Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of Phase-Separated *super*-H-shaped Triblock Architectures: Poly(L-lactide) Grafted From Telechelic Polyisoprene

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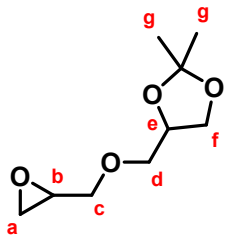
A. ADDITIONAL EXPERIMENTAL DETAILS

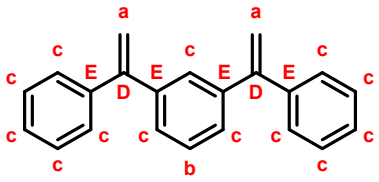
1,2-Isopropylidene glyceryl glycidyl ether (IGG)



^{1}H NMR (300 MHz, benzene-d_6) δ[ppm]: 4.17 – 4.03 (m, 1.00H, e), 3.86 – 3.75 (m, 1.05H, f), 3.71 – 3.59 (m, 1.05H, f'), 3.46 – 3.21 (m, 3.16H, c, d), 3.11 – 2.98 (m, 1.05H, c'), 2.76 (ddt, $J_{b,c}$ = 5.5 Hz, $J_{b,a}$ = 4.1 Hz, $J_{b,a'}$ = 2.6 Hz, 1.01H, b), 2.24 (dd, $J_{a,a'}$ = 5.3 Hz, $J_{a,b}$ = 4.1 Hz, 1.05H, a), 2.13 – 2.08 (m, 1.06H, a), 1.41 (s, 3.17H, g), 1.29 (s, 3.19H, g')

^{13}C NMR (75 MHz, benzene-d_6) δ[ppm]: 109.34 (C_q), 75.12 (E), 72.49 (C, D), 67.09 (F), 50.56 (B), 43.45 (A), 27.10 (G), 25.66 (G).

1,3-Bis(1-phenylethenyl) benzene (PEB)



^{1}H NMR (400 MHz, DMSO-d_6) δ[ppm]: 7.40 – 7.22 (m, 12.75H, c), 7.12 (t, $J_{b,c}$ = 1.8 Hz, 1.02H, b), 5.45 dd, $J_{a,a}$ = 6.1 Hz, $J_{a,a'}$ = 1.1 Hz, 4.00H, a);

^{13}C NMR (101 MHz, DMSO-d_6) δ[ppm]: 148.91 (D), 140.97 – 140.34 (E), 128.81 – 127.22 (B, C), 114.99 (A).

PEB initiated polymerization. The carbanionic polymerization could be visually tracked by the color change of the reaction solution. This is due to the difference at the active chain end. After addition of *sec*-BuLi to the colorless PEB stock solution, a deep red solution was formed, indicating a benzylic anionic charge. By the addition of isoprene, the color changed to yellow, corresponding to the living chain end of polyisoprenyl lithium. Protonation by the addition of methanol again led to a colorless solution. **Figure S1** shows an example of these color changes.

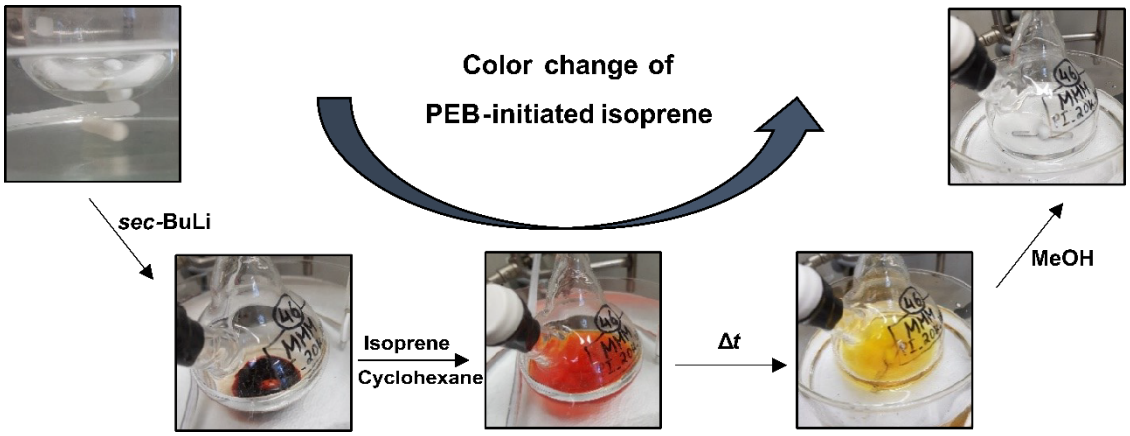


Figure S1. Color change during the PEB initiated polymerization of isoprene in cyclohexane.

DBU catalyzed lactide polymerization. The amount of DBU used for the lactide polymerization was varied. Deviating from the ratio [ROH]/[DBU]=5, sample $PLLA_{81}PI_{617}PLLA_{81}$ was prepared with ratio 4.2 and sample $PLLA_{64}PI_{254}PLLA_{64}$ with 2.1.

B. ADDITIONAL NMR SPECTRA

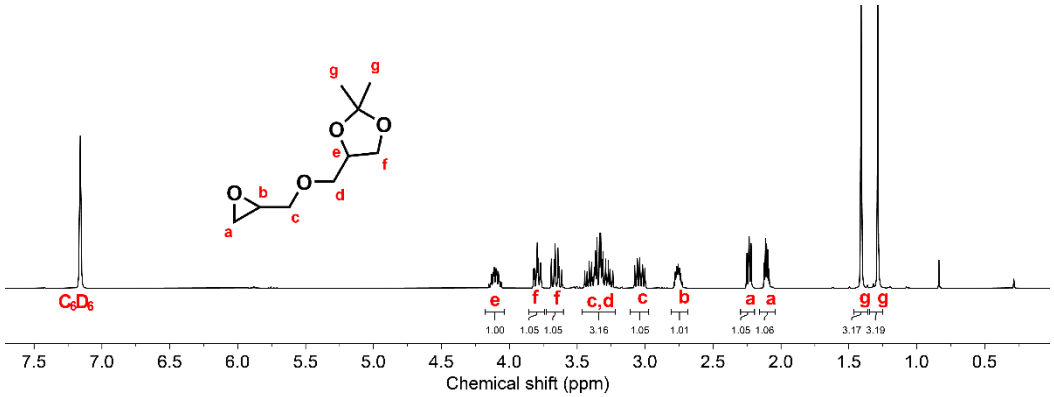


Figure S2. ^{1}H NMR spectrum of IGG (C_6D_6, 300 MHz).

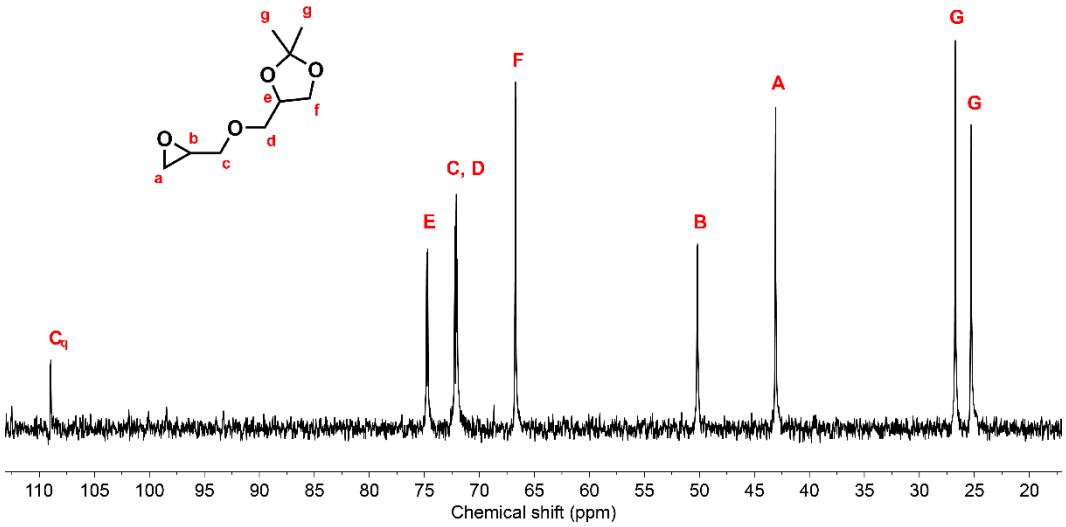


Figure S3. ^{13}C NMR spectrum of IGG (C_6D_6, 75 MHz).

