Supporting Information

for

Surface-attached poly(phosphoester)-hydrogels with benzophenone groups

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Materials. All reagents were used without further purification unless otherwise stated. Solvents, dry solvents (over molecular sieves) and deuterated solvents were purchased from Acros Organics, Sigma-Aldrich, Deutero GmbH or Fluka. Furfuryl alcohol, 2-chloro-2-oxo-1,3,2-dioxaphospholane, pyridine, 1-pentanol, 4-hydroxybenzophenone, triethylamine, 3-buten-1-ol, potassium carbonate, 2-bromoethanol, 2-(benzyloxy)ethanol, 2-ethyl-1-butanol, sodium hydride, 1,8-diazabicyclo[5.4.0]undec-7-ene, bromoacetate, hexamethyldisiloxane (HDMSO), triethoxysilane, platinum on activated charcoal (10wt%), trimethox(propyl)silane, (3-aminopropyl)triethoxysilane, allyl bromide, 1-propanethiol, cysteamine, pentaerythritol tetrakis(3-mercaptopropionate), dodecyl mercaptan, dodecyl amine, maleic anhydride, sodium acetate, and 2,2′-azobis(2-methylpropionitrile) were purchased from Sigma-Aldrich. $MgSO_4$ was purchased from Fisher Scientific. 3,5-bis(trifluoromethyl)phenylisothiocyanate was purchased from Alfa Aesar GmbH & Co KG. Lithium aluminum hydride (2.4 M in THF) and cyclohexylamine were purchased from Acros Organics. 3-Butenyltriethoxysilane was purchased from Gelest Inc., USA. 3-(benzyloxy)ethanol, 1-pentanol, 2-ethyl-1-butanol, triethylamine and 3-buten-1-ol was dried with NaH prior to use, distilled, and stored over molecular sieves.

1,8-diazabicyclo[5.4.0]undec-7-ene was distilled prior to use, and stored over molecular sieve at 4 °C. The silicon wafer substrates used were single or double side polished (for FT-IR measurements), with [100] orientation, 1.5x1.5 cm in size, and about 700 µm thickness, purchased from Si-Mat, Kaufering, Germany.

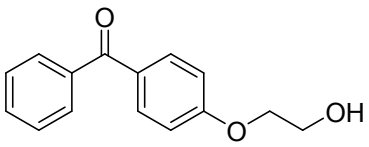
Instrumentation and Characterization Techniques. Size exclusion chromatography (SEC) measurements were performed in DMF (containing 0.25 g/L of lithium bromide as an additive) on an Agilent 1100 Series as an integrated instrument, including a PSS GRAM columns (1000/1000/100 g), a UV detector (270 nm), and a RI detector at a flow rate of 1 mL/min at 60 °C. Calibration was carried out using PEO standards provided by Polymer Standards Service. For nuclear magnetic resonance analysis ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AVANCE III 300, 500, 700 or 850 MHz spectrometer. All spectra were measured in either d_6-DMSO, $CDCl_3$ or d_2-DCM at 298 K. The spectra were calibrated against the solvent signal and analyzed using MestReNova 8 from Mestrelab Research S.L. DOSY spectra were analyzed with TOPSPIN 3.2 software. For the quantitative ^{31}P-NMR experiments for copolymerization studies a 5 mm triple resonance TXI ^{1}H/^{13}C/^{15}N probe equipped with a z-gradient on the 850 MHz Bruker AVANCE III system was used. The ^{31}P NMR (334 MHz) measurements were obtained with inverse gated decoupling,[24] which allows the integration of the ^{31}P-NMR signals. The used relaxation delay was fixed at 10 s with a scan number of 32 and a 90° flip angle of 27 µs and a spectral width of 34000Hz (100ppm). For the control ^{1}H NMR measurements one transient was used with a 90° pulse of 10.8 µs, a spectral width of 17000 Hz (20 ppm) and a recycling delay of 5 s. The temperature was kept at 253, 263 or 273 K and regulated by a standard ^{1}H methanol NMR sample using the topspin 3.1 software (Bruker). The control of the temperature was realized with a VTU (variable temperature unit) and an accuracy of +/- 0.1 K. 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 a N_2 atmosphere (30 mL/min) with a heating and cooling rate of 10 °C/min. The used spin-coater was a SPIN150-NPP (SPS-Europe, Netherlands) or a Delta 80 BM Lackschleuder (Süss MicroTech, Germany) The UV irradiation unit was a BIO-LINK-Box (Vilber Lourmat GmbH, Germany) or a UV-Stratalinker 2400 (Stratagene®, California), each with 254 nm light bulbs. The thickness of the dry PPE layers on silicon wafers was measured by ellipsometry with an "auto-nulling imaging" ellipsometer Nanofilm EP^3 (Nanofilm Technologie GmbH, Göttingen, Germany), equipped with a 532 nm solid-state laser. A refractive index of 1.4734 for **P2** and 1.4805 for **P4** was used, for other samples the refractive index was set to 1.5. The angle of incidence was varied from 70-80° for silicon and from 64-74° for gold substrates. The average value from 2-3 different positions was taken, and the EP4-model used to fit the data. Static, advancing and receding contact angles of PPE-networks (CA) were measured with the CA system OCA 20 (Dataphysics GmbH, Filderstadt, Germany). The average value was determined from three measurements on three different samples. The water droplet to determine the static CA had a volume of 5 µL; for the dynamic CA measurement, a volume reduction speed of 2 µL/s was used. The static CAs were calculated with the Laplace−Young method, the advancing and receding CAs with the elliptical and the tangent method, respectively. FT-IR spectra of monomers and polymers were recorded using a Thermo Scientific iS10 FT-IR spectrometer equipped with a diamond ATR unit. ATR-FT-IR spectra of PPE-networks were measured on a Bio-Rad Excalibur spectrometer (Bio-Rad, Munich, Germany). PPE-networks on double-sided polished silicon wafers, immobilized on one side, were measured under nitrogen atmosphere. A non-coated silicon wafer was used as background sample. 64 scans were taken for each measurement. The spectra were recorded from 4000 to 400 cm^{-1}. The topography of the surfaces was imaged by atomic force microscopy (AFM) with a Dimension Icon from Bruker. Commercially

