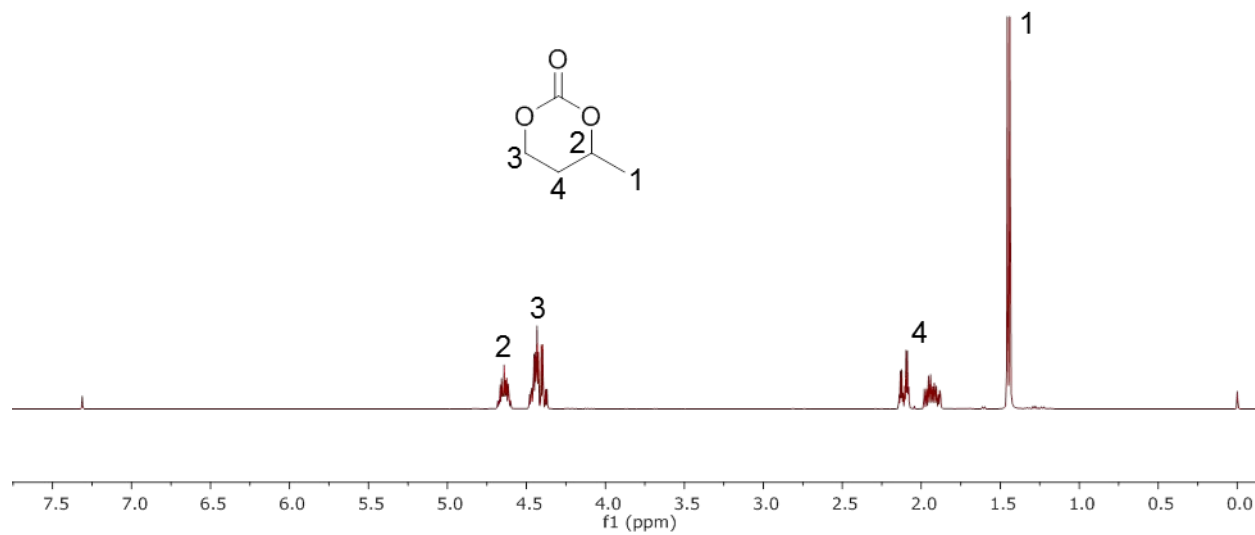


Figure S1 ^1H NMR of *rac*-1-MeTMC.