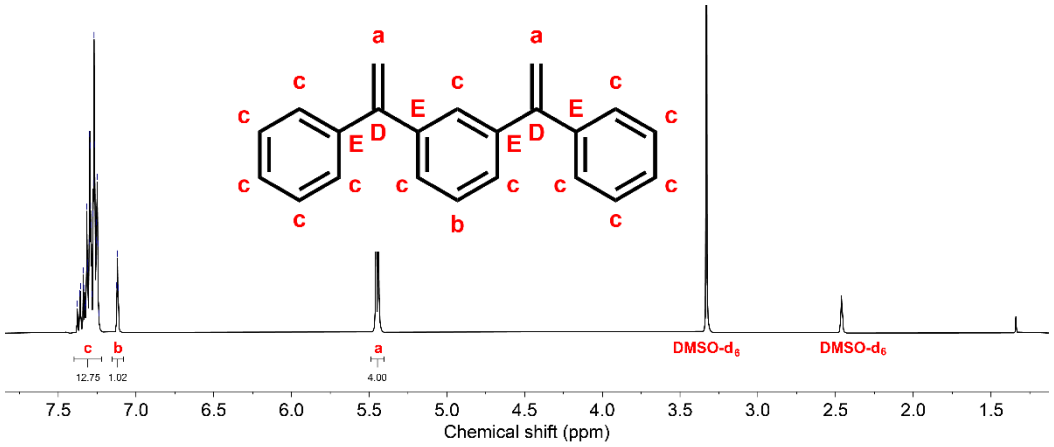


Figure S4. ^{1}H NMR spectrum of 1,3-di-(1-phenylethyl)-benzene (PEB) (DMSO-d_6, 400 MHz).

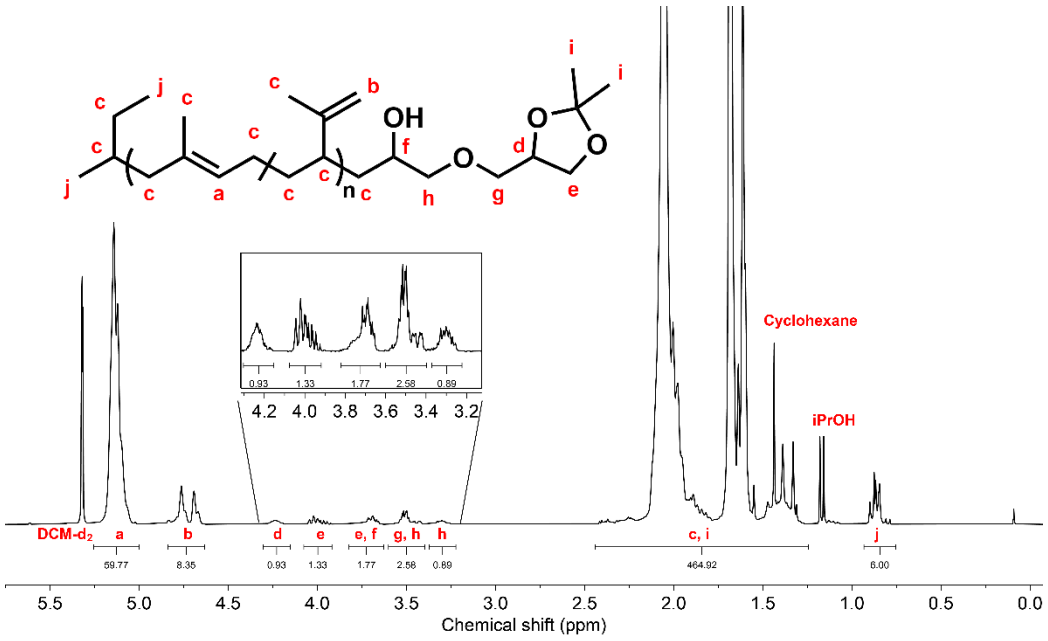


Figure S5. ^{1}H NMR spectrum of sample $PI_{64}IGG_{0.94}$ with respective signals, used for the exemplary calculations.

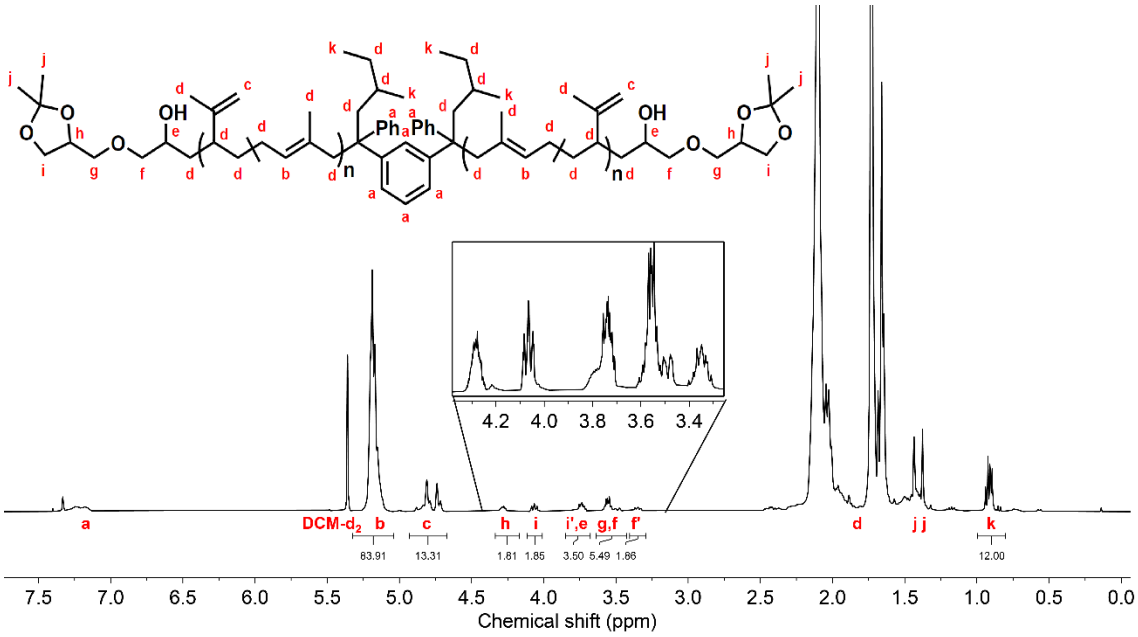


Figure S6. ^{1}H NMR spectrum of sample $IGG_{0.91}PI_{91}IGG_{0.91}$ ($DCM\text{-}d_2$, 400 MHz).

