Copolymerization of Cyclic Phosphonate and Lactide: Synthetic Strategies towards Control of Amphiphilic Microstructure

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EXPERIMENTAL SECTION

General Considerations

The preparation and characterization of all metal complexes were carried out under an inert argon atmosphere using standard Schlenk or glovebox techniques, as described in previously published work.\(^1\)

2-Ethyl-2-oxo-1,3,2-dioxaphospholane (EtPPn) was synthesized at the Max Planck Institute following procedures previously published.\(^2\) Prior to use EtPPn was lyophilised twice and stored under inert conditions. Chemicals used were purchased from Sigma-Aldrich and used as received. Exceptions include lactide (LA) which was recrystallized twice from dry toluene and stored in an Ar-regulated glovebox. Dry solvents used in handling metal complexes and polymerizations were obtained \textit{via} SPS (solvent purification system) and dried over 3Å molecular sieves. Benzyl alcohol (BnOH), toluene-\(d\)\(_8\) and CDCl\(_3\) was dried over CaH\(_2\), distilled prior to use and stored over 3Å molecular sieves. 1,4-benzenedimethanol was recrystallized twice from Et\(_2\)O, prior to storing under argon. Materials characterization (SEC, MALDI-ToF) facilities were provided through the Chemical Characterisation and Analysis Facility (CCAF) at the University of Bath.

NMR Spectroscopy

\(^1\)H and \(^31\)P NMR spectra of polymerizations were recorded on a Bruker 400 MHz instrument and referenced to residual solvent peaks. All spectra were processed with the MestReNova 9.0.1-13254 software. Coupling constants are given in Hertz. Polymerization conversion when carried out in CDCl\(_3\) was determined from the integration of the methine region of the polymer (5.12 – 5.20 ppm) against that of the monomer (4.94 – 5.01) in the case of LA and (1.74 – 1.85 ppm) for the polymer and (1.93-2.03 ppm) for the monomer in the case of EtPPn, unless stated otherwise. Conversions of EtPPn were also taken and compared from integration of all polymer signals in the \(^31\)P NMR spectra \{number of scans (ns) = 64, D1 = 5 seconds\}, \(i.e\) in CDCl\(_3\) polymer signals (34.0 – 36.0 ppm) against the monomer signals (53.0 – 53.5 ppm) or in the case of toluene-\(d\)\(_8\) (33.0 – 35.1 ppm) for the polymer and (48.2 – 49.6 ppm) for the monomer. In homopolymerization reactions a small quantity of ring-opened methoxy terminated side product was seen (37.0 ppm in CDCl\(_3\)) upon quenching with methanol. When this side product was apparent, conversion was taken from integration of the polymer signals over that of the sum of the monomer and side-product signals. Expected % EtPPn in the copolymer was calculated from conversion and feed ratios from the crude product. Molecular weight measurements obtained from NMR analysis were carried out by comparing the integral of the aromatic signals of BnO- end group (7.28 – 7.43 ppm) with the EtPPn polymer backbone signal (4.13 – 4.39 ppm) and the methine region of the PLA unit. In the case of using 1,4-benzenedimethanol as an initiator polymers were integrated against the singlet aromatic signal at 7.30 ppm. \textit{In-situ} NMR experiments were carried out in J-Young’s NMR tubes in 0.7 mL toluene-\(d\)\(_8\). Timings were recorded from sample preparation. Upon heating to elevated temperatures the sample was allowed to stabilise for 10 minutes prior to manual shimming.
Successive $^1$H (ns = 16) and $^{31}$P (ns =32, D1= 5s) NMR spectra were acquired every 10 minutes via a staggering run sequence.

**Diffusion Ordered Spectroscopy (DOSY)**

All $^1$H and $^{31}$P DOSY NMR experiments were recorded on a Bruker Avance III 500 MHz spectrometer at concentrations of 10 mg mL$^{-1}$. NMR samples were equilibrated at the measurement temperature of 25 °C for 5 min before data collection. Spinning was deactivated to avoid convection. 1D $^1$H spectra were acquired with the zg30 pulse program from the Bruker library. 2D DOSY spectra were acquired using a double stimulated echo sequence (“dstegp2s”) for convection compensation and with monopolar gradient pulses. Diffusion delay of 5 seconds, 64,000 data points and 32 scans per gradient level was used. Ten gradient strengths were used between 2 and 95 %. In the case of $^{31}$P NMR diffusion delays were set at 10 seconds with 64 scans per gradient level. The spectra were multiplied with an exponential window function before Fourier transformation (xf2) and subsequently phase corrected. The diffusion coefficients were obtained on MestReNova processing software by fitting a peak heights fit method to the spectra. Diffusion constants are reported alongside the solvent diffusion signals and compared to those recorded in the literature.$^{3,4}$

**Size-Exclusion Chromatography (SEC)**

Size-exclusion chromatography (SEC) was carried out on an Agilent 1260 Infinity series instrument at 1 mL min$^{-1}$ at 35 °C with a THF eluent using a PLgel 5 μm MIXED-D 300 × 7.5 mm column. Detection was carried out using triple detection methods, using a differential refractive index (RI) detector (referenced to 11 polystyrene standards of narrow molecular weight, ranging from $M_w$ 615 – 568000 Da), a viscometer detector and a light scattering detector (90°, with a calculated dn/dc range = 0.095 – 0.11 g$^{-1}$ mL, as calculated from the RI). Multi analysis software was used to process the data. For polymers which were not fully soluble in THF, i.e all homo-polymers of EtPPn and select copolymers SEC analysis was performed at the Max Planck Institute for Polymer Research in DMF (containing 0.25 g L$^{-1}$ of lithium bromide as an additive) at 60 °C at a flow rate of 1 mL min$^{-1}$ with an Agilent 1100 Series as an integrated instrument, including a PSS HEMA column (106 /105 /104 g mol$^{-1}$) and a refractive index (RI) detector. Calibration was carried out using poly(ethylene glycol) standards provided by Polymer Standards Service.

**Differential Scanning Calorimetry (DSC)**

Thermal transitions were recorded on a Thermal analysis Q20 DSC from TA instruments, equipped with a Thermal Advantage Cooling System 90 under nitrogen. Samples were measured from –70 °C to 150 °C with 10 °C min$^{-1}$ heating and 10 °C / min cooling, following a standard heating-cooling-heating-sequence. $T_g$ data was presented is that obtained from the second cycle.

**MALDI-ToF Mass Spectrometry**

MALDI-ToF analysis was carried out on a Bruker Autoflex speed instrument in reflector positive mode, using DCTB as the matrix at a concentration of 10 mg mL$^{-1}$. 50 μL of this solution was co-applied with
2 μL of 0.1 mol L⁻¹ NaTFA solution and 10 μL of the analyte at a concentration of 10 mg mL⁻¹. 1 μL of this homogenised solution was applied to a steel target plate for analysis.

**Thermal-Gravimetric Analysis (TGA)**

Thermal-gravimetric analysis was carried out on a Setsys Evolution TGA 16/18. Calisto software was employed to collect and process the data. The sample was loaded onto a pre-weighed 170 μL alumina crucible. Following a 30 minute purge at 30 °C under argon flow at 20 mL min⁻¹ the sample was heated at a rate of 20 °C a minute the required temperature.

**Standard synthetic Protocols**

In a typical procedure, copolymerization from a monomer mixture was carried out by loading EtPPn (0.1 mL, 8.6 × 10⁻⁴ mol), L-LA (123 mg, 8.6 × 10⁻⁴ mol) into 2.25 mL solution of toluene in an ampule fitted with a J-Youngs cap. 250 μL of a premade 0.00688 mol L⁻¹ solution of catalyst and benzyl alcohol in toluene was added. The ampule was then stirred at 80 °C for 16 hours prior to quenching with a few drops of methanol and removal of the solvent *in-vacuo*. Crude NMR were obtained in CDCl₃ to ascertain conversion. Twice repeated precipitation in Et₂O, centrifugation and drying in a vacuum controlled oven at 30 °C for 24h yielded the pure polymer.

