Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for:

Increasing the solubility range of polyesters by tuning their microstructure with comonomers

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Theoretical diad distribution calculation from semi-quantitative ^{13}C NMR.

The probability to have a ω-PDL unit depends on the theoretical degree of polymerization and is corrected with the conversion:

$$P_{\omega-PDL} = \frac{DP_{n,th,\,\omega-PDL}.\,conv(\omega\text{–}PDL)}{DP_{n,th,\,\omega-PDL}.\,conv(\omega-PDL) + DP_{n,th,\,M}.\,conv(M)}$$

$$P_{M} = \frac{DP_{n,th,\,M}.\,conv(M)}{DP_{n,th,\omega-\,PDL}.\,conv(\omega-PDL) + DP_{n,th,\,M}.\,conv(M)}$$

The theoretical diad distributions correspond to the product of the probabilities:

$$\omega\text{–}PDL^{*} - \omega\text{–}PDL = {P_{\omega-PDL}}^{2}$$

$$M^{*} - M = {P_{M}}^{2}$$

$$\omega\text{–}PDL^{*} - M = M^{*} - \omega\text{–}PDL = P_{\omega-PDL}.P_{M}$$

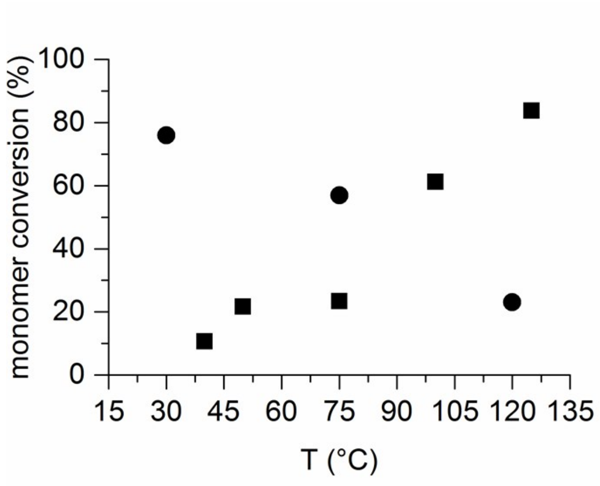

Figure S1. Temperature dependence of bulk homopolymerizations (BnOH/ω-PDL 1/20 and BnOH/δ-UDL 1/15) with ω-PDL (black square) and δ-UDL (black circle) conversions after 60 min.

