Supporting Information for

Polymerizing phostones: A fast way to in-chain poly(phosphonate)s with adjustable hydrophilicity

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1. General Information

All chemicals and solvents were purchased from Sigma-Aldrich, Acros Organics or Fluka and used as received unless otherwise stated. Monomers and Initiator were distilled from $MgSO_4$ and stored over molecular sieves. Deuterated solvents were purchased from Sigma-Aldrich and used as received. ^{tBu}[salen]AlMe was synthesized according to well-established literature procedures.[1-2]

Instrumentation and Characterization Techniques

NMR. ^{1}H ^{13}C and ^{31} P NMR spectra were recorded using a Bruker Avance III 250, a Bruker Avance 300 or a Bruker Avance III 500. All spectra were referenced internally to residual proton signals of the deuterated solvent.

FTIR. FT-IR spectra were recorded using a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

SEC. For the size exclusion chromatography (SEC) measurements two different methods were used. ***Method a***: SEC measurements of standard polymers were performed in DMF (containing 1 gL^{-1} of lithium bromide as an additive) at 60 °C and a flow rate of 1 mL min^{-1} with a PSS SECurity as an integrated instrument, including a set of 3 PSS GRAM columns (porosity of 100 Å and 1000 Å) and a refractive index (RI) Detector. Calibration was carried out using polyethylene glycol standards provided by Polymer Standards Service. ***Method b***: SEC measurements were performed in DMF (containing 1 gL^{-1} of lithium bromide as an additive) at 50 °C with an Agilent 1100 Series as an integrated instrument, including a HEMA column (300/100/40) from MZ Analysentechnik, a UV (275 nm), and a refractive index (RI) detector. Calibration was carried out using poly(ethylene glycol) standards provided by Polymer Standards Service.

DSC. The thermal properties of the synthesized polymers have been measured by differential scanning calorimetry (DSC) on a Mettler Toledo DSC 823 calorimeter. Three scanning cycles of heating-cooling were performed in an N_2-atmosphere 30 mL/min) with a heating and cooling rate of 10 °C/min.

TGA was measured on a Mettler Toledo ThermoSTAR TGA/SDTA 851-Thermowaage in a nitrogen atmosphere. The heating rate was 10 °C/min in a range of temperature between 25 °C and 600 – 900 °C.

DLS. Dynamic light scattering (DLS) measurements were performed on an ALV spectrometer consisting of a goniometer and an ALV-5004 multiple-tau full-digital correlator(320 channels) which allows measurements over an angular range from 30° to 150. A He-Ne Laser (wavelength of 632.8 nm) is used as

light source. For temperature controlled measurements the light scattering instrument is equipped with a thermostat from Julabo.

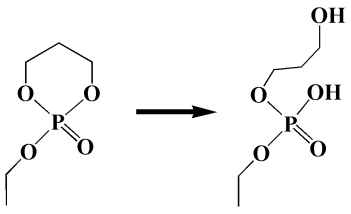
Acetylcholinesterase Assay. Inhibition of acetylcholinesterase was tested with the colorimetric Acetylcholinesterase Activity Assay Kit from Sigma Aldrich. The tests were performed according to the general protocol.

Determination of the cloud point. Cloud points were determined in MilliQ water and detected by the optical transmittance of a light beam (λ = 500 nm) through a 1 cm sample cell. The measurements were performed in a Jasco V-630 photo spectrometer with a Jasco ETC-717 Peltier element. The intensity of the transmitted light was recorded versus the temperature of the sample cell. The heating/ cooling rate was 1 °C min^{-1}, and values were recorded every 0.1 °C.

Density functional calculations. All calculations were carried out using Gaussian 09 package. The structures were optimized at the B3LYP level of theory and the aug-cc-pVTZ basis set. Ring strain energies were calculated as a difference between energies of cyclic molecules and their strain-free, linear counterparts, which are shown in Scheme S1. The energies of optimized molecules and relative strains are given in **Error! Reference source not found.**.

Table S1. Formation energies (Hartree) of cyclic compounds and their linear counterparts, their differences, and relative with respect to **M5** strain energies.

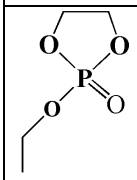
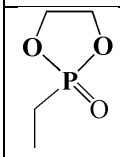
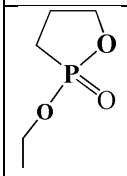
compound	cyclic, Hartree	linear, Hartree	Difference, kcal/mol	Relative strain, kcal/mol
M1	-764.46	-840.93	47988.68	2.14
M3	-725.13	-801.61	47990.88	4.34
M4	-800.40	-876.88	47990.23	3.69
M5	-839.73	-916.21	47986.54	0



Scheme S1. Cyclic and linear structures of **M4** used to compute the ring strain energies. We also assumed the same changes for **M1**, **M3**, and **M5**.

Ionization potentials (IP) and electron affinities (EA) with relaxed geometries of cations and anions, chemical potential $\mu = -\frac{1}{2}(\mathrm{IP} + \mathrm{EA})$, chemical hardness $\eta = \mathrm{IP} - \mathrm{EA}$, and electrophilicity index $\omega^{+} = \frac{\mu^2}{2\eta}$ are summarized in Table S2.

Table S2. Calculated ionization potential (IP), electron affinity (EA), chemical potential (μ), chemical hardness (η), and electrophilicity index (ω^{+}). All values are in eV.

	IP	EA	μ	η	ω^{+}
	0.36	−0.21	−4.75	9.91	1.14
	0.35	−0.18	−4.73	9.81	1.14
	0.34	−0.22	−4.57	9.58	1.09

2. Synthetic Procedures

2-ethoxy-1,2-oxaphospholane 2-oxide (M1). M1 was synthesized according to a literature procedure.[3] Triethyl phosphite (131 g, 0.8 mol, 2 eq) and 1,3-dibromopropane (80 g, 0.4 mol, 1 eq) were combined in a round bottom flask equipped with a distillation apparatus to remove evolving ethyl bromide. The mixture was heated up to 120 °C until 1,3-dibromopropane was consumed completely (the consumption of the alkyl halide was monitored by NMR measurements since no solvent is used for the reaction). The crude monomer was separated from the oligomeric side product by distillation (55-60 °C, 0.1 mbar) and purified by fractional distillation. 12.5 g (0.08 mol, 20%) 2-ethoxy-1,2-oxaphospholane-2-oxide is obtained as colorless liquid.

^{1}H NMR. ^{1}H NMR (300 MHz, chloroform-*d*) δ 4.25 – 3.96 (m, 4H, -P-O-CH_2-), 2.37 – 2.06 (m, 2H), 1.90 – 1.65 (m, 2H, -P-CH_2-), 1.28 (t, *J* = 7.1 Hz, 3H, -CH_3). ^{13}C NMR (176 MHz, chloroform-*d*) δ 67.26 (-O-***C***H_2-CH_2-), 62.18 (-O-***C***H_2-CH_3), 23.92 (-P-***C***H_2-), 18.49 (-P-CH_2-***C***H_2-), 16.47 (-***C***H_3). ^{31}P NMR (121 MHz, chloroform-*d*) δ 49.25. FTIR (cm^{-1}): 2988, 2904, 1451, 1415 (P-CH_2-), 1392, 1364, 1266, 1235 (P=O), 1160, 1043 (P−O−C), 980 (P−O−C), 960, 894, 807, 775

2-butoxy-1,2-oxaphospholane 2-oxide (M2). Tributyl phosphite (198 g, 0.8 mol, 2 eq) and 1,3-dibromopropane (80 g, 0.4 mol, 1 eq) were combined in a round bottom flask equipped with a distillation apparatus to remove evolving butyl bromide. The mixture was heated up to 120 °C until 1,3-dibromopropane was consumed completely (the consumption of the alkyl halide was monitored by NMR measurements since no solvent is used for the reaction). The crude monomer was separated from the oligomeric side product by distillation and purified by column chromatography using ethyl acetate as eluent to remove side products. The product can be removed from the column by using acetone as eluent to yield 15.6 g (21%) of a colorless liquid.

^{1}H NMR (300 MHz, chloroform-*d*) δ 4.24 – 3.94 (m, 4H, -P-O-CH_2-), 2.34 – 2.02 (m, 2H), 1.92 – 1.69 (m, 2H), 1.71 – 1.52 (m, 2H), 1.46 – 1.23 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H, -CH_3). ^{13}C NMR (176 MHz, chloroform-*d*) δ 67.24 (-O-***C***H_2-CH_2-), 66.16 (-O-***C***H_2-C_3H_7), 32.71 (-O-CH_2-***C***H_2-), 29.83 (-***C***H_2-CH_3), 24.12(-P-***C***H_2-), 19.10(-P-CH_2-***C***H_2-), 13.73 (-***C***H_3). ^{31}P NMR (122 MHz, chloroform-*d*) δ 49.28. FTIR (cm^{-1}): 2959, 2867, 1458, 1413(P-CH_2-), 1379, 1358, 1269 (P=O), 1235, 1151, 1062, 1020 (P−O−C), 978 (P−O−C), 897, 851, 796, 737

General Procedure for the ROP of M1 and M2 using TBD as a catalyst. The reaction was conducted either in dry dichloromethane or dry toluene at different temperatures with 2-(benzyloxy) ethanol as the

initiator and TBD as the catalyst. All Schlenk-tubes were flame-dried prior to use. M1/M2 and a stock solution of 2-(benzyloxy) ethanol (65.7 mmol L^{-1}) were introduced into a tube via syringe. TBD was freeze-dried with benzene before use and a stock solution (0.36 mol L^{-1}) in the dry solvent was prepared. The initiator stock solution was added to the monomer and the concentration was adjusted to an overall concentration of 2 mol/L of the monomer with the respective solvent. The reaction tube, as well as the TBD stock solution, were cooled down to 0 °C and the polymerization was initiated by the rapid addition of the TBD solution (5 equivalents in respect to the initiator) to the stirred monomer/initiator solution via syringe. Polymerizations were quenched by addition of an excess of acetic acid (20 mg mL^{-1}) in the respective solvent. The polymers were purified by precipitation into diethyl ether or hexane (for (**P(2)**) and subsequent dialysis (to remove the organocatalyst; a dialysis membrane with an MWCO of 1000 g/mol was used).

General Procedure for the ROP of M1 and M2 using TU/DBU or Tris-Urea/TU.

All Schlenk-tubes were flame-dried prior to use. 2-(benzyloxy) ethanol was used as the initiator. TU/Tris-Urea was introduced into a flame-dried Schlenk-tube, dissolved in dry benzene, and dried by lyophilization. M1/M2 was introduced into the Schlenk-tube. A Stock solution of the initiator (65.7 mmol L^{-1}) in the respective dry solvent was prepared. A calculated amount of the initiator stock solution was added to the stirred solution of monomer and co-catalyst. In all cases, a certain amount of dry solvent was added to the monomer/co-catalyst solution to give a total reaction concentration of 2 mol L^{-1}. The temperatures were adjusted and the polymerization was started by rapid addition of DBU to the reaction mixture by a microliter syringe. The polymerizations of M1 with TU/DBU as a catalyst were conducted with 5 equivalents with respect to the initiator. The polymerizations with Tris-Urea/DBU as a catalyst were conducted with 2 equivalents with respect to the initiator for M1 and with 4 equivalents for the polymerization of M2. Polymerizations were quenched by addition of an excess of acetic acid in the respective solvent. The polymers were purified by precipitation into diethyl ether or hexane (for (P(2)) and subsequent dialysis.

Representative NMR data for P(1)

^{1}H NMR (300 MHz, Methylene Chloride-d_2) δ 7.27 (d, J = 3.9 Hz, aromatic C***H***), 4.47 (s, aryl-C***H***$_2$-), 4.15 – 3.81 (m, backbone /side chain –P-O-C***H***$_2$-), 2.00 – 1.60 (m, backbone –P-C***H***$_2$-C***H***$_2$-), 1.23 (t, J = 7.0 Hz, side chain –C***H***$_3$).^{13}C NMR (126 MHz, Chloroform-d) δ 64.91 (-P-C_2H_4-***C***H_2-), 62.00 (-O-***C***H_2-CH_3), 23.88(-P-***C***H_2-CH_2-), 21.32 (-P-CH_2-***C***H_2-), 16.48, (-***C***H_3).