available ScanAsyst Air cantilevers (length: 115 µm; width: 25 µm; spring constant: 0.4 N/m; resonance frequency: 70 kHz) were used. All AFM images were recorded in ScanAsyst Mode in air. The obtained images were analyzed and processed with the software 'Nanoscope Analysis 1.5'. For each sample, the root-mean-square (RMS) average roughness from three images of an area of 5 × 5 μm^2 at different positions was taken.

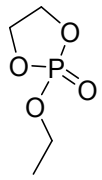
Additional synthetic procedures

4-(2-hydroxyethoxy)benzophenone: The alcohol was synthesized according to literature.[24] 4-Hydroxybenzophenone (15.00 g, 75.7 mmol, 1 eq.) and potassium carbonate (20.92 g, 151.4 mmol, 2 eq.) were suspended in 150 mL acetone and refluxed for 1 h under argon-atmosphere. Bromoethanol (18.91 g, 151.4 mmol, 2 eq.) was added via syringe and the reaction refluxed overnight. The reaction was cooled down to room temperature and water was added. The aqueous phase was extracted with diethyl ether three times and the combined organic phases washed with brine once. The organic phase was concentrated. Column chromatography (silica gel, dichloromethane/ethyl acetate 4:1, R_f=0.67) gave the pure product, colorless crystals. Yield: 7.76 g, 42%. ^{1}H NMR (300 MHz, DMSO-d_6): δ [ppm] 7.78-7.50 (m, 7H, aromat. H), 7.10 (d, 2H, aromat. H), 4.94 (t, 1H, -O*H*), 4.10 (t, 2H, Ar-O-CH_2-CH_2-OH), 3.75 (q, 2H, Ar-O-CH_2-CH_2-OH).



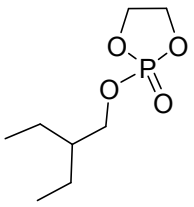
2-ethoxy-2-oxo-1,3,2-dioxaphospholane (EEP, **2***):* The monomer was synthesized according to literature. Briefly, a flame-dried 500mL three-neck flask, equipped with a dropping funnel, was charged with 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP) (50.00 g,

0.35 mol) dissolved in dry THF (100 mL). A solution of dry ethanol (16.17 g, 0.35 mol) and dry triethylamine (35.51 g, 0.35 mol) in dry THF (70 mL) was added dropwise to the stirring solution of COP at -20 °C under argon atmosphere. During the reaction, hydrogen chloride was formed and precipitated as pyridinium hydrochloride. The reaction was stirred at 4 °C overnight. The salt was removed by filtration and the filtrate concentrated in vacuo. The residue was purified by distillation under reduced pressure to give a fraction at 105-110 °C/0.095 mbar, obtaining the clear, colorless, liquid product EEP. Yield: 34.60 g (0.23 mol), 65%. ^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] 4.47-4.34 (m, 4H, O-C*H*$_2$-C*H*$_2$-O), 4.11-4.04 (m, 2H, O-C*H*$_2$-CH$_3$), 1.25 (t, 3H, O-CH$_2$-C*H*$_3$). ^{13}C{H} NMR (126 MHz, DMSO-d_6): δ [ppm] 66.35 (-O-*C*H$_2$-*C*H$_2$-O-), 64.18 (-O-*C*H$_2$-CH$_3$), 15.96 (-O-CH$_2$-*C*H$_3$). ^{31}P{H} NMR (202 MHz, DMSO-d_6): δ [ppm] 16.83. FTIR (cm^{-1}): 2985 (-CH$_2$- and –CH$_3$ stretching), 2915 (-CH$_2$- and –CH$_3$ stretching), 1477 (O-CH$_2$- deformation), 1445, 1393, 1369 (-CH$_3$ deformation), 1282 (P=O stretching), 1225, 1166 (-CH$_3$ rocking), 1101, 1056, 1016 (P-O-C stretching), 980 (P-O-C stretching), 926, 831 (P-O-C stretching), 752 (-CH$_2$- rocking).