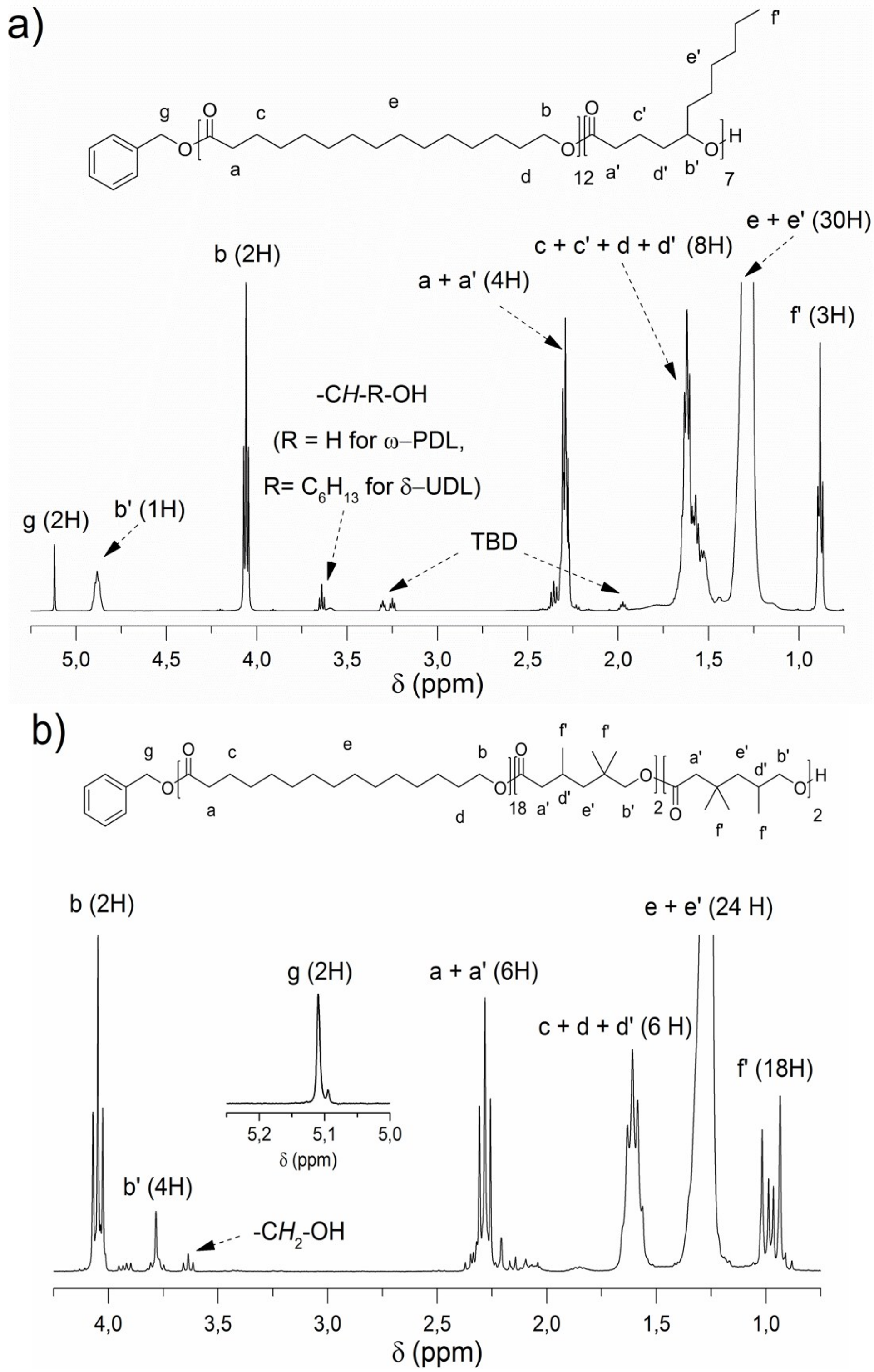

Figure S2. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of purified copolymers a) poly(ω-PDL-*co*-δ-UDL) (Table 1, entry **3**); and b) poly(ω-PDL-*co*-TMCL) (Table 1, entry **6**).