Representative NMR data for P(2)

^{1}H NMR (300 MHz, Methylene Chloride-d_2) δ 7.26 (d, J = 4.0 Hz, aromatic C***H***), 4.47 (s, aryl-C***H***$_2$-), 4.17 – 3.77 (m, backbone /side chain –P-O-C***H***$_2$-), 1.96 – 1.44 (m, backbone –P-C***H***$_2$-C***H***$_2$– and side chain –C***H***$_2$-C_2H_5), 1.32 (dq, J = 14.4, 7.3 Hz, side chain -C***H***$_2$-CH_3), 0.86 (t, J = 7.3 Hz, side chain –C***H***$_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) 65.68 (backbone -O-***C***H_2-), 65.01(side chain -O-***C***H_2-CH_3), 32.58(side chain –O-CH_2-***C***H_2-), 23.94 (backbone –P-***C***H_2-) 21.28 (backbone –CH_2-***C***H_2-CH_2-), 18.74 (side chain –***C***H_2–CH_3), 13.61 (side chain –***C***H_3).^{31}P NMR (121 MHz, Methylene Chloride-d_2) δ 31.42, 30.83.

Synthesis of P(1)-5. Octadecanol and TU were dried by lyophilization with benzene. M1 (490 mg, 3.26 mmol, 40 eq) was added to the dried TU. A stock solution of octadecanol in dry toluene was prepared with a concentration of 0.07 mol L^{-1}. 1.1mL (22.0 mg, 0.084 mmol, 1 eq) of the initiator stock solution was added to the monomer resulting in a monomer concentration of 3 mol L^{-1}. The polymerization was initiated by the addition of 60 µL of DBU (62 mg, 0.41 mmol, 5eq). Polymerization was conducted at 0 °C and terminated after 20 h by the rapid addition of an excess of acetic acid dissolved in dichloromethane with a concentration of 20 mg mL^{-1}. The polymer was obtained by three-times precipitation in cold diethyl ether and subsequent dialysis against water to yield 396 mg (77%) of a colorless amorphous polymer.

^{1}H NMR (500 MHz, chloroform-*d*) δ 4.22 – 3.83 (m), 1.99 – 1.69 (m), 1.27 (t, J = 7.0 Hz), 0.81 (t, J = 6.9 Hz, 3H). ^{31}P NMR (202 MHz, chloroform-*d*) δ 31.43. ^{13}C NMR (126 MHz, chloroform-*d*) δ 64.99, 61.71, 29.68, 22.50, 21.36, 16,51.

General Procedure for the kinetic studies of the ROP of M1/M2. All reaction kinetics were conducted at a monomer concentration of 2 mol L^{-1}. At different time points, 100 µL of the reaction mixture was removed and terminated in 1 mL $CDCl_3$ containing 20 mg acetic acid. These solutions were divided into two parts each containing 0.5 mL. One part was freed from solvent under reduced pressure and analyzed without further purification by SEC. The other part was directly analyzed by ^{31}P NMR spectroscopy without purification to determine the conversion. M_n was determined by ^{1}H NMR spectroscopy of the purified polymer sample. The reaction mixture was purified by three-times precipitation into diethyl ether (3x) and vacuum dried.

Synthesis of P(3)-1. 2-ethyl-1,3,2-dioxaphospholane-2-oxide (457 mg, 3.36 mmol, 40 eq) was placed in a flame-dried Schlenk tube. A stock solution of octadecanol in dry toluene was prepared with a concentration of 0.07 mol L^{-1}. 1.13mL (22.7 mg, 0.084 mmol, 1 eq) of the initiator stock solution was added to the monomer resulting in a monomer concentration of 3 mol L^{-1}. The polymerization was initiated by the addition of 62 µL of DBU (64 mg, 0.42mmol, 5eq). Polymerization was conducted at

room temperature and terminated after 19 h by the rapid addition of an excess of acetic acid dissolved in dichloromethane with a concentration of 20 mg mL^{-1}. The polymer was obtained by three-times precipitation in cold diethyl ether and subsequent dialysis against water to yield 448mg (93%) of a colorless amorphous polymer.

^{1}H NMR (500 MHz, chloroform-*d*) δ 4.38 – 4.09 (m), 1.83 (dq, *J* = 18.4, 7.7 Hz), 1.19 (dt, *J* = 20.5, 7.6 Hz, 126H), 0.86 (t, *J* = 6.9 Hz). ^{13}C NMR (126 MHz, chloroform-*d*) δ 64.50, 29.69, 19.36, 18.22. ^{31}P NMR (202 MHz, chloroform-*d*) δ 35.23.

3. spectra

monomers

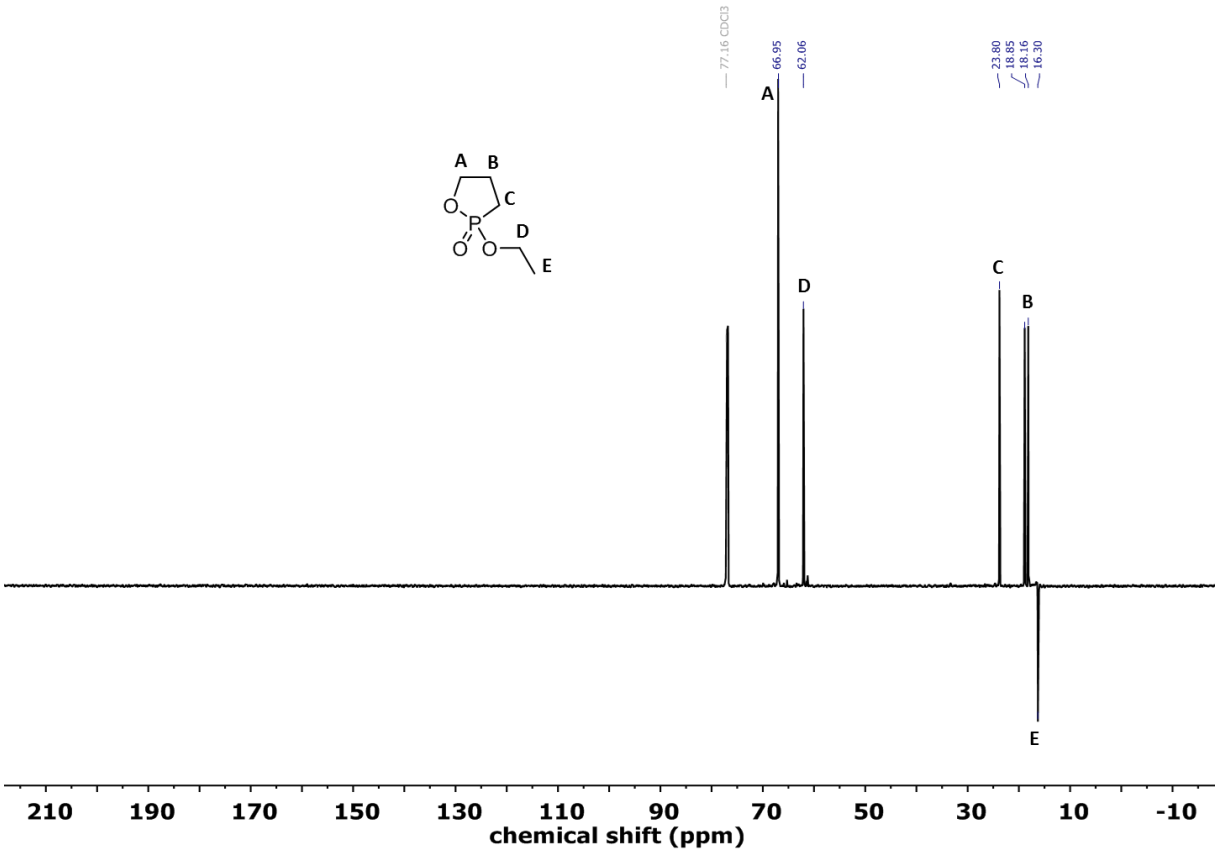


Figure S1. J MOD ^{13}C NMR (176 MHz) of **M1** in $CDCl_3$ at 298 K.

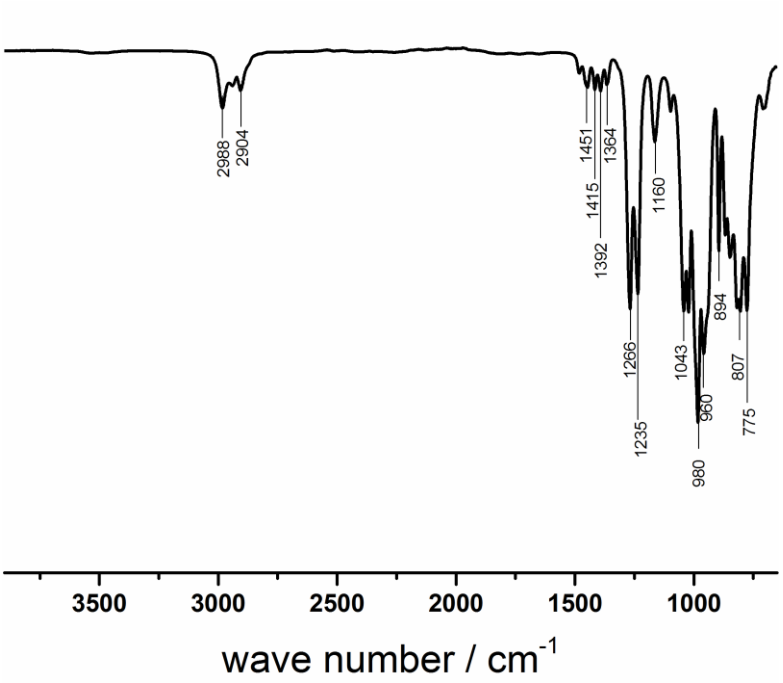


Figure S2: IR spectrum of **M1**.

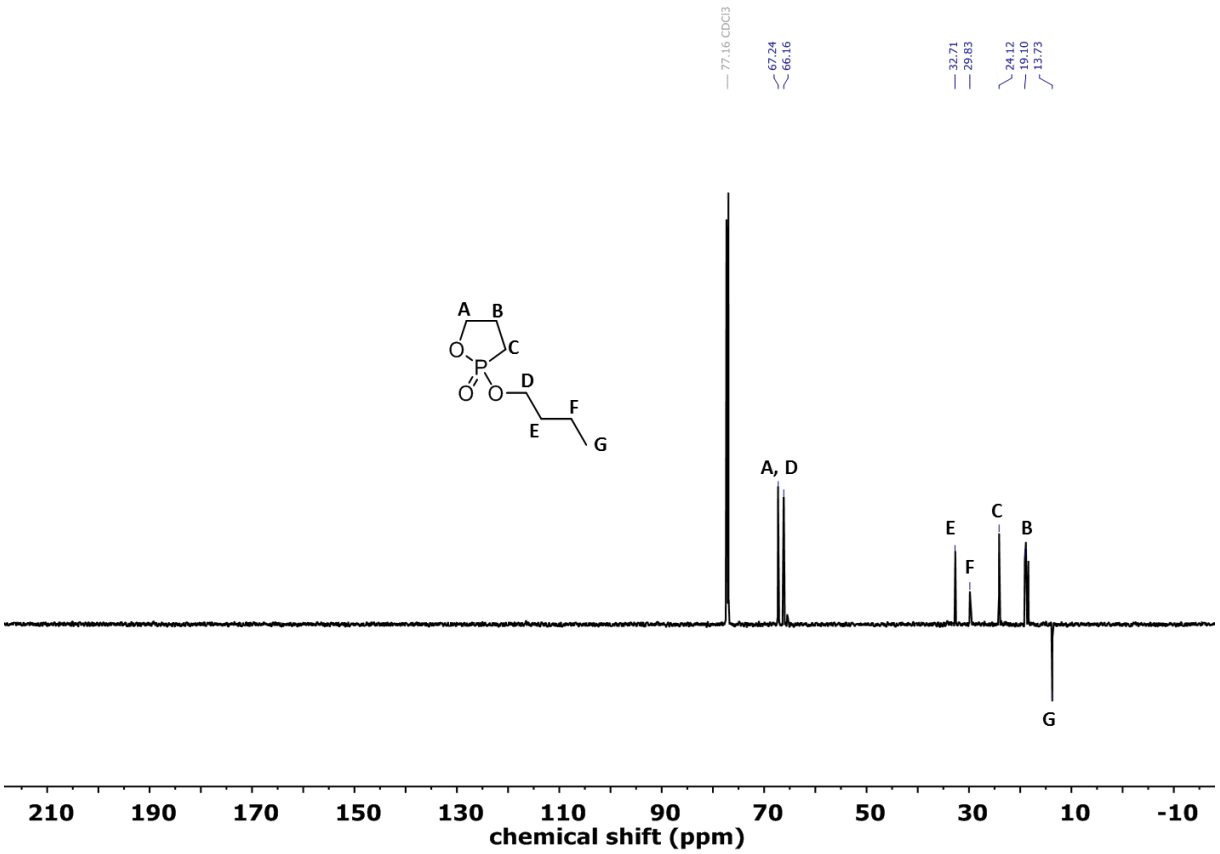


Figure S3. J MOD ^{13}C NMR (176 MHz) of **M2** in $CDCl_3$ at 298 K.

