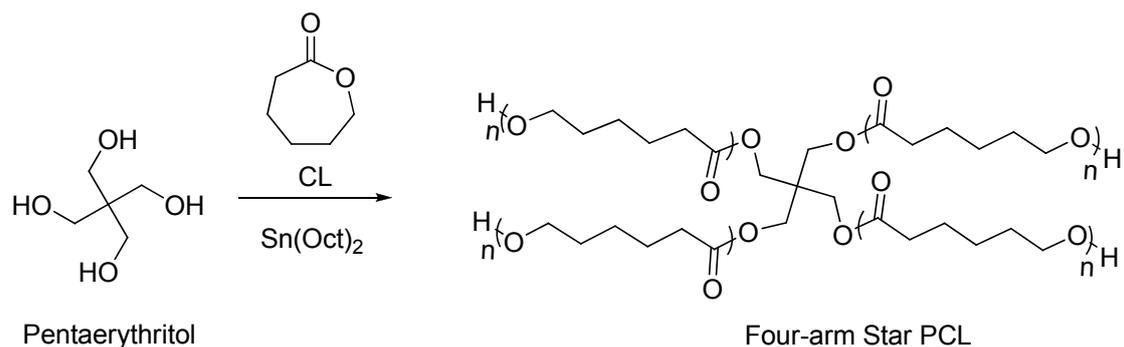


Supplementary Material: Molecular Differentiated Initiator Reactivity in the Synthesis of Poly(caprolactone)-Based Hydrophobic Homopolymer and Amphiphilic Core Corona Star Polymers

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Scheme S1. Synthesis of four-arm star PCL using CH and MWH with pentaerythritol (PTOL) and Sn(Oct)₂ as initiator/catalyst system.

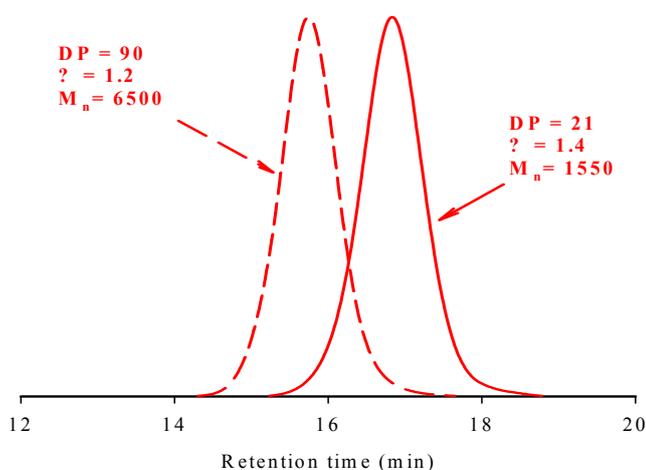


Figure S1. GPC traces of 3-arm star PCL (DP = 90 and DP = 21) initiated by TMP.

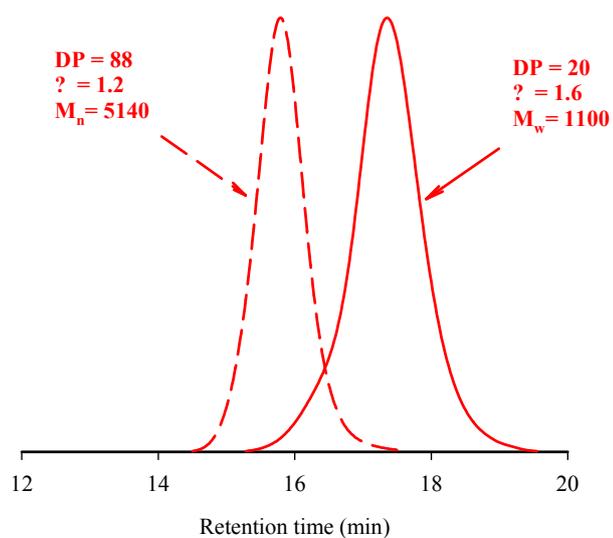


Figure S2. GPC traces of 4-arm star PCL (DP = 88 and DP = 20) initiated by pentaerythritol (PTOL).