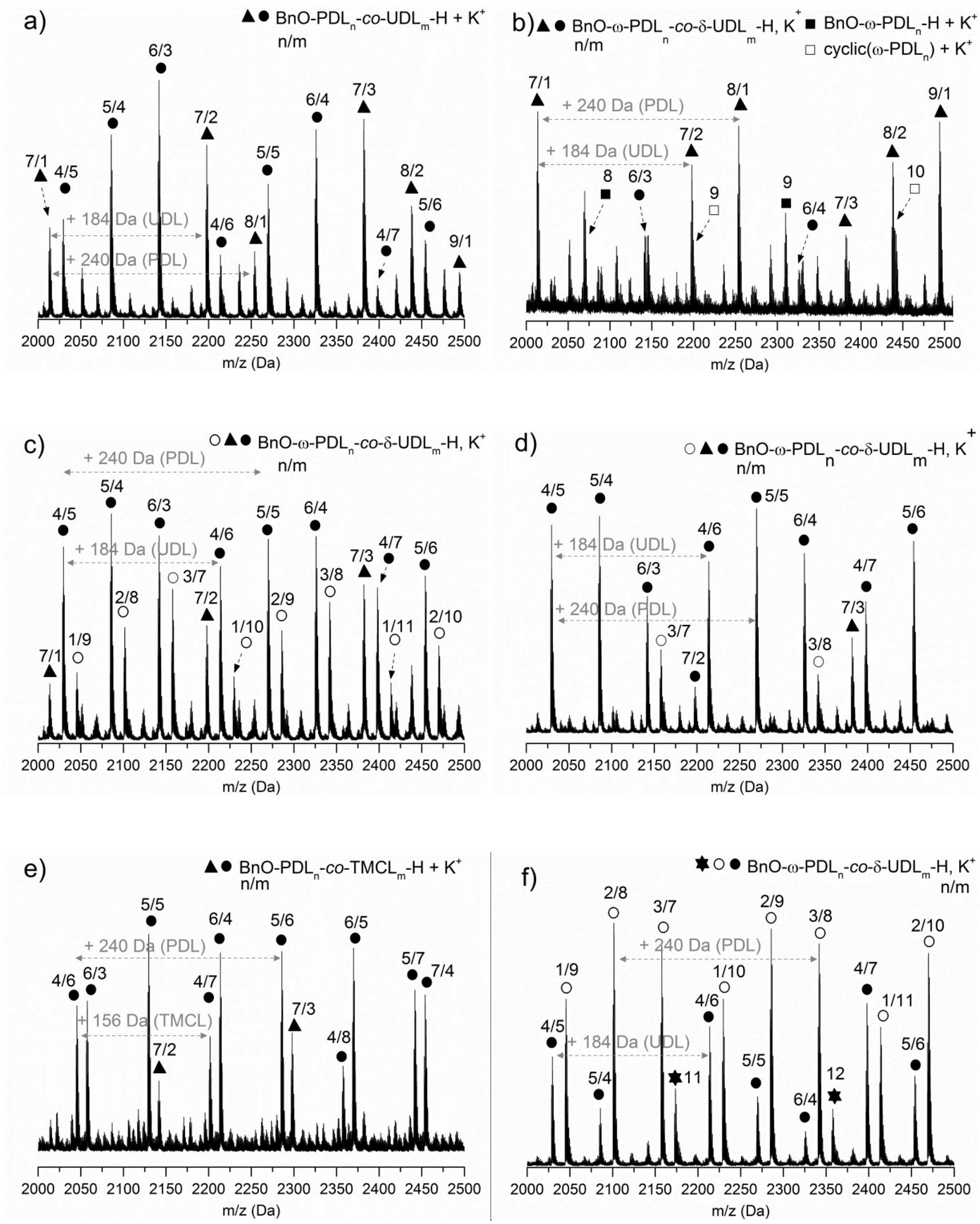

Figure S3. MALDI-ToF spectra of a) poly(ω-PDL-*co*-δ-UDL) synthesized with a feed ratio of 12/4 ω-PDL/ δ-UDL in one-pot; b) poly(ω-PDL-*co*-δ-UDL) synthesized with a feed ratio of 12/4 ω-PDL/ δ-UDL with ω-PDL added to δ-UDL; c) poly(ω-PDL-*co*-δ-UDL) synthesized with a feed ratio of 12/4 ω-PDL/ δ-UDL with δ-UDL added to ω-PDL; d) poly(ω-PDL-*co*-δ-UDL) synthesized with a feed ratio of 8/8 ω-PDL/ δ-UDL in one-pot; e) poly(ω-PDL-co-TMCL) with ω-PDL/TMCL feed ratio of 8/8 in one-pot, and f) poly(ω-PDL-*co*-δ-UDL) synthesized with a feed ratio of 4/12 ω-PDL/ δ-UDL in one-pot. Squares indicate PPDL homopolymers (black for linear and empty for cyclics) and black stars indicate PUDL homopolymers. Black triangles indicate copolymers with ω-PDL ratio > 0.7, empty circles indicate copolymers with ω-PDL ratio < 0.3 and black circles indicate copolymers with 0.3 < ω-PDL ratio < 0.7.