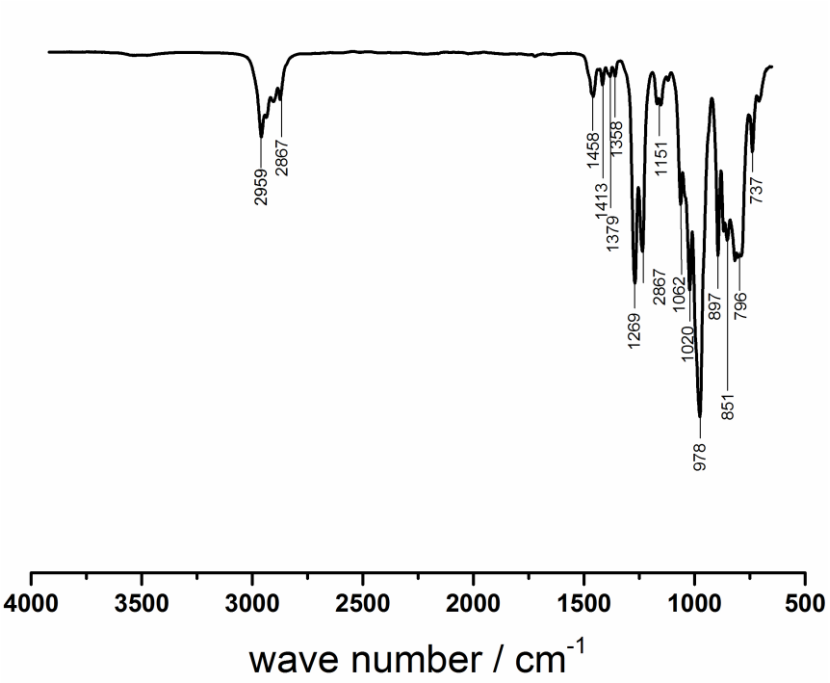


Figure S4. IR spectrum of **M2**.

Polymers

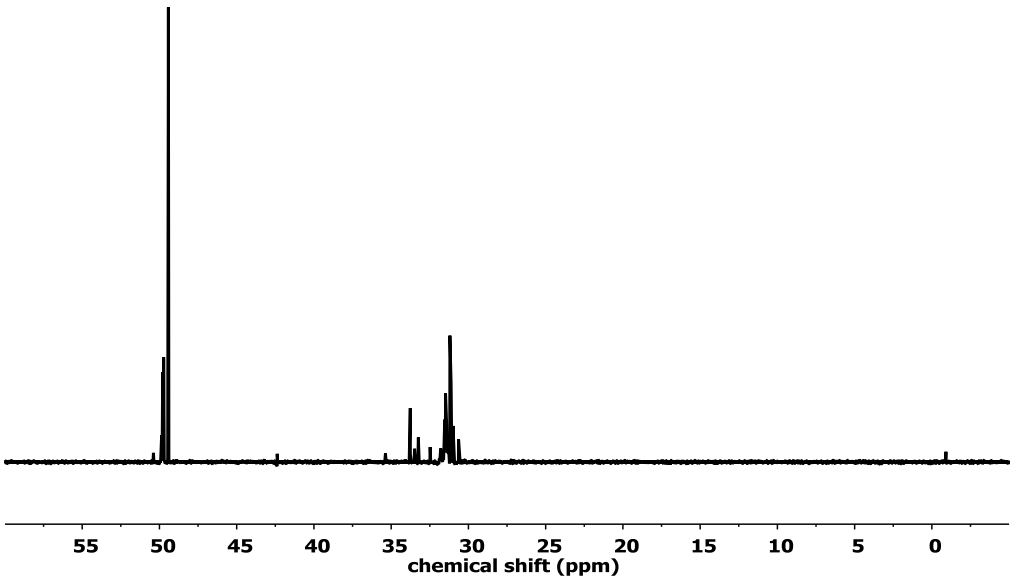


Figure 5. ^{31}P NMR (121 MHz) in $CDCl_3$ at 298 K of the polymerization of M1 with $Sn(Oct)_2$ after 18h at 95°C in toluene with a ratio $[M]_0$:$[I]_0$:[cat.] 50:1:5.7

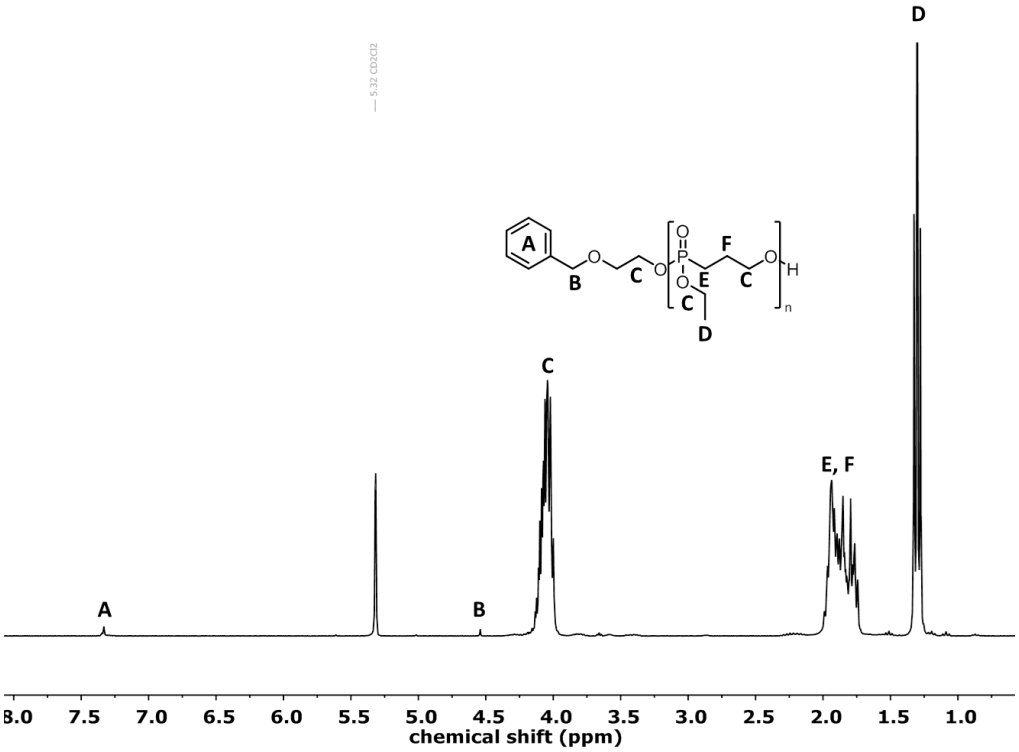


Figure S6. ^{1}H NMR (300 MHz) of P(1)-4 in CD_2Cl_2 at 298 K.

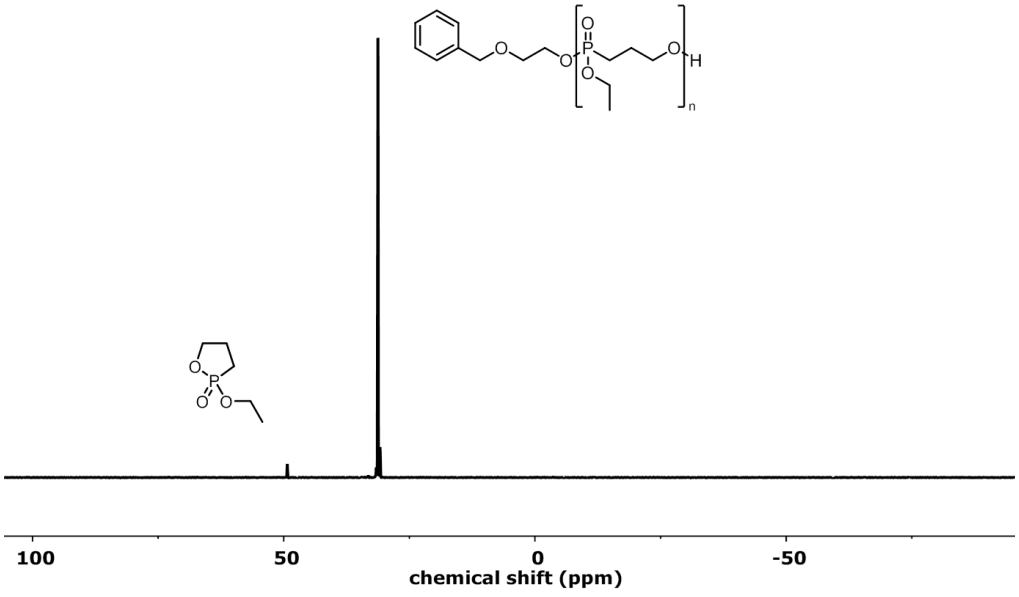


Figure 7. ^{31}P NMR (202 MHz) of P(1)-4 in CD_2Cl_2 at 298 K. The spectra shows 2% of residual monomer at 49.3 ppm.

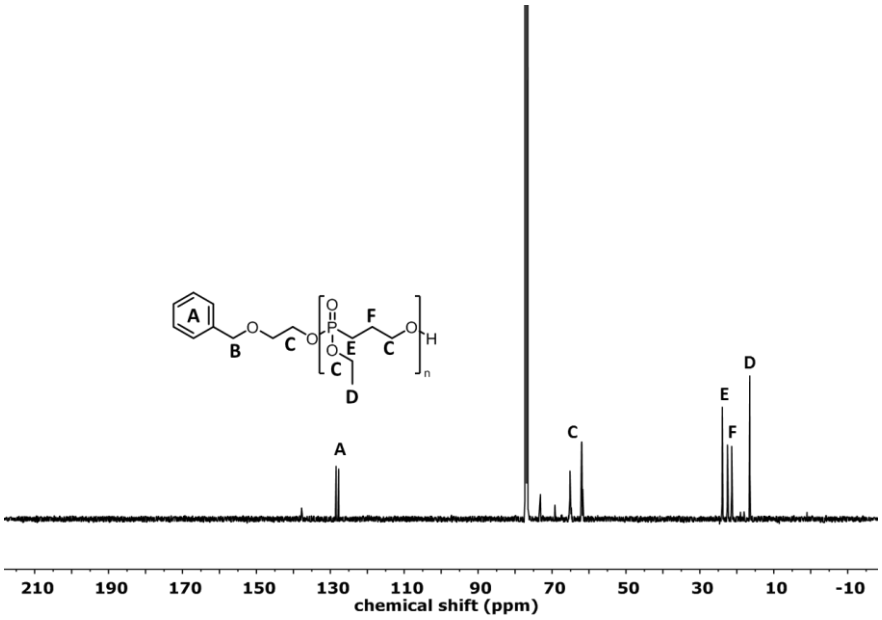


Figure S8. ^{13}C NMR (126 MHz) of P(1)-1 in $CDCl_3$ at 298 K.

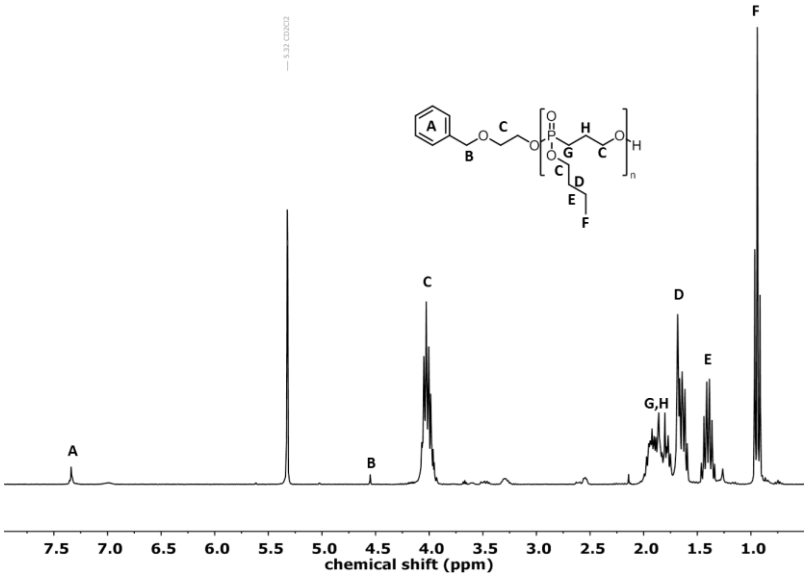


Figure S9. ^{1}H NMR (300 MHz) of P(2)-3 in $CDCl_3$ at 298 K.

