

# **SUPPORTING INFORMATION**

## **Polyester Macromonomer Syntheses and Radical Copolymerization**

### **Kinetics with Styrene**

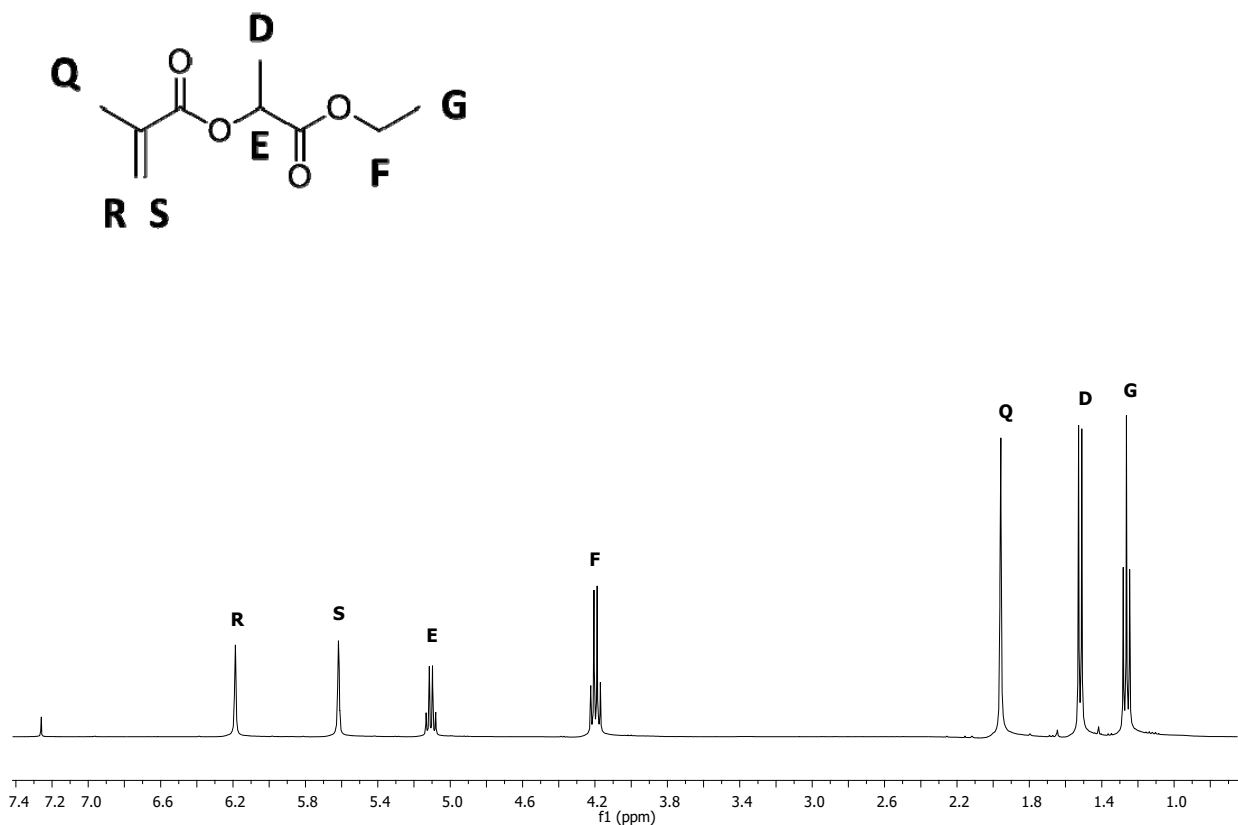
Thomas R. Rooney, Otlaitla Monyatsi, Robin A. Hutchinson\*

---

Department of Chemical Engineering, Dupuis Hall, Queen's University, Kingston, ON, K7L  
3N6, Canada (robin.hutchinson@queensu.ca)

**Macromonomer Synthesis** (see Experimental Section and Scheme 1 of manuscript for abbreviations)

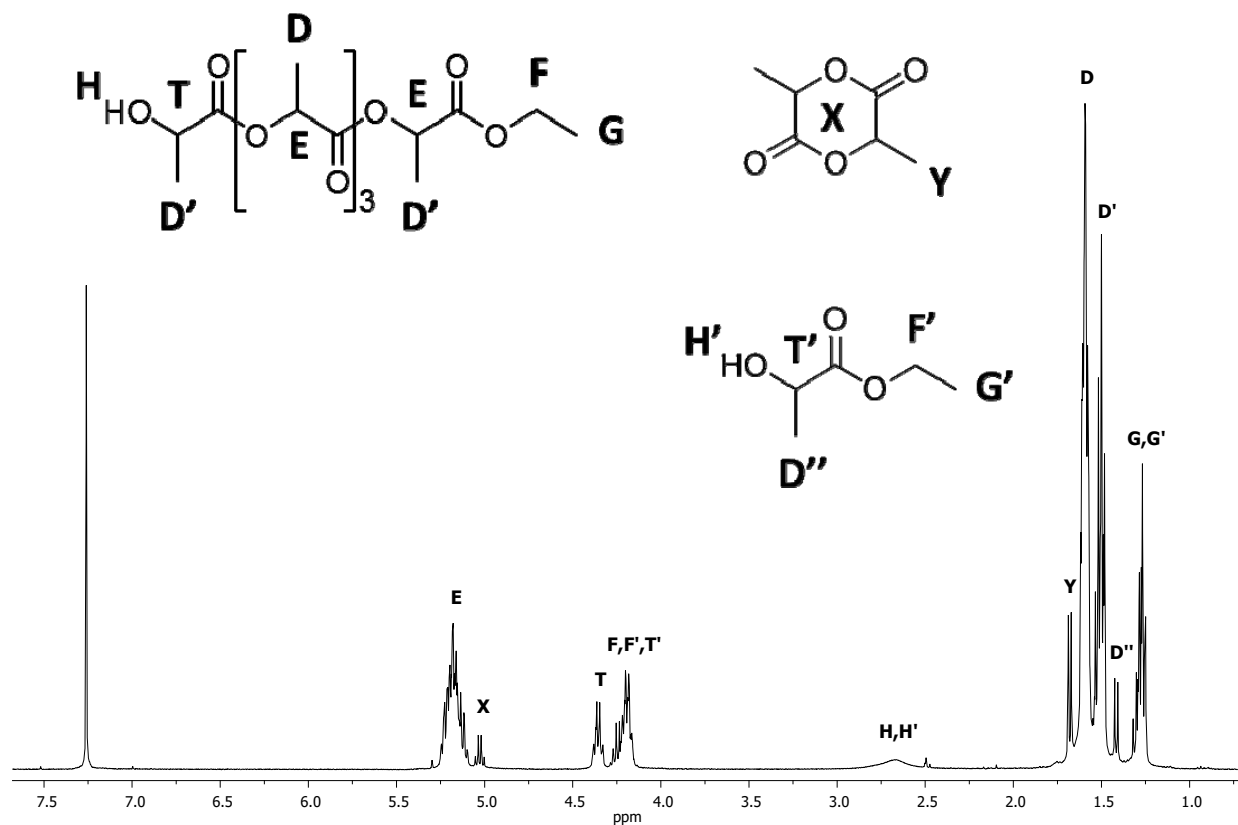
**PLA<sub>1</sub>EMA**



**Figure S1: Proton NMR spectrum with peak assignment for PLA<sub>1</sub>EMA in CDCl<sub>3</sub> at 25 °C.**

PLA<sub>1</sub>EMA <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.19 ppm (s, 1.0H, R), δ = 5.62 ppm (s, 1.0H, S), δ = 5.10 ppm (q, 0.9H, E), δ = 4.20 ppm (q, 2.0H, F), δ = 1.96 ppm (s, 3.0H, Q), δ = 1.52 ppm (d, 3.0H, D), δ = 1.26 ppm (t, 3.0H, G).

# PLA<sub>5</sub>E



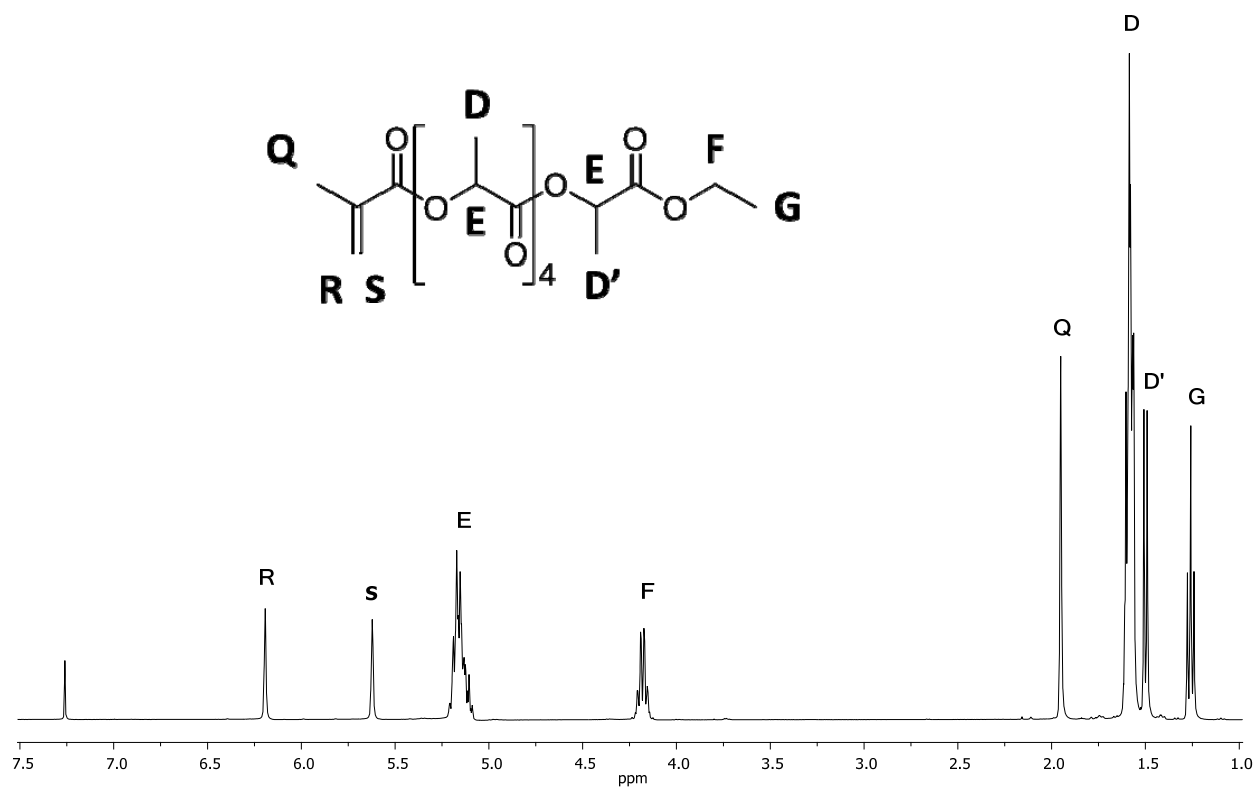
**Figure S2: Proton NMR spectrum with peak assignment for PLA<sub>5</sub>E in CDCl<sub>3</sub> at 25 °C.**