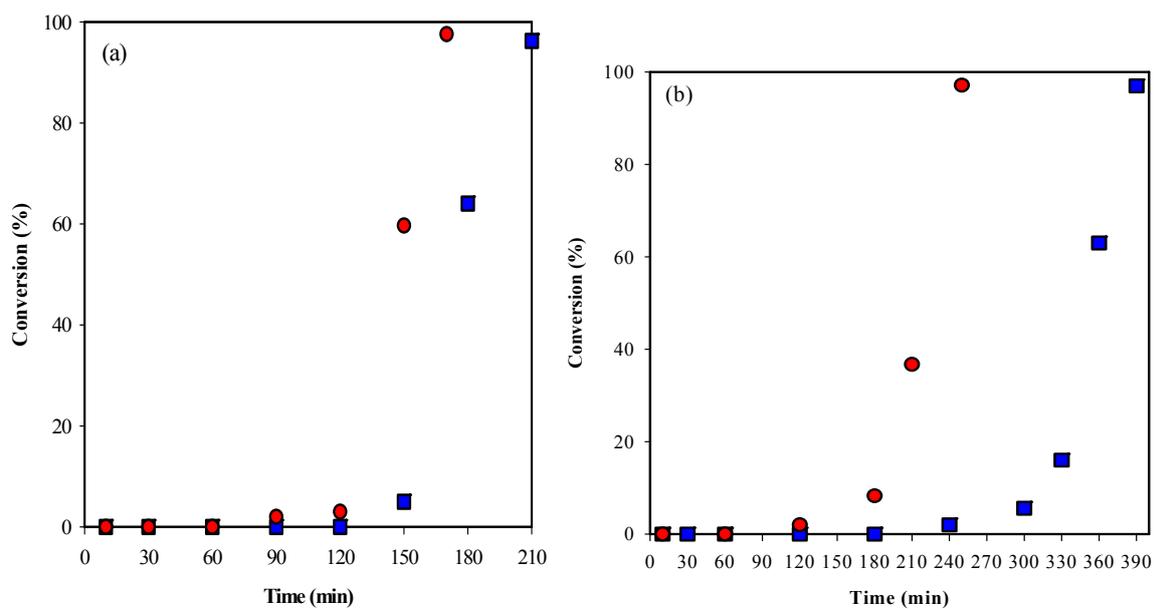
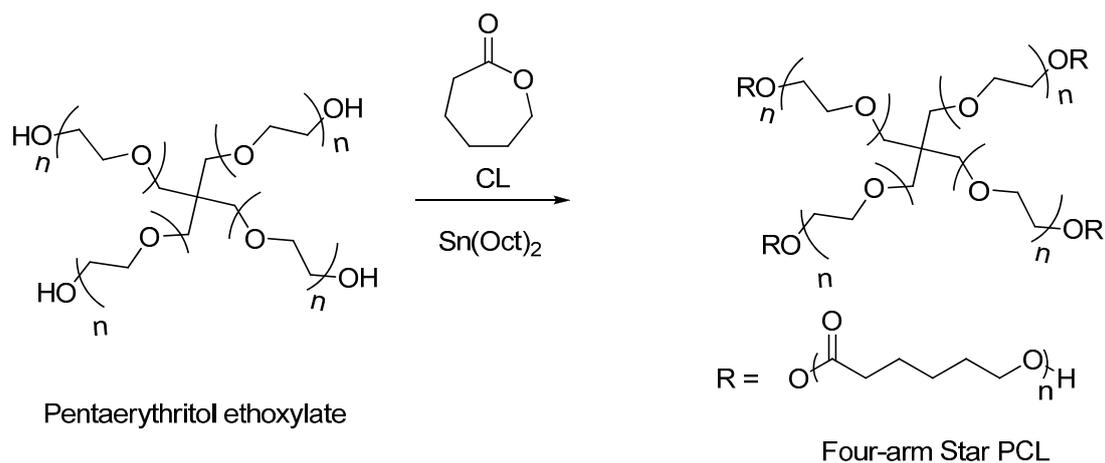


Figure S3. Comparison of the kinetics of the ROP initiated with PTOL, conducted in a round bottom flask using CH (■) and MWH (●) (150 °C, DP (a) 88 and (b) 20).



Scheme S2. Synthesis of four-arm star PCL using CH and MWH with PTOLE and Sn(Oct)₂ as initiator/catalyst system.