For sequential addition reactions a typical procedure was carried out by loading LA (123 mg, 8.6 × 10⁻⁴ mol) into 1.00 mL solution of toluene in an ampule fitted with a J-Youngs cap. 250 μL of a premade 0.00688 mol L⁻¹ solution of catalyst and benzyl alcohol in toluene was added and the solution was heated to 80 °C and stirred for 16 h. To the stirred solution cooled to 25 °C, under a flow of argon, EtPPn (0.1 mL 8.6 × 10⁻⁴ mol) in 1.25 mL of toluene was added via a purged syringe. The solution was then stirred at 25 °C for a further hour prior to quenching with a few drops of methanol and quick removal of the solvent *in-vacuo*. Crude NMR were obtained in CDCl₃ to ascertain conversion. Twice repeated precipitation in Et₂O, centrifugation and drying in a vacuum controlled oven at 30 °C for 24h yielded the pure polymer.
**HOMOPOLYMERIZATION**

Polymerization data

Table S1) Selected data for the polymerization of EtPPn using 1.

| Entry | Temperature °C | Solvent | Time (hours) | Concentration mol L⁻¹ | Conv₃ % | Mₙtheory g mol⁻¹ | MₙSEC d g mol⁻¹ | D |
|-------|---------------|---------|--------------|------------------------|---------|-----------------|-----------------|---|
| 1ᵃ    | 25            | N/A     | 0.05         | Bulk                   | 76      | 5280            | -               | - |
| 2ᵃ    | 25            | N/A     | 0.08         | Bulk                   | 90      | 6230            | 4300            | 1.11 |
| 3     | 25            | DCM     | 3            | 0.35                   | 96      | 6640            | 5300            | 1.14 |
| 4     | 25            | Tol     | 3            | 0.35                   | 83      | 5750            | -               | - |
| 5     | 25            | Tol     | 24           | 0.35                   | 89      | 6150            | 4900            | 1.32 |
| 6     | 25            | Tol     | 120          | 0.35                   | 94      | 6500            | 3300            | 1.42 |
| 7     | 25            | Tol     | 24           | 0.7                    | 99      | 6850            | 4800            | 1.38 |
| 8     | 80            | Tol     | 2            | 0.35                   | 49      | 3400            | 2800            | 1.26 |
| 9     | 80            | Tol     | 4            | 0.35                   | 55      | 3650            | 3050            | 1.20 |
| 10    | 80            | Tol     | 16           | 0.35                   | 100     | 6900            | 7600            | 1.17 |
| 11    | 80            | Tol     | 4            | 0.7                    | 90      | 6230            | 5300            | 1.21 |
| 12    | 80            | Tol     | 24           | 0.7                    | 64      | 4450            | 2850            | 1.25 |

Feed ratios of 50:1:1 [(EtPPn)ₙ·[I]₀·[BnOH]₀]. Bulk polymerization was carried out by adding the initiator to a stirred solution of 1.72 × 10⁻³ moles of EtPPn and 3.4 × 10⁻⁵ moles BnOH, quenching was done by dropping into an excess of CDCl₃ and CH₃OH in a 95:5 ratio. Conversion quoted is taken from integration of the CH₂ region in the polymer (1.74 – 1.85 ppm) against the monomer (1.93 – 2.03 ppm) from the ¹H NMR spectra and compared to that obtained from ¹³P NMR spectroscopy. 

Mₙtheory values = [(Conversion [M]₀/100 × [M]₀/[I]₀) × Mw M] +Mw end group (defined as BnO- and H-). MₙSEC data of all homopolymers was obtained from SEC analysis in DMF, with an RI detector using poly(ethylene glycol) standards.
**$^1$H and $^{31}$P NMR analysis**

**Figure S1** (Entry 1, Table S1) $^1$H NMR spectra in CDCl$_3$ of the polymerization of EtPPn at feed ratios of 50:1:1 ([([EtPPn])=1][BnOH]), in neat EtPPn 20 °C, 3 minutes. Quenching was carried out by dropping the polymer into a solution of CDCl$_3$ and CD$_3$OD (95:5). (top right; conversion of EtPPn taken from the integration of PC$_2$H$_2$ region of the polymer (1.74 – 1.85 ppm) against the monomer (1.93 – 2.03 ppm) = 75.9 %). $M_n^{NMR}$ is taken from the integral of PC$_2$H$_2$ polymer signal over that of observed bound PhCH$_2$O- end group. $M_n^{NMR} = 2866.2$ g mol$^{-1}$, $M_n^{theo} = 5162.3$ g mol$^{-1}$.

**Figure S2** (Entry 1, Table S1) $^{31}$P NMR spectra in CDCl$_3$ of the polymerization of EtPPn at feed ratios of 50:1:1 ([([EtPPn])=1][BnOH]), in neat EtPPn 20 °C, 3 minutes. Conversion of 69 % can be read from the integration of polymeric phosphorus signals (34.5 – 36.2 ppm) against the monomer (53.0 – 53.5 ppm) and methoxy terminated side product.
Figure S3) (Entry 2, Table S1) $^1$H NMR spectra in CDCl$_3$ of the polymerization of EtPPn at feed ratios of 50:1:1 {([EtPPn]₀:[1]₀:[BnOH]₀)}, in neat EtPPn 20 °C, 5 minutes. (top right; conversion of EtPPn taken from the integration of PCH$_2$ region of the polymer (1.74 – 1.85 ppm) against the monomer (1.93 – 2.03 ppm) = 89.7 %). $M_n^\text{NMR}$ is taken from the integral of PCH$_2$ polymer signal over that of observed bound PhCH$_2$O- end group. $M_n^\text{NMR} = 5572.3$ gmol$^{-1}$, $M_w^{\text{bio}} = 6208$ gmol$^{-1}$.

Figure S4) (Entry 1, Table S1) $^3$P NMR spectra in CDCl$_3$ of the polymerization of EtPPn at feed ratios of 50:1:1 {([EtPPn]₀:[1]₀:[BnOH]₀)}, in neat EtPPn 20 °C, 5 minutes. Conversion of 88 % can be read from the integration of polymeric phosphorus signals (34.5 – 36.2 ppm) against the monomer (53.0 – 53.5 ppm) and methoxy terminated side product.
Figure S5 (Entry 1, Table 1) $^1$H DOSY spectra in CDCl$_3$ of the homopolymerization of EtPPn at feed ratios of 50:1:1 ([EtPPn]:[1]:[BnOH]), [LA] = 0.69 mol L$^{-1}$ in Toluene, 80 °C, 16 h. Diffusion rates are compared to the solvent for comparison. $D_{\text{sol}} = 2.29 \times 10^{-9}$ m$^2$s$^{-1}$, $D_{\text{poly}} = 2.55 \times 10^{-10}$ m$^2$s$^{-1}$
COPOLYMERIZATION STUDIES

Polymerization data

Table S2) Polymerization data for the copolymerization of rac-LA and EtPPn from a monomer mixture.

| Entry | Initiator | Feed ratio [LA] [EtPPn] [I] [BnOH] | % Conversion LA | % Conversion EtPPn | Expected % EtPPn in polymer | $M_\text{n,SEC}$ (g/mol) | $M_\text{n,NMR}$ (g/mol) | $M_\text{n,LS}$ (g/mol) | $T_g$ (°C) | Triads ratio PPP-PL-PLP |
|-------|-----------|------------------------------------|-----------------|-------------------|-----------------------------|-------------------------|------------------------|------------------------|-----------|--------------------------|
| 1     | 1         | 50:50:1:1                          | 75              | 100               | 57                          | 15550 [1.06]            | 13250                  | 12300                  | -9.7      | 51:22:27                 |
| 2     | 1         | 100:50:1:1                         | 77              | 98                | 39                          | 12480 [1.02]            | 8600                   | 17900                  | -3.1      | 59:28:13                 |
| 3     | 1         | 100:20:1:1                         | 83              | 100               | 19                          | 16200 [1.27]            | 16550                  | 14800                  | 19.6      | 45:28:27                 |
| 4     | 1         | 100:10:1:1                         | 95              | 100               | 10                          | 12900 [1.23]            | 11650                  | 15150                  | 27.4      | 15:44:41                 |
| 5*    | 1         | 50:50:1:1                          | 73              | 100               | 58                          | 21000 [1.12]            | 9500                   | 12200                  | 18.7      | 62:21:17                 |
| 6*    | 1         | 100:100:1:1                        | 67              | 90                | 57                          | 22850                  | 22300                  | -8.6       | 53:23:24                 |
| 7*    | 1         | 100:50:1:1                         | 75              | 100               | 40                          | 20600 [1.06]            | 20100                  | 17600                  | 23.3      | 38:29:33                 |
| 8*    | 1         | 50:50:1:1                          | 30              | 96                | 76                          | 6100 [1.31]*            | 7650                   | 8800                   | -35.8     | 87:8.5                   |
| 9*    | 2         | 50:50:1:1                          | 85              | 67                | 45                          | 4300 [1.10]             | 8550                   | 10500                  | 2.9       | 35:45:20                 |
| 10*   | 2         | 50:50:1:1                          | 81              | 46                | 35                          | 4750 [1.18]             | 8600                   | 9350                   | 7.9       | 35:32:34                 |
| 11b,c | 2         | 50:50:1:1                          | 91              | 18                | 17                          | 3150 [1.10]             | 7200                   | 7900                   | 18.1      | 14:40:46                 |

Toluene at 80 °C for 16h, [LA]₀ = [EtPPn]₀ = 0.69 mol L⁻¹, • L-LA,  5 L-LA, T = 25 °C, time = 120 h, [EtPPn]₀ = [LA]₀ = 0.35 M.  • L-LA, [M]₀ = 0.35 mol L⁻¹, • CHCl₃, T = 25 °C, $M_\text{n,SEC}$ data was obtained from SEC analysis in THF using Triple detection methods. *SEC analysis carried out in DMF using RI detection methods with a poly(ethylene glycol) standard.