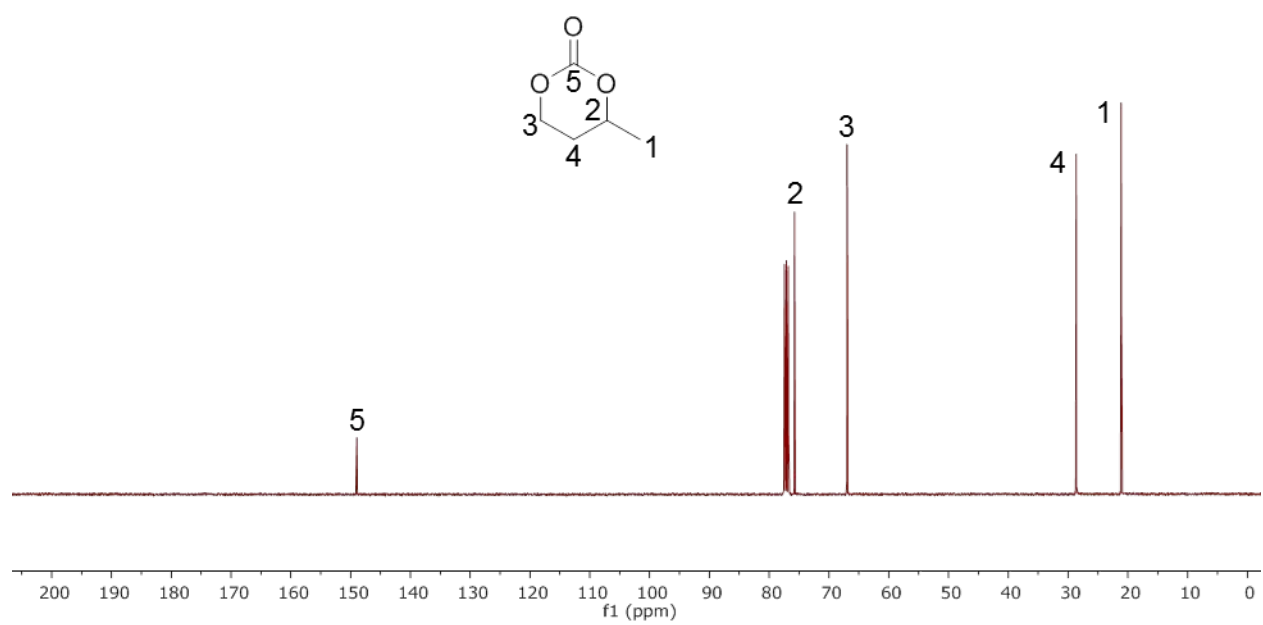


Figure S2 ^{13}C NMR of *rac*-1-MeTMC.

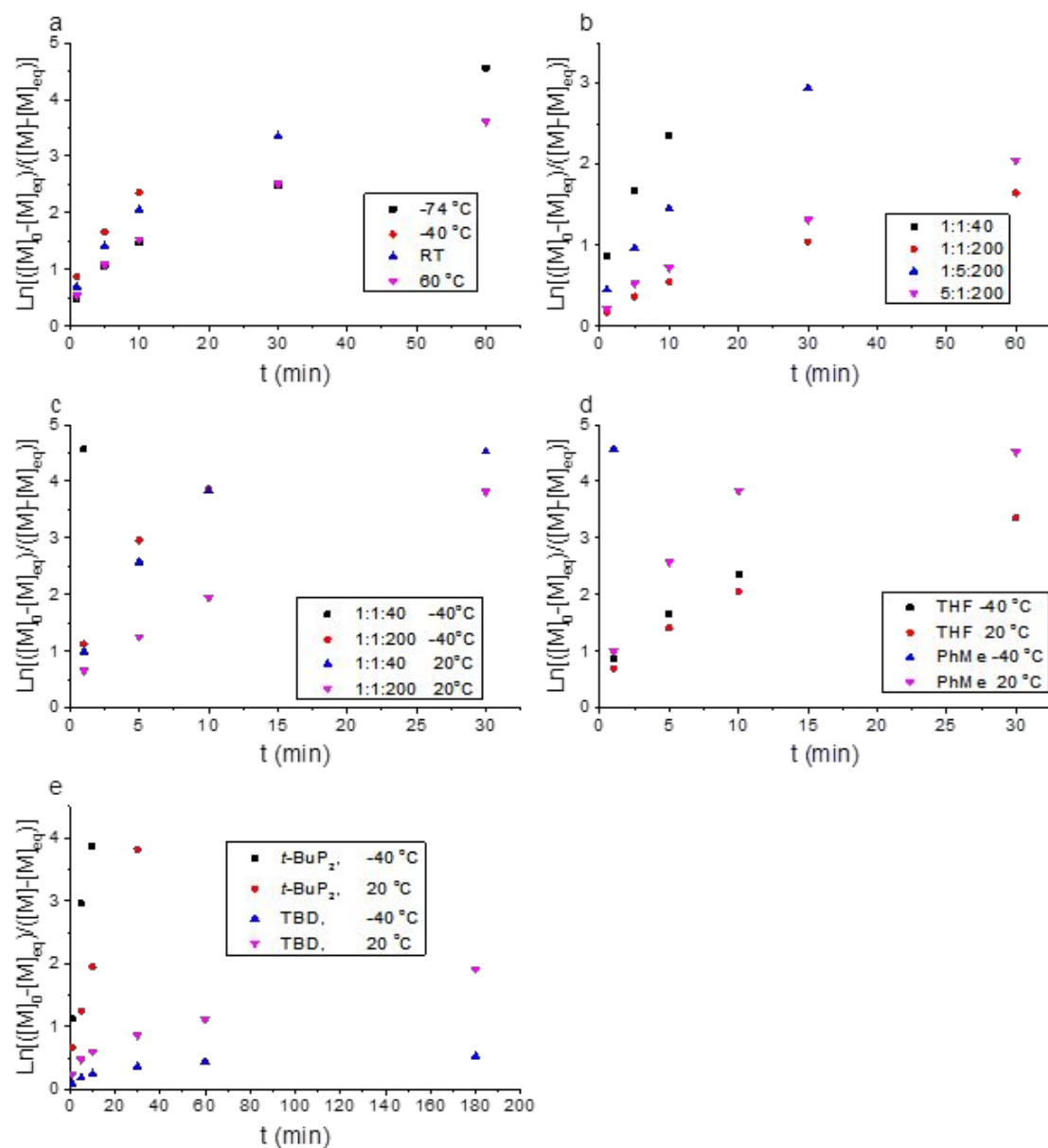


Figure S3 Semilogarithmic plots of monomer conversion over time for comparative sets of reactions. Each plot corresponded to the following figure in the manuscript: a) temperature dependence in THF (Figure 1a); b) reactant ratios dependence in THF (Figure 1b); c) temperature and reactant dependence in toluene (Figure 2a); d) solvent and temperature dependence (Figure 2b); e) catalyst and temperature dependence (Figure 3a).