PLA<sub>5</sub>EMA <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak T: δ = 5.29–5.07 ppm (m, 4.5H, E), δ = 5.03 ppm (q, 0.5H, X), δ = 4.35 ppm (q, 1.0H, T), δ = 4.30–4.13 ppm (m, 2.4H, F+F'+T'), δ = 1.68 ppm (d, 0.9H, Y), δ = 1.62–1.56 ppm (m, 10.5H, D), δ = 1.54–1.47 ppm (m, 6.8H, D'), δ = 1.42 ppm (d, 0.6H, D''), δ = 1.33–1.24 ppm (m, 3.6H, G+G').

$$n = \frac{\int E + \int T}{T} = \frac{4.7 + 1}{1} = 5.5$$

$$\%LA_{conv.} = \frac{\int E}{\int X + \int E} = \frac{4.5}{0.3 + 4.5} \times 100\% = 94\%$$

## PLA<sub>5</sub>EMA

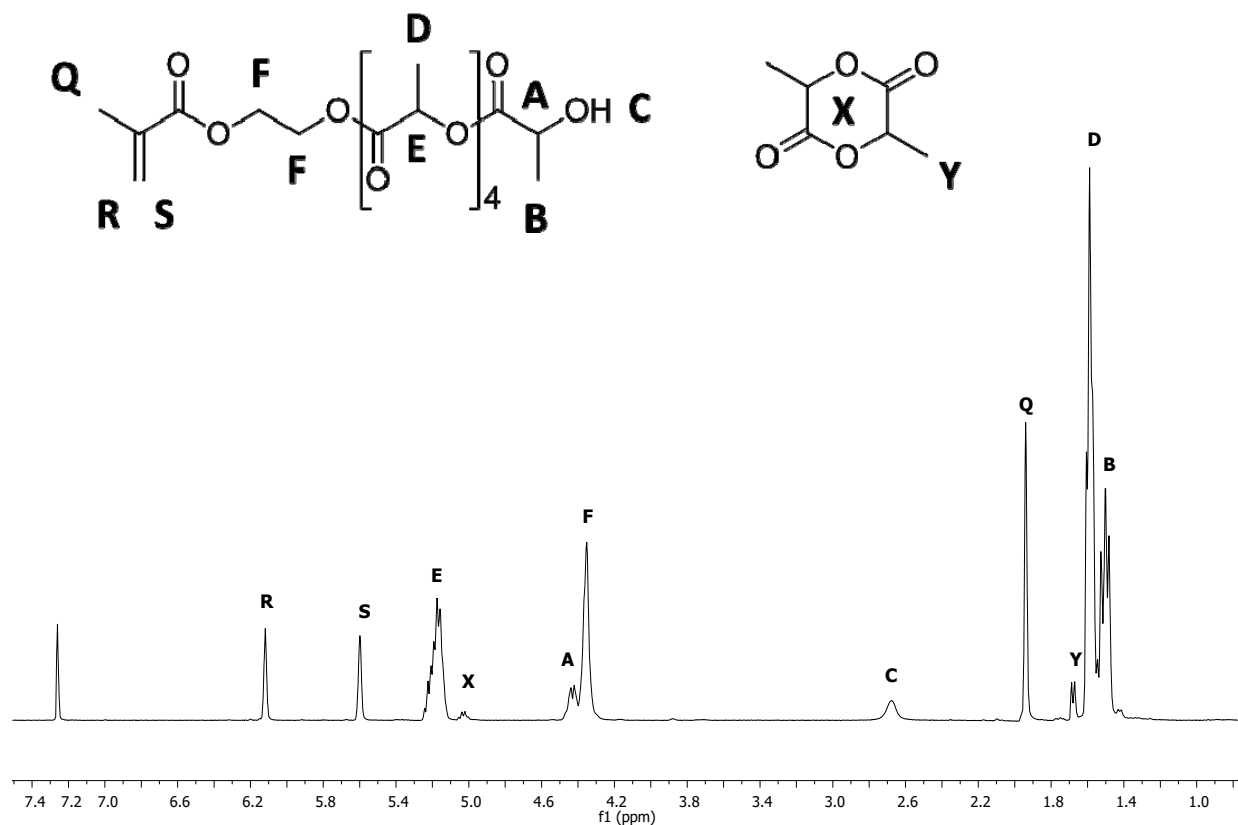


**Figure S3: Proton NMR spectrum with peak assignment for PLA<sub>5</sub>EMA in CDCl<sub>3</sub> at 25 °C.**

PLA<sub>5</sub>EMA <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S:  $\delta = 6.20$  ppm (s, 1.0H, R),  $\delta = 5.63$  ppm (s, 1.0H, S),  $\delta = 5.26\text{--}5.06$  ppm (m, 5.3H, E),  $\delta = 4.19$  ppm (q, 2.0H, F),  $\delta = 1.96$  ppm (s, 3.0H, Q),  $\delta = 1.68\text{--}1.54$  ppm (m, 12.9H, D),  $\delta = 1.51$  ppm (d, 3.0H, D'),  $\delta = 1.27$  ppm (t, 3.0H, G).

$$n = \frac{\int E}{\int S} = \frac{5.3}{1} = 5.3$$

# HEMA-PLA<sub>5</sub>



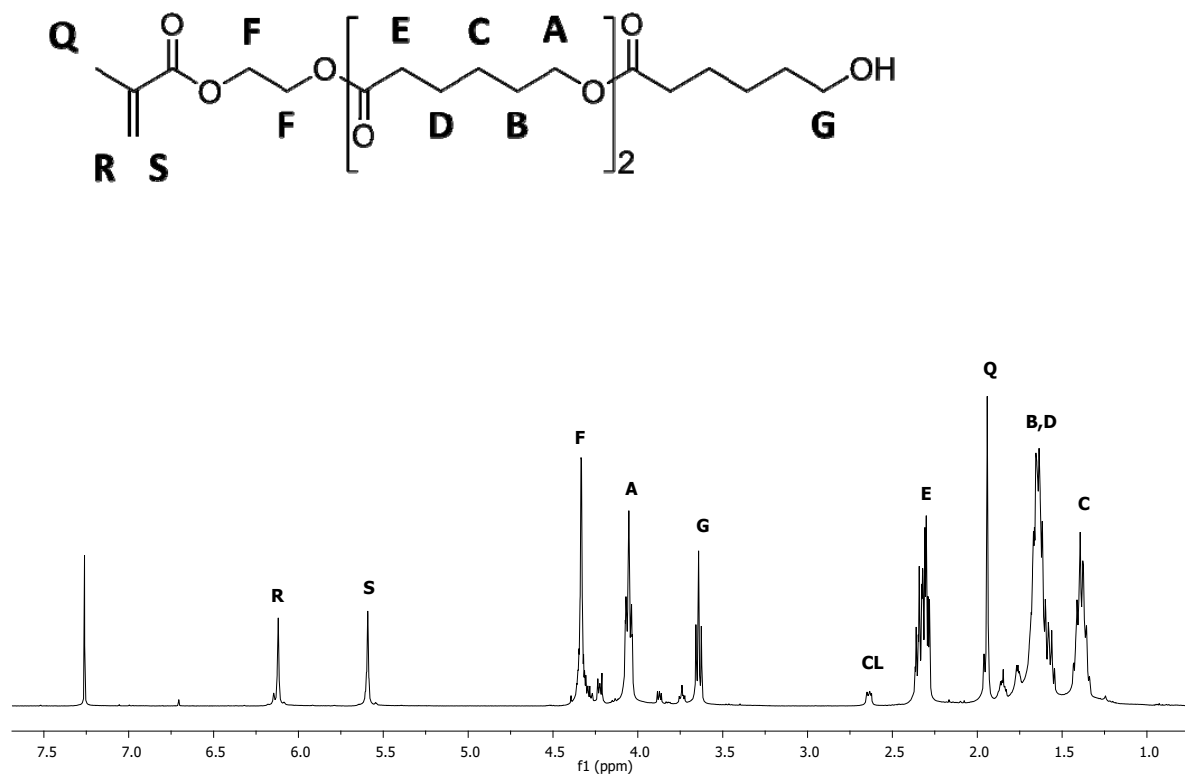
**Figure S4: Proton NMR spectrum with peak assignment for HEMA-PLA<sub>5</sub> in CDCl<sub>3</sub> at 25 °C.**