Table S3) Polymerization data for the copolymerization of L-LA and EtPPn using 1 as catalyst under varying reaction conditions.

| Entry | Monomer added | Step 1 | Step 2 | % Conversion LA | % Conversion EtPPn* | Expected % EtPPn in polymer* | $M_\text{n,SEC}$ (g/mol) | $M_\text{n,NMR}$ (g/mol) | $M_\text{n,LS}$ (g/mol) | $T_g$ (°C) | Triads ratio PPP-PL-PLP |
|-------|---------------|--------|--------|-----------------|---------------------|----------------------------|-------------------------|------------------------|------------------------|-----------|--------------------------|
| 1     | EtPPn         | 80,2   | LA     | 80,16           | 22                  | 45                        | 66.6                    | 2545 [1.25]            | 4100                   | 4750      | -68:24:8                  |
| 2     | EtPPn         | 25,24  | LA     | 25,24           | 28                  | 92                        | 76.6                    | -                      | -8800                  | -         | 86:8.6                   |
| 3     | EtPPn         | 25,24  | LA     | 25,120          | 51                  | 100                       | 66.2                    | -                      | 6250                   | 10550     | -21.5                    |
| 4     | LA            | 80,24  | EtPPn  | 80,1            | 96                  | 78                        | 44.8                    | 4100 [1.53]*            | 11200                  | 12300     | 63.9 (-48.0)             |
| 5     | LA            | 80,24  | EtPPn  | 25,1            | 96                  | 88                        | 47.8                    | 9850 [1.31]*            | 11900                  | 13000     | 64.9 (-43.4)            |
| 6*    | LA            | 80,24  | EtPPn  | 25,1            | 92                  | 48                        | 34.3                    | -                      | 16830                  | 19900     | 62.1 (-55.8)            |
| 7b    | LA            | 80,24  | -      | -               | 95                  | -                         | 15400 [1.36]            | 13440                  | 13800                  | 62.4      | -                        |
| 8*    | LA            | 80,16  | EtPPn  | 25,1            | 94                  | 82                        | 43.7                    | -                      | 20860                  | 24800     | -23.2                    |
| 9*    | LA            | 80,6   | EtPPn  | 25,1            | 66                  | 82                        | 57.7                    | -                      | 20310                  | 21470     | -24.5                    |
| 10*   | EtPPn & LA    | 25,0.16| -      | 80,1            | 60                  | 100                       | 62.5                    | -                      | 71150                  | 12500     | 1.0                     |
| 11    | EtPPn & LA    | 25,6   | -      | 80,13           | 71                  | 89                        | 55.6                    | -                      | 6500                   | 11300     | -                       |
| 12*   | EtPPn & LA    | 25,2   | -      | 80,16           | 71                  | 82                        | 53.6                    | -                      | 9800                   | 10800     | 5.3                     |
| 13*   | EtPPn & LA    | 25,6   | -      | 80,1            | 71                  | 82                        | 53.6                    | -                      | 12682                  | 10800     | 3.4                     |
| 14*   | EtPPn & LA    | 80,16  | -      | 25,0.5          | 81                  | 95                        | 54.5                    | -                      | 7650                   | 12400     | -77.15:8                 |

Feed ratios of 50:50:1:1 [EtPPn]₀/[L-LA]₀/[I]₀/[BnOH]₀, [L-LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹, • Feed ratio of 100:100:1:1 [EtPPn]₀/[L-LA]₀/[I]₀/[BnOH]₀, [L-LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹, b 1.4 benzenedimethanol as initiator at feed ratios of 100:100:2:1 [EtPPn]₀/[L-LA]₀/[I]₀/[BnOH]₀, [L-LA]₀ = [EtPPn]₀. c [M]₀ = 3.6 mol L⁻¹, d in-situ NMR analysis. * Taken from 'H NMR spectra.  • SEC analysis in THF using Triple detection methods.  •SEC analysis carried out in DMF using RI detection methods with a poly(ethylene glycol) standard.  • Taken from integration of polymer signals against those of initiator in the purified polymer.  • Taken from the conversion of monomer units relative to the feed ratio of monomers in the crude polymer.
\(^{1}\text{H} \) and \(^{31}\text{P} \) NMR analysis

Di-block copolymers from sequential addition

**Figure S6** \(^{1}\text{H} \) NMR spectra in CDCl\(_3\) of the crude co-block (LA-\(b\)-EtPPn) synthesised from the sequential copolymerization of \(L\)-LA with EtPPn at ratios of 50:50:1:1 \([\text{[LA]}_{0}\text{:[EtPPn]}_{0}\text{:[I]}_{0}\text{:[BnOH]}_{0}], [\text{LA}]_{0} = 0.35 \text{ mol L}^{-1} \) in toluene (Entry 5, Table S3). \(M_n^{\text{NMR}}\) is calculated from the integration of the polymer proton environments (LA: 5.13 – 5.19 ppm, EtPPn 4.19 – 4.29 ppm) over that of the single BnO- end group seen at 7.34 ppm. Conversion; LA: 96 %, EtPPn: 88 %, \(M_n^{\text{theo}} = 12300 \text{ g mol}^{-1}\). \(M_n^{\text{NMR}} = 11900 \text{ g mol}^{-1}, M_n^{\text{SEC}} = 9850 \text{ g mol}^{-1}\).

**Figure S7** \(^{31}\text{P} \) NMR spectra in CDCl\(_3\) of the co-block (LA-\(b\)-EtPPn) synthesised from the sequential copolymerization of \(L\)-LA with EtPPn at ratios of 50:50:1:1 \([\text{[LA]}_{0}\text{:[EtPPn]}_{0}\text{:[I]}_{0}\text{:[BnOH]}_{0}], [\text{LA}]_{0} = 0.35 \text{ mol L}^{-1} \) in toluene (Entry 5, Table S3). Conversion of EtPPn from \(^{31}\text{P} \) NMR is taken from the integral of the polymer (34.0 – 36.0 ppm) region over that of the monomer (52.0 – 53.0 ppm). Triad linkages can be obtained showing a 2:98:0 ratio of P-P-L, P-P-P and L-P-L.
Figure S8) $^{31}$P DOSY spectra in CDCl$_3$ of the co-block (LA-b-EtPPn) synthesized from the sequential copolymerization of L-LA with EtPPn at ratios of 50:50:1:1 ([LA]:[EtPPn]:[1]:[BnOH]$_0$), [LA]$_0$ = 0.35 mol L$^{-1}$. in toluene (Entry 5, Table S3). The reaction involved polymerization of L-LA at 80 °C for 24 hours and then sequential addition of a 0.35 mol L$^{-1}$ solution of EtPPn in toluene. The reaction was stirred for a further hour prior to quenching.

Figure S9) $^1$H NMR spectra in CDCl$_3$ of the crude co-block (LA-b-EtPPn) synthesized from the sequential copolymerization of L-LA with EtPPn at ratios of 100:100:1:1 ([LA]:[EtPPn]:[1]:[BnOH]$_0$), [LA]$_0$ = 0.35 mol L$^{-1}$ in toluene (Entry 6, Table S3). $M_n$NMR is calculated from the integration of the polymer proton environments (LA: 5.13 – 5.19 ppm, EtPPn 1.71 – 1.82 ppm) over that of the single BnO- end group seen at 7.30 ppm. Conversion: LA: 92 %, EtPPn: 48 %, $M_n$NMR = 19900 g mol$^{-1}$, $M_n$NMR = 16830 g mol$^{-1}$.
Figure S10) $^{31}$P NMR spectra in CDCl$_3$ of the co-block (LA-b-EtPPn) synthesized from the sequential copolymerization of L-LA with EtPPn at ratios of 50:50:1:1 ([LA]:[EtPPn]:[I]:[BnOH])$_0$, [LA]$_0$ = 0.35 mol L$^{-1}$ in toluene. (Entry 6, Table S3). Conversion of EtPPn from $^{31}$P NMR is taken from the integral of the polymer (34.0 – 36.0 ppm) region over that of the monomer (52.0 – 53.0 ppm). Triad linkages can be obtained showing a 4:95:1 ratio of P-P-L, P-P-P and L-P-L.