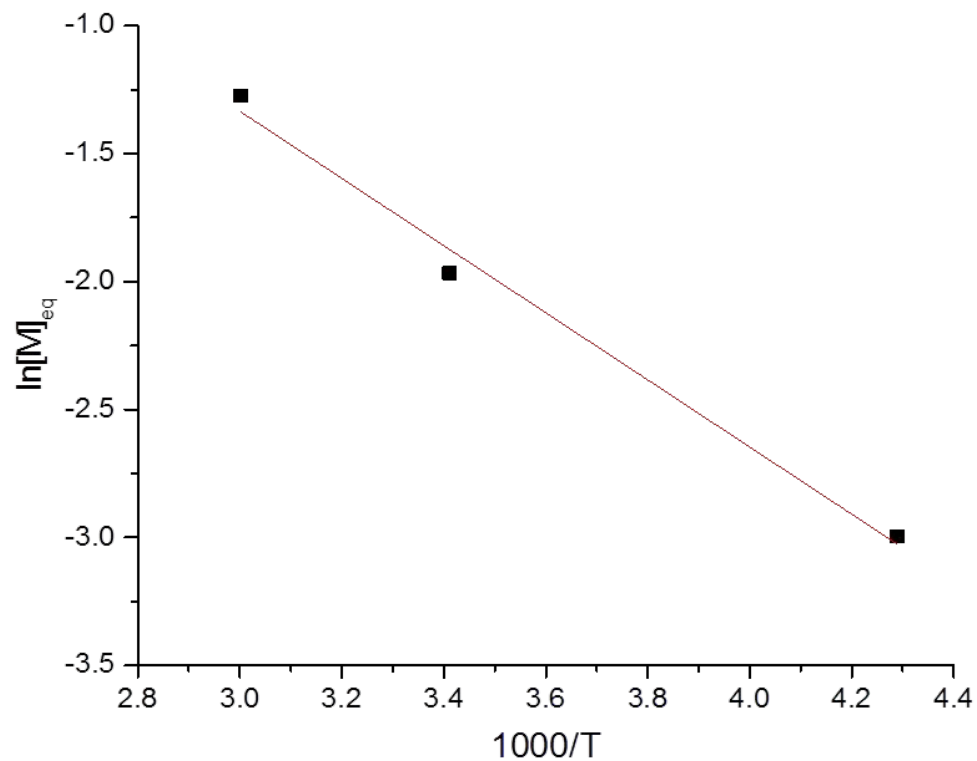


Figure S4 Relationship between $\ln[M]_{eq}$ and $1000/T$ in the system using THF as a solvent and with $[I]:[cat.]:[M]_0=1:1:40$. The linear fitting of the data points gives the following equation according to Dainton's equation¹ $\ln[M]_{eq} = \Delta H_p/RT - \Delta S_p/R$: $\ln[M]_{eq} = 2.60373 - 1312.48/T$. The calculated values are: $\Delta H_p \approx -10.91 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S_p \approx -21.647 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