HEMA-PLA<sub>5</sub> <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.12 ppm (s, 1.0H, R), δ = 5.25–5.10 ppm (m, 4.3H, E), δ = 5.03 ppm (q, 0.2H, X), δ = 4.43 ppm (q, 1.0H, A), δ = 4.35 ppm (s, 4.0H, F), δ = 1.94 ppm (s, 3.0H, Q), δ = 1.68 ppm (d, 0.6H, Y), δ = 1.63–1.45 ppm (m, 16.0, D,B).

$$n = \frac{\int E + \int A}{\int S} = \frac{4.3 + 1}{1} = 5.3$$

$$\%LA_{conv.} = \frac{\int E + \int A}{\int E + \int A + \int X} = \frac{4.3 + 1}{4.3 + 1 + 0.2} \times 100\% = 96\%$$

# HEMA-PCL<sub>3</sub>



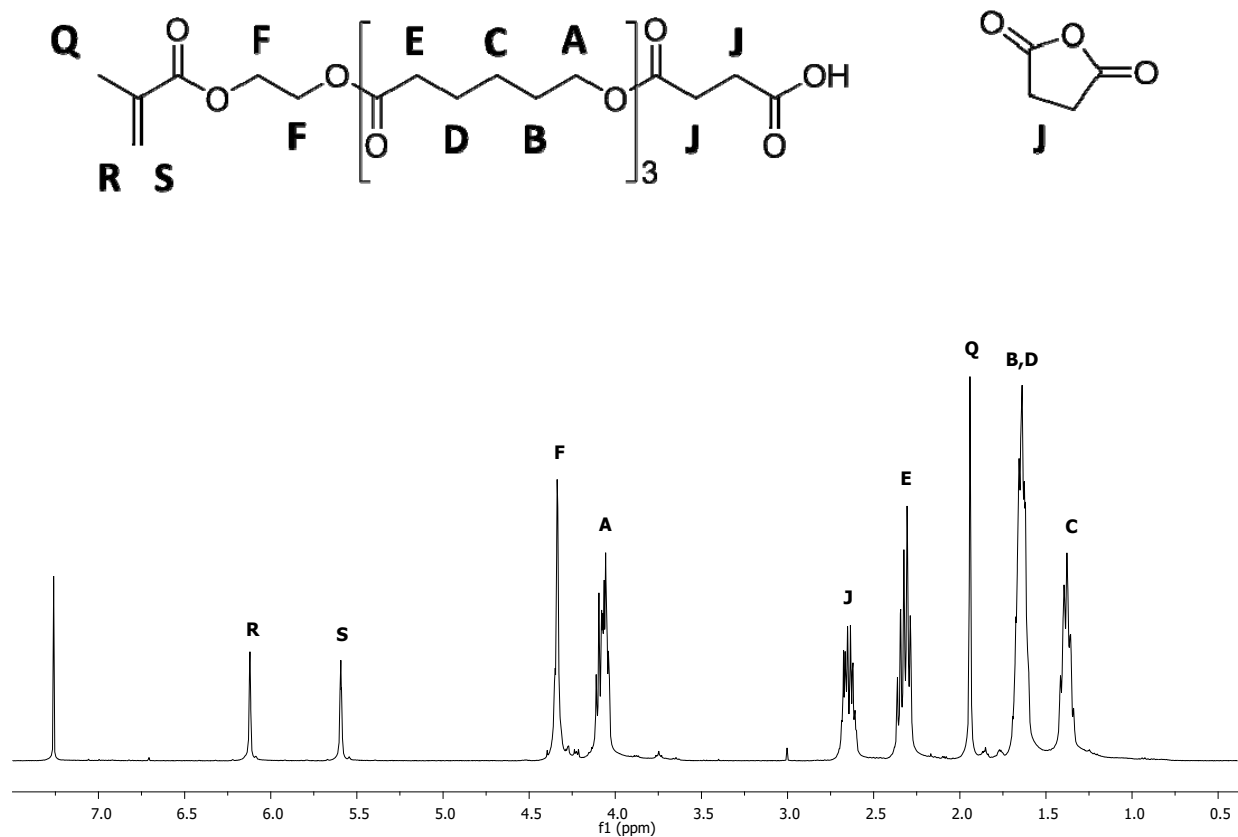
**Figure S5: Proton NMR spectrum with peak assignment for HEMA-PCL<sub>3</sub> in CDCl<sub>3</sub> at 25 °C.**

HEMA-PCL<sub>3</sub> <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.12 ppm (s, 1.0H, R), δ = 5.59 ppm (s, 1.0H, S), δ = 4.33 ppm (s, 4.0H, F), δ = 4.05 ppm (t, 4.6H, A), δ = 3.64 ppm (t, 2.0H, G), δ = 2.65 ppm (t, 0.4H, CL), δ = 2.40–2.25 ppm (m, 6.6H, E), δ = 1.94 ppm (s, 3.0H, Q), δ = 1.70–1.54 ppm (m, 14.4H, B,D), δ = 1.44–1.32 ppm (m, 6.7H, C).

$$n = \frac{\int E}{\int S} = \frac{6.6/2}{1} = 3.3$$

$$\% CL_{conv.} = \frac{\int E}{\int E + \int CL} = \frac{6.6}{6.6 + 0.4} \times 100\% = 94\%$$

# HEMA-PCL<sub>3</sub>-COOH

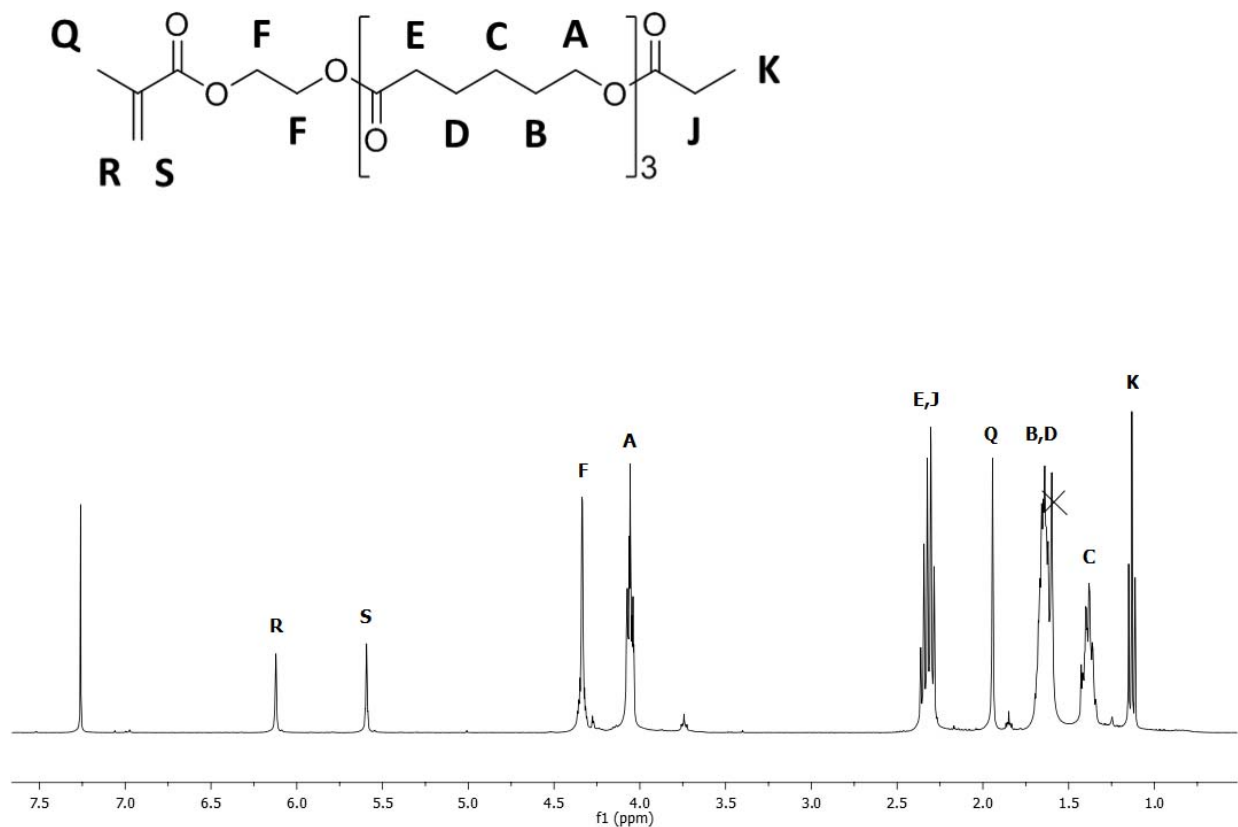


**Figure S6: Proton NMR spectrum with peak assignment for HEMA-PCL<sub>3</sub>-COOH in CDCl<sub>3</sub> at 25 °C.**

HEMA-PCL<sub>3</sub>-COOH <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.12 ppm (s, 1.0H, R), δ = 5.59 ppm (s, 1.0H, S), δ = 4.34 ppm (s, 4.0H, F), δ = 4.14–3.97 ppm (m, 6.7H, A), δ = 2.71–2.57 ppm (m, 4.4H, J), δ = 2.40–2.22 ppm (m, 6.7H, E), δ = 1.94 ppm (s, 3.0H, Q), δ = 1.70–1.54 ppm (m, 13.2H, B,D), δ = 1.44–1.32 ppm (m, 6.7H, C).