**Tri-block polymers from sequential addition**

Figure S11) $^1$H NMR spectra in CDCl$_3$ of the crude tri-block (EtPPn-b-LA-b-EtPPn) synthesized from the sequential copolymerization of L-LA and EtPPn using 1,4-benzenedimethanol as initiator ([LA]:[EtPPn]:[I]:[Bn(CH$_2$OH)$_2$])$_0$ = 100:100:2:1, [LA] = 0.35 mol L$^{-1}$ (Entry 8 Table S3). Spectra highlights the assignation of conversion peaks. The reaction involved polymerization of L-LA at 80 °C for 16 hours and then sequential addition of a 0.35 mol L$^{-1}$ solution of EtPPn in toluene. The reaction was stirred for a further hour prior to quenching. Conversion; LA: 94%, EtPPn: 82%, $M_\text{NMR}$ = 24800 g mol$^{-1}$, $M_\text{NMR}$ = 20900 g mol$^{-1}$. 
\[ \text{Figure S12: } ^{31}P \text{ NMR spectra in CDCl}_3 \text{ of the tri-block (EtPPn-}b\text{-LA-}b\text{-EtPPn) synthesised from the sequential copolymerization of L-LA and EtPPn using 1,4-benzenedimethanol as initiator (}[[\text{LA}]_0]:[[\text{EtPPn}]_0]:[\text{I}]_0:[\text{Bn(CH}_2\text{OH)}_2]_0 = 100:100:2:1\), [LA] = 0.35 mol L\(^{-1}\) (Entry 8 Table S3). Triad linkages can be obtained showing a 4:95:1 ratio of P-P-L, P-P-P and L-P-L.\]

\[ \text{Figure S13} \) (Entry 9, Table S3) \(^1\text{H} \text{ DOSY spectra in CDCl}_3 \text{ of the tri-block (EtPPn-}b\text{-LA-}b\text{-EtPPn) synthesized from the sequential copolymerization of L-LA and EtPPn using 1,4-benzenedimethanol as initiator (}[[\text{LA}]_0]:[[\text{EtPPn}]_0]:[\text{I}]_0:[\text{Bn(CH}_2\text{OH)}_2]_0 = 100:100:2:1\), [LA] = 0.35 mol L\(^{-1}\) (Entry 8 Table S3). Diffusion rates are compared to the solvent for comparison. \( D_{\text{sol}} = 2.29 \times 10^{-9} \text{ m}^2 \text{s}^{-1}, D_{\text{poly}} = 1.86 \times 10^{-10} \text{ m}^2 \text{s}^{-1}. \]
**Figure S14** $^1$H NMR spectra in CDCl$_3$ of the purified tri-block (EtPPn-b-LA-b-EtPPn) synthesized from the sequential copolymerization of $L$-LA and EtPPn using 1,4-benzenedimethanol as initiator ([LA]$_0$:[EtPPn]$_0$:I$_0$:Bn(CH$_2$OH)$_2$)$_0 = 100:100:2:1$, [LA] = 0.35 mol L$^{-1}$ (Entry 9 Table S3). The reaction involved polymerization of $L$-LA at 80 °C for 6 hours and then sequential addition of a 0.35 mol L$^{-1}$ solution of EtPPn in toluene. The reaction was stirred for a further hour prior to quenching. Integration is highlighted relative to proton signals on the bound initiator group. Conversion; LA: 66%, EtPPn: 82%, $M_n$tho = 21450 g mol$^{-1}$, $M_n$NMR = 20310 g mol$^{-1}$.

**Figure S15** $^{31}$P NMR spectra in CDCl$_3$ of the tri-block (EtPPn-b-LA-b-EtPPn) synthesised from the sequential copolymerization of $L$-LA and EtPPn using 1,4-benzenedimethanol as initiator ([LA]$_0$:[EtPPn]$_0$:I$_0$:Bn(CH$_2$OH)$_2$)$_0 = 100:100:2:1$, [LA] = 0.35 mol L$^{-1}$ (Entry 9 Table S3).
Figure S16) $^1$H DOSY spectra in CDCl$_3$ of the tri-block (EtPPn-b-LA-b-EtPPn) synthesised from the sequential copolymerisation of L-LA and EtPPn using 1,4-benzenedimethanol as initiator ([LA]:[EtPPn]:[1]:[Bn(CH$_2$OH)$_2$]$_2$)$_0$ = 100:100:2:1), [LA] = 0.35 mol L$^{-1}$ (Entry 9 Table S3). Diffusion rates are compared to the solvent for comparison. $D_{\text{sol}} = 2.27 \times 10^{-9}$ m$^2$ s$^{-1}$, $D_{\text{poly}} = 1.08 \times 10^{-10}$ m$^2$ s$^{-1}$.
Copolymers from monomer mixtures

Figure S17  $^1$H NMR spectra in CDCl$_3$ of the copolymerization of rac-LA with EtPPn at ratios of 100:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[I]$_0$:[BnOH]$_0$), [LA]$_0$ = 0.69 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 2, Table S2). $M_n^{NMR}$ = 8600 g mol$^{-1}$, $M_n^{SEC}$ = 12480 g mol$^{-1}$, $M_n^{theo}$ = 17900 g mol$^{-1}$.

Figure S18  $^{31}$P NMR spectra in CDCl$_3$ of the copolymerization of rac-LA with EtPPn at ratios of 100:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[I]$_0$:[BnOH]$_0$), [LA]$_0$ = 0.69 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 2, Table S2). Conversion of EtPPn is taken from the integral of the polymer (34.0 – 37.0 ppm) region over that of the monomer (48.4 – 49.5 ppm) = 100 %. Triad linkages can be obtained showing a 59:28:13 ratio of P-P-P, P-P-L and L-P-L.
Figure S19) $^1$H NMR spectra in CDCl$_3$ of the copolymerization of rac-LA with EtPPn at ratios of 100:10:1:1 ([LA]$_0$:EtPPn$_0$:1[BnOH]$_0$), [LA]$_0$ = 0.69 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 4, Table S2). $M_n$NMR = 11650 g mol$^{-1}$, $M_n$SEC = 12950 g mol$^{-1}$, $M_n$theo = 15150 g mol$^{-1}$.

Figure S20) $^{31}$P NMR spectra in CDCl$_3$ of the copolymerization of rac-LA with EtPPn at ratios of 100:10:1:1 ([LA]$_0$:EtPPn$_0$:1[BnOH]$_0$), [LA]$_0$ = 0.69 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 4, Table S2). Conversion of EtPPn is taken from the integral of the polymer (34.0 – 37.0 ppm) region over that of the monomer (48.4 – 49.5 ppm) = 100 %. Triad linkages can be obtained showing a 15:44:41 ratio of P-P-P, P-P-L and L-P-L. This can be translated to a unit ratio in the polymer of 2:4:4 (P-P-P, P-P-L and L-P-L).
Figure S21) $^1$H NMR spectra in CDCl$_3$ of the copolymerization of rac-LA with EtPPn at ratios of 100:100:1:1 ([LA]$_0$:[EtPPn]$_0$:[BnOH]$_0$), [LA]$_0$ = [EtPPn]$_0$ = 0.35 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 6, Table S2). $M_n$NMR = 22850 g mol$^{-1}$, $M_n$theo = 22300 g mol$^{-1}$.

Figure S22) $^{31}$P NMR spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at ratios of 100:100:1:1 ([LA]$_0$:[EtPPn]$_0$:[BnOH]$_0$), [LA]$_0$ = [EtPPn]$_0$ = 0.35 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 6, Table S2). Triad linkages can be obtained showing a 53:23:24 ratio of P-P-P, P-P-L and L-P-L.
Figure S23) $^{31}$P NMR spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at ratios of 50:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[2][BnOH]$_0$), [LA]$_0$ = 0.69 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 9, Table S2). Triad linkages can be obtained showing a 34:29:37 ratio of P-P-P, P-P-L and L-P-L.

Figure S24) $^{31}$P NMR spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at ratios of 50:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[1][BnOH]$_0$), [LA]$_0$ = [EtPPn]$_0$ = 3.4 mol L$^{-1}$ in toluene, 80 °C, 16 h (Entry 10, Table S3). Reaction followed a temperature sequence; #1: 25 °C 10 mins, #2 80°C 1h. Triad linkages can be obtained showing a 83:9:7 ratio of P-P-P, P-P-L and L-P-L.
Figure S25) (Entry 8, Table S2) $^1$H DOSY spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at ratios of 50:50:1:1 $\{[\text{L-LA}]_0:[\text{EtPPn}]_0:[\text{I}]_0:[\text{BnOH}]_0\}$, $[\text{L-LA}]_0 = 0.69$ mol L$^{-1}$ in toluene, 25 °C, 120 h. Conversion; LA = 30 %, EtPPn = 96 %. Diffusion rates are compared to the solvent for comparison. $D_{\text{sol}} = 2.07 \times 10^{-9}$ m$^2$ s$^{-1}$, $D_{\text{poly}} = 2.31 \times 10^{-10}$ m$^2$ s$^{-1}$.