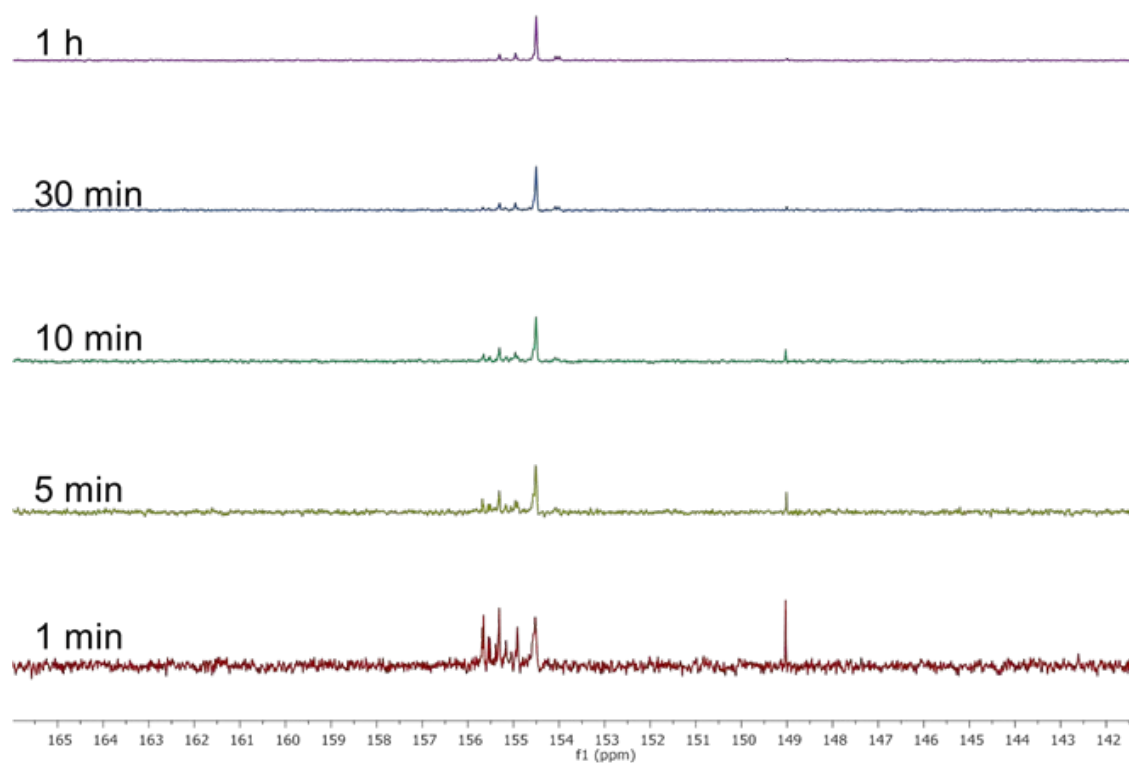


Figure S5 Compiled ^{13}C NMR spectra showing the carbonyl region of the raw product after the respected reaction time, using entry 6 as the model system.

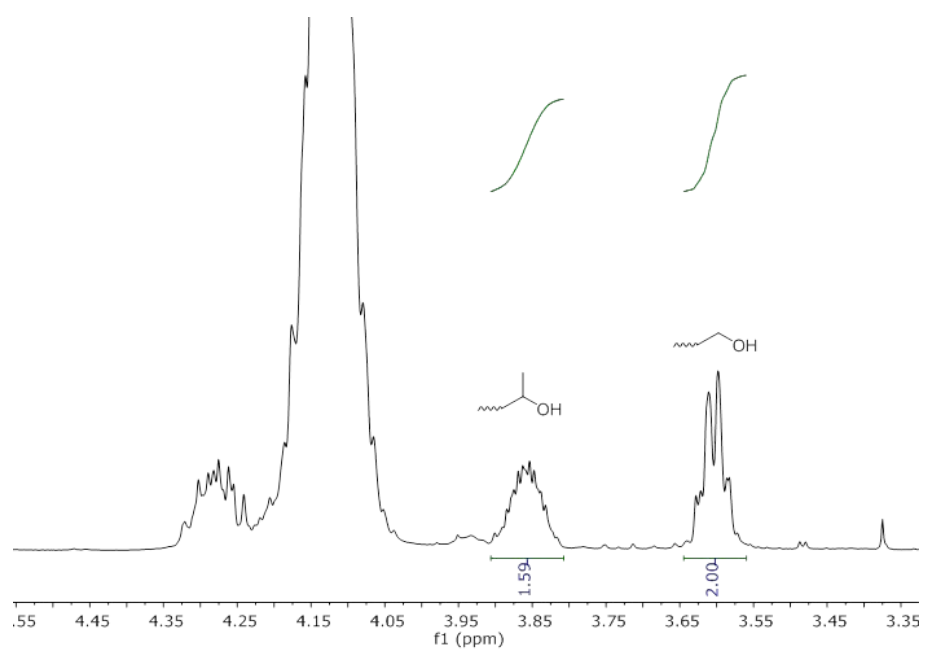


Figure S6 ^1H NMR showing a slight preference of secondary alcohol as chain-end over primary alcohol as chain-end.