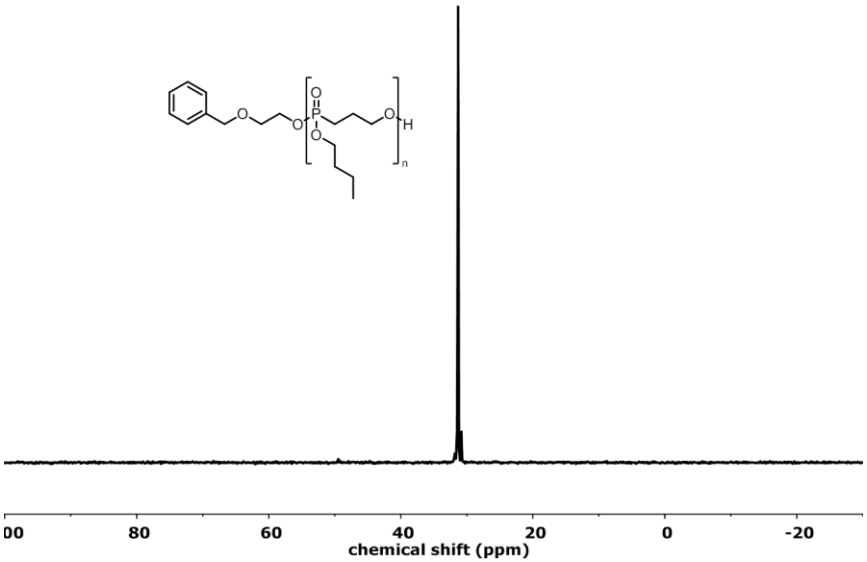


Figure 10. ^{31}P NMR (121 MHz) of P(2) with DP=75 (product of the reaction kinetic with Tris-Urea/DBU) in CD_2Cl_2 at 298 K.

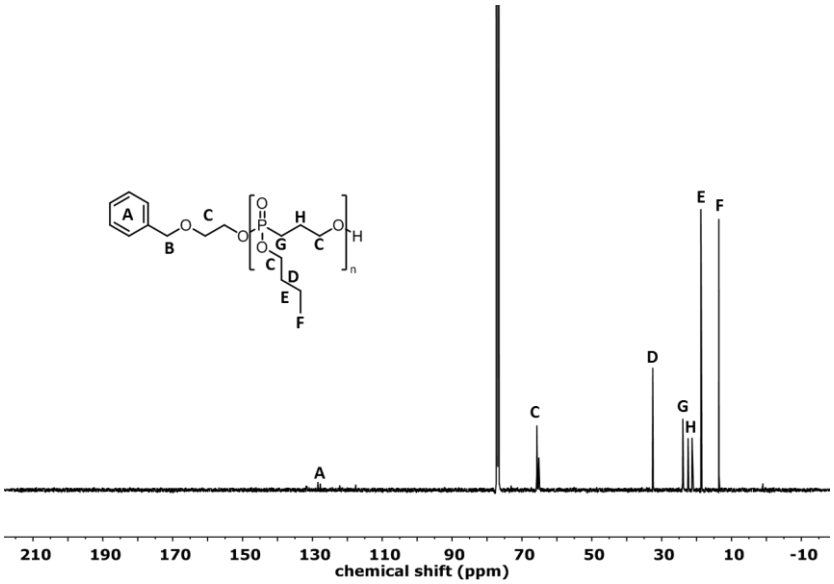


Figure S11.^{13}C NMR (126 MHz) of P(2)-3 in $CDCl_3$ at 298 K.

4. SEC-Elugrams

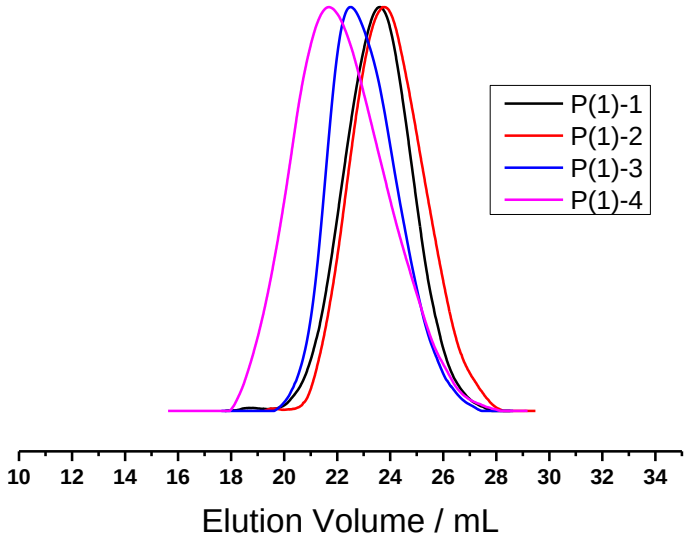


Figure S12. SEC-elugrams of polymers P(1)-1in DMF at 50°C (*method b*).

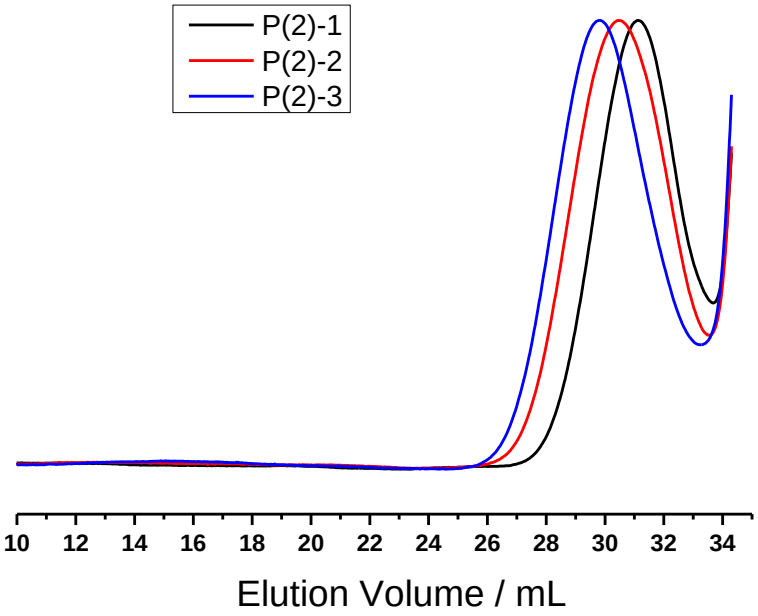


Figure S13. SEC-elugrams of polymers P(2) in DMF at 60°C (*method a*).

5. Thermal Characterization

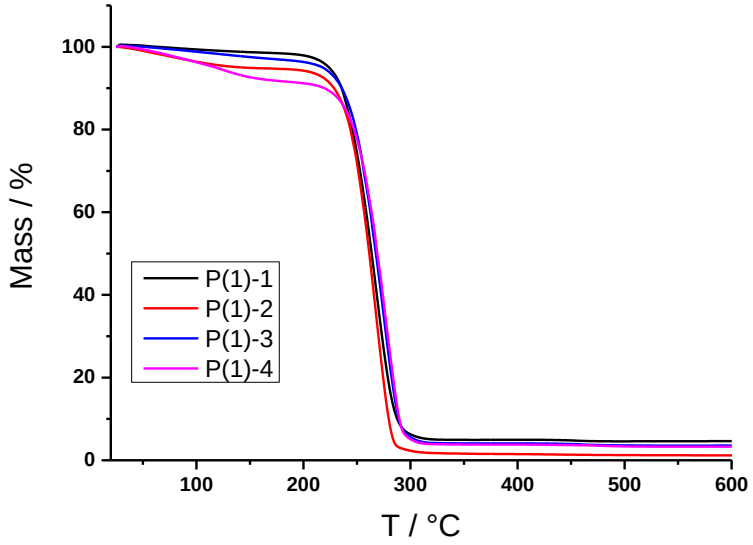


Figure S14. TGA measurements of polymers P(1).

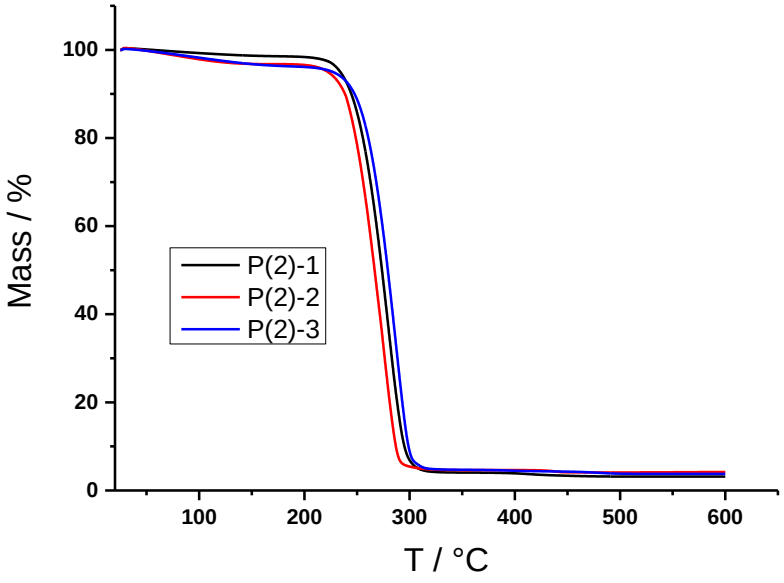


Figure S15. TGA thermograms of polymers P(2).

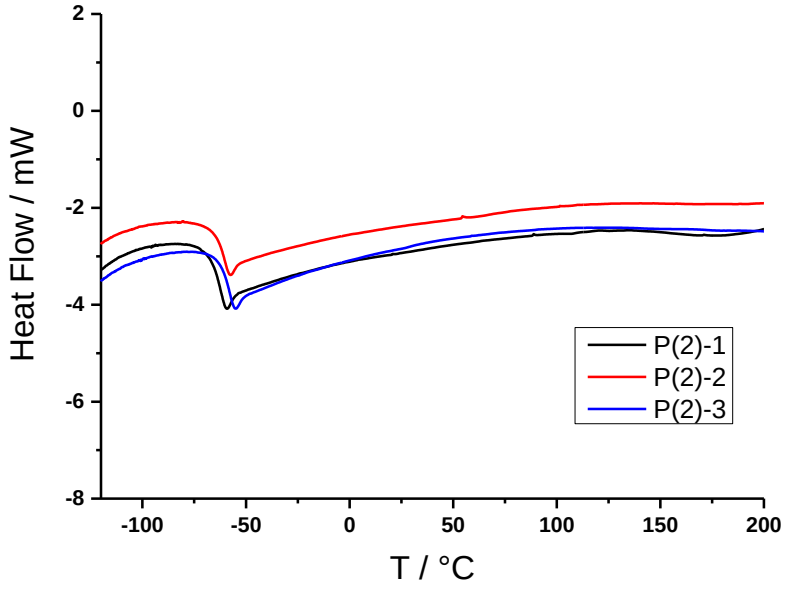


Figure S16. DSC thermograms of polymers P(2) at a heating rate of 10 K min^{-1} (depicted is the second heating phase).

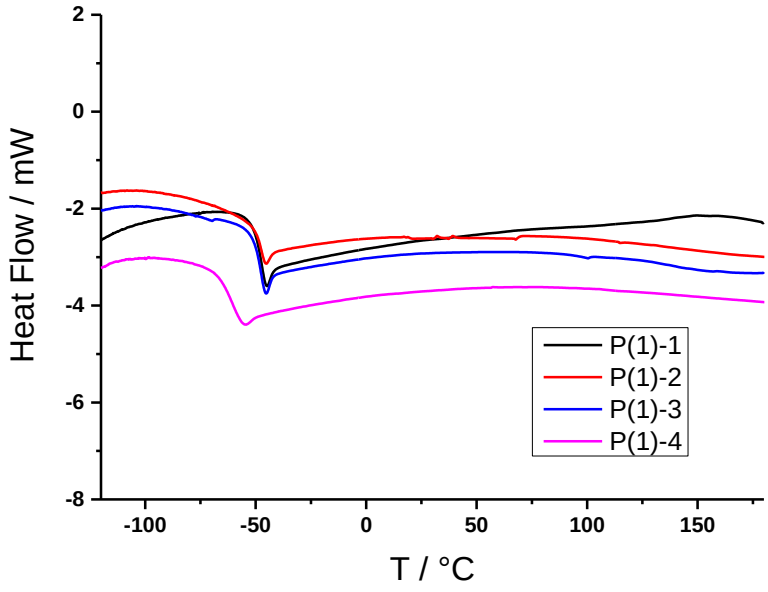


Figure S17. DSC thermograms of Poly(2)-polymers P(1) at a heating rate of 10 K min^{-1} (depicted is the second heating phase second heating).