Figure S26) (Entry 7, Table S2) $^1$H DOSY spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at feed ratios of 100:50:1:1 $\{[\text{L-LA}]_0:[\text{EtPPn}]_0:[\text{I}]_0:[\text{BnOH}]_0\}$, $[\text{L-LA}]_0 = 0.69$ mol L$^{-1}$ in toluene, 80 °C, 16 h. Conversion; LA = 77 %, EtPPn = 98 %. Diffusion rates are compared to the solvent for comparison. $D_{\text{sol}} = 2.07 \times 10^{-9}$ m$^2$ s$^{-1}$, $D_{\text{poly}} = 2.31 \times 10^{-10}$ m$^2$ s$^{-1}$.
Figure S27) (Entry 11, Table S3) $^1$H DOSY spectra in CDCl$_3$ of the copolymerization of L-LA with EtPPn at feed ratios of 50:50:1:1 ([L-LA]:[EtPPn]:[I]:[BnOH]), [L-A]$_0$ = 0.35 mol L$^{-1}$. Reaction was carried out via a sequential temperature sequence in toluene, #1 25 °C, 2 h, #2 80 °C, 16 h. Conversion; LA = 71 %, EtPPn = 89 %. Diffusion rates are compared to the solvent for comparison. $D_{sol}$ = $2.09 \times 10^{-9}$ m$^2$s$^{-1}$, $D_{poly}$ = $2.13 \times 10^{-10}$ m$^2$s$^{-1}$.

Figure S28) (Entry 13, Table S3) $^1$H DOSY spectra in CDCl$_3$ of the in-situ NMR monitored copolymerization of L-LA with EtPPn at feed ratios of 50:50:1:1 ([L-LA]:[EtPPn]:[I]:[BnOH]), [L-A]$_0$ = 0.35 mol L$^{-1}$. In toluene-d$_8$ 80 °C, 16 h. Conversion; LA = 71 %, EtPPn = 82 %. Prior to DOSY experimentation the polymer was quenched and extracted from the crude mixture. Diffusion rates are compared to the solvent for comparison. $D_{sol}$ = $2.18 \times 10^{-9}$ m$^2$s$^{-1}$, $D_{poly}$ = $2.19 \times 10^{-10}$ m$^2$s$^{-1}$. 


COPOLYMERISATION KINETICS

Figure S29: Conversion over time for the copolymerization of EtPPn in a mixture with L-LA at ratios 50:50:1:1 ([EtPPn]₀:[L-LA]₀:[2]ₜ[BnOH]₀ in toluene-d₈ at 25 °C using DBU as the initiator. [LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. ● LA conversion is taken from integration of the methine region in the polymer against the CH₃ region of the monomer in the ¹H NMR spectra. ● Conversion of EtPPn taken from ³¹P NMR from integration of the polymer region (33.07 – 35.01 ppm) against the monomer signal (48.6 – 49.37 ppm).

Figure S30: Pseudo-first order plot for the polymerization of EtPPn in a mixture with L-LA at ratios 50:50:1:1 ([EtPPn]₀:[L-LA]₀:[2]ₜ[BnOH]₀ in toluene-d₈ at 25 °C using DBU as the initiator. [LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. ● LA conversion is taken from integration of the methine region in the polymer against the CH₃ region of the monomer. ● Conversion of EtPPn taken from ³¹P NMR from integration of the polymer region (33.07 – 35.01 ppm) against the monomer signal (48.6 – 49.37 ppm). ● $k_{obs,LA} = 6.5 \times 10^{-3}$ min⁻¹, ● $k_{obs,EtPPn} = 4.0 \times 10^{-4}$ min⁻¹.
Figure S31) Stacked plot of $^{31}$P NMR spectra of pEtPPn synthesized from copolymerization with $L$-LA at ratios of 50:50:1:1 ([LA]₀:[EtPPn]₀:[2]₀:[BnOH]₀) at 80 °C in toluene-d₈ using DBU as the initiator. [LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. Red spectra indicates initial acquisition at 30 mins, with 4 % conversion, with an end acquisition identified by the purple spectra taken at 900 minutes with 25 % EtPPn conversion. A small shift towards higher field in the monomer signal is indicative of changing in chemical make-up of the solution.

Figure S32) Plots of conversion (left y-axis) and linkage proportion (right y axis) of incorporated units polymer against time. Data obtained through $^1$H and $^{31}$P NMR kinetic experiments for the copolymerization of EtPPn and $L$-LA at 80 °C for 900 using DBU as the initiator. Assignment of triad linkages follows 34.8 (L-P-L), 34.1 (P-P-P) and 33.6 (P-P-L) ppm in the $^{31}$P NMR spectra.
Figure S33) Conversion over time for the copolymerization of EtPPn in a mixture with L-LA at ratios 50:50:1:1 \([\text{[EtPPn]}_0 : \text{[L-LA]}_0 : \text{[1]}_0 : \text{[BnOH]}_0]\) in toluene-\(d_8\) at 25 °C, \([\text{L-LA}}_0 = \text{[EtPPn]}_0 = 0.35 \text{ mol L}^{-1}\). ● LA conversion is taken from integration of the methine region in the polymer against the \(\text{CH}_3\) region of the monomer. ● Conversion of EtPPn taken from \(^1\text{H NMR}\) from integration of the \(\text{CH}_2\) of polymer region (1.76 – 1.86 ppm) and the \(\text{CH}_2\) of the monomer (1.94 – 2.05 ppm).

\[
y = 0.0077x + 0.6075 \\
R^2 = 0.9895
\]

Figure S34) Pseudo-first order plot for the polymerization of EtPPn in a mixture with L-LA at ratios 50:50:1:1 \([\text{[EtPPn]}_0 : \text{[L-LA]}_0 : \text{[1]}_0 : \text{[BnOH]}_0]\) in toluene-\(d_8\) at 25 °C, \([\text{L-LA}}_0 = \text{[EtPPn]}_0 = 0.35 \text{ mol L}^{-1}\). ● Conversion of EtPPn taken from \(^1\text{H NMR}\) from integration of the \(\text{CH}_2\) of polymer region (1.76 – 1.86 ppm) and the \(\text{CH}_2\) of the monomer (1.94 – 2.05 ppm).\(k_{\text{obs, EtPPn}} = 7.7 \times 10^{-3} \text{ min}^{-1}\).
Figure S35) Conversion vs time graph for copolymerization of EtPPn with L-LA at ratios of 50:50:1:1 ([L-A][EtPPn][1][BnOH]) at following a sequential heating run of 25 °C for 100 minutes and then at 80 °C for a further 800 minutes, [L-A]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. Conversion is taken from the ¹H NMR spectra.

Figure S36) Pseudo-first order plot for the co-polymerization of EtPPn with L-LA at ratios 50:50:1:1 ([EtPPn][L-LA][1][BnOH]) in toluene-d₈ at 80 °C following an initial sequence of 25 °C for 80 minutes, [L-A]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. Data presented is during the sequence when appreciable conversion of both monomers is seen. $k_{obs}^{EtPPn} = 2.3 \times 10^{-3}$ min⁻¹, $k_{obs}^{LA} = 2.7 \times 10^{-3}$ min⁻¹.
Figure S37) Stacked plot of $^{31}$P NMR spectra of pEtPPn synthesised from copolymerization with L-LA at ratios of 50:50:1:1 ([LA]₀:[EtPPn]₀:[1]:[BnOH]₀) following a sequential heating run of 25 °C for 100 minutes and then at 80 °C for 800 minutes, [LA]₀ = [EtPPn]₀ = 0.35 mol L⁻¹. Red spectra indicates initial acquisition at 120 minutes, with 69 % conversion, with an end acquisition identified by the purple spectra taken at 400 minutes with 80 % EtPPn conversion. Early time data is omitted from this spectra (20-120 minutes).

Figure S38) Plots of conversion (left y-axis) and linkage proportion (right y axis) against time. Taken from kinetic experiment for the copolymerization of EtPPn and L-LA at ratios of 50:50:1:1 ([LA]₀:[EtPPn]₀:[1]:[BnOH]₀). Sequential temperatures runs of 25 °C for 110 minutes followed by 80 C for 860 minutes. Assignment of triad linkages follows; 34.8 (L-P-L), 34.1 (P-P-L) and 33.6 (P-P-P) ppm in the $^{31}$P NMR spectra.
Figure S39) Conversion vs time graph for co-polymerization of EtPPn with L-LA at ratios of 50:50:1:1 \([\text{[LA]}_0:\text{[EtPPn]}_0:\text{[1]}_0:\text{[BnOH]}_0]\) at 80 °C for 940 minutes followed by 25 °C for 100 minutes and then at 80 °C for a further 30 minutes, \([\text{[LA]}_0 = \text{[EtPPn]}_0 = 0.35 \text{ mol L}^{-1}\). Conversion are taken from the \(^1\text{H}\) NMR spectra.