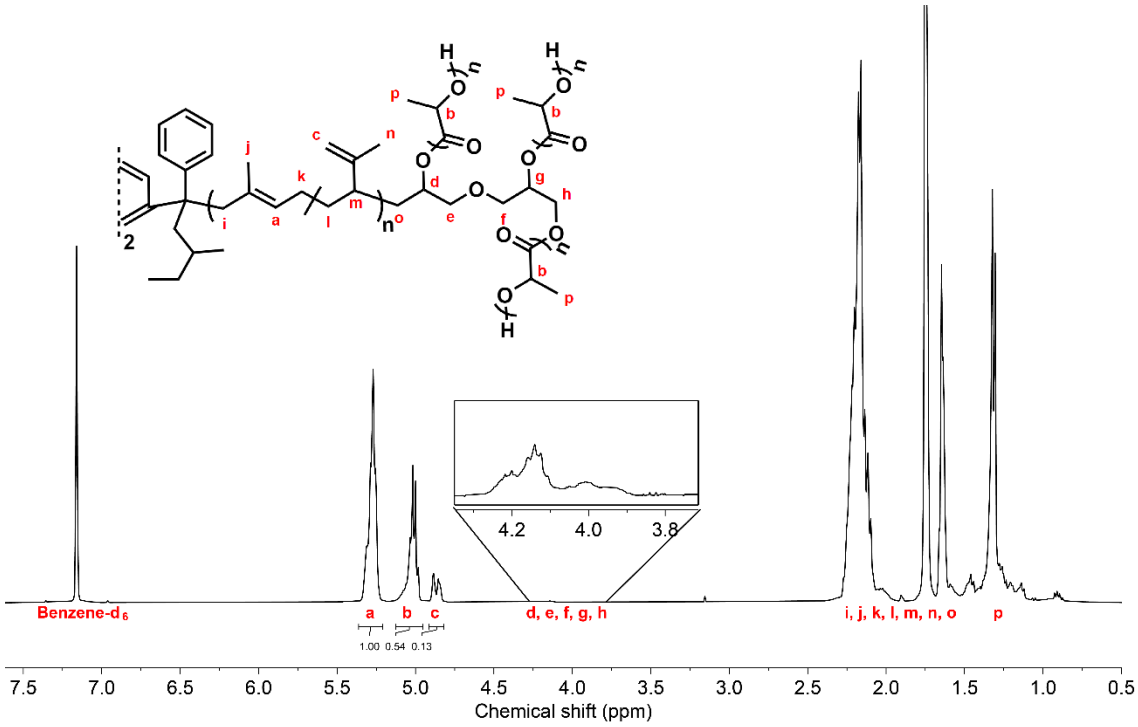


Figure S7. ^{1}H NMR spectrum of sample $PLLA_{64}PI_{254}PLLA_{64}$ (C_6D_6, 400 MHz).

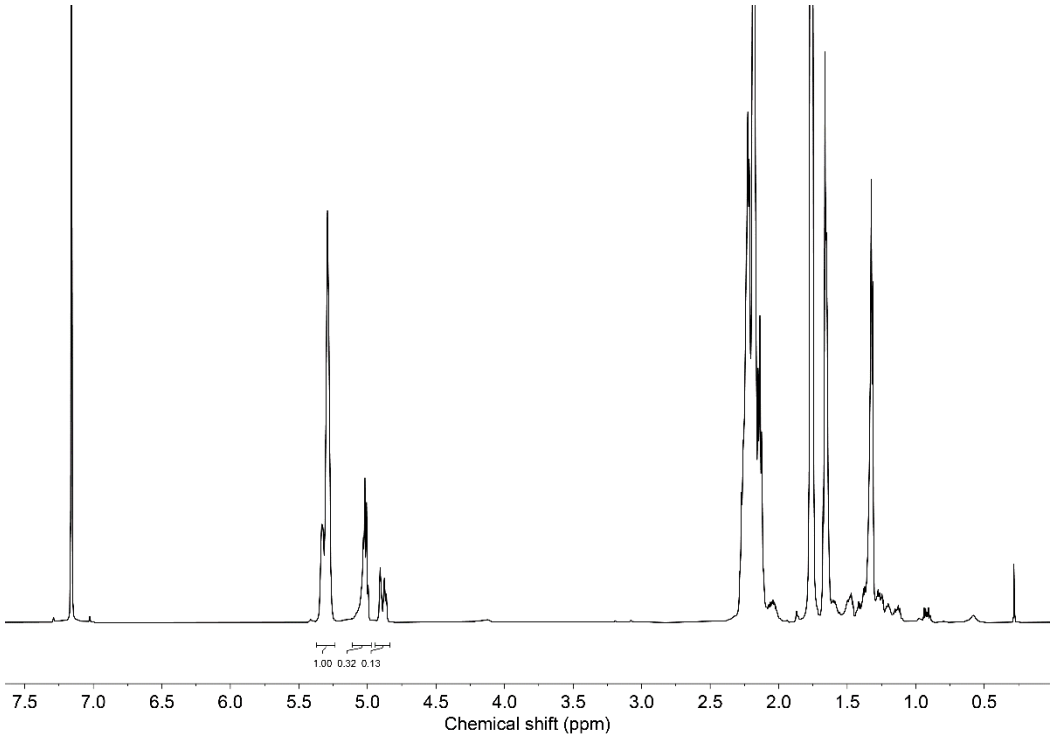


Figure S8. ^{1}H NMR spectrum of sample $PLLA_{38}PI_{254}PLLA_{38}$ (C_6D_6, 400 MHz).

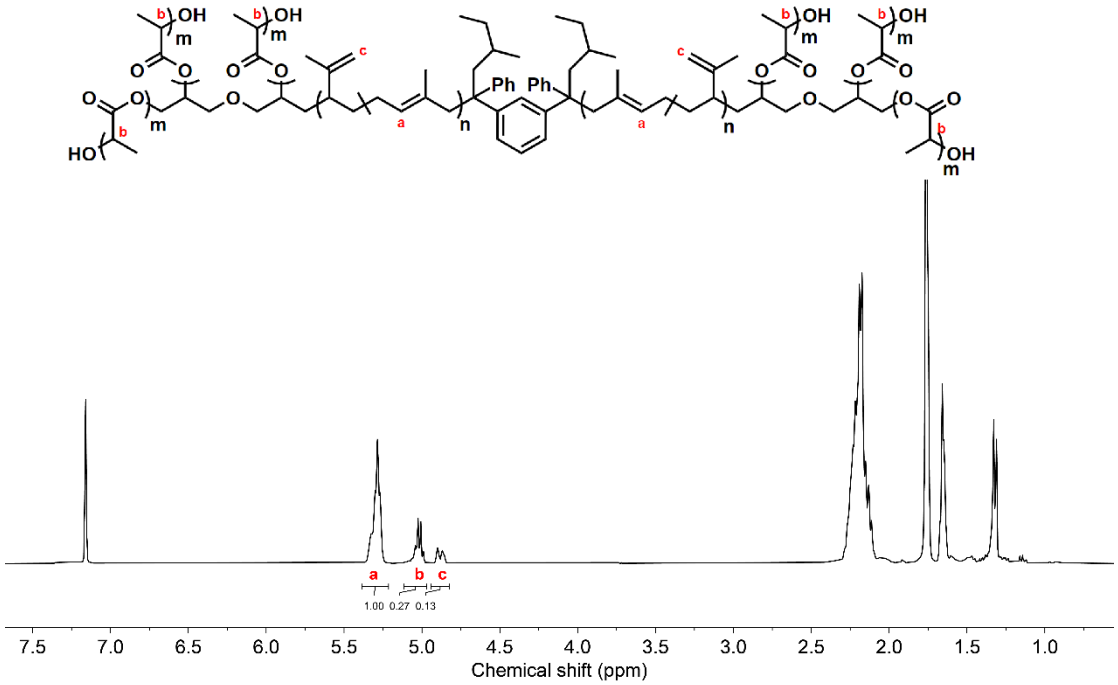


Figure S9. ^{1}H NMR spectrum of sample $PLLA_{58}PI_{459}PLLA_{58}$ (C_6D_6, 400 MHz).