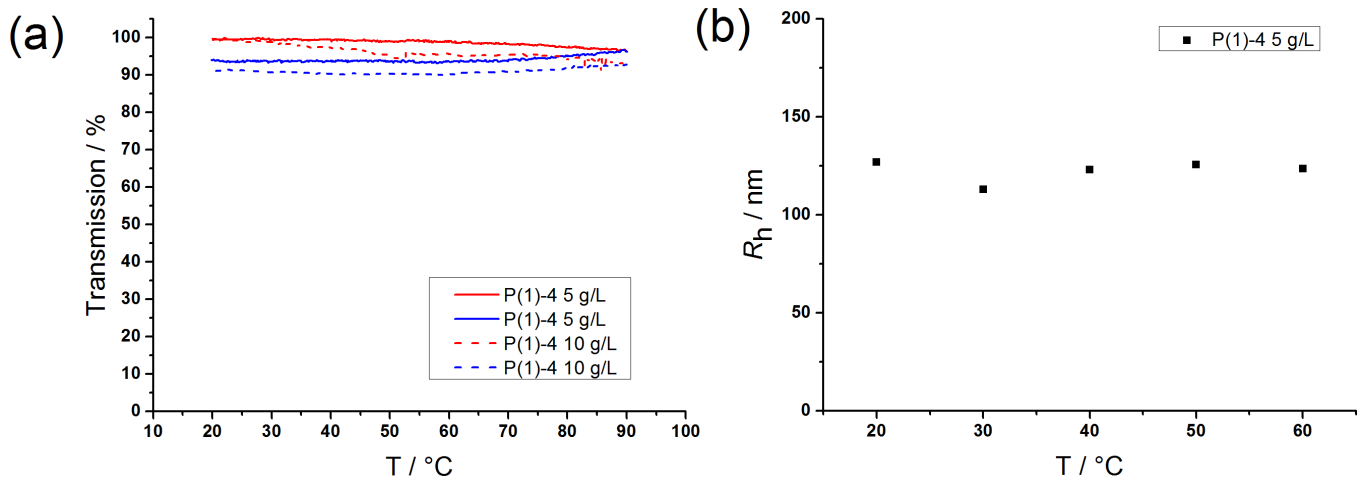


Figure S18. (a) Turbidity measurements of P(1)-4 in H_2O at a heating rate of 1°C min^{-1} .Transmission was measured at 500 nm for two concentrations (5, 10 g L^{-1}). (b) DLS measurements for P(1)-4 in H_2O at a concentration of 5 g L^{-1} showed the formation of aggregates with hydrodynamic radii of ~120 nm.

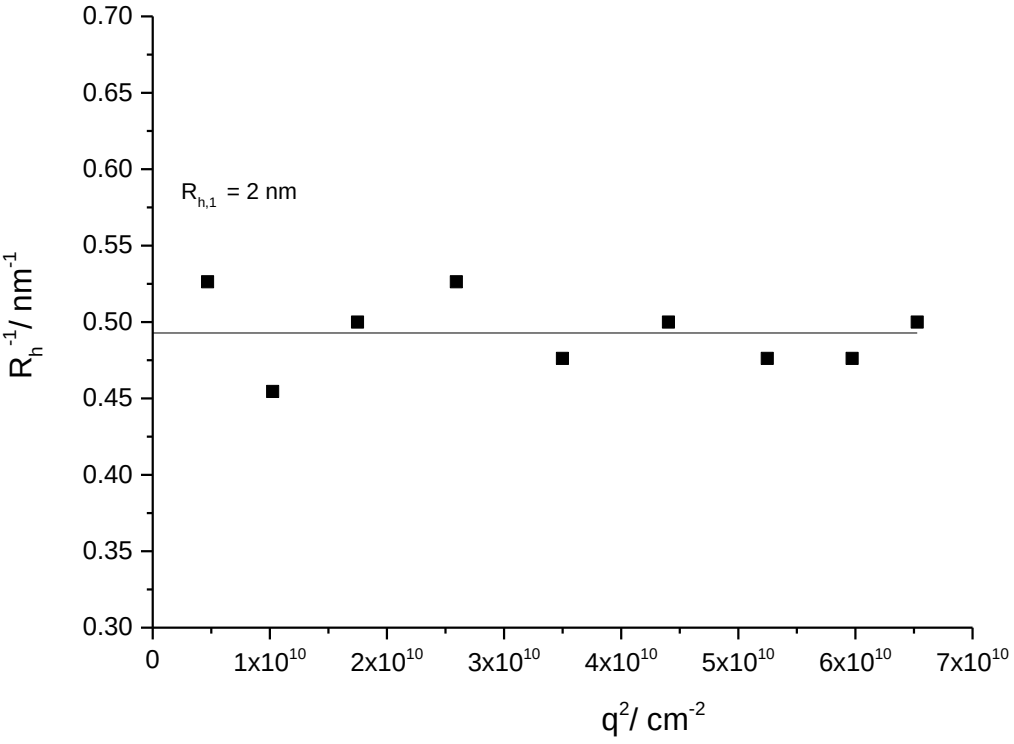


Figure 19. DLS measurements for P(3) DP=50 in H_2O at a concentration of 10 g L^{-1}.

6. Kinetic studies for the polymerization of M1

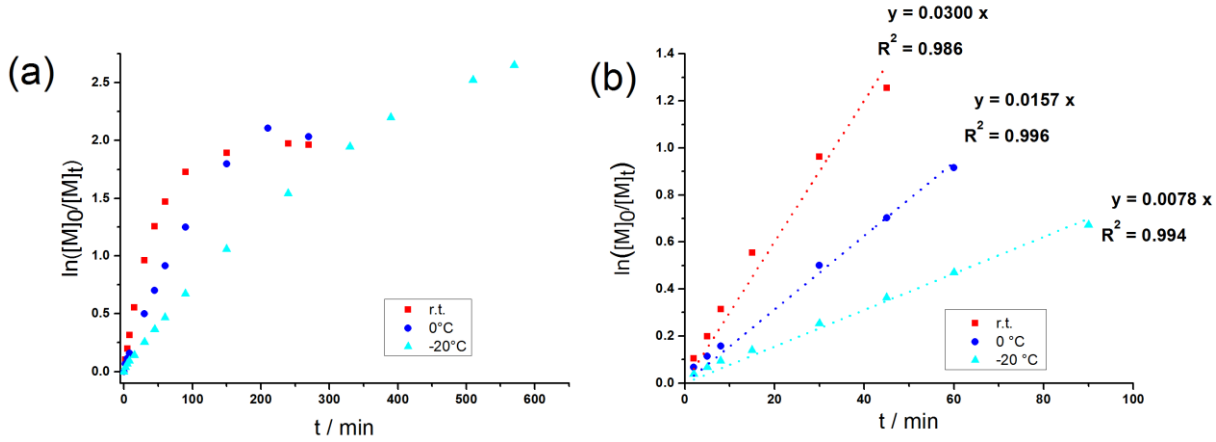


Figure S20. (a) Kinetic plots of ($\ln([M]_0/[M]_t)$) *vs* time obtained from ^{31}P NMR spectra for the polymerization of M1 with TBD as catalyst at r.t., 0 °C, -20 °C. The ratio of monomer : initiator : catalyst was 100 : 1 : 5 (data listed in Table S2). (b) Linear area of the conversion ($\ln([M]_0/[M]_t)$) *vs* time.

Table S2. Kinetic data for the polymerization of M1 by organocatalytic ROP using 2-(benzyloxy)ethanol as initiator and TBD as catalyst at different temperatures. Polymerizations were conducted at a monomer concentration of 2 mol L^{-1}.

#	$[M]_0/[I]_0/[cat.]$	T / °C	solvent	Time / min	Conv. [a] / %	n [b]	M_n [a]	M_n [b] / gmol^{-1}	Đ [c]
1	100:1:5	0	tol	2	7	n.d.	1200	n.d.	n.d.
2	100:1:5	0	tol.	5	12	n.d.	2000	n.d.	1.10
3	100:1:5	0	tol.	8	15	n.d.	2400	n.d.	1.17
4	100:1:5	0	tol.	30	40	53	6200	8100	1.41
5	100:1:5	0	tol.	45	52	n.d.	8000	n.d.	1.41

6	100:1:5	0	tol.	60	60	71	9200	10800	1.49
7	100:1:5	0	tol.	90	71	82	10800	12500	1.63
8	100:1:5	0	tol.	150	84	n.d.	12800	n.d.	1.76
9	100:1:5	0	tol.	210	88	93	13400	14100	1.71
10	100:1:5	0	tol.	270	87	n.d.	13200	n.d.	n.d.
11	100:1:5	r.t.	tol.	2	10	n.d.	1700	n.d.	1.12
12	100:1:5	r.t.	tol.	5	18	n.d.	2900	n.d.	1.23
13	100:1:5	r.t.	tol.	8	27	37	4200	5700	1.22
14	100:1:5	r.t.	tol.	15	43	52	6600	8000	1.32
15	100:1:5	r.t.	tol.	30	62	67	9500	10200	1.43
16	100:1:5	r.t.	tol.	45	72	75	11000	11410	1.46
17	100:1:5	r.t.	tol.	60	77	78	11700	11900	1.44
18	100:1:5	r.t.	tol.	90	82	81	12500	12300	1.52
19	100:1:5	r.t.	tol.	150	85	86	12900	13100	1.58
20	100:1:5	r.t.	tol.	240	86	86	13100	13100	n.d.
21	100:1:5	r.t.	tol.	270	86	n.d.	13100	n.d.	1.60
22	100:1:5	-20	tol.	2	4	n.d.	800	n.d.	1.05
23	100:1:5	-20	tol.	5	6	n.d	1100	n.d	1.08
24	100:1:5	-20	tol.	8	9	n.d.	1500	n.d.	1.09
25	100:1:5	-20	tol.	15	13	n.d.	2100	n.d.	1.12
26	100:1:5	-20	tol.	30	23	n.d.	3600	n.d.	1.19
27	100:1:5	-20	tol.	45	31	34	4800	5300	n.d.

28	100:1:5	-20	tol.	60	38	53	5900	8100	1.29
29	100:1:5	-20	tol.	90	49	n.d.	7500	n.d.	1.37
30	100:1:5	-20	tol.	150	65	67	9900	10200	1.60
31	100:1:5	-20	tol.	240	79	79	12000	12000	1.65
32	100:1:5	-20	tol.	330	85	n.d.	12900	n.d.	1.75
33	100:1:5	-20	tol.	390	89	n.d.	13500	n.d.	1.83
34	100:1:5	-20	tol.	510	92	n.d.	14000	n.d.	1.81
35	100:1:5	-20	tol.	570	93	n.d.	14100	n.d.	1.89

Conv.[a]: monomer conversions were obtained from ^{31}P NMR spectra on aliquots taken from the polymerization mixtures. M_n[a] was calculated from the monomer conversion obtained by ^{31}P NMR spectroscopy. M_n[b] was calculated from the monomer to initiator ratio based on 1H NMR of the purified aliquots. Đ[c] was measured by SEC calibrated using PEG standards.