![Conversion vs time graph](image)

**Figure S40**) Pseudo-first order plot for the co-polymerization of EtPPn with L-LA at ratios 50:50:1:1 \([\text{[EtPPn]}_0:\text{[L-LA]}_0:\text{[1]}_0:\text{[BnOH]}_0]\) in toluene-d\(_8\) at 80 °C for 940 minutes followed by 25 °C for 100 minutes and then at 80 °C for a further 30 minutes, \([\text{[LA]}_0 = \text{[EtPPn]}_0 = 0.35 \text{ mol L}^{-1}\). Data presented is during the sequence when appreciable conversion of both monomers is seen. \(k_{\text{obs,EtPPn}} = 9.1 \times 10^{-3} \text{ min}^{-1}\), \(k_{\text{obs,L-A}} = 4.4 \times 10^{-3} \text{ min}^{-1}\).
Stacked plot of $^{31}$P NMR spectra of pEtPPn synthesized from co-polymerisation with L-LA at ratios of 50:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[1]$_0$:[BnOH]$_0$) at 80 °C in toluene d$_8$. [LA]$_0$ = [EtPPn]$_0$ = 0.35 mol L$^{-1}$. Red spectra indicates initial acquisition at 30 mins, with 70% conversion, with an end acquisition identified by the purple spectra taken at 930 minutes with 88% EtPPn conversion. A small shifting in the monomer signal is indicative of changing in chemical make-up of the solution.

Plots of conversion and linkage proportion of incorporated units polymer against time. Taken from ‘in-situ’ kinetic experiment for the copolymerization of EtPPn and L-LA at temperatures of 80 °C for 900 minutes at ratios of 50:50:1:1 ([LA]$_0$:[EtPPn]$_0$:[1]$_0$:[BnOH]$_0$) in toluene d$_8$. Linkage proportion is calculated based on overall 100% Assignment of triad linkages follows; 34.8 (L-P-L), 34.1 (P-P-P) and 33.6 (P-P-L) ppm in the $^{31}$P NMR spectra.
Figure S43) Stacked plot of $^1$H NMR spectra of pEtPPn synthesised from ‘ex-situ’ co-polymerization with L-LA at ratios of 50:50:1:1 $[\text{LA}]_0:[\text{EtPPn}]_0:[\text{I}]_0:[\text{BnOH}]_0$ in toluene. $[\text{LA}]_0 = [\text{EtPPn}]_0 = 0.35$ mol L$^{-1}$. The experiment followed a sequential temperature ramp in a stirred monomer mixture, #1 25 °C 6h. #2 80 °C 16h. Sampling was taken by removing aliquots from the stirred mixture under a flow of argon.

Figure S44) Stacked plot of $^{31}$P NMR spectra of pEtPPn synthesised from ‘ex-situ’ co-polymerization with L-LA at ratios of 50:50:1:1 $[\text{LA}]_0:[\text{EtPPn}]_0:[\text{I}]_0:[\text{BnOH}]_0$ in toluene. $[\text{LA}]_0 = [\text{EtPPn}]_0 = 0.35$ mol L$^{-1}$. The experiment followed a sequential temperature ramp in a stirred monomer mixture, #1 25 °C 6h. #2 80 °C 16h. Sampling was taken by removing aliquots from the stirred mixture under a flow of argon.
Figure S45) $M_0^{\text{theo}}$ and $M_0^{\text{NMR}}$ vs conversion graph for the $^1$H NMR tracked copolymerization of EtPPn : L-LA at ratios 50:50:1:1 $[[\text{EtPPn}]:[[\text{L-LA}]]:[[1]]:[[\text{BnOH}]]$ in toluene-d$_8$ following a sequential heating run of 25 °C for 100 minutes and then at 80 °C for 800 minutes, $[\text{LA}]_0 = [\text{EtPPn}]_0 = 0.35$ mol L$^{-1}$. $M_0^{\text{NMR}} = M_0^{\text{NMR,LA}} + M_0^{\text{NMR,EtPPn}}$. Conversion is taken from total monomer conversions.
REACTIVITY RATIO ANALYSIS

Fitting of the real-time NMR data using 1

**Figure S46.** Fit of the real-time NMR data of EtPPn using 1 at feed ratios 50:50:1:1 \([\text{EtPPn}]_0: [\text{LA}]_0: [\text{BnOH}]_0: [\text{I}]_0\), 80 °C, 16h to \(t = 0\). Since most methods for estimating reactivity ratios are only applicable to low to medium conversions it was necessary to fit the real-time NMR data to \(t = 0\) for the reaction using 1.\(^3\)

**Figure S47.** Fit of the real-time NMR data of LA using 1 at feed ratios 50:50:1:1 \([\text{EtPPn}]_0: [\text{LA}]_0: [\text{BnOH}]_0: [\text{I}]_0\), 80 °C, 16h to \(t = 0\). Since most methods for estimating reactivity ratios are only applicable to low to medium conversions it was necessary to fit the real-time NMR data to \(t = 0\) for the reaction using 1.\(^3\)
Estimation of reactivity ratios via the Meyer-Lowry equation

Integration of the Mayo-Lewis equation results in the Meyer-Lowry model. This model can be used for the estimation of reactivity ratios from low to moderate conversions by fitting the experimental compositional drift of $f_i$ against the total conversion $X_n$.  

**Equation S1.** Meyer-Lowry model for the estimation of reactivity ratios.$^5$

$$X_n = 1 - \left( \frac{f_1}{f_{10}} \right)^{\alpha} \left( \frac{f_2}{f_{20}} \right)^{\beta} \left( \frac{f_{10} - \delta}{f_1 - \delta} \right)^{\gamma}$$

$$\alpha = \frac{r_2}{(1 - r_2)}; \quad \beta = \frac{r_1}{(1 - r_1)}; \quad \gamma = \frac{1 - r_1 r_2}{(1 - r_2)(1 - r_2)}; \quad \delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

**Figure S48.** Meyer-Lowry fit from the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 1 at feed ratios 50:50:1:1 \{[EtPPn][LA][BnOH][I]\}, 80 °C, 16h which was extrapolated to $t = 0$.

**Figure S49.** Meyer-Lowry fit from the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 2 at feed ratios 50:50:1:1 \{[EtPPn][L-LA][BnOH][I]\}, 80 °C, 16h.
Estimation of reactivity ratios via the logarithmic Meyer-Lowry equation

Another form of the Meyer-Lowry equation is the logarithmic form which can also be used for the estimation of reactivity ratios.\(^6\)

**Equation S2.** Logarithmic Meyer-Lowry model for the estimation of reactivity ratios.\(^6\)

\[
\log\left(\frac{[M_2]}{[M_{20}]}\right) = \frac{r_2}{1-r_2} \log\left(\frac{[M_{20}][M_3]}{[M_2][M_3]}\right) - \frac{1-r_2}{(1-r_1)(1-r_2)} \cdot \log\left(\frac{(r_1 - 1)}{(r_1 - 1)} - r_2 + 1 \right)
\]

**Figure S50.** Logarithmic Meyer-Lowry fit from the real-time NMR data of EtPPn (r\(_1\)) and LA (r\(_2\)) using 1 at feed ratios 50:50:1:1 \([\text{EtPPn}:\text{LA}:\text{BnOH}:\text{I}]\), 80 °C, 16h which was extrapolated to \(t = 0\).

**Figure S51.** Logarithmic Meyer-Lowry fit from the real-time NMR data of EtPPn (r\(_1\)) and LA (r\(_2\)) using 2 at feed ratios 50:50:1:1 \([\text{EtPPn}:\text{L-LA}:\text{BnOH}:\text{I}]\), 80 °C, 16h.
An alternative approach for estimating reactivity ratios is the direct numerical integration of the differential copolymer composition equation.\textsuperscript{7}

**Equation S3.** Differential copolymer composition equation. With $X_n$ as the total conversion, $f_i$ as the mole fraction of unreacted monomer and $F_i$ as the instantaneous copolymer composition.\textsuperscript{7}

\[
\frac{df_1}{X_n} = \frac{f_1 - F_1}{1 - X_n}
\]

**Figure S52.** Direct numerical integration of the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 1 at feed ratios 50:50:1:1 \([\text{EtPPn}]_0:[\text{LA}]_0:[\text{BnOH}]_0:[\text{I}]_0\), 80 °C, 16h which was extrapolated to $t = 0$.