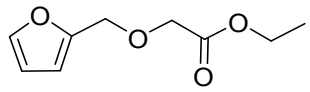
2-(2-ethyl butoxy)-2-oxo-1,3,2-dioxaphospholane (EBP, **4***):* The monomer was synthesized according to a modified literature protocol[27]. Briefly, a flame-dried 500mL three-neck flask, equipped with a dropping funnel, was charged with a solution of dry 2-ethyl-1-butanol (11.60 g, 0.11 mol, 1.1eq.) and dry triethylamine (11.48 g, 0.11 mol, 1.1eq.) in dry THF (100 mL). 2-chloro-2-oxo-1,3,2-dioxaphospholane (14.70 g, 0.10 mol, 1eq.) dissolved in dry THF (50 mL) was added dropwise to the stirring solution at 0 °C under argon atmosphere. During the reaction, hydrogen chloride was formed and precipitated as triethylammonium

hydrochloride. The reaction was stirred at 0 °C for 4h and stored in the freezer overnight. The salt was removed by filtration with a Schlenk-frit and the filtrate concentrated in vacuo. The residue was purified by distillation under reduced pressure to give a fraction at 130 °C/1 mbar, obtaining the clear, colorless, liquid product EBP. Yield: 11.70 g, 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 4.43-4.25 (m, 4H, O-C*H*$_2$-C*H*$_2$-O), 4.02-3.97 (m, 2H, (CH_3-CH_2)$_2$-CH-C*H*$_2$-O-), 1.52-1.41 (m, 1H, (CH_3-CH_2)$_2$-C*H*-CH_2-O-), 1.37-1.27 (quintett, 4H, (CH_3-C*H*$_2$)$_2$-CH-CH_2-O-), 0.84 (t, 6H, (C*H*$_3$-CH_2)$_2$-CH-CH_2-O-). ^{13}C{H} NMR (76 MHz, $CDCl_3$): δ [ppm] 70.80 ((CH_3-CH_2)$_2$-CH-*C*H_2-O-), 65.99 (-O-*C*H_2-*C*H_2-O-), 41.60 ((CH_3-CH_2)$_2$-*C*H-CH_2-O-), 22.69 ((CH_3-*C*H_2)$_2$-CH-CH_2-O-), 10.86 ((*C*H_3-CH_2)$_2$-CH-CH_2-O-). ^{31}P{H} NMR (202 MHz, $CDCl_3$): δ [ppm] 17.63. FTIR (cm^{-1}): 2963 (-CH_2- and –CH_3 stretching), 2934 (-CH_2- and –CH_3 stretching), 2877 (-CH_2- and –CH_3 stretching), 1463 (O-CH_2- deformation), 1385, 1367 (-CH_3 deformation), 1285 (P=O stretching), 1225, 1151 (-CH_3 rocking), 1103, 1016 (P-O-C stretching), 975 (P-O-C stretching), 928, 836 (P-O-C stretching), 774 (-CH_2- rocking).

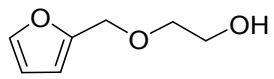


Ethyl-2-(furan-2-ylmethoxy)acetate: The acetate was synthesized according to literature.[33] Briefly, furfuryl alcohol (25.00 g, 254.8 mmol, 1 eq.) was dissolved in 200 mL dry THF in a flame-dried round-bottom flask under argon atmosphere. Sodium hydride (7.34 g, 305.8 mmol, 1.2 eq.) was added and the reaction was refluxed for 1 h. Bromoacetate (46.81 g, 280.3 mmol, 1.1 eq.) was added and refluxed overnight. Then, water was slowly added. The aqueous phase was extracted with ethyl acetate twice and the organic phase with brine once. The organic phase was dried over $MgSO_4$ and concentrated. Column chromatography (silica gel, dichloromethane/ethyl acetate 98:2, R_f=0.94) gave the pure product. Yield: 75%. ^{1}H

NMR (300 MHz, $CDCl_3$): δ [ppm] 7.42 (s, 1H, -O-C*H*=CH-), 6.36 (m, 2H, -O-CH=C*H*-C*H*=), 4.54 (s, 2H, O-C(=CH)-CH_2-O-), 4.21 (q, 2H, -O-CH_2-CH_3), 4.08 (t, 2H, -O-CH_2-C(=O)-O-), 1.28 (t, 3H, -CH_3).