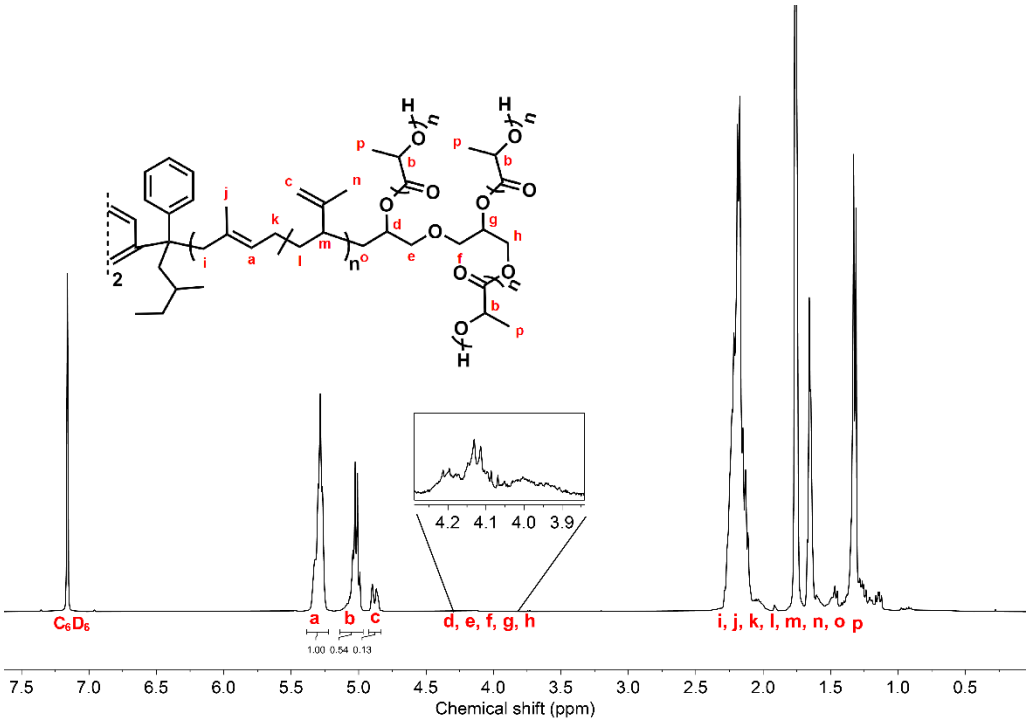


Figure S10. ^{1}H NMR spectrum of sample $PLLA_{116}PI_{459}PLLA_{116}$ (C_6D_6, 400 MHz).

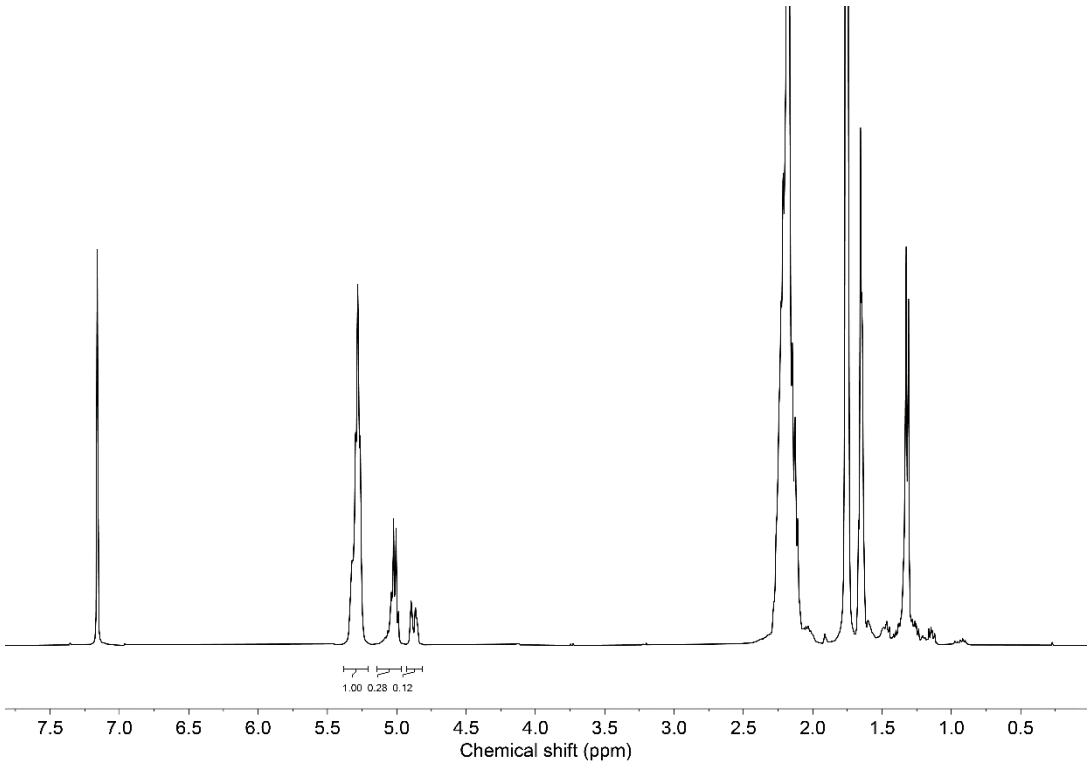


Figure S11. ^{1}H NMR spectrum of sample $PLLA_{81}PI_{617}PLLA_{81}$ (C_6D_6, 400 MHz).

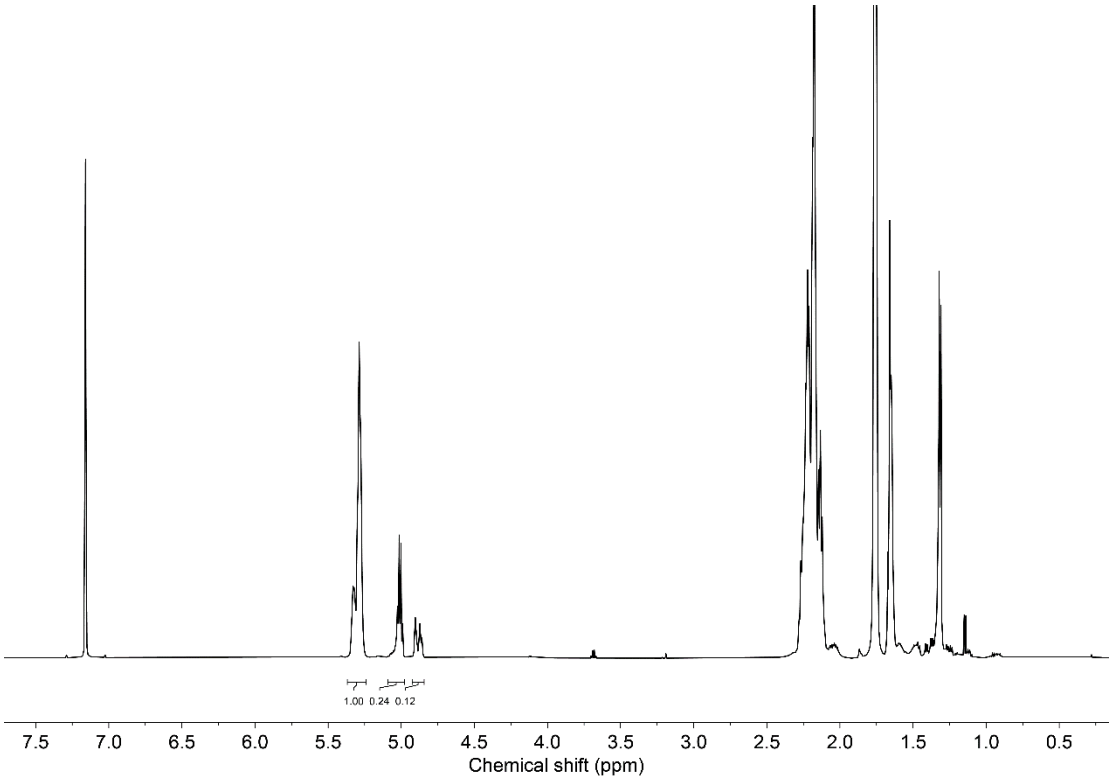


Figure S12. ^{1}H NMR spectrum of sample PLLA$_{70}$-*b*-PI$_{617}$-*b*-PLLA$_{70}$ (C_6D_6, 400 MHz).