$$n = \frac{\int E}{\int S} = \frac{6.7/2}{1} = 3.35$$

## HEMA-PCL<sub>3</sub>-ET



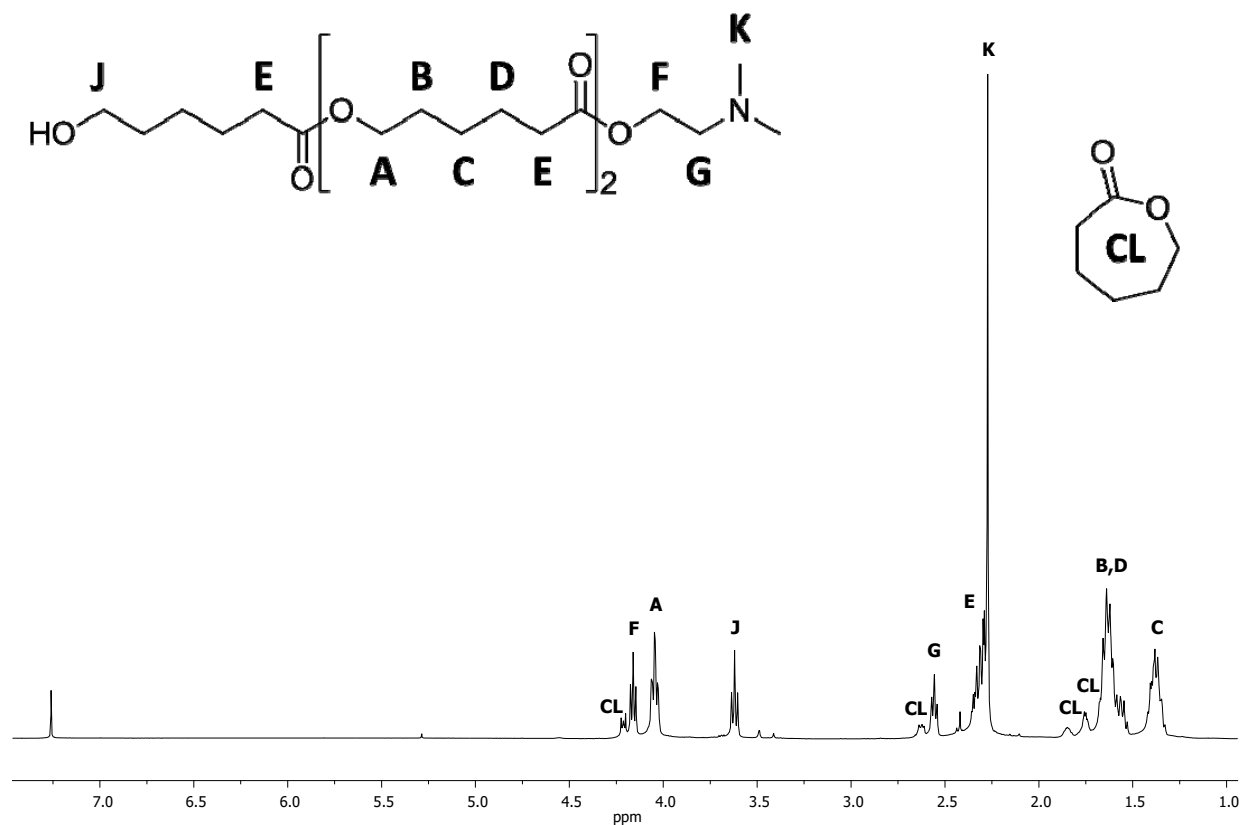
**Figure S7: Proton NMR spectrum with peak assignment for HEMA-PCL<sub>3</sub>-ET in CDCl<sub>3</sub> at 25 °C.**

HEMA-PCL<sub>3</sub>-ET <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.12 ppm (s, 1.0H, R), δ = 5.59 ppm (s, 1.0H, S), δ = 4.34 ppm (s, 4.0H, F), δ = 4.06 ppm (t, 6.6H, A), δ = 2.40–2.26 ppm (m, 8.6H, E+J), δ = 1.94 ppm (s, 3.0H, Q), δ = 1.70–1.54 ppm (m, N/A, B+D+H<sub>2</sub>O), δ = 1.44–1.32 ppm (m, 7.4H, C), δ = 1.44–1.32 ppm (t, 3.0H, K).

$$n = \frac{\frac{\int(E,J) - 2}{2}}{\int S} = \frac{\frac{8.6 - 2}{2}}{1} = 3.3$$



**PCL<sub>3</sub>De**



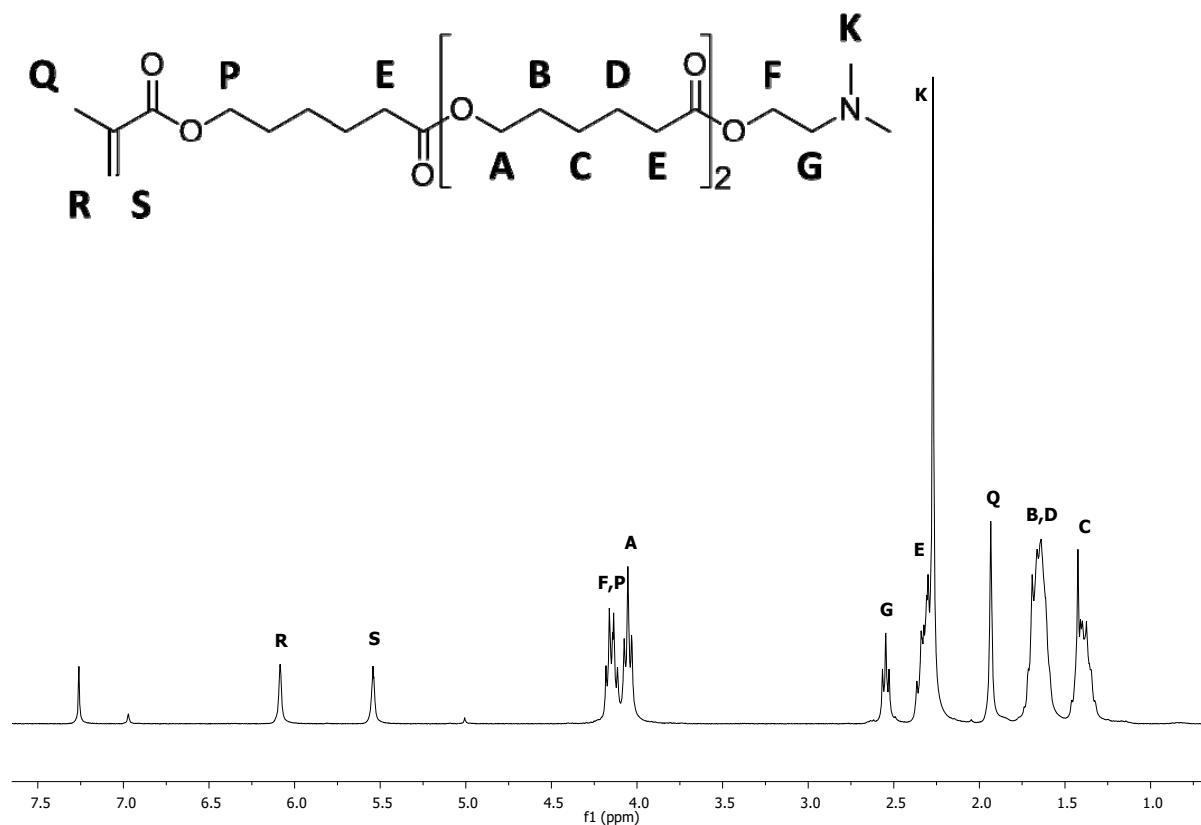
**Figure S8: Proton NMR spectrum with peak assignment for PCL<sub>3</sub>De in CDCl<sub>3</sub> at 25 °C.**

PCL<sub>3</sub>De <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak J:  $\delta = 4.23$  ppm (t, 0.4H, CL),  $\delta = 4.17$  ppm (t, 2.0H, F),  $\delta = 4.06$  ppm (m, 4.0H, A),  $\delta = 3.64$  ppm (t, 2.0H, J),  $\delta = 2.64$  ppm (t, 0.4H, CL),  $\delta = 2.56$  ppm (t, 2.0H, G),  $\delta = 2.44$ – $2.24$  ppm (m, 12.3H, E+K),  $\delta = 1.86$  ppm (m, 0.4H, CL),  $\delta = 1.71$ – $1.51$  ppm (m, 13.2, B+D),  $\delta = 1.46$ – $1.33$  ppm (m, 6.2 H, C).

$$n = \frac{\int J + \int A}{\int J} = \frac{2.0 + 4.0}{2.0} = 3.0$$

$$\%CL_{conv.} = \frac{\int J + \int A}{\int J + \int A + \int CL} = \frac{2.0 + 4.0}{2.0 + 4.0 + 0.4} \times 100\% = 94\%$$