**Figure S53.** Direct numerical integration of the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 2 at feed ratios 50:50:1:1 \([\text{EtPPn}]_0:[\text{L-LA}]_0:[\text{BnOH}]_0:[\text{I}]_0\), 80 °C, 16h.
Estimation of reactivity ratios by using the Jaacks model

The Jaacks model estimates the reactivity ratios under the assumption of an ideal copolymerization $r_1*r_2=1$. Using this assumption the following equation can be used to fit the experimental data.

**Equation S4.** Copolymerization equation of an ideal copolymerization.$^6$

\[
\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}
\]

\[
\frac{[M_1]}{[M_{10}]} = \left( \frac{[M_2]}{[M_{20}]} \right)^{r_1}
\]

\[
\log \left( \frac{[M_1]}{[M_{10}]} \right) = r_1 \log \left( \frac{[M_2]}{[M_{20}]} \right)
\]

\[
r_2 = \frac{1}{r_1}
\]

**Figure S54.** Jaacks fit of the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 1 at feed ratios 50:50:1:1 ([EtPPn]$_0$:[LA]$_0$:[BnOH]$_0$:[I]$_0$), 80 °C, 16h which was extrapolated to $t = 0$.

**Figure S55.** Jaacks fit of the real-time NMR data of EtPPn ($r_1$) and LA ($r_2$) using 2 at feed ratios 50:50:1:1 ([EtPPn]$_0$:[L-LA]$_0$:[BnOH]$_0$:[I]$_0$), 80 °C, 16h.
Calculation of the copolymer microstructure

The copolymer microstructure can be calculated by the previously obtained \( r \) parameters. Therefore the instantaneous copolymer composition \( F_1 \) is plotted against the total conversion \( X_n \).\(^6\)

**Equation S5.** Equations used for the calculation of the copolymer microstructure. With \( X_n \) as the total conversion and \( F_1 \) as the instantaneous copolymer composition.

\[
X_n = 1 - \frac{[M_1] + [M_2]}{[M_{10}] + [M_{20}]}
\]

\[
t = \frac{[M_1]}{[M_2]}
\]

\[
\varepsilon = \frac{1 + r_1 t}{1 + r_2 t^{-1}}
\]

\[
F_1 = \frac{\varepsilon}{1 + \varepsilon}
\]

**Figure S56.** Mean composition \((F)\) of EtPPn and LA using 1 at feed ratios 50:50:1:1 {\([\text{EtPPn}]_0:\text{[LA]}_0:\text{[BnOH]}_0:\text{[I]}_0\)}, 80 °C, 16h which was extrapolated to \( t = 0 \).

**Figure S57.** Mean composition \((F)\) of EtPPn and LA using 2 at feed ratios 50:50:1:1 {\([\text{EtPPn}]_0:\text{[L-LA]}_0:\text{[BnOH]}_0:\text{[I]}_0\)}, 80 °C, 16h versus the total conversion determined using the \( r \) parameters estimated by the Meyer–Lowry fit.
Overview of the determined reactivity ratios for the comonomer pairs EtPPn and LA using 1 and 2

Table S4. Overview of the determined reactivity ratios for the comonomer pairs EtPPn and LA using 1

| Methods          | $r_{EtPPn}$ | $r_{LA}$ | $r_{EtPPn} \cdot r_{LA}$ |
|------------------|-------------|----------|-------------------------|
| Meyer-Lowry      | 18.411      | 0.836    | 15.393                  |
| Meyer-Lowry log  | 18.475      | 0.842    | 15.549                  |
| Jaacks           | 9.668       | 0.103    | 0.999                   |
| Direct Numerical Integration | 18.500 | 0.844 | 15.610 |

Copolymerisation of EtPPn and L-LA monitored from via ‘in-situ’ NMR experimentation, at feed ratios 50:50:1:1 ([EtPPn]:[L-LA]:[BnOH]:[I]_0), 80 °C, 16h which was extrapolated to $t = 0$. A fit of data is required due to restrictions of the mathematical model requiring data < 30% conversion to carry out calculation.

Table S5. Overview of the determined reactivity ratios for the comonomer pairs EtPPn and LA using 2 at feed ratios 50:50:1:1 ([EtPPn]:[L-LA]:[BnOH]:[I]_0), 80 °C, 16h.

| Methods          | $r_{EtPPn}$ | $r_{LA}$ | $r_{EtPPn} \cdot r_{LA}$ |
|------------------|-------------|----------|-------------------------|
| Meyer-Lowry      | 0.195       | 19.737   | 3.851                   |
| Meyer-Lowry log  | 0.117       | 17.433   | 2.041                   |
| Jaacks           | 0.067       | 14.739   | 0.984                   |
| Direct Numerical Integration | 0.104 | 17.006 | 1.764 |

Copolymerisation of EtPPn and L-LA monitored from via ‘in-situ’ NMR experimentation, at feed ratios 50:50:1:1 ([EtPPn]:[L-LA]:[BnOH]:[I]_0), 80 °C, 16h which was extrapolated to $t = 0$. A fit of data is required due to restrictions of the mathematical model requiring data < 30% conversion to carry out calculation.
SELECTED SEC TRACES

Figure S58) Example SEC of rac-LA : EtPPn copolymer at ratios of 100:20:1:1 ([LA]₀:[EtPPn]₀:[I]₀:[BnOH]₀) (Entry 3, Table 1.1). SEC ran in THF using detection methods. $M_{\text{theo}} = 14792 \text{ g mol}^{-1}$, $M_{\text{SEC}} = 16200 \text{ g mol}^{-1}$, $D = 1.27$.

Figure S59) Example SEC of rac-LA : EtPPn copolymer at ratios of 100:10:1:1 ([LA]₀:[EtPPn]₀:[I]₀:[BnOH]₀) (Entry 3, Table S2). SEC ran in THF using detection methods. $M_{\text{theo}} = 13575 \text{ g mol}^{-1}$, $M_{\text{SEC}} = 12900 \text{ g mol}^{-1}$, $D = 1.23$. 

Figure S60) Example SEC spectra of L-LA : EtPPn copolymer with feed ratios of 50:50:1:1 ([LA]₀:EtPPn₀:1:[BnOH]₀) carried out at 25 °C in toluene-d₈. SEC ran in THF using detection methods. $M_n^{theo} = 12176 \text{ g mol}^{-1}$, $M_n^{SEC} = 21000 \text{ g mol}^{-1}$, $D = 1.12$. 
**SELECTED TGA TRACES**

Figure S61) TGA trace of pEtPPn (Entry 2, Table S1). Onset of degradation at 139 °C, with derivative maxima 210 °C. No further degradation is recorded past 230 °C. ([EtPPn]:[I]=[Bn(CH₂OH)₂]:0 = 50:1:1), [LA] = 0.35 mol L⁻¹. Conversion = 90 %, \( M_n^{\text{SEC}} = 4300 \text{ g mol}^{-1} \), \( M_n^{\text{theo}} = 6200 \text{ g mol}^{-1} \).

Figure S62) TGA trace of PLA synthesised from the polymerization of L-LA using 1,4-benzenedimethanol as initiator ([LA]:[I]:[Bn(CH₂OH)₂]₀ = 100:2:1), [LA] = 0.35 mol L⁻¹ (Entry7, Table S3). Conversion = 90 % \( M_n^{\text{SEC}} = 15400 \text{ g mol}^{-1} \), \( M_n^{\text{NMR}} = 13800 \text{ g mol}^{-1} \), Onset of degradation at 174 °C, with derivative maxima 315 °C. No further degradation is recorded past 415 °C.
Figure S63) TGA trace of EtPPn : rac-LA copolymer synthesized from feed ratios of 50:50:1:1 ([LA]:[EtPPn]:[I]:[BnOH]) carried out at 80 °C for 16 h (Entry 1, Table S2). Conversion(LA) = 75 %, Conversion(EtPPn) = 100 %, triad ratios of 51:22:27 (P-P-P : P-P-L : P-L-P) $M_n^{SEC} = 15500$ g mol$^{-1}$, $M_n^{NMR} = 12300$ g mol$^{-1}$, $M_n^{NMR} = 15550$ g mol$^{-1}$. Onset of degradation at 113 °C, multiple derivative curves are present with derivative maxima at 286 °C. No further degradation is recorded past 418 °C.

Figure S64) TGA trace of EtPPn : $L$-LA copolymer synthesized from feed ratios of 100:100:1:1 ([LA]:[EtPPn]:[I]:[BnOH]) carried out at 80 °C for 16 h (Entry 6, Table S3). Conversion(LA) = 67 %, Conversion(EtPPn) = 90 %, triad ratios of 53:25:22 (P-P-P : P-P-L : P-L-P), $M_n^{SEC} = 22300$ g mol$^{-1}$, $M_n^{NMR} = 22850$ g mol$^{-1}$. Onset of degradation at 171 °C, with derivative maxima 322 °C. No further degradation is recorded past 390 °C.
Figure S65) TGA trace of EtPPn-L-LA copolymer, synthesized from the sequential addition of EtPPn to a stirred solution of PLLA at 80 °C, then kept at 80 °C for 1h with feed ratios of 50:50:1:1 ([LA]₀:[EtPPn]₀:[1]₀:[BnOH]₀) (Entry 4, Table S3). % EtPPn in polymer = 54.8 % with triad ratios equal to P-P-P : P-P-L : L-P-L ratios of (96:1:3). Three distinct mass loss sequences are seen with the onset of degradation at 138 °C, with a first derivative maxima at 222 °C, second at 279 °C and third at 322.4 °C. No further degradation is recorded past 350 °C.

Figure S66) TGA trace of the block EtPPn-b-L-LA copolymer, synthesized from the sequential addition of EtPPn to a stirred solution of PLLA at 80 °C, then kept at 25 °C for 1h, with feed ratios of 50:50:1:1 ([LA]₀:[EtPPn]₀:[1]₀:[BnOH]₀) (Entry 5, Table S3). % EtPPn in polymer = 47.8 % with triad (P-P-P : P-P-L : L-P-L) ratios of (98:2:0). Two distinct mass loss sequences are seen with the onset of degradation at 143 °C, with a first derivative maxima at 227 °C resulting in a 47 % mass loss with the second occurring at 337 °C, resulting in a further 37.8 % mass loss. No further degradation is recorded past 370 °C.
Figure S67) TGA trace of the block EtPPn-b-L-LA copolymer, synthesized from the sequential addition of EtPPn to a stirred solution of PLLA at 80 °C, then kept at 25 °C for 1h (Entry 6, Table S3). Feed ratios of 100:100:1:1 ([LA]c:[EtPPn]c:[1c][BnOH]c) % EtPPn in polymer = 47.8 % with triad (P-P-P : P-P-L : L-P-L) ratios of (95:4:1). Two distinct mass loss sequences are seen with a first derivative maxima at 226 °C with the second occurring at 353 °C, resulting in a further 37.8 % mass loss. No further degradation is recorded past 404 °C.

Figure S68) TGA trace of the triblock EtPPn-b-L-LA-b-EtPPn copolymer, synthesized from the sequential addition of EtPPn to a stirred solution of PLLA (synthesized at 6h 80 °C) at 25 °C for 1h (Entry 6, Table S3). Feed ratios of 100:100:2:1 ([LA]c:[EtPPn]c:[1c][Bn(CH2OH)]c) = 100:100:2:1, [LA] = 0.35 mol L−1 (Entry 9 Table S3). Conversion(1LA) = 66 % Conversion(EtPPn) = 82 %, % EtPPn in polymer = 58 % with triad (P-P-P : P-P-L : L-P-L) ratios of (94:3:3). M\text{NMR} = 21500 g mol−1, M\text{NMR} = 20300 g mol−1. Two distinct mass loss sequences are seen with a first derivative maxima at 268 °C (62.7 % mass loss) with the second occurring at 352 °C, resulting in a further 37.4 % mass loss. No further degradation is recorded past 397 °C.
SELECTED DSC TRACES

Figure S69) DSC chromatogram for copolymer with unit ratio of [EtPPn]_{49}[rac-LA]_{77} (Entry 2, Table S2). \( T_g = -3.1^\circ C \).

Figure S70) DSC chromatogram for copolymer with unit ratio of [EtPPn]_{20}[rac-LA]_{83} (Entry 3, Table S2). \( T_g = 19.6^\circ C \).
Figure S71) DSC chromatogram for copolymer with unit ratio of [EtPPn]_{16}[rac-LA]_{86} (Entry 4, Table S2). \( T_g = 27.4 \, ^\circ\text{C} \).

Figure S72) DSC chromatogram for copolymer with unit ratio of [EtPPn]_{48}[L-LA]_{44} (Entry 2, Table S3). \( T_g = -43.4 \, ^\circ\text{C}, 64.9 \, ^\circ\text{C} \).
Figure S73) DSC chromatogram for copolymer with unit ratio of \([\text{EtPPn}]_{50}: [L-LA]_{30}\) (Entry 6, Table S3). \(T_g = 1.37 \, ^\circ C\).

Figure S74) DSC chromatogram for copolymer with unit ratio of \([\text{EtPPn}]_{41}: [L-LA]_{36}\) (Entry 7, Table S3). \(T_g = 5.3 \, ^\circ C\).
Figure S75) MALDI-ToF spectra of EtPPn-rac-LA copolymer synthesized from feed ratios of 100:20:1:1. \([\text{rac-LA}] : \text{EtPPn} : \text{I} : \text{BnOH}\], Conv(LA) = 83 %, Conv(EtPPn) = 100 %. \(M_n^{\text{theo}} = 12176 \text{ g mol}^{-1}, M_n^{\text{SEC}} = 16550 \text{ g mol}^{-1}, D = 1.27\) (Entry 3, Table S2). Only cyclic material is seen evidenced by no clear end group.
Figure S76) MALDI-ToF spectra of EtPPn-LA copolymer synthesized from feed ratios of 100:50:1:1, \([L-LA]_c[EtPPn]_c[I]_c[BnOH]_a\), Conv(LA) = 75 %, Conv(EtPPn) = 100 %. \(M_n^{[\text{theo}]} = 17577 \text{ g mol}^{-1}\), \(M_n^{[\text{SEC}]} = 20100 \text{ g mol}^{-1}\), \(D = 1.06\) (Entry 6, Table S2). Only cyclic material is seen evidenced by no clear end group.
Figure S77: MALDI-ToF spectra of EtPPn-rac-LA copolymer synthesized from feed ratios of 100:50:1:1. $[^{[rac-LA]}_{c}[^{EtPPn}]_{c}[^{I}]_{c}[^{BnOH}]_{c}]$, Conv(LA) = 77 %, Conv(EtPPn) = 98 %. $M_{n \text{theo}} = 18010$ g mol$^{-1}$, $M_{n \text{SEC}} = 12480$ g mol$^{-1}$, $D = 1.02$ (Entry 2, Table S2). Only cyclic material is seen evidenced by no clear end group.
**Figure S78** MALDI-ToF spectra of EtPPn-rac-LA copolymer synthesized from feed ratios of 50:50:1:1. ([rac-LA]c:[EtPPn]c:[I]c:[BnOH]a). Conv(LA) = 73%, Conv(EtPPn) = 100%. $M_n^{Theo}$ = 12173 g mol$^{-1}$, $M_n^{SEC}$ = 21000 g mol$^{-1}$, $D$ = 1.12 (Entry 5, Table S2). Only cyclic material is seen evidenced by no clear end group.
REFERENCES

(1) Beament, J.; Mahon, M. F.; Buchard, A.; Jones, M. D. Aluminum Complexes of Monopyrrolidine Ligands for the Controlled Ring-Opening Polymerization of Lactide. *Organometallics* **2018**, *37*, 1719–1724.

(2) Wolf, T.; Steinbach, T.; Wurm, F. R. A Library of Well-Defined and Water-Soluble Poly(Alkyl Phosphonate)s with Adjustable Hydrolysis. *Macromolecules* **2015**, *48* (12), 3853–3863.

(3) Neufeld, R.; Stalke, D. Accurate Molecular Weight Determination of Small Molecules via DOSY-NMR by Using External Calibration Curves with Normalized Diffusion Coefficients. *Chem. Sci.* **2015**, *6* (6), 3354–3364.

(4) Evans, R.; Deng, Z.; Rogerson, A. K.; McLachlan, A. S.; Richards, J. J.; Nilsson, M.; Morris, G. A. Quantitative Interpretation of Diffusion-Ordered NMR Spectra: Can We Rationalize Small Molecule Diffusion Coefficients? *Angew. Chemie - Int. Ed.* **2013**, *52* (11), 3199–3202.

(5) Kazemi, N.; Duever, T. A.; Penlidis, A. Reactivity Ratio Estimation from Cumulative Copolymer Composition Data. *Macromol. React. Eng.* **2011**, *5* (9–10), 385–403.

(6) Patino-Leal, H.; Reilly, P. M.; O’Driscoll, K. F. On the Estimation of Reactivity Ratios. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18* (3), 219–227.

(7) Hauch, E.; Zhou, X.; Duever, T. A.; Penlidis, A. Estimating Reactivity Ratios from Triad Fraction Data. *Macromol. Symp.* **2008**, *271* (1), 48–63.

(8) Jaacks, V. A Novel Method of Determination of Reactivity Ratios in Binary and Ternary Copolymerizations. *Macromol. Chem. Phys.* **1972**, *161* (1), 161–172.

(9) Painter, P. C.; Coleman, M. M. *Essentials of Polymer Science and Engineering*; Raymond F. Boyer Library Collection; DEStech Publications, Incorporated, 2008.