C. ADDITIONAL DSC MEASURMENTS

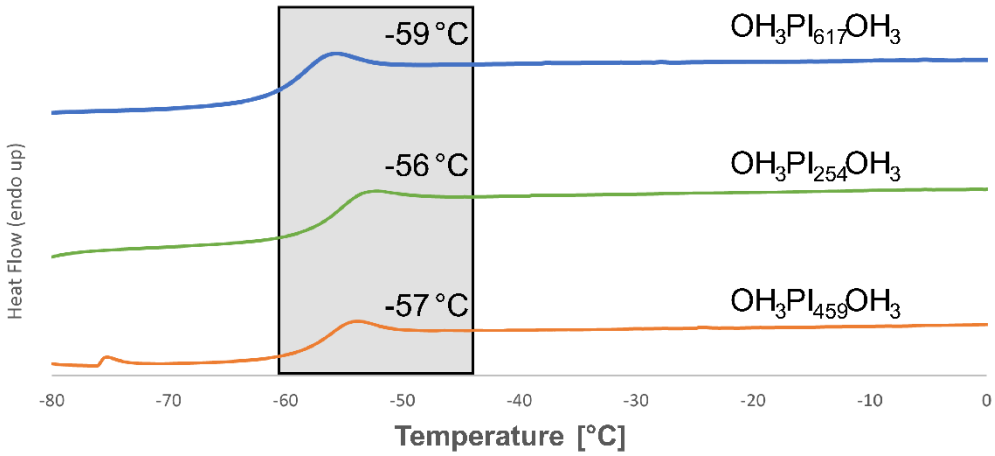


Figure S13. DSC measurements of all PI-macro initiators, second heating curve, heating rate: 20 °C/min.

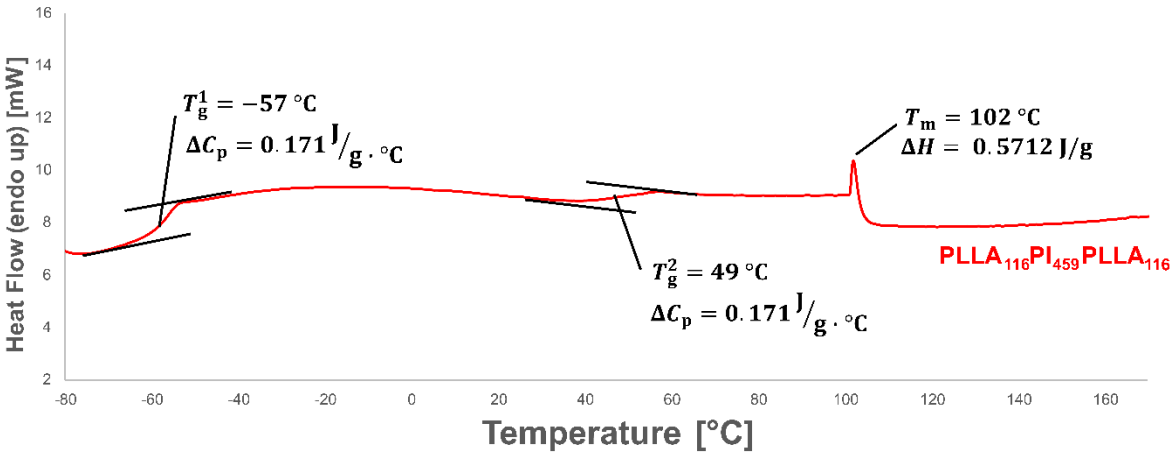


Figure S14. DSC measurement, second heating curve of sample $PLLA_{116}PI_{459}PLLA_{116}$; heating rate: 20 K/min.

D. ADDITIONAL DOSY MEASURMENTS

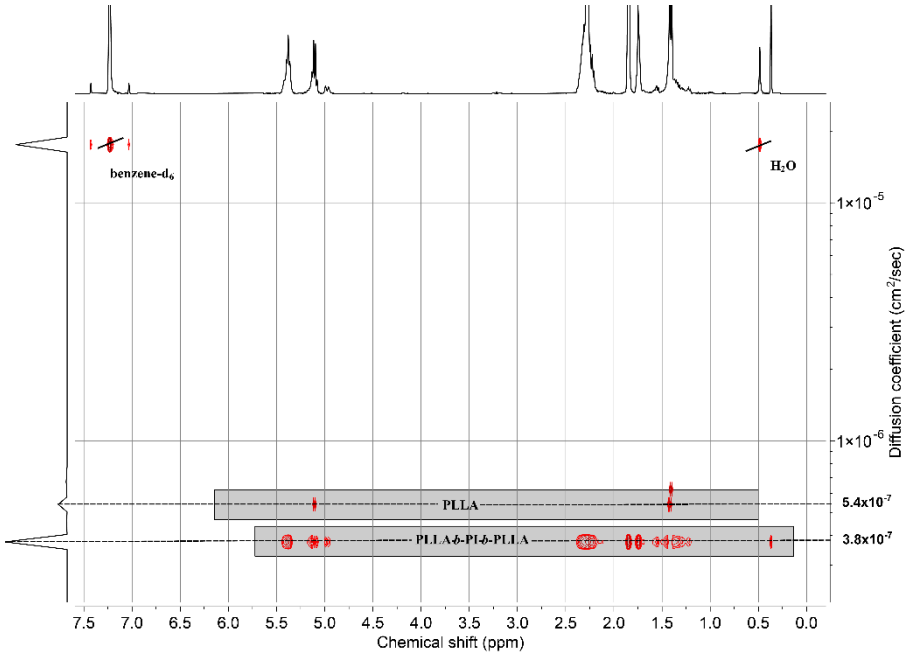


Figure S15. DOSY NMR of lactide polymerization attempt using $OH_3PLLA_{617}OH_3$ and ([ROH]/[DBU]=2.1) (C_6D_6). The result shows PLLA homopolymer contamination.