# PCL<sub>3</sub>DeMA

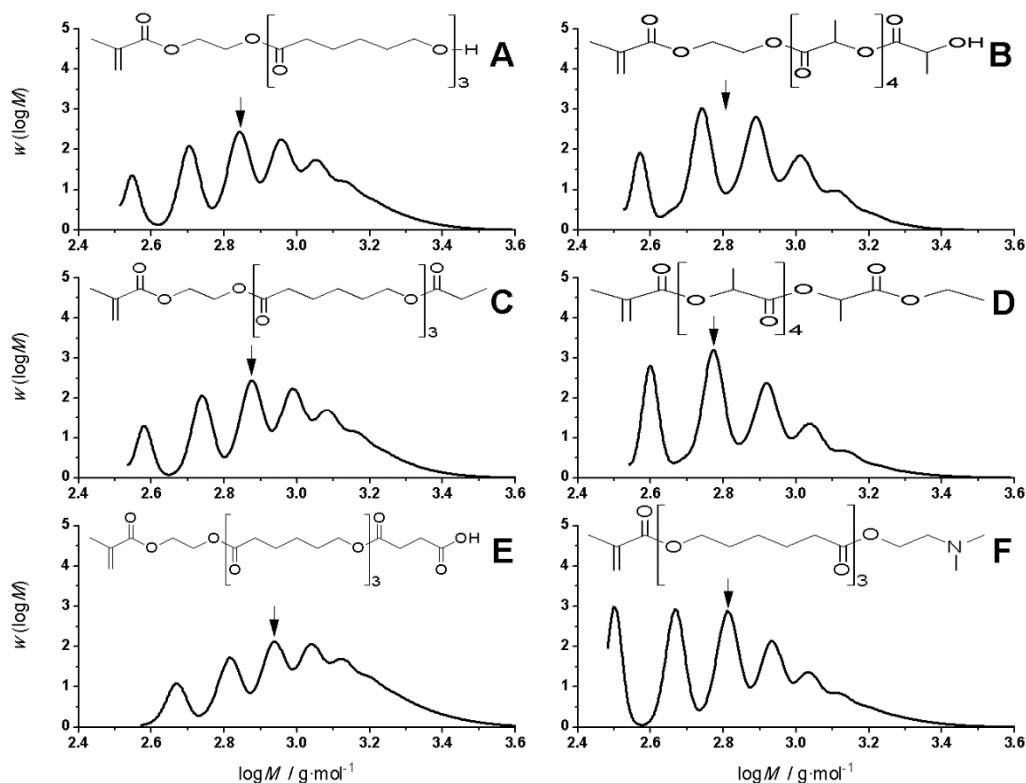


**Figure S9: Proton NMR spectrum with peak assignment for PCL<sub>3</sub>DeMA in CDCl<sub>3</sub> at 25 °C.**

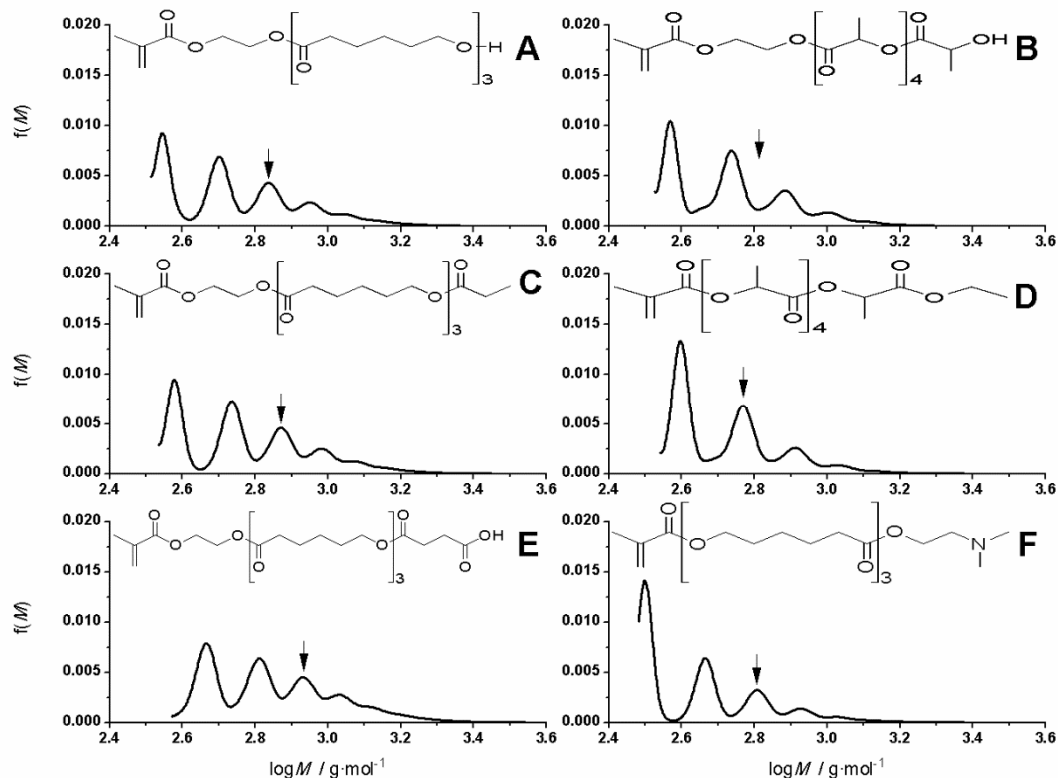
PCL<sub>3</sub>DeMA <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) with integrations relative to Peak S: δ = 6.09 ppm (s, 1.0H, R), δ = 5.54 ppm (s, 1.0H, S), δ = 4.19–4.10 ppm (m, 4.0H, F+P), δ = 4.05 ppm (t, 4.1H, A), δ = 2.55 ppm (t, 2.0H, G), δ = 2.38–2.24 ppm (m, 12.4H, E+K), δ = 1.93 ppm (s, 3.0H, Q), δ = 1.70–1.52 ppm (m, 12.8H, B+D), δ = 1.45–1.31 ppm (m, 6.4H, C).

$$n = \frac{\frac{\int(A + F, P) - \int G}{2}}{\int S} = \frac{\frac{8.1 - 2}{2}}{1} = 3.05$$

## Macromonomer Oligomeric Distributions



**Figure S10: Molar mass distributions measured by size exclusion chromatography in THF and analyzed as polymethyl methacrylate equivalents for HEMA-PCL<sub>3</sub> (panel A), HEMA-PLA<sub>5</sub> (panel B), HEMA-PCL<sub>3</sub>-ET (panel C), PLA<sub>5</sub>EMA (panel D), HEMA-PCL<sub>3</sub>-COOH (panel E), and PCL<sub>3</sub>DeMA (panel F). Arrows indicate expected location of target  $n$  (see Table 1 of main text).**



**Figure S11: Number distributions (normalized by area) measured by size exclusion chromatography in THF and analyzed as polymethyl methacrylate equivalents for HEMA-PCL<sub>3</sub> (panel A), HEMA-PLA<sub>5</sub> (panel B), HEMA-PCL<sub>3</sub>-ET (panel C), PLA<sub>5</sub>EMA (panel D), HEMA-PCL<sub>3</sub>-COOH (panel E), and PCL<sub>3</sub>DeMA (panel F). Arrows indicate expected location of target  $n$  (see Table 1 of main text).**

### **(Macro)monomer Copolymerization Kinetics**

In order to estimate monomer conversion, a reference peak invariant with time must be established from the proton NMR spectra, as shown in Figure S12. The integral of the aromatic region does not change with time, but the broadness of the copolymer aromatic signals overlaps peak C of styrene (ST) monomer. Since the integrations of peaks C and A are equivalent throughout the reaction, a reference integral is established as the difference in integrations of peak A (which is distinct) and the aromatic region, as summarized by Eqn. S1. Then, the absolute moles of methacrylate (xMA) and ST are calculated as a function of time by Eqn. S2 and S3 in order to determine monomer molar composition and molar conversion by Eqn. S4 and S5, respectively. The composition drift is normalized by initial composition according to Eqn. S6.

$$Ref. = \int Aromatics - \int A \quad S1$$

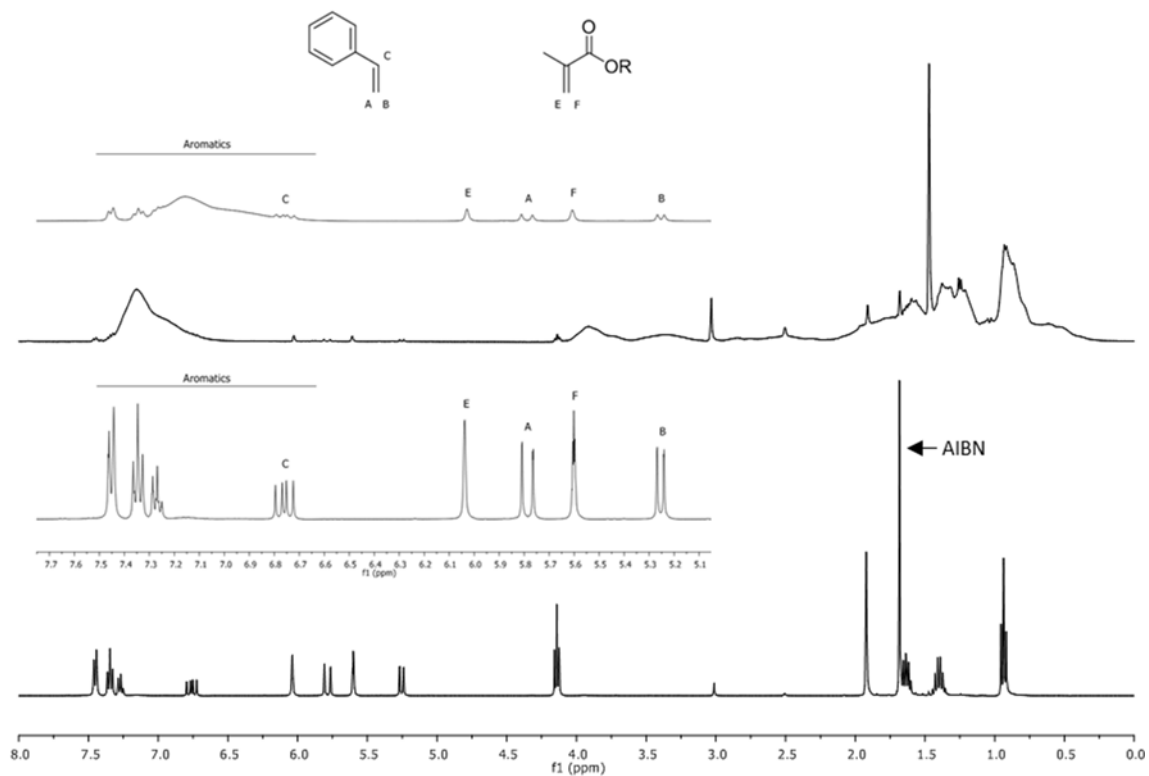
$$n_{xMA} = \frac{\int E}{Ref.} \quad S2$$

$$n_{ST} = \frac{\int A}{Ref.} \quad S3$$

$$f_{xMA} = \frac{\int E}{\int A + \int E} \quad S4$$

$$\chi = 1 - \frac{n_{xMA} + n_{ST}}{n_{xMA,0} + n_{ST,0}} \quad S5$$

$$Normalized f_{xMA} = \frac{f_{xMA}}{f_{xMA,0}} \quad S6$$



**Figure S12: Relevant peak assignments for representative  $^1\text{H}$ -NMR spectra of BMA/ST copolymerization at 0% (bottom) and at 98% (top; inset at 80%) conversions performed in 80 wt% DMSO- $d_6$  at 80 °C with  $f_{\text{xMA},0} = 0.5$  and 3.5 wt% AIBN.**