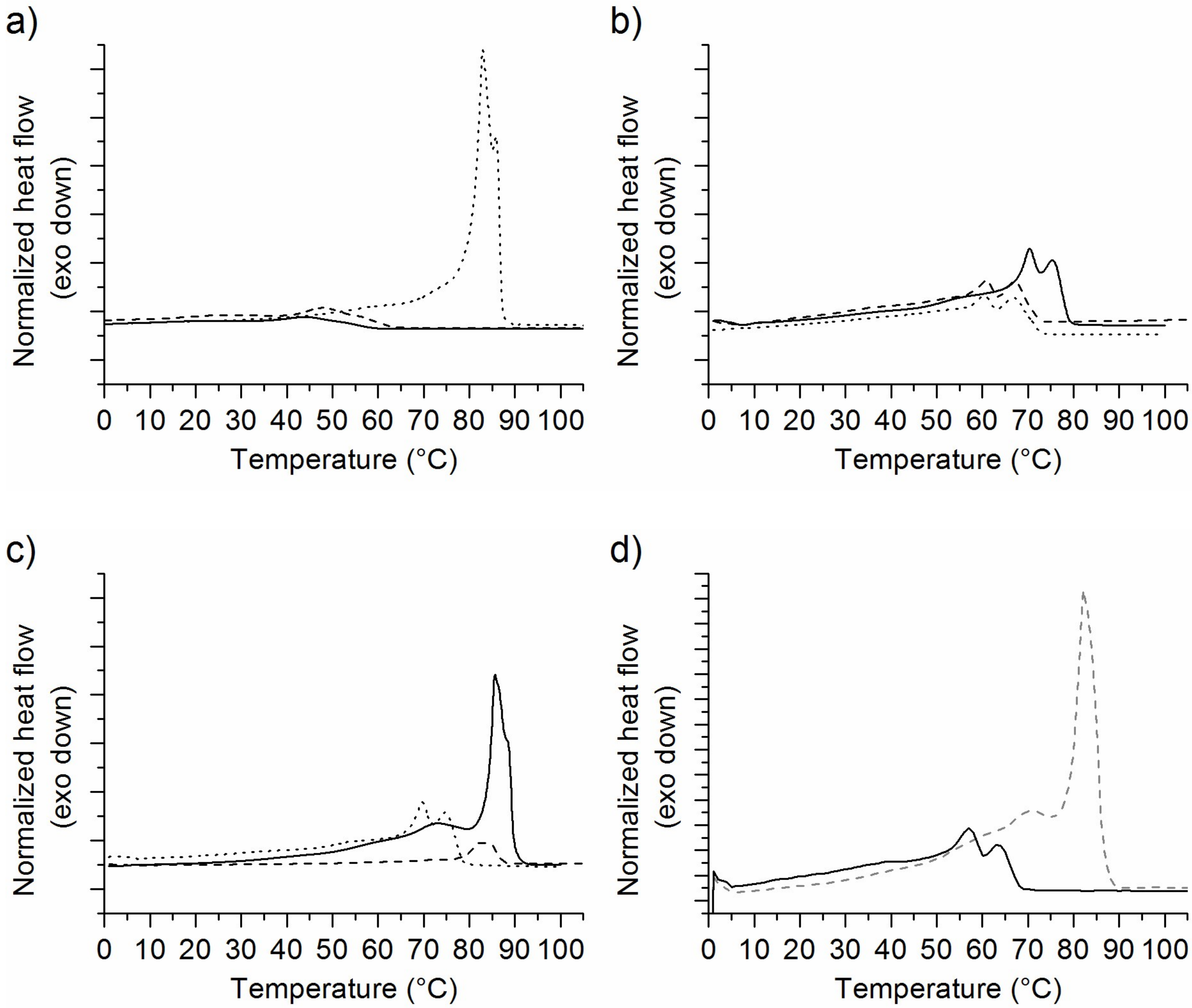

Figure S4. DSC thermographs (2nd heating) of poly(ω-PDL-*co*-δ-UDL) synthesized in one-pot (black full line), with ω-PDL addition to δ-UDL (black dashed line) and with δ-UDL addition to ω-PDL (black dotted line) with feeding ratios of ω-PDL/ δ-UDL of a) 4/12, b) 8/8, and c) 12/4. d) DSC thermographs of poly(ω-PDL-*co*-TMCL) synthesized in one-pot with feeding ratios of ω-PDL/TMCL of 8/8 (full line) and 12/4 (dashed line).