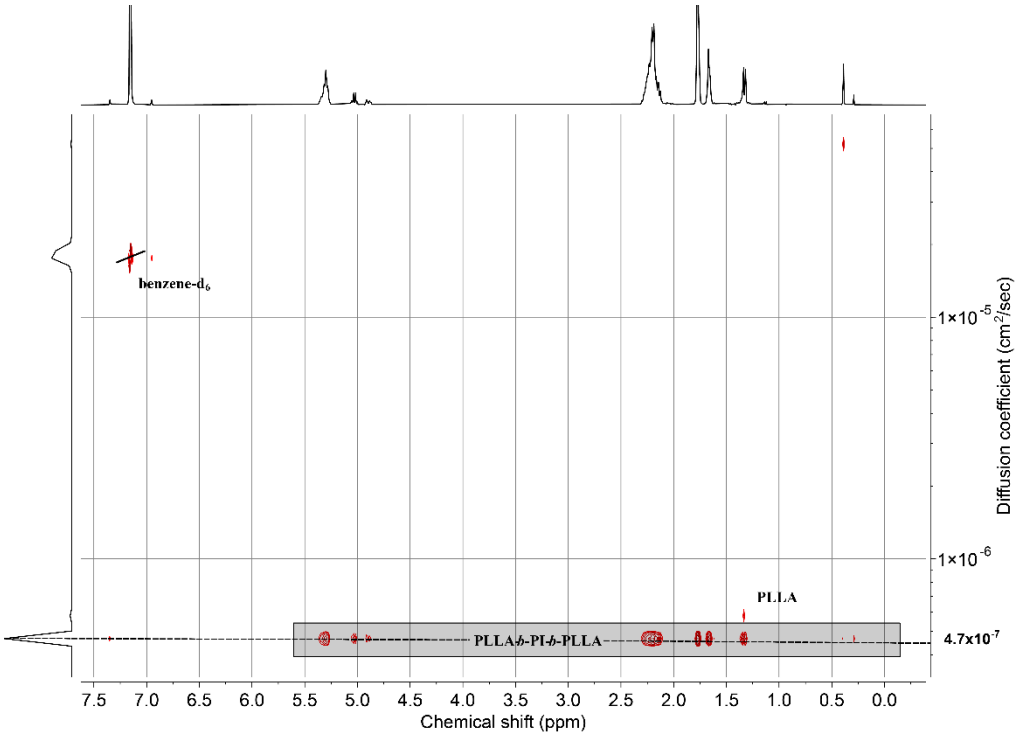


Figure S16. DOSY NMR of lactide polymerization attempt using $OH_3PLLA_{617}OH_3$ and ([ROH]/[DBU]=5) resulting in the sample: $PLLA_{70}PI_{617}PLLA_{70}$ (C_6D_6).

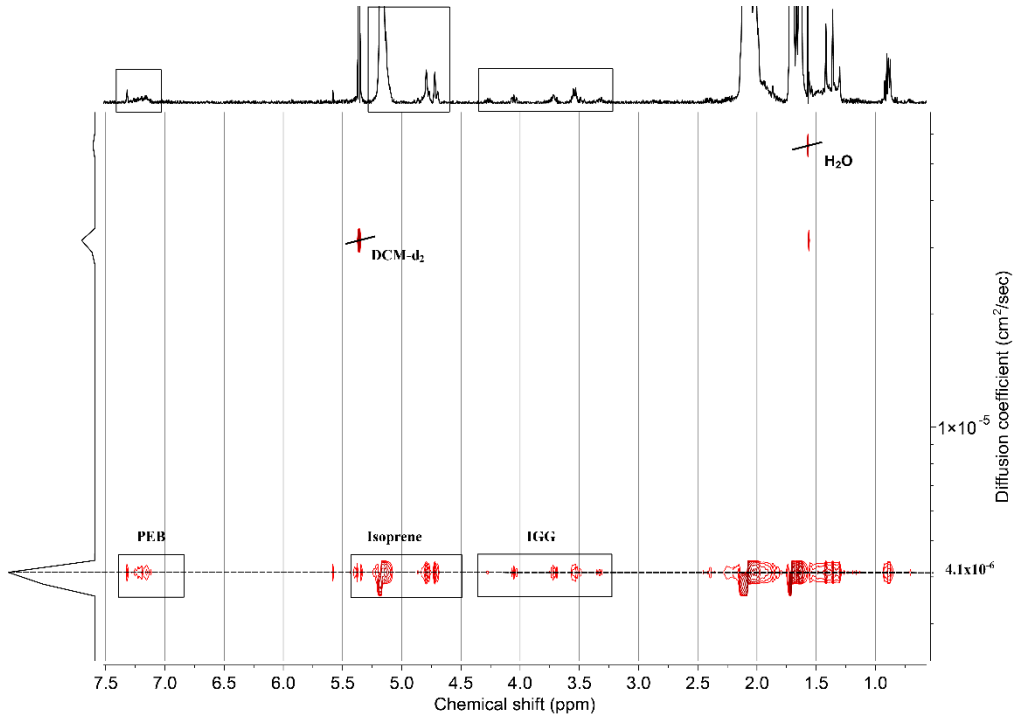


Figure S17. DOSY NMR of sample $IGG_{0.91}PI_{91}IGG_{0.91}$ in DCM-d_2.

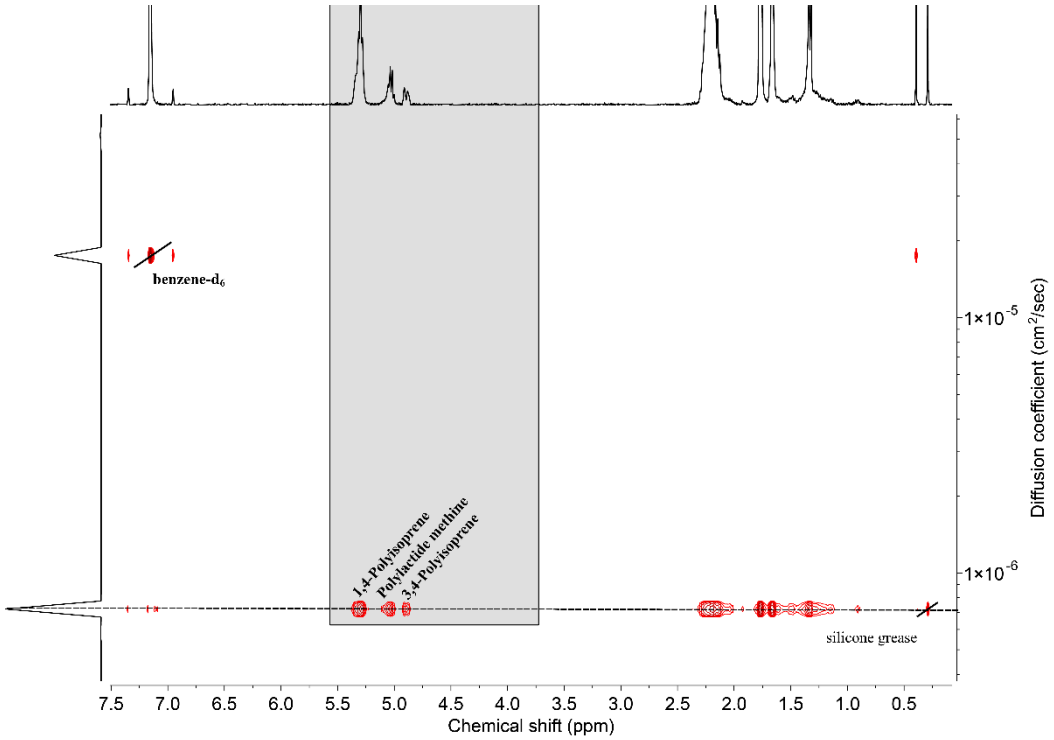


Figure S18. DOSY NMR of sample $PLLA_{38}PI_{254}PLLA_{38}$ in C_6D_6, showing the absence of PLLA homopolymer contamination.

E. ADDITIONAL SEC RESULTS

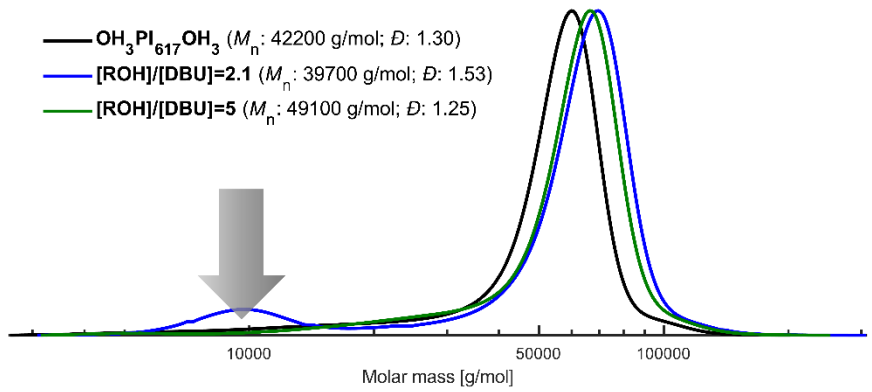


Figure S19. SEC traces of lactide polymerization experiments using different [ROH]/[DBU] ratios, measured in THF using PI calibration.