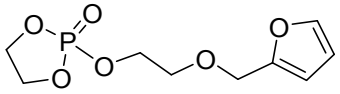


2-(furan-2-ylmethoxy)ethan-1-ol: The alcohol was synthesized according to literature.[33] Briefly, lithium aluminum hydride (2.4 M in THF, 47.79 mL, 114.7 mmol, 0.6 eq.) was dissolved in 100L dry diethyl ether in a flame-dried 3-necked round-bottom flask. Ethyl 2-(furan-2-ylmethoxy)acetate (35.21 g, 191.2 mmol, 1 eq.) in 50 mL dry diethyl ether was added dropwise in the way that the reaction gently refluxed. It was stirred overnight at room temperature and then water was slowly added. The aqueous phase was extracted with diethyl ether twice and the organic phase with brine once. The organic phase was dried over $MgSO_4$ and concentrated. Column chromatography (silica gel, dichloromethane/acetone 19:1, R_f=0.42) gave the pure product. Yield: 36%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.40 (s, 1H, -O-C*H*=CH-), 6.32 (m, 2H, -O-CH=C*H*-C*H*=), 4.49 (s, 2H, O-C(=CH)-CH_2-O-), 3.73 (m, 2H, .O-CH_2-CH_2-OH), 3.59 (m, 2H, .O-CH_2-CH_2-OH), 2.31 (s, 1H, -O*H*).



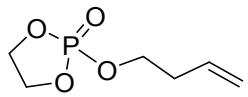
2-(2-(furan-2-ylmethoxy)ethoxy)-2-oxo-1,3,2-dioxaphospholane (FEP, **5***):* 2-(furan-2-ylmethoxy)ethan-1-ol (5.00 g, 35.3 mmol, 1 eq.) was dissolved in 100 mL dry THF in a flame-dried 3-necked round-bottom flask. Dry pyridine (2.78 g, 35.2 mmol, 1 eq.) was added and the mixture was cooled to 0°C. 2-chloro-2-oxo-1,3,2-dioxaphospholane (7.52 g, 52.8 mmol, 1.5 eq.) in 35 mL dry THF was added over a period of 1h, stirred for 4 h and kept at -20°C for additional 8h. During the reaction, hydrogen chloride was formed and precipitated as pyridinium hydrochloride. The ice-cold reaction mixture was then filtered

under inert-gas atmosphere and concentrated under reduced pressure. Column chromatography with an RP-1 column (silica gel deactivated with 5v% hexamethyldisiloxane, dichloromethane/ethyl acetate 1:3, R_f=0.77) afforded 4.09 g (47%) of the pure product FEP as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] 7.37 (s, 1H, -O-C*H*=CH-), 6.35 (m, 2H, -O-CH=C*H*-C*H*=), 4.52 (s, 2H, O-C(=CH)-C*H*$_2$-O-), 4.43-4.23 (m, 6H, -O-CH$_2$-C*H*$_2$-O-P(-O-)-O-C*H*$_2$-C*H*$_2$-), 3.72-3.68 (s, 2H, -O-C*H*$_2$-CH$_2$-O-P(-O-)-O-). ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ [ppm] 151.36 (O-*C*(=CH)-CH$_2$-O-), 143.21 (-O-*C*H=CH-), 110.46 (-O-CH=CH-*C*H=), 109.67 (-O-CH=*C*H-CH=), 68.18 (O-C(=CH)-*C*H$_2$-O-), 67.02 (-O-*C*H$_2$-CH$_2$-O-P(-O-)-O-), 66.40 (-O-P(-O-)-O-*C*H$_2$-*C*H$_2$-), 63.88 (-O-CH$_2$-*C*H$_2$-O-P(-O-)-O-). ^{31}P{H} NMR (202 MHz, $CDCl_3$): δ [ppm] 17.75. FTIR (cm^{-1}): 3119 (–CH= stretching), 3034 (–CH= stretching), 2956 (-CH$_2$- stretching), 2914 (-CH$_2$- stretching), 2868 (-CH$_2$- stretching), 1503 (C=C stretching), 1479 (O-CH$_2$- deformation), 1356, 1285 (P=O stretching), 1225, 1150 (=CH- stretching), 1103, 1063, 1023 (P-O-C stretching), 987 (P-O-C stretching), 927, 884, 866, 838 (O-CH$_2$- stretching), 749 (-CH$_2$- rocking), 684 (C-H deformation).