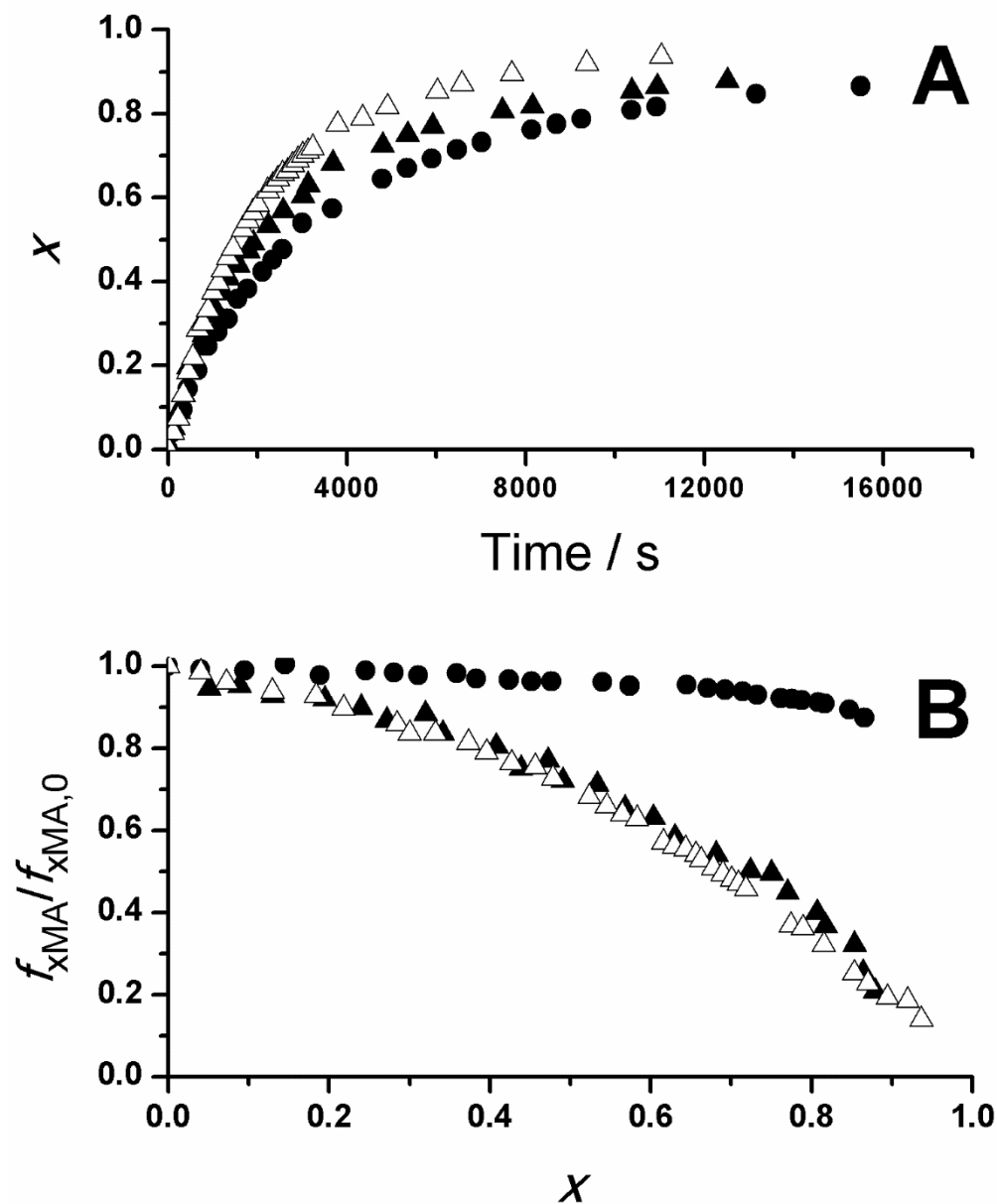


Figure S13: Overall monomer conversion vs time profiles (panel A) and normalized monomer composition vs conversion (panel B) for ST copolymerizations with  $f_{\text{xMA},0} = 0.2$  for BMA (circles) and HEMA (triangles) in 80 wt% (closed symbols) as well as 60 wt% (open symbols) toluene-d8 performed at 80 °C with 3.5 wt% AIBN.

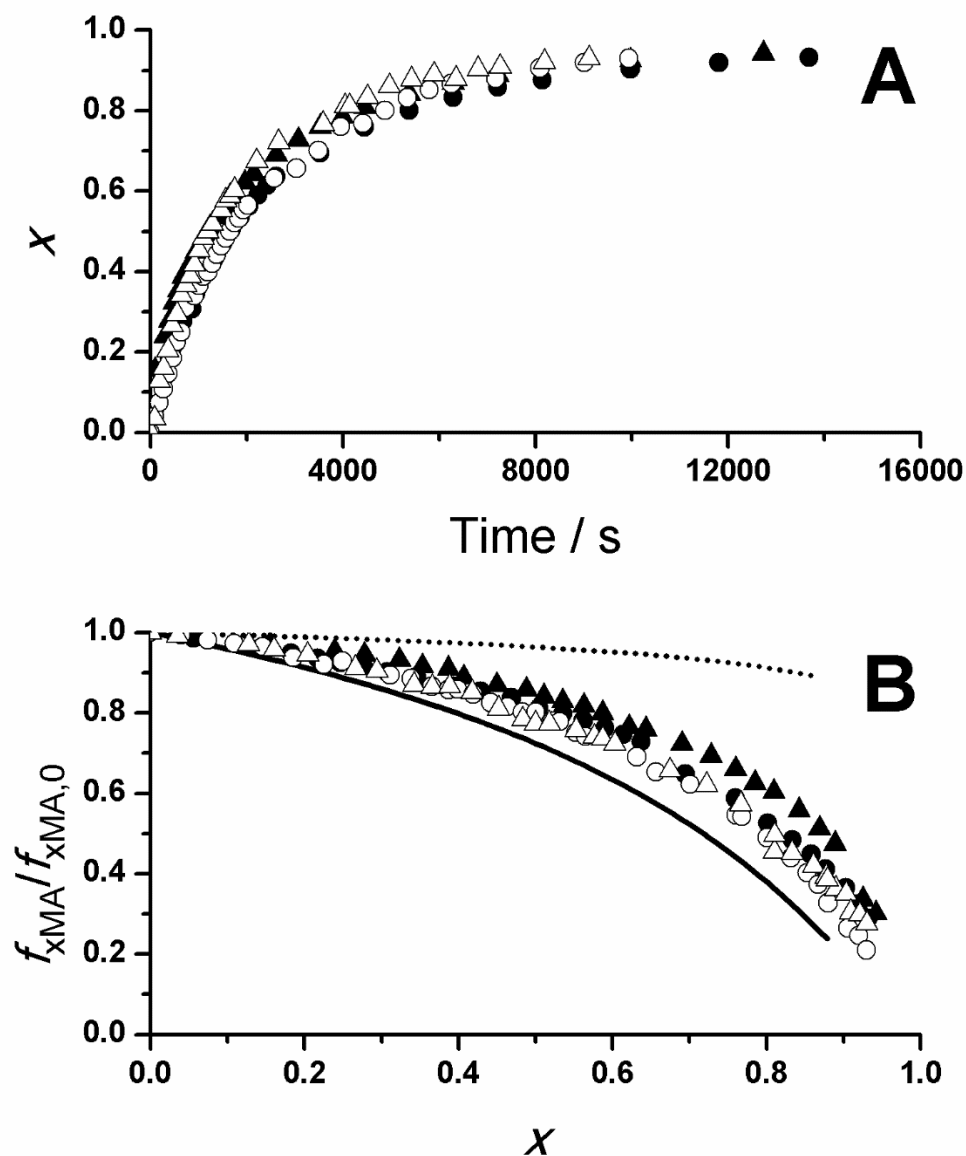


Figure S14: Overall monomer conversion vs time profiles (panel A) and normalized monomer composition vs conversion (panel B) for ST copolymerizations with  $f_{\text{xMA},0} = 0.2$  for BMA (circles) and HEMA (triangles) in 80 wt% (closed symbols) as well as 60 wt% (open symbols) DMSO-d6 performed at 80 °C with 3.5 wt% AIBN. Best fit lines for HEMA/ST (solid line) and BMA/ST (dotted line) in 80 wt% toluene-d8 are provided as visual guides.