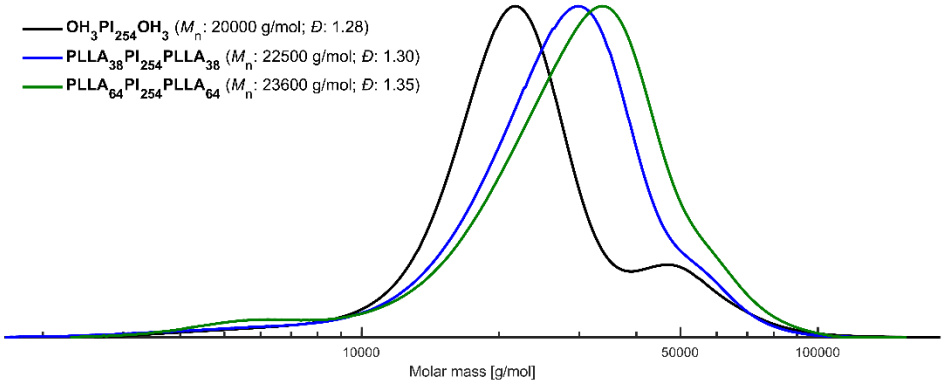


Figure S20. SEC traces of both lactide polymerizations using the 20k polyisoprene macroinitiator, measured in THF using a PI calibration.

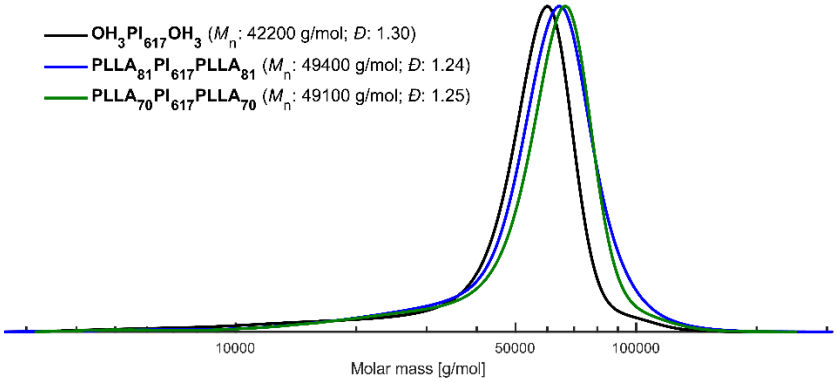


Figure S21. SEC traces of both lactide polymerizations using the 40k polyisoprene macroinitiator, measured in THF using a PI calibration.

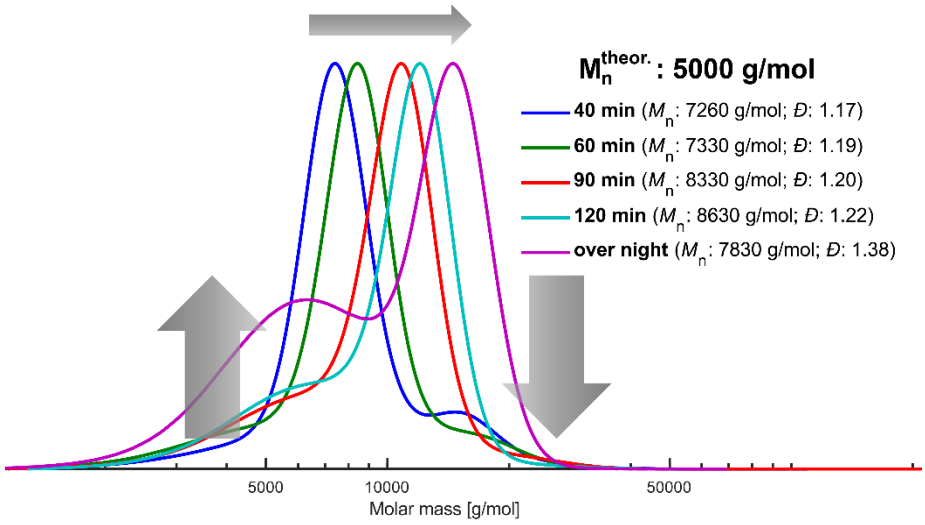


Figure S22. SEC-Results of PEB initiated PI-polymerization with various activation times carried out at room temperature. For each polymerization a Mw of 5000 g/mol was targeted, RI detector, eluent: THF, PI calibration.

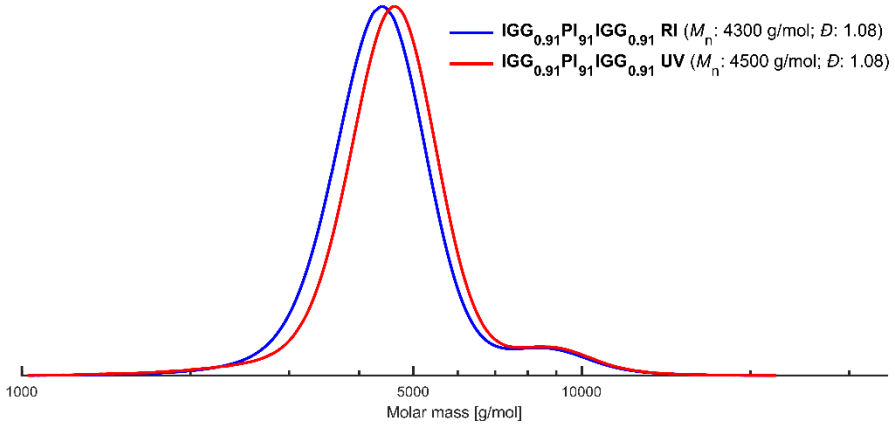


Figure S23. SEC-results of low M_n PEB initiated PI sample ($IGG_{0.91}PI_{91}IGG_{0.91}$), UV detector showing an additional signal to RI detector; eluent: THF, using a PI calibration.

F. ADDITIONAL ANALYTIC MEASURMENTS

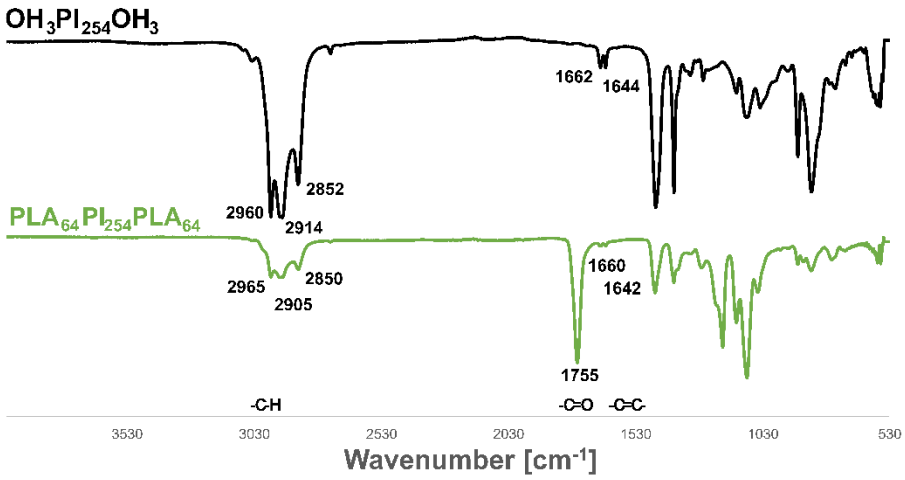


Figure S24. FT-IR spectra showing the presence of the lactide signals after polymerization, using the 20k polyisoprene macroinitiator, measured on a Nicolet iS10FT-IR, Thermo Fisher Scientific.