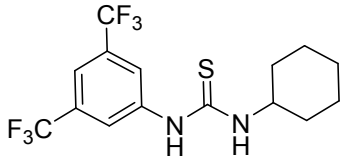
2-(but-3-en-1-yloxy)-2-oxo-1,3,2-dioxaphospholane (BuEP, **6***)*[23]*:* The monomer was synthesized according to a modified literature protocol for EEP[34]. Briefly, a flame-dried 500mL three-neck flask, equipped with a dropping funnel, was charged with a solution of dry 3-buten-1-ol (10.12 g, 0.14 mol, 1eq.) and dry triethylamine (14.21 g, 0.14 mol, 1eq.) in dry THF (100 mL). 2-chloro-2-oxo-1,3,2-dioxaphospholane (20.00 g, 0.14 mol, 1eq.) dissolved in dry THF (50 mL) was added dropwise to the stirring solution at 0 °C under argon atmosphere. During reaction, hydrogen chloride was formed and precipitated as triethylammonium hydrochloride. The reaction was stirred at 0 °C for 4h and stored in the freezer overnight. The salt was removed by filtration with a Schlenk-frit and the filtrate concentrated in vacuo. The

residue was purified by distillation under reduced pressure to give a fraction at 85-91 °C/0.048-0.071 mbar, obtaining the clear, colorless, liquid product BuEP. Yield: 20.33 g, 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 5.85-5.68 (m, 1H, CH_2=C*H*-CH_2-CH_2-O-), 5.20-5.04 (m, 2H, C*H*$_2$=CH-CH_2-CH_2-O-), 4.50-4.27 (m, 4H, O-C*H*$_2$-C*H*$_2$-O), 4.22-4.09 (m, 2H, CH_2=CH-CH_2-C*H*$_2$-O-), 2.50-2.36 (q, 2H, CH_2=CH-C*H*$_2$-CH_2-O-). ^{13}C{H} NMR (76 MHz, $CDCl_3$): δ [ppm] 132.99 (-P-O-CH_2-CH_2-*C*H=CH_2), 117.88 (-P-O-CH_2-CH_2-CH=*C*H$_2$), 67.84 (d, -P-O-*C*H$_2$-CH_2-CH=CH_2), 65.97 (d, -O-*C*H$_2$-*C*H$_2$-O-P), 34.59 (d, -P-O-CH_2-*C*H$_2$-CH=CH_2).^{31}P{H} NMR (121 MHz, $CDCl_3$): δ [ppm] 17.49. FTIR (cm^{-1}): 3080 (-CH=CH_2 stretching), 2982 (-CH_2- and =CH_2 stretching), 2913 (-CH= stretching), 1642 (C=C stretching), 1475 (O-CH_2- deformation), 1433, 1368, 1285 (P=O stretching), 1228, 1154, 1067, 1015 (P-O-C stretching), 994 P-O-C stretching), 925, 832 (P-O-C stretching), 760 (-CH_2- rocking).



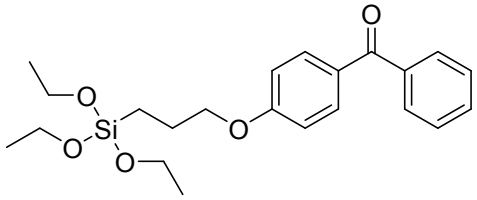
N-cyclohexyl-N'-(3,5-bis(trifluoromethyl)phenyl)thiourea (TU): TU was synthesized according to the method described previously[35]. Briefly, in a flame-dried 50 mL flask 3,5-bis(trifluoromethyl)phenylisothiocyanate (2.00 g, 7.4*10^{-3}mol) was dissolved in 10 mL dry THF under argon atmosphere. Cyclohexylamine (0.73 g, 7.2*10^{-3}mol) was added dropwise at room temperature to the stirring solution. After the reaction mixture was stirred for 5 h, the solvent was removed *in vacuo*. The colorless residue was recrystallized from boiling chloroform. It was filtered hot and cooled down. Colourless needles precipitated in a yellowish solution. The product, TU, was collected by filtration, washed with cold chloroform and dried under reduced pressure. Yield: 1.77g, 370.36 g/mol, 4.8 mmol, 67%. ^{1}H NMR (300 MHz, DMSO-d_6): δ [ppm] 9.84 (s, 1H, Ar-N*H*-C(=S)-NH-Cy), 8.23 (s, 1H, *p*-Ar-NH), 8.17

(s, 2H, *o*-Ar-NH), 7.72 (s, 1H, Ar-NH-C(=S)-N*H*-Cy), 4.11 (s, 1H, Ar-NH-C(=S)-NH-(*H*)Cy), 1.94-1.15 (m, 10H, Ar-NH-C(=S)-NH-*Cy*).



4-(3-triethoxysilyl)propyloxybenzophenone: The benzophenone silane was synthesized according to literature.[36] Briefly, 4-hydroxybenzophenone (5 g, 25.2 mmol, 1 eq.) and potassium carbonate (3.49 g, 25.2 mmol, 1 eq.) were dissolved in about 100 mL acetone and heated to reflux for 1 h. Allyl bromide (3.36 g, 27.8 mmol, 1.1 eq.) was then added to the mixture and refluxed for 18 h. Water was added at room temperature, and extracted with diethyl ether three times. The combined organic phases were washed with 10 wt% NaOH solution, dried over $MgSO_4$, filtered, and concentrated. The product was recrystallized from boiling methanol to yield 4-allyloxybenzophenone as off-white crystals. Yield: 4.40 g, 238.29 g/mol, 18.5 mmol, 73%.