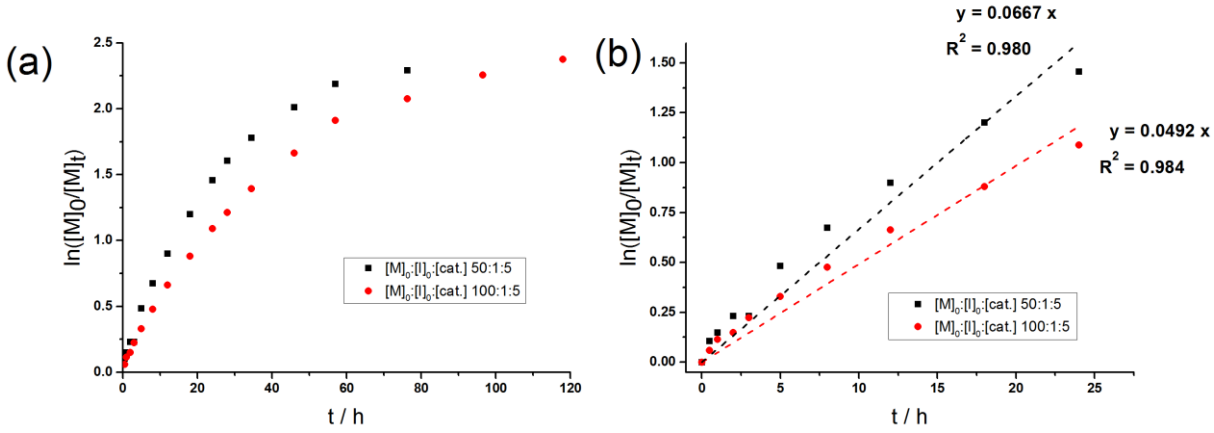


Figure S21. (a) Kinetic plots of ($\ln([M]_0/[M]_t)$) *vs* time obtained from ^{31}P NMR spectra for the polymerization of M1 with TU/DBU as catalyst system with different ratios of $[M]_0/[I]_0/[cat.]$ (data listed in Table S3). (b) Linear fit of the conversion ($\ln([M]_0/[M]_t)$) *vs* time.

Table S3. Kinetic data for the polymerization of M1 by organocatalytic ROP using 2-(benzyloxy)ethanol as initiator and a DBU/TU as a catalyst with different ratios of $[M]_0/[I]_0/[cat.]$. Polymerizations were conducted at a monomer concentration of 2 mol L^{-1}.

#	$[M]_0$:$[I]_0$:[cat.]	T / °C	solvent	Time / h	Conv. [a] / %	n	M_n[a] / gmol^{-1}	M_n[b] / gmol^{-1}	Đ[c]
1	50:1:5	0	tol.	0.5	10	n.d.	900	n.d.	n.d.
2	50:1:5	0	tol.	1	14	n.d.	1200	n.d.	1.05
3	50:1:5	0	tol.	2	21	23	1800	3600	1.14
4	50:1:5	0	tol.	5	38	23	3000	3600	1.23
5	50:1:5	0	tol.	8	49	27	3900	4200	1.28
6	50:1:5	0	tol.	12	59	n.d.	4700	n.d.	1.35
7	50:1:5	0	tol.	18	70	n.d.	5400	n.d.	1.39
8	50:1:5	0	tol.	24	77	n.d.	6000	n.d.	1.45
9	50:1:5	0	tol.	28	80	39	6200	6000	1.45
10	50:1:5	0	tol.	34.5	83	n.d.	6500	n.d.	1.48
11	50:1:5	0	tol.	46	87	n.d.	6600	n.d.	1.48
12	50:1:5	0	tol.	57	89	n.d.	6900	n.d.	n.d.
13	50:1:5	0	tol.	76.25	90	n.d.	6900	n.d.	n.d.
14	100:1:5	0	tol.	0.5	6	n.d.	1100	n.d.	n.d.
15	100:1:5	0	tol.	1	11	n.d.	1800	n.d.	n.d.
16	100:1:5	0	tol.	2	14	n.d.	2300	n.d.	1.14
17	100:1:5	0	tol.	3	20	31	3200	4800	1.18

18	100:1:5	0	tol.	5	28	n.d.	4400	n.d.	1.29
19	100:1:5	0	tol.	8	38	n.d.	5900	n.d.	1.32
20	100:1:5	0	tol.	12	48	43	7400	6600	1.36
21	100:1:5	0	tol.	18	59	60	9000	9200	1.34
22	100:1:5	0	tol.	24	66	n.d.	10100	n.d.	1.45
23	100:1:5	0	tol.	28	70	n.d.	10700	n.d.	1.46
24	100:1:5	0	tol.	34.5	75	n.d.	11400	n.d.	1.50
25	100:1:5	0	tol.	46	81	80	12300	12200	1.55
26	100:1:5	0	tol.	57	85	n.d.	12900	n.d.	n.d.
27	100:1:5	0	tol.	76.25	87	n.d.	13200	n.d.	1.69
28	100:1:5	0	tol.	96.5	90	n.d.	13700	n.d.	1.67
29	100:1:5	0	tol.	118	91	n.d.	13800	n.d.	1.64

Conv.[a]: monomer conversions were obtained from ^{31}P NMR spectra on aliquots taken from the polymerization mixtures. M_n[a] was calculated from the monomer conversion obtained by ^{31}P NMR spectroscopy. M_n[b] was calculated from the monomer to initiator ratio based on ^{1}H NMR of the purified aliquots. Đ[c] was measured by SEC calibrated using PEG standards.

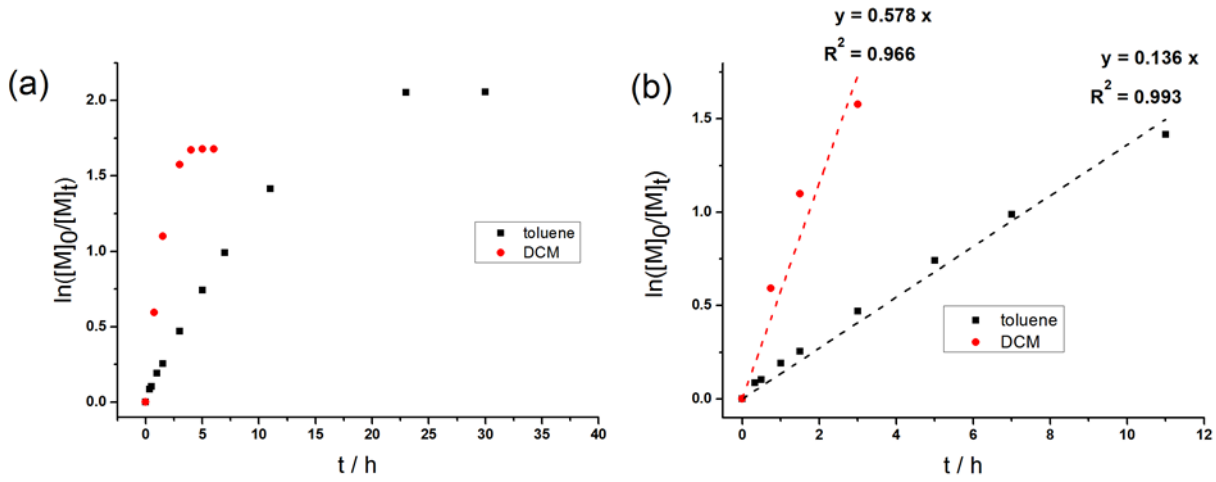


Figure S22. Kinetic plots of ($\ln([M]_0/[M]_t)$) *vs* time obtained from ^{31}P NMR spectra for the polymerization of M1 with Tris-Urea/DBU as catalyst system with different in different solvents (data listed in Table S4). (B) Linear fit of the conversion ($\ln([M]_0/[M]_t)$) *vs* time.

Table S4. Kinetic data for the polymerization of M1 by organo catalytic ROP using 2-(benzyloxy)ethanol as initiator and a DBU/TU as a catalyst with different ratios of $[M]_0/[I]_0/[cat.]$

#	$[M]_0/[I]_0/[cat.]$	T / °C	solvent	Time / h	Conv. [a] / %	n	M_n[a]/ gmol^{-1}	M_n[b]/ gmol^{-1}	Đ[c]
1	100:1:2	0	tol	0.33	8	n.d.	1400	n.d.	n.d.
2	100:1:2	0	tol	0.5	10	n.d.	1700	n.d.	n.d.
3	100:1:2	0	tol	1	17	n.d.	2700	n.d.	n.d.
4	100:1:2	0	tol	1.5	22	n.d.	3500	n.d.	n.d.
5	100:1:2	0	tol	3	38	44	5900	6800	n.d.
6	100:1:2	0	tol	5	52	58	8000	8900	n.d.
7	100:1:2	0	tol	7	63	69	9600	10500	1.36
8	100:1:2	0	tol	11	76	79	11600	12000	1.33
9	100:1:2	0	tol	23	87	87	13200	13200	1.40
10	100:1:2	0	tol	30	87	n.d.	13200	n.d.	1.40
11	100:1:2	0	DCM	0.75	45	52	6900	8000	1.26
12	100:1:2	0	DCM	1.5	67	71	10200	10810	1.46
13	100:1:2	0	DCM	3	79	77	12000	11700	1.53
14	100:1:2	0	DCM	4	81	78	12300	11900	1.53
15	100:1:2	0	DCM	5	81	n.d.	12300	n.d.	1.38
16	100:1:2	0	DCM	6	81	81	12300	12300	1.44

17	170:1:2	0	tol.	14.5	63	n.d.	9600	n.d.	n.d.
18	170:1:2	0	tol.	20	73	147	18800	22200	n.d.
19	170:1:2	0	tol.	26.5	82	150	21200	22700	n.d.
20	170:1:2	0	tol.	38.5	88	166	22700	25100	1.56

Conv.[a]: monomer conversions were obtained from ^{31}P NMR spectra on aliquots taken from the polymerization mixtures. M_n[a] was calculated from the monomer conversion obtained by ^{31}P NMR spectroscopy. M_n[b] was calculated from the monomer to initiator ratio based on ^{1}H NMR of the purified aliquots. Đ[c] was measured by SEC calibrated using PEG standards.

7. Kinetic studies for the polymerization of M2

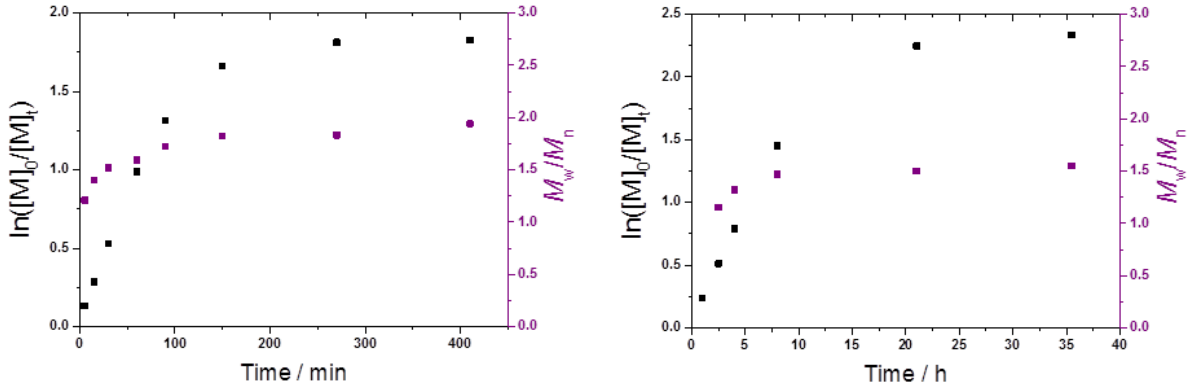


Figure 23. Plots of monomer conversion ($\ln([M]_0/[M]_t)$) *vs* time obtained from ^{31}P NMR spectra for the polymerization of M2 with TBD (A) and DBU/Tris-Urea (B). The ratio of monomer : initiator : catalyst was 100 : 1 : 5 for (A) and 100 : 1 : 4 for (B).

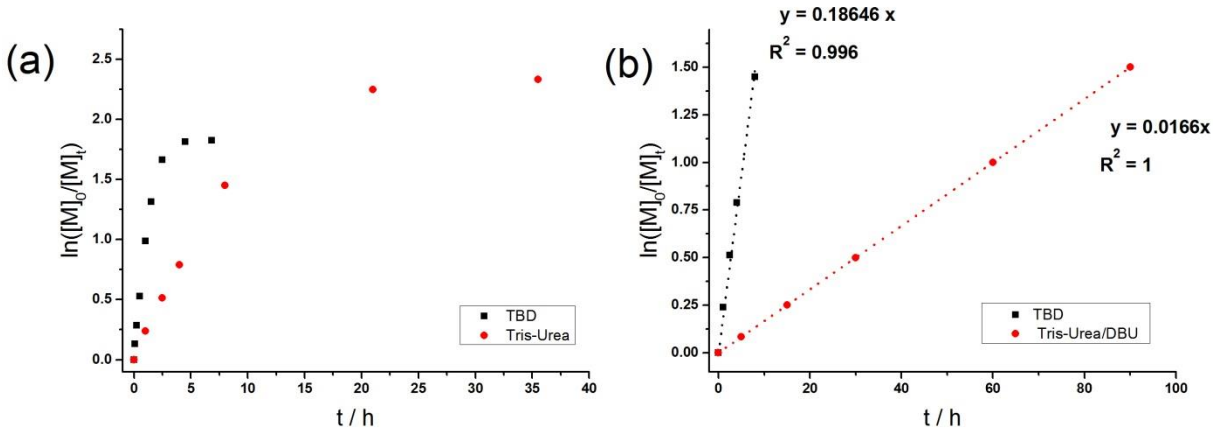


Figure S24. Kinetic plots of ($\ln([M]_0/[M]_t)$) *vs* time obtained from ^{31}P NMR spectra for the polymerization of M2 with Tris-Urea/DBU and TBD as a catalyst. The ratio of monomer : initiator : catalyst was 100 : 1 : 5 for the polymerization with TBD and 100:1:4 for the polymerization with Tris-Urea/DBU (data listed in Table S5). (b) Linear fit of the conversion ($\ln([M]_0/[M]_t)$) *vs* time.