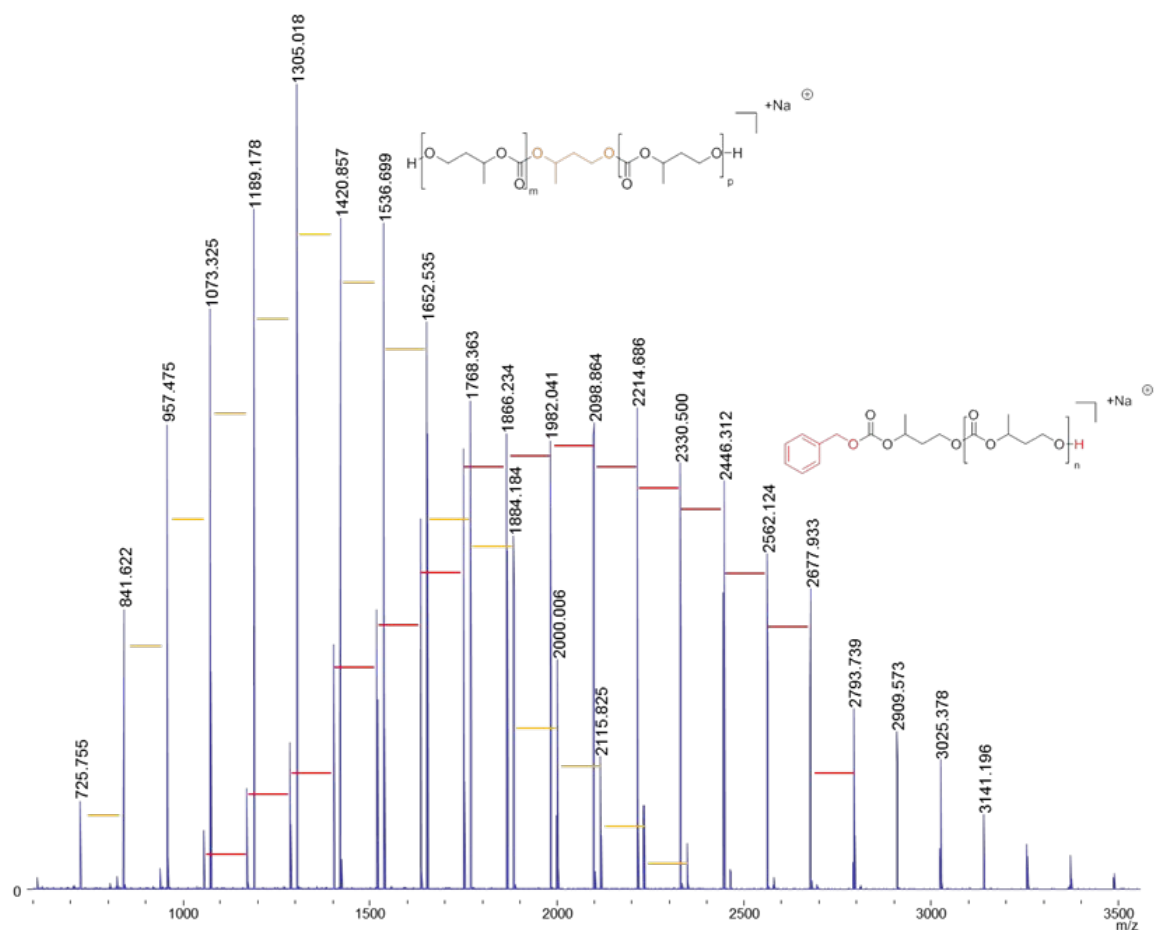


Figure S7 MALDI-ToF of the raw polymerization product using monomer with impurities. The molecular structure of each population is color coded respectively. The apparatus and sample preparation were used according to previous literature.²

Reference

- (1) Olsén, P.; Undin, J.; Odelius, K.; Keul, H.; Albertsson, A.-C. Switching from Controlled Ring-Opening Polymerization (CROP) to Controlled Ring-Closing Depolymerization (CRCDP) by Adjusting the Reaction Parameters That Determine the Ceiling Temperature. *Biomacromolecules* **2016**, *17* (12), 3995–4002.
- (2) Hua, G.; Odelius, K. Exploiting Ring-Opening Aminolysis–Condensation as a Polymerization Pathway to Structurally Diverse Biobased Polyamides. *Biomacromolecules* **2018**, *19* (5), 1573–1581.