4-allyloxybenzophenone (0.5 g, 2.1 mmol, 1eq.) was dissolved in triethoxysilane (5 mL, 22.2 mmol) at room temperature under inert gas atmosphere. Platinum on activated charcoal (5 mg, 10%) was added to the mixture and stirred at room temperature for 2 d until the reaction was completed (petrol ether/acetone 5:1, product R_f=0.22). The catalyst was removed by filtration and residual triethoxysliane under high vacuum to quantitatively yield the product as off-white solid. The product was used without further purification.



Determination of the reactivity ratios for monomers 1 and 2. The reactivity ratios for the monomer pair **EEP** and **BeEP** was determined exemplarily for **P1** from the real-time ^{1}H NMR copolymerization. The data is listed below:

	EEP (2)	**Initiator**	**BeEP (1)**
m/mg	35.97	0,30	4.12
n/µmol	236.50	1,97	11.83
c (µmol/mL)	394.17	3,29	19.72
c (mol/L)	0.3942	0,0033	0.0197
k_{app}	$1.42 \cdot 10^{-5}$		$4.97 \cdot 10^{-5}$
k_p	0.0043		0.0151
$\mathbf{r_1}$			**3.5**
$\mathbf{r_2}$	**0.3**		

Monomers and Polymers

a. NMR spectra

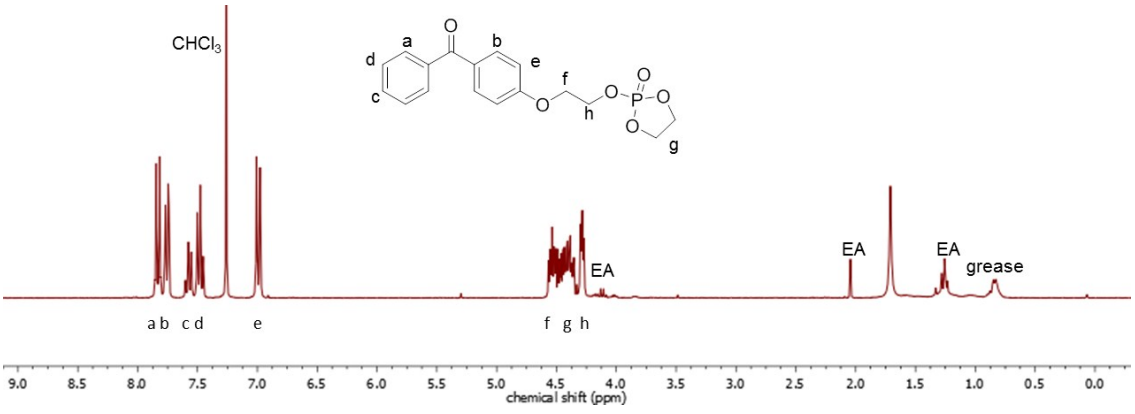


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) of **BeEP** (**1**) at 298 K.

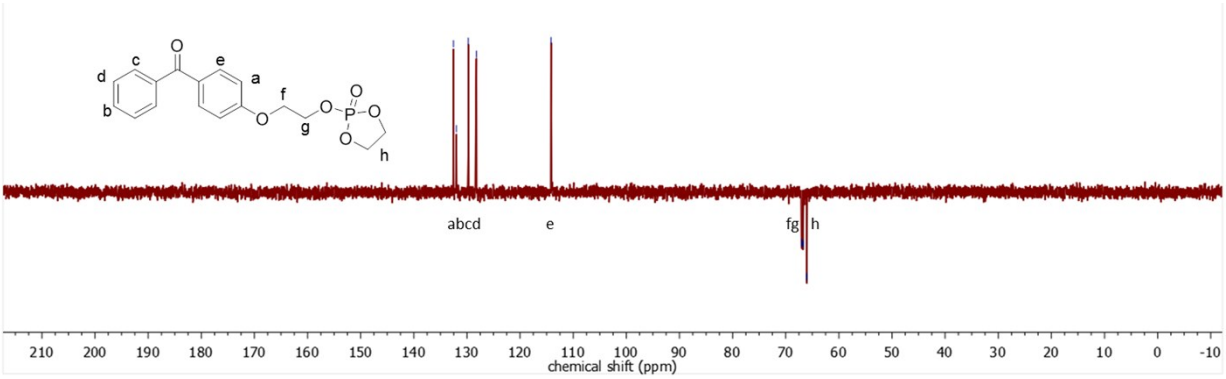


Figure S2. $^{13}C\{H\}$-DEPT NMR (76 MHz, $CDCl_3$) of **BeEP**(**1**) at 298 K (Note: quaternary C-atoms are not depicted).