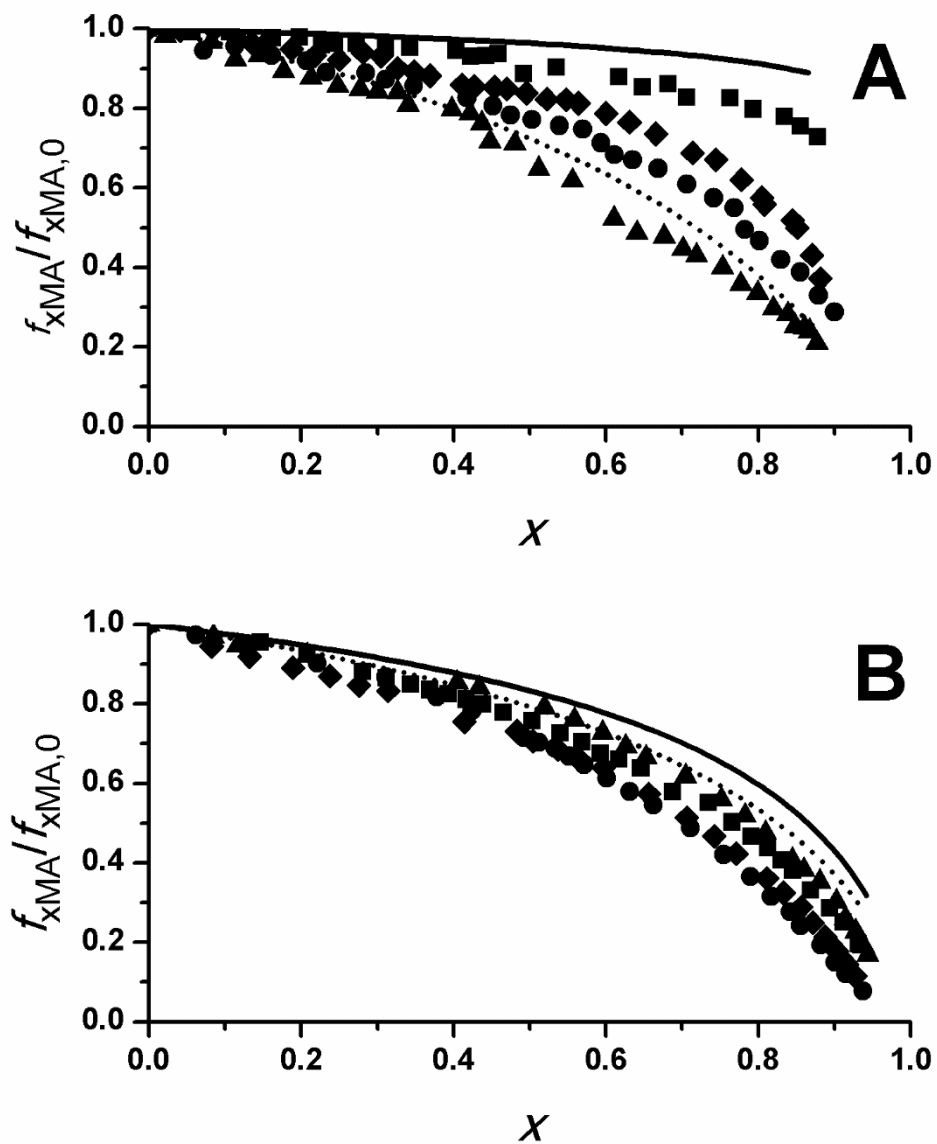


Figure S15: Normalized monomer composition drifts of ST copolymerizations with  $f_{xMA,0} = 0.2$  for PLA<sub>1</sub>EMA (●), HEMA-COOH (▲), DMAEMA (■), and GMA (◆) in 80 wt% toluene-d<sub>8</sub> (panel A) and 80 wt% DMSO-d<sub>6</sub> (panel B) performed at 80 °C with 3.5 wt% AIBN. Best fit lines for HEMA/ST (solid lines) and BMA/ST (dotted lines) in their respective solutions are provided as visual guides.

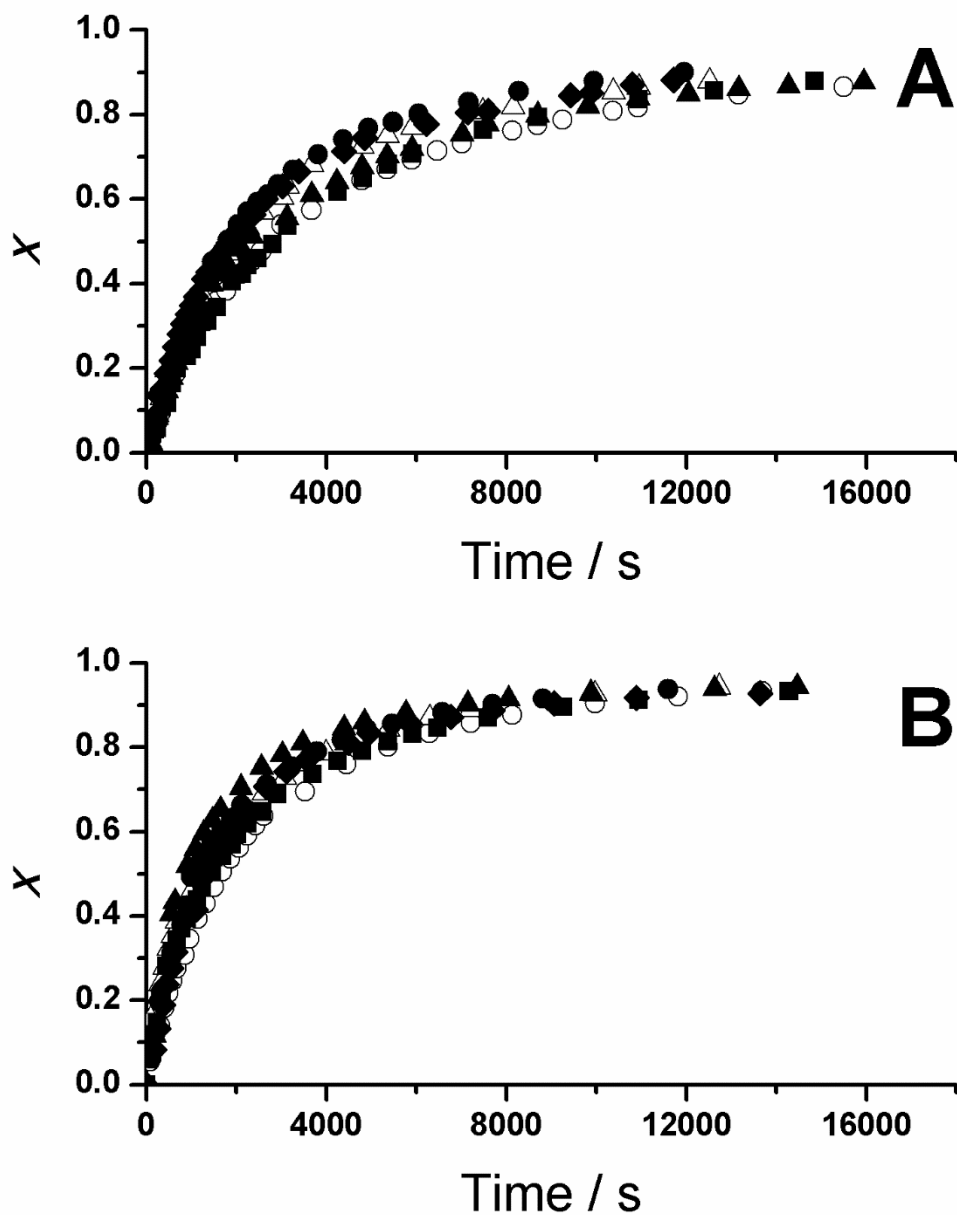


Figure S16: Overall monomer conversion profiles for ST copolymerizations with  $f_{\text{xMA},0} = 0.2$  for BMA ( $\circ$ ), HEMA ( $\Delta$ ), PLA<sub>1</sub>EMA ( $\bullet$ ), HEMA-COOH ( $\blacktriangle$ ), DMAEMA ( $\blacksquare$ ), and GMA ( $\blacklozenge$ ) in 80 wt% toluene-d<sub>8</sub> (panel A) and 80 wt% DMSO-d<sub>6</sub> (panel B) performed at 80 °C with 3.5 wt% AIBN.