Table S5. Kinetic data for the polymerization of M2 by organo catalytic ROP using 2-(benzyloxy)ethanol as initiator.

#	**cat**	$[M]_0$:$[I]_0$:[cat]	T / °C	solvent	Time / h	Conv.[a] / %	n	M_n[a] /gmol^{-1}	M_n[b]/ gmol^{-1}	Đ[c]
1	TrisU/DBU	100:1:4	0	tol.	1	21	n.d.	3900	n.d.	n.d.
2	TrisU/DBU	100:1:4	0	tol.	2,5	40	n.d.	7300	n.d.	1.15
3	TrisU/DBU	100:1:4	0	tol.	4	55	n.d.	10000	n.d.	1.32
4	TrisU/DBU	100:1:4	0	tol.	8	77	n.d.	13900	n.d.	1.47
5	TrisU/DBU	100:1:4	0	tol.	21	90	94	16200	16900	1.50
6	TBD	100:1:5	0	DCM	0.08	12	n.d.	2300	n.d.	1.21
7	TBD	100:1:5	0	DCM	0.25	25	n.d.	4600	n.d.	1.40
8	TBD	100:1:5	0	DCM	0.5	41	48	7500	8700	1.52
9	TBD	100:1:5	0	DCM	1	63	60	11400	10800	1.59
10	TBD	100:1:5	0	DCM	1.5	73	68	13200	12300	1.82
11	TBD	100:1:5	0	DCM	2.5	84	86	15100	15500	1.83
12	TBD	100:1:5	0	DCM	6.8	84	86	15100	15500	1.94

Conv.[a]: monomer conversions were obtained from ^{31}P NMR spectra on aliquots taken from the polymerization mixtures. M_n[a] was calculated from the monomer conversion obtained by ^{31}P NMR spectroscopy. M_n[b] was calculated from the monomer to initiator ratio based on ^{1}H NMR of the purified aliquots. Đ[c] was measured by SEC calibrated using PEG standards.

8. Degradation studies

Degradation studies were conducted in an NMR tube and followed by ^{1}H and ^{31}P NMR spectroscopy. For the degradation at pH 12, a 0.01 M KOH solution was prepared with 10% D_2O. For the degradation at pH 1, a 0.1M HCl solution was prepared containing 10% D_2O. For the degradation at pH 10 a

Degradation of P(1) at pH 1

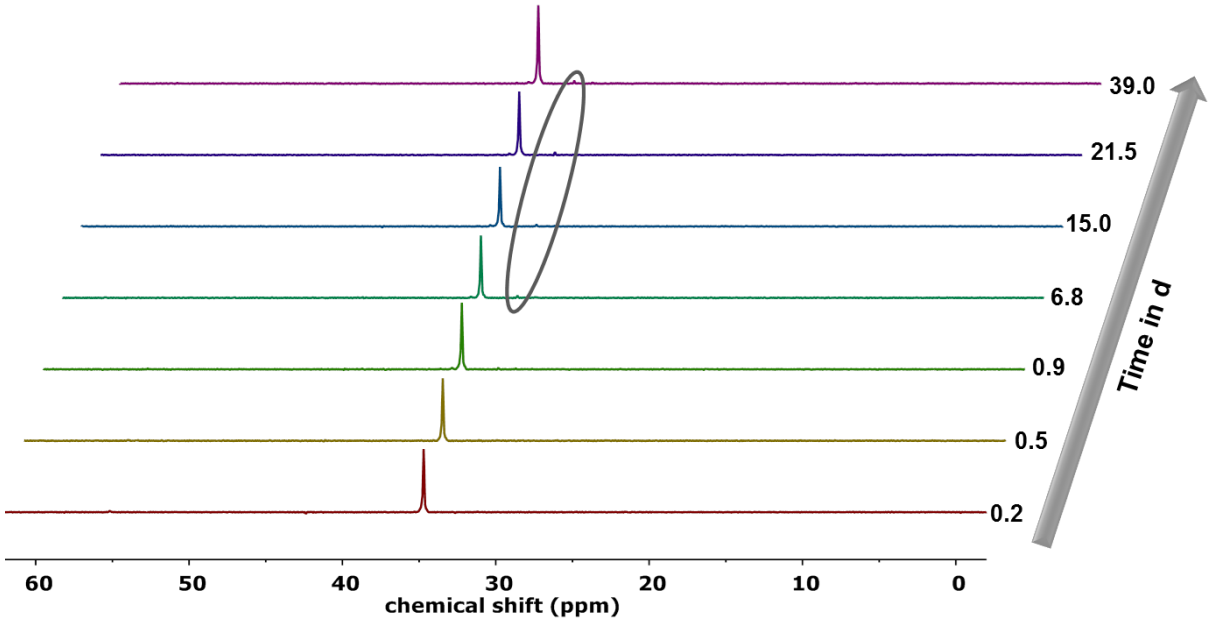


Figure S25. ^{31}P NMR spectra (H_2O/ D2O (9:1), 121 MHz, 298K) of the degradation of P(1)-4 at pH 1 at different time points. After 6 days the evolution of a signal at 32.36 ppm indicates starting degradation.

Degradation of P(1) at pH 12

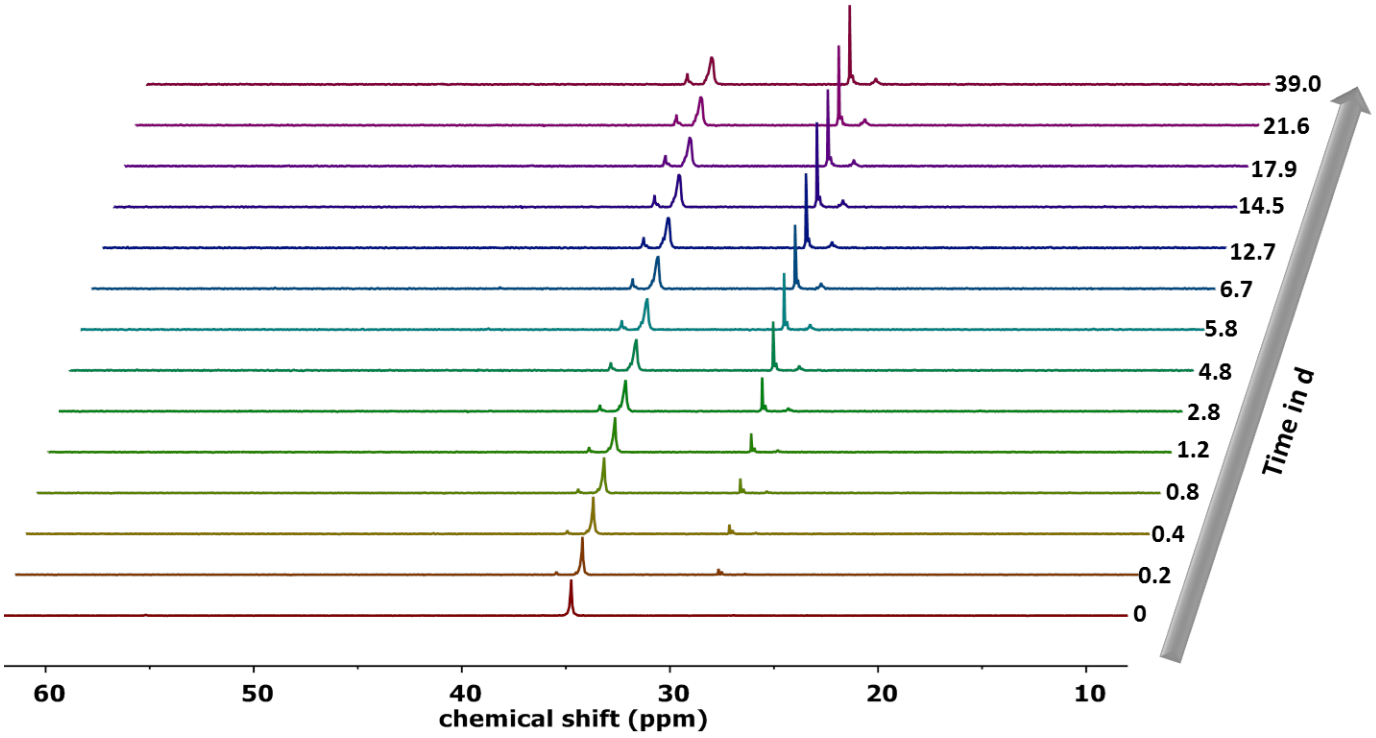


Figure 26. Overlay of the ^{31}P NMR spectra (H_2O/ D2O (9:1), 121 MHz, 298K) during the degradation of P(1)-4 at pH 12 at different time points.

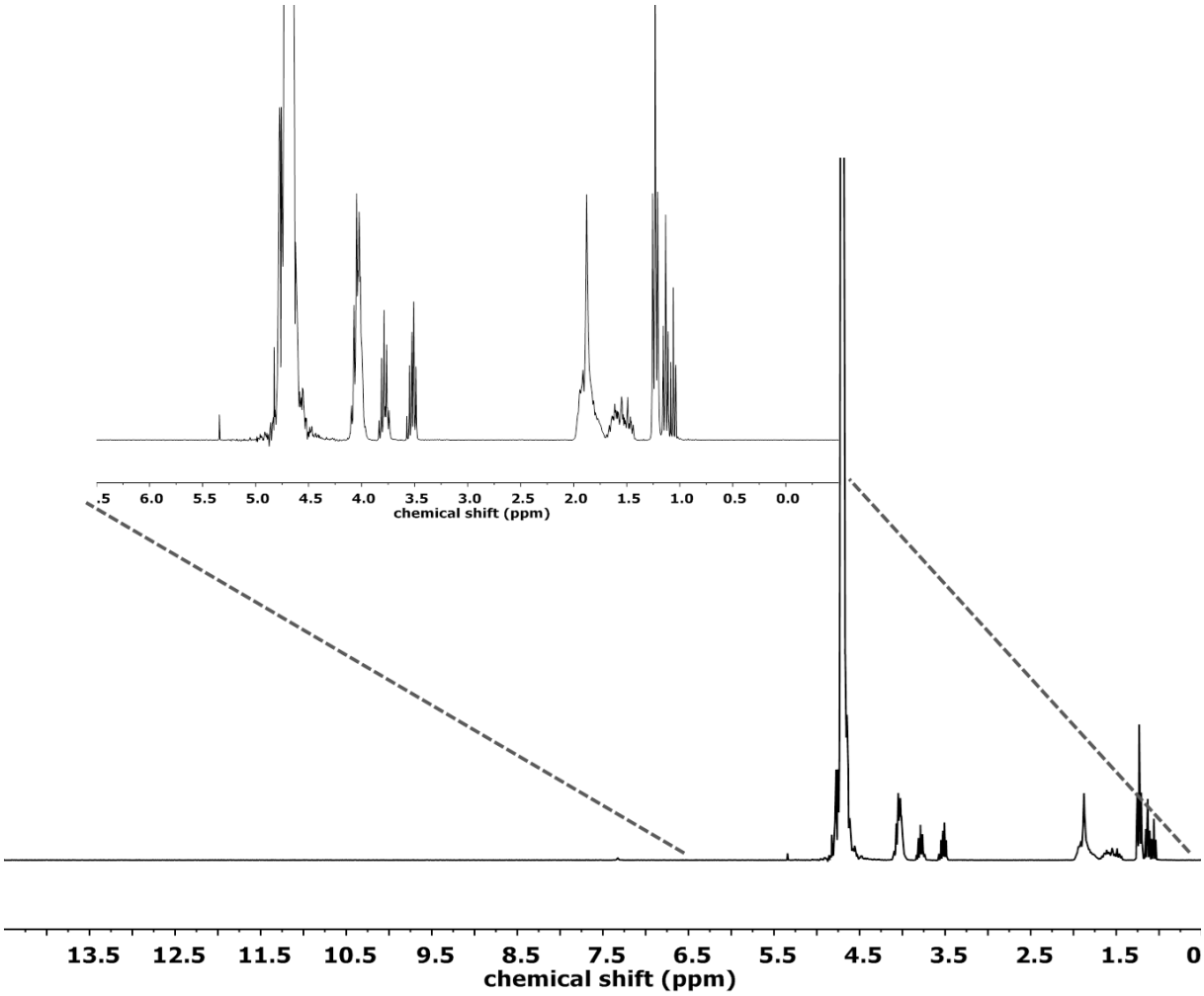


Figure S27. ^{1}H NMR spectrum (300MHz) of the degradation of P(1)-4 after 39 days in D_2O at 298K.