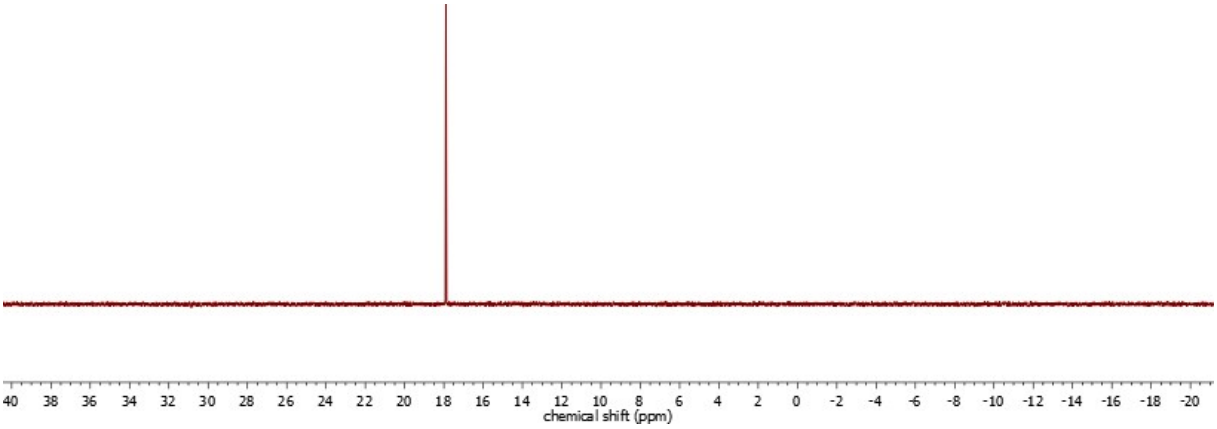


Figure S3. $^{31}P\{H\}$ NMR (121 MHz, $CDCl_3$) of **BeEP** (**1**) at 298 K.

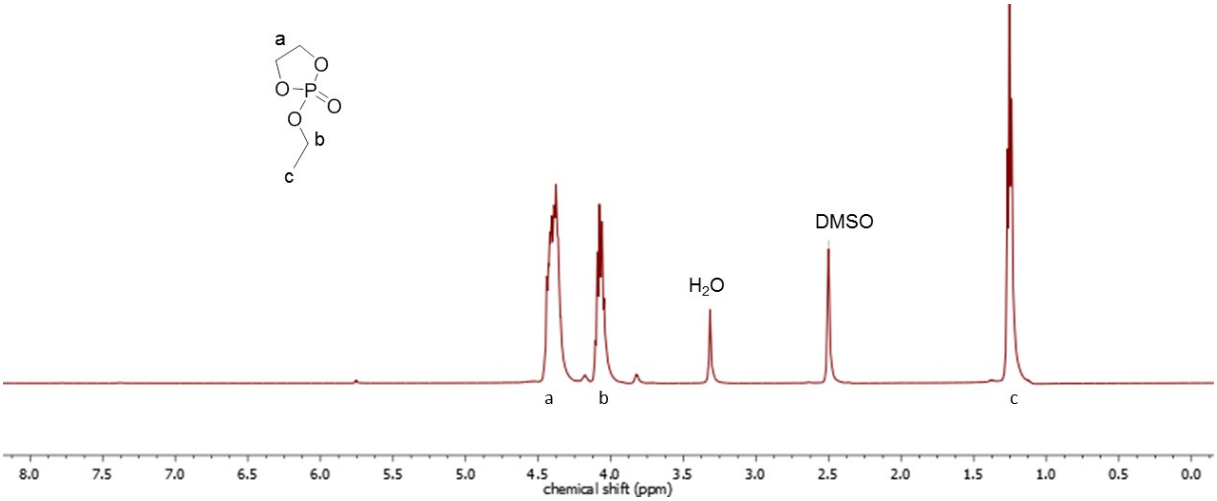


Figure S4. ^{1}H NMR (500 MHz, DMSO-d_6) of **EEP** (**2**) at 298 K.