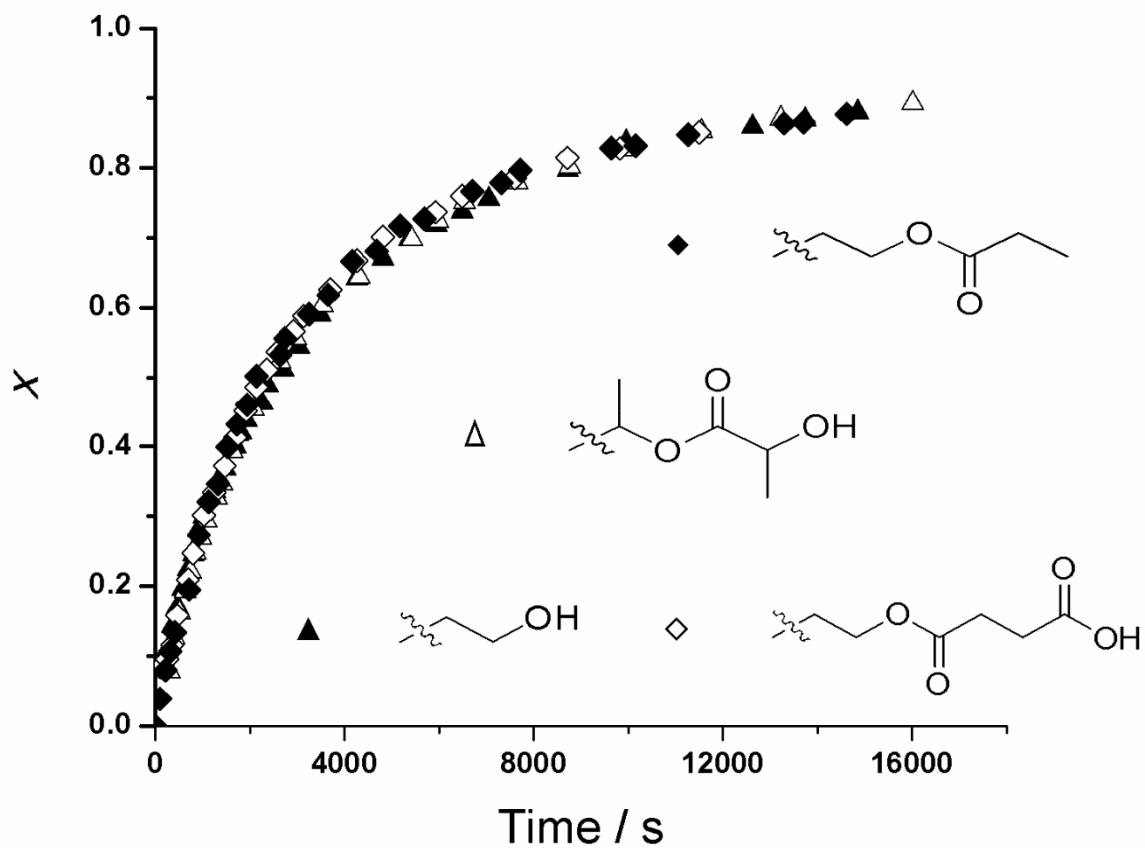


Figure S17: Overall monomer conversion profiles for ST copolymerizations with  $f_{\text{xMA},0} = 0.2$  for HEMA-PCL<sub>3</sub> (▲), HEMA-PLA<sub>5</sub> (△), HEMA-PCL<sub>3</sub>-COOH (◆), and HEMA-PCL<sub>3</sub>-ET (◇) in 80 wt% toluene-d<sub>8</sub> performed at 80 °C with 3.5 wt% AIBN.

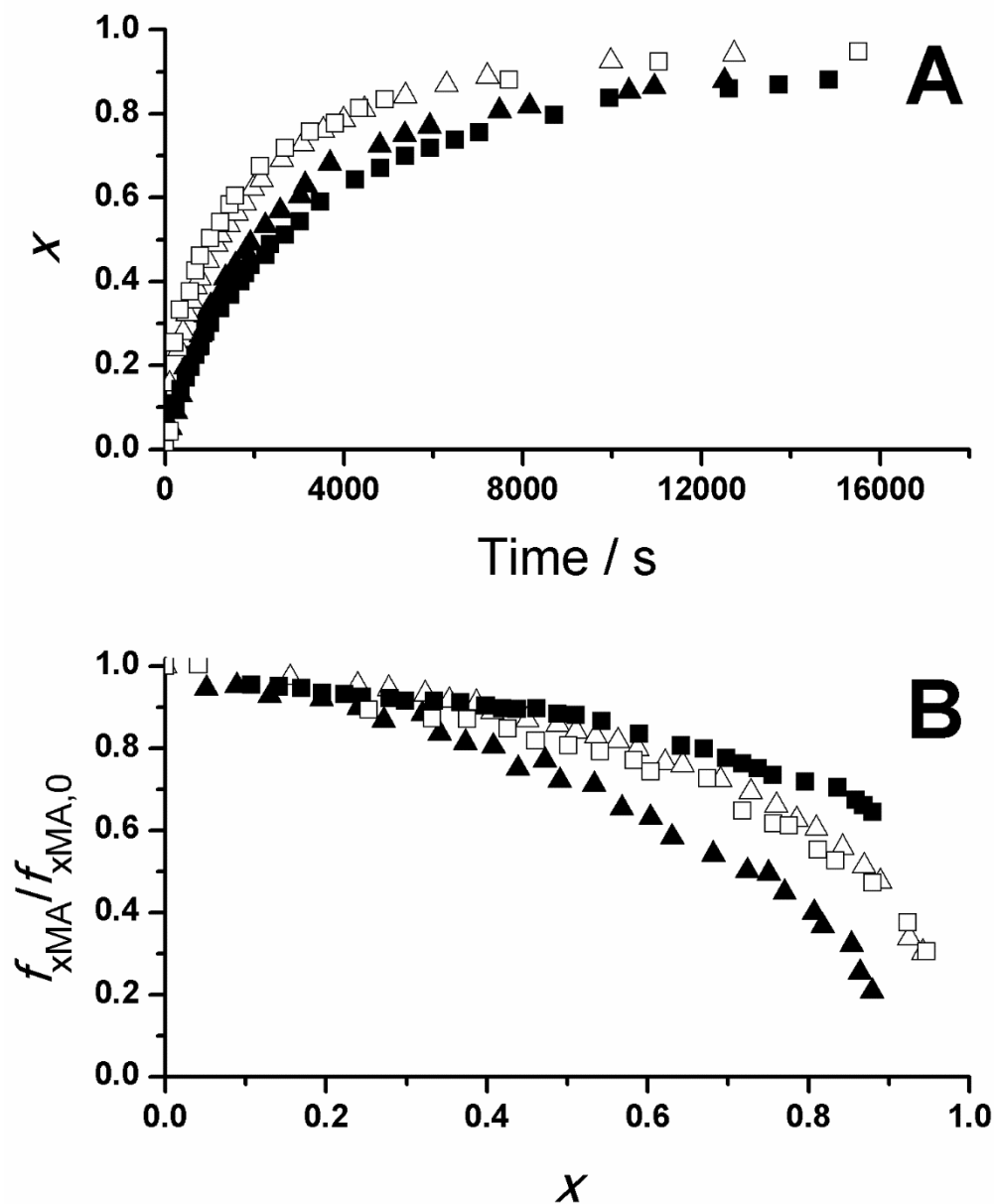
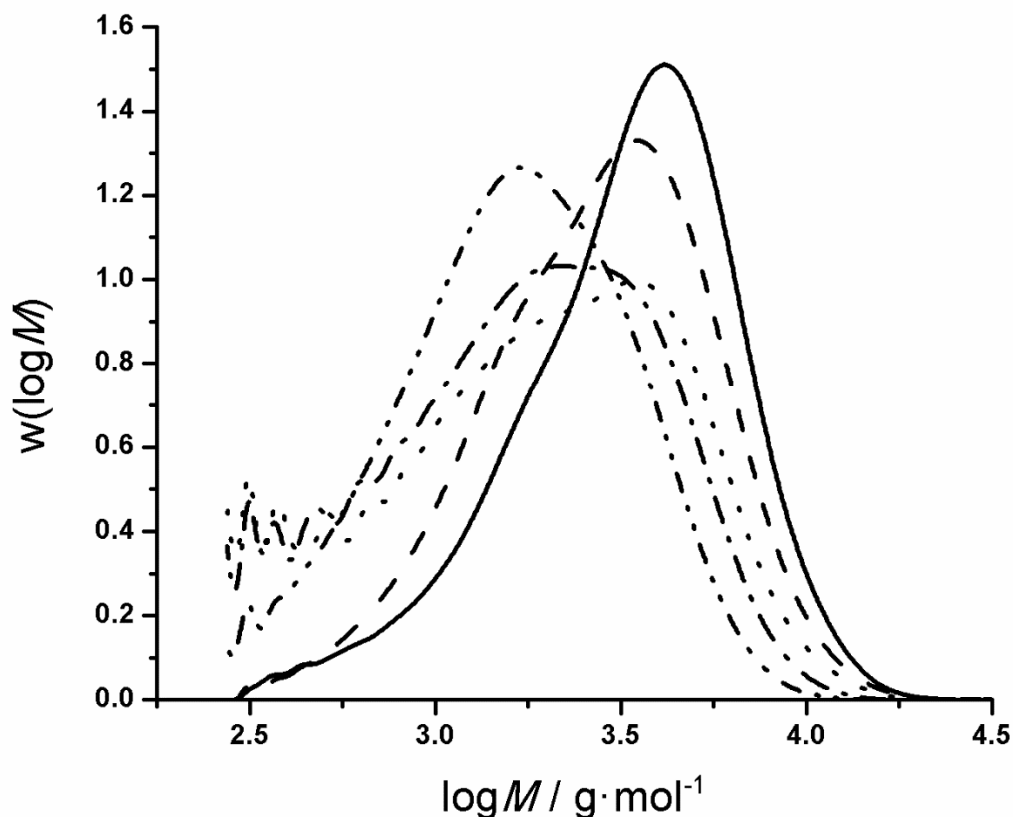


Figure S18: Overall monomer conversion vs time profiles (panel A) and normalized monomer composition vs conversion (panel B) for ST copolymerizations with  $f_{xMA,0} = 0.2$  for HEMA (triangles) and HEMA-PCL<sub>3</sub> (squares) in 80 wt% toluene-d<sub>8</sub> (closed symbols) and 80 wt% DMSO-d<sub>6</sub> (open symbols) performed at 80 °C with 3.5 wt% AIBN.

**Table S1: Weight-average molar masses ( $M_w$ ) and dispersities ( $\mathcal{D}$ ) measured by light scattering for high conversion batch xMA/ST ( $f_{\text{xMA},0} = 0.2$ ) copolymers produced at 80 °C in 80 wt% toluene-d8 with 3.5 wt% AIBN.**

xMA	$M_w$	$\mathcal{D}$
	kg·mol <sup>-1</sup>	
PLA <sub>5</sub> EMA	5.3	-
HEMA	3.7	1.4
HEMA-PCL <sub>3</sub>	3.0	1.7
PCL <sub>3</sub> DeMA	3.0	1.3
BMA	2.2	1.5



**Figure S19: Polymer molar mass distributions in polystyrene equivalents for high conversion batch xMA/ST ( $f_{\text{xMA},0} = 0.2$ ) copolymers produced at 80 °C in 80 wt% toluene-d8 with 3.5 wt% AIBN for PLA<sub>5</sub>EMA (solid), HEMA (dash), HEMA-PCL<sub>3</sub> (dot), PCL<sub>3</sub>DeMA (dash dot), and BMA (dash dot dot) as xMA comonomer.**