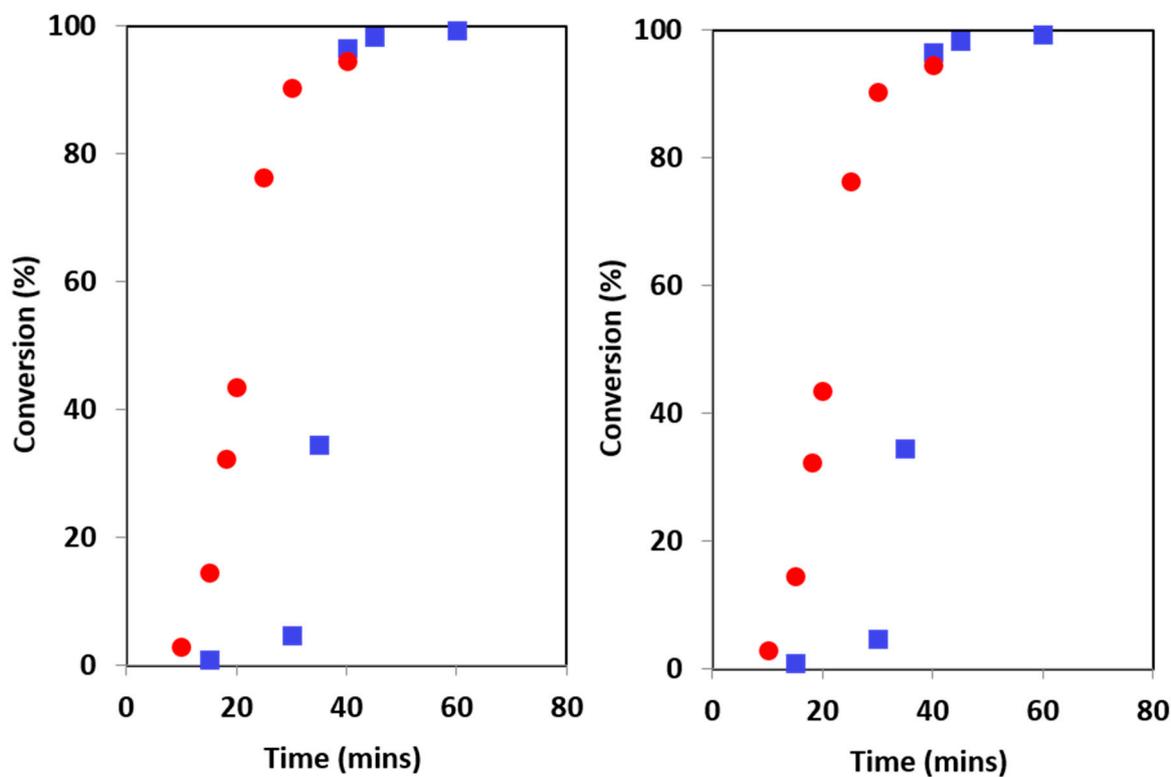


Figure S4. Comparison of G (left) and GE (right) initiated ROP the kinetics using CH (■) and MWH (●) (150 °C, DP90).

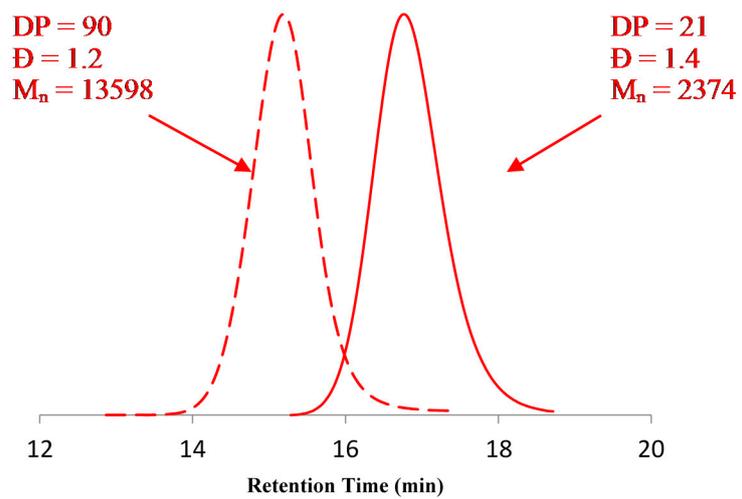


Figure S5. GPC traces of 3-arm star PCL (DP = 90 and DP = 21) initiated by TMPE.