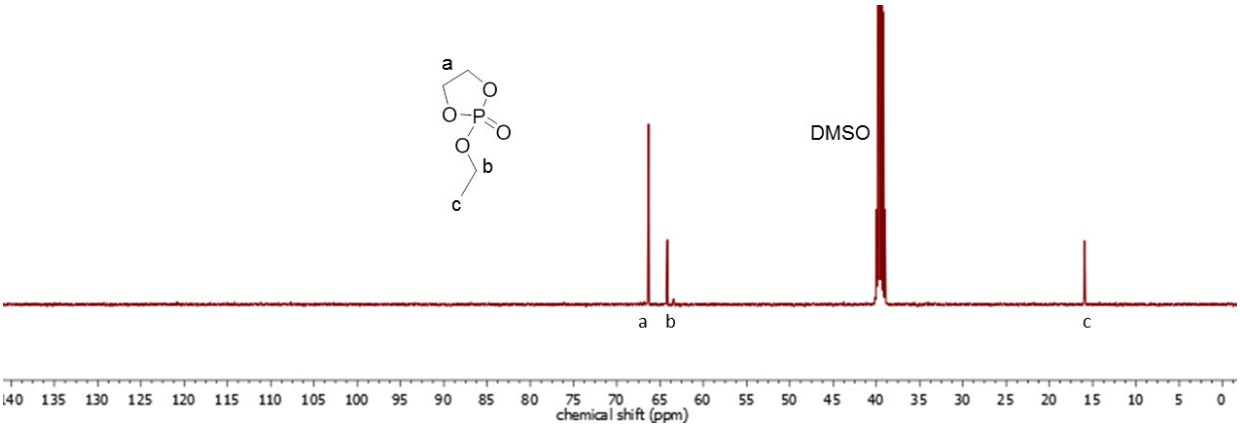


Figure S5. $^{13}C\{H\}$ NMR (126 MHz, DMSO-d_6) of **EEP** (**2**) at 298 K.

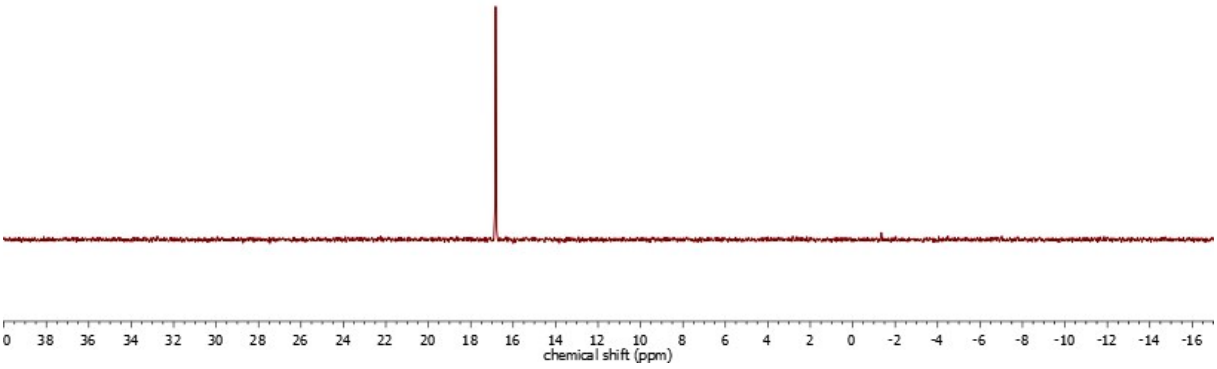


Figure S6. $^{31}P\{H\}$ NMR (202 MHz, DMSO-d_6) of **EEP** (**2**) at 298 K.

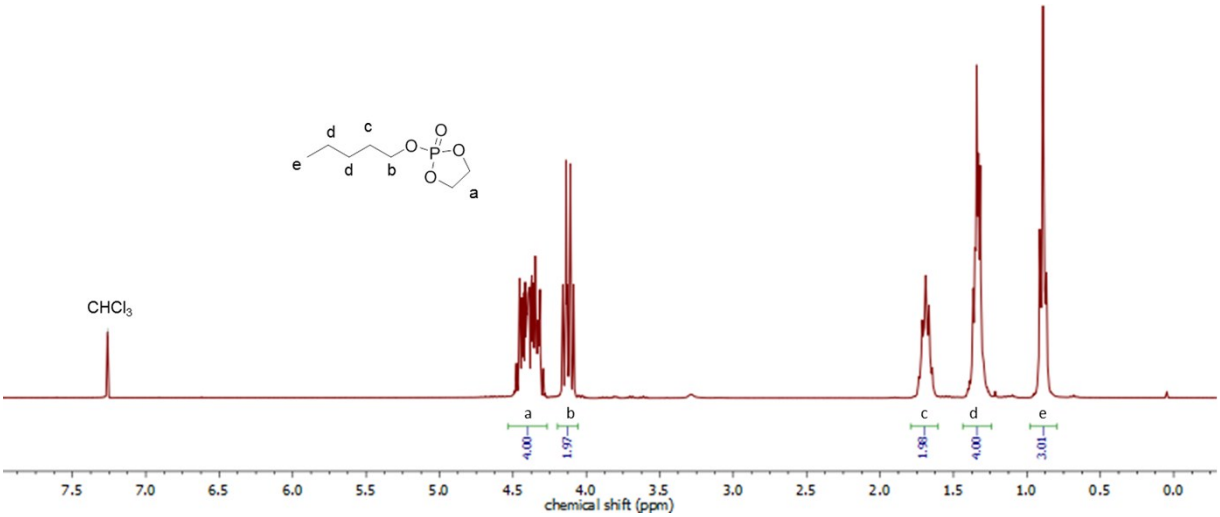


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) of **PEP** (**3**) at 298 K.