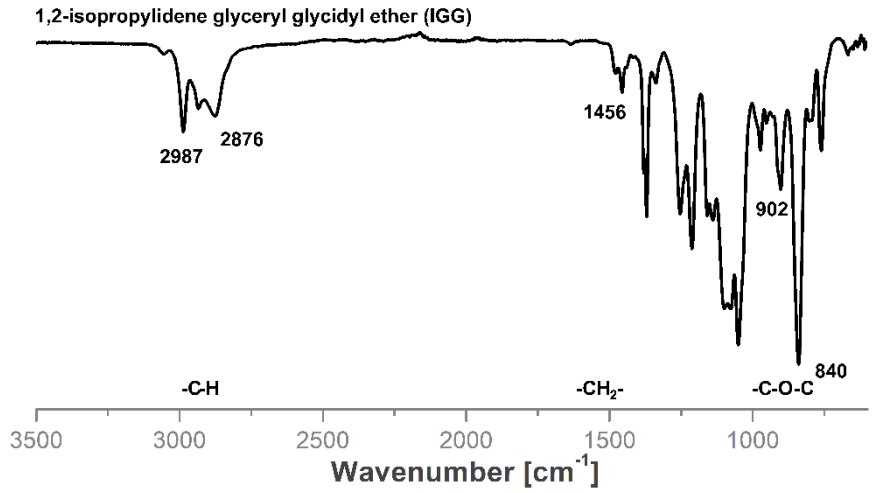


Figure S25. FT-IR spectrum of 1,2-isopropylidene glyceryl glycidyl ether (IGG), measured on a Nicolet iS10FT-IR, Thermo Fisher Scientific.

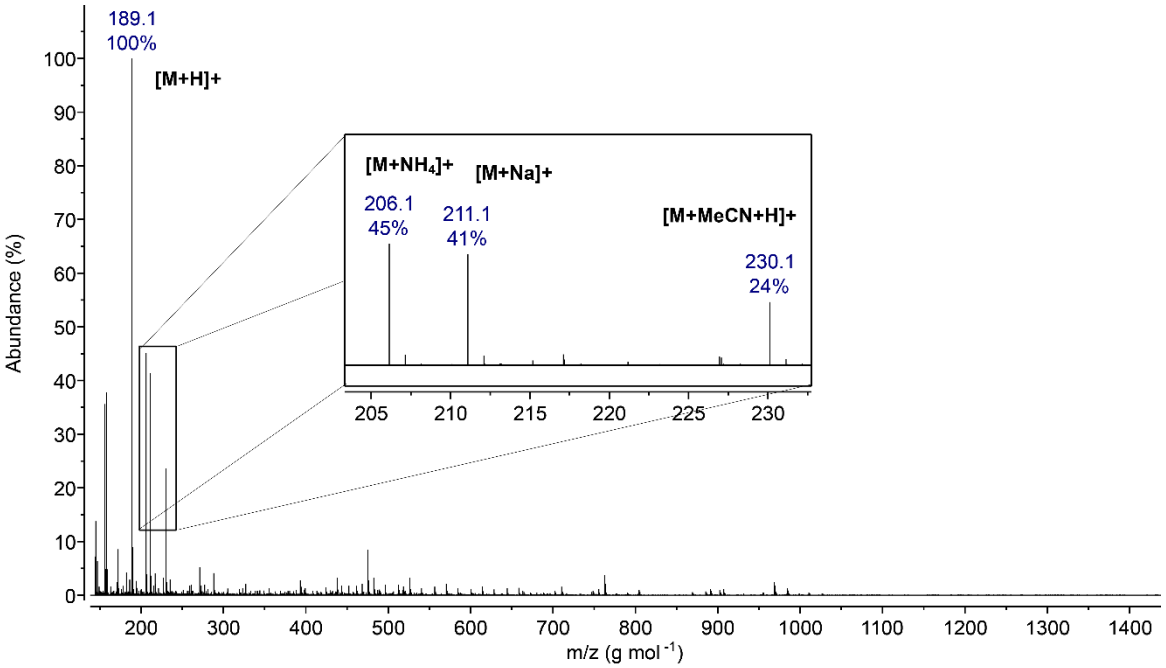


Figure S26. High-resolution MS ESI+ measurement of 1,2-isopropylidene glyceryl glycidyl ether (IGG), measured on an Agilent 6545 QTOF-HRAM-MS instrument.

G. MATHEMATIC CALCULATIONS

I. Microstructure of polyisoprene [$PI_{1,4}$-content]

Values were taken from sample $PI_{64}IGG_{0.94}$ (**Figure S5**):

$$PI_{1,4} = \frac{I(Methine)}{I(Methine) + (I(Methylidene) \cdot 0.5)} \cdot 100\% = \frac{59.77}{59.77 + (8.35 \cdot 0.5)} \cdot 100\% \cong 93\%$$

II. Degree of polymerization of polyisoprene [P_n(PI)]

Values were taken from sample $PI_{64}IGG_{0.94}$ (**Figure S5**):

$$P_n(PI) = \frac{6 \cdot (I(Methine) + (I(Methylidene) \cdot 0.5))}{I(Methyl\ of\ BuLi)} = \frac{6 \cdot (59.77 + (8.35 \cdot 0.5))}{6} \cong 64$$

III. Degree of polymerization of polylactide [P_n(PLLA)]

Values were taken from sample $PLLA_{64}PI_{254}PLLA_{64}$ (**Figure S7**):

$$P_n(PLLA)\ (PLLA_{64}PI_{254}PLLA_{64}) = \frac{I(Methine\ (PLLA))}{I(Methine\ (PI)) + (I(Methylidene\ (PI)) \cdot 0.5)} \cdot P_n(PI) = \frac{0.54}{1 + (0.13 \cdot 0.5)} \cdot 254 \cong 129$$

IV. Degree of end functionalization [E.F.]

Values were taken from sample $PI_{64}IGG_{0.94}$ (**Figure S5**), corresponding to the characteristic signals of the IGG protons:

$$E.F. = \frac{6 \cdot I(d+e+f+g+h)}{8 \cdot I(j)} = \frac{6 \cdot (0.93 + 1.33 + 1.77 + 2.58 + 0.89)}{8 \cdot 6} \cdot 100\% \cong 94\%$$

V. Molecular weight by NMR [M_n(NMR)]

Values were taken from sample $PLLA_{64}PI_{254}PLLA_{64}$ (**Figure S7**):

$$M_n^{NMR}(PLLA_{64}PI_{254}PLLA_{64}) = M(C_4H_9) + P_n(PI) \cdot M(C_5H_8) + E.F. \cdot M(C_9H_{17}O_4)$$

$$= 57.12\frac{g}{mol} + 64 \cdot 68.12\frac{g}{mol} + 0.94 \cdot 189.23\frac{g}{mol} \cong 4600\frac{g}{mol}$$

VI. Volume fraction of polylactide [Φ(LA)]

Exemplary calculation for sample $PLLA_{64}PI_{254}PLLA_{64}$ (**Figure S7**) based on the calculation done by Fang et al.[1], assuming density values of the polymers measured at 140 °C. Amorphous polylactide (with 10% *meso*-PLA) $\rho(PLLA) = 1.154\frac{g}{cm^3}$ [2] and PI $\rho(PI) = 0.830\frac{g}{cm^3}$ [1]:

$$\Phi_{LA} = \frac{P_n(PLLA) \cdot M(LLA)/\rho(PLLA)}{P_n(PLLA) \cdot M(LLA)/\rho(PLLA) + P_n(PI) \cdot M(I)/\rho(PI)} = \frac{129 \cdot 72.06\frac{g}{m}}{129 \cdot 72.06\frac{g}{mol} \Big/ 1.154\frac{g}{cm^3}}$$

$$\cong 0.28$$

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(2) Witzke, D. R.; Narayan, R.; Kolstad, J. J. Reversible Kinetics and Thermodynamics of the Homopolymerization of l -Lactide with 2-Ethylhexanoic Acid Tin(II) Salt. *Macromolecules* **1997**, *30* (23), 7075–7085. DOI: 10.1021/ma970631m.