Degradation of P(3) at pH 10

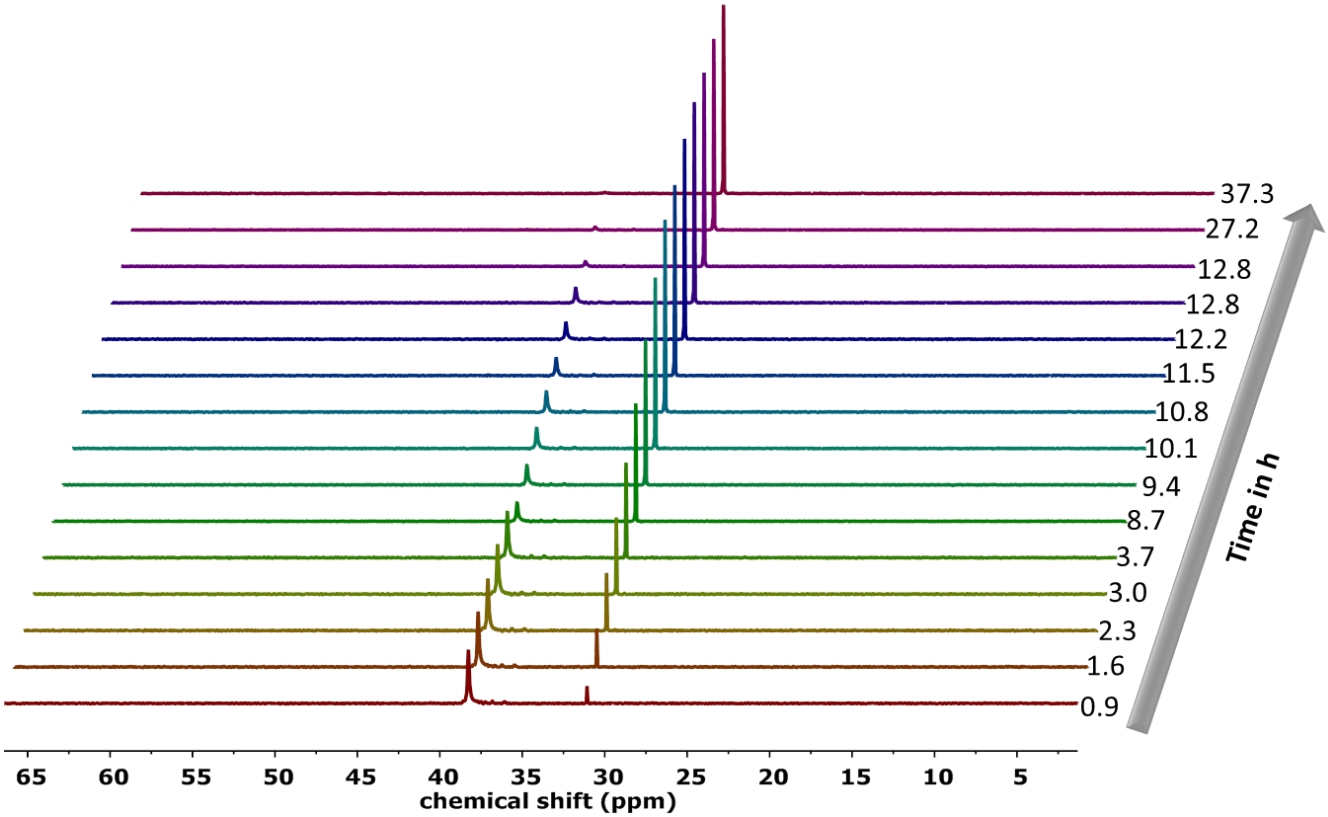


Figure S28. ^{31}P NMR spectra (H_2O/ D2O (9:1), 121 MHz 298K) of the degradation of polymer P(3) at pH 10

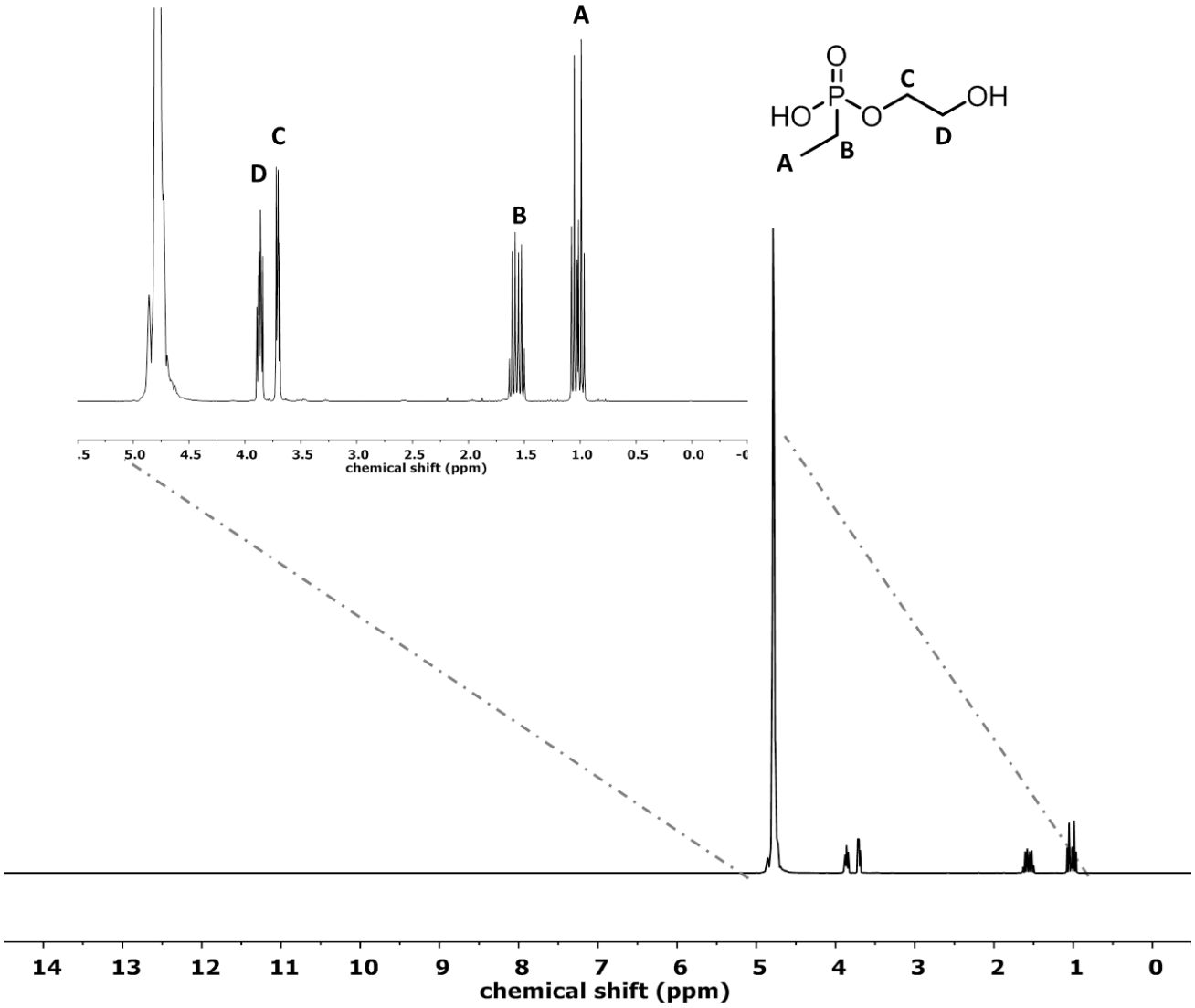


Figure S29. ^{1}H NMR spectrum (300MHz) of the final breakdown product of P(3) at pH 10 in D_2O at 298K

9. Monomer stability in D_2O

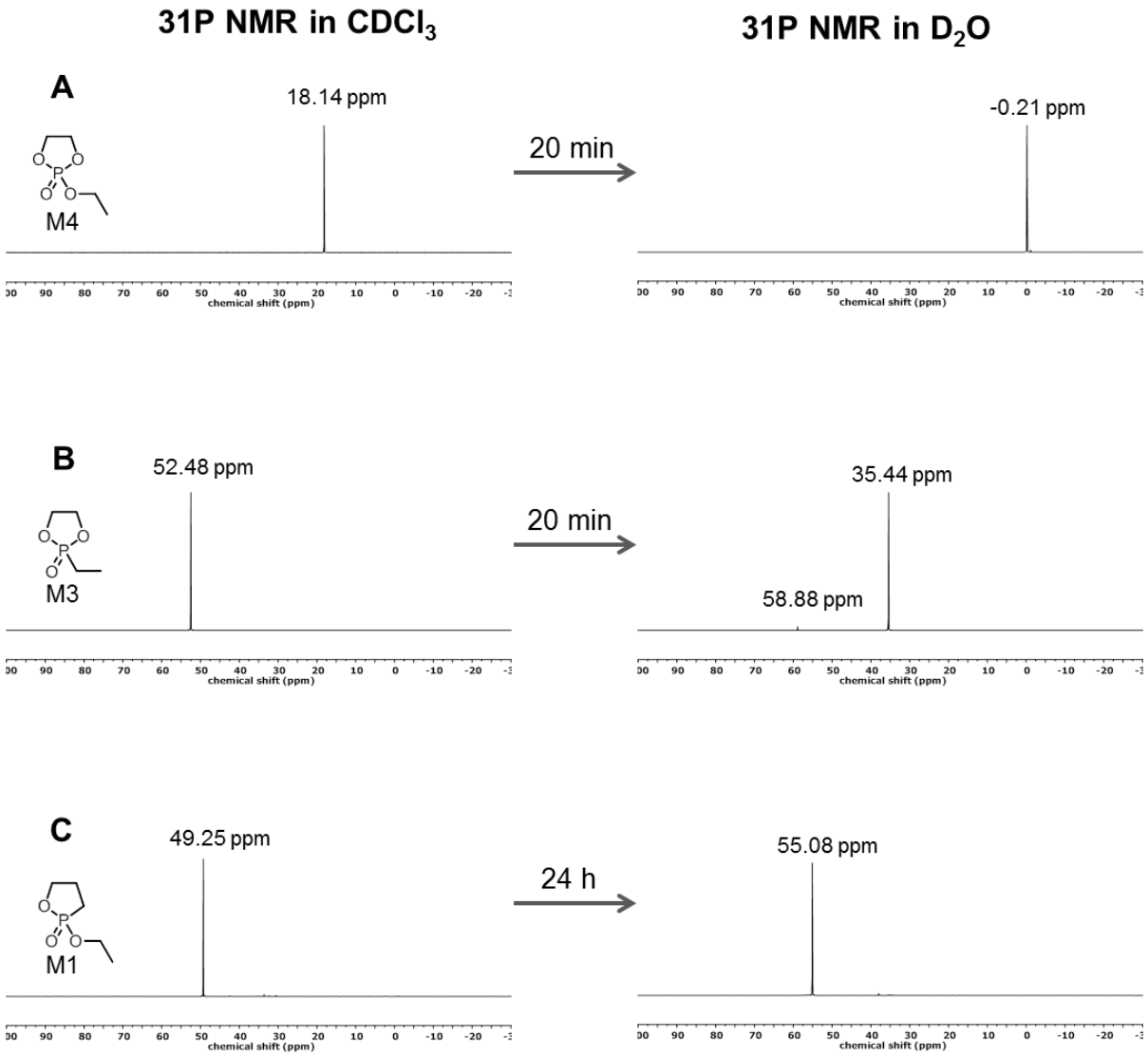


Figure S30: ^{31}P NMRs M4 (A), M3 (B), M1(C) in $CDCl_3$ and D_2O MHz

10. References

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3. A.Y. Garner, Phosphonic acid phostones. U.S. Patent 2,953,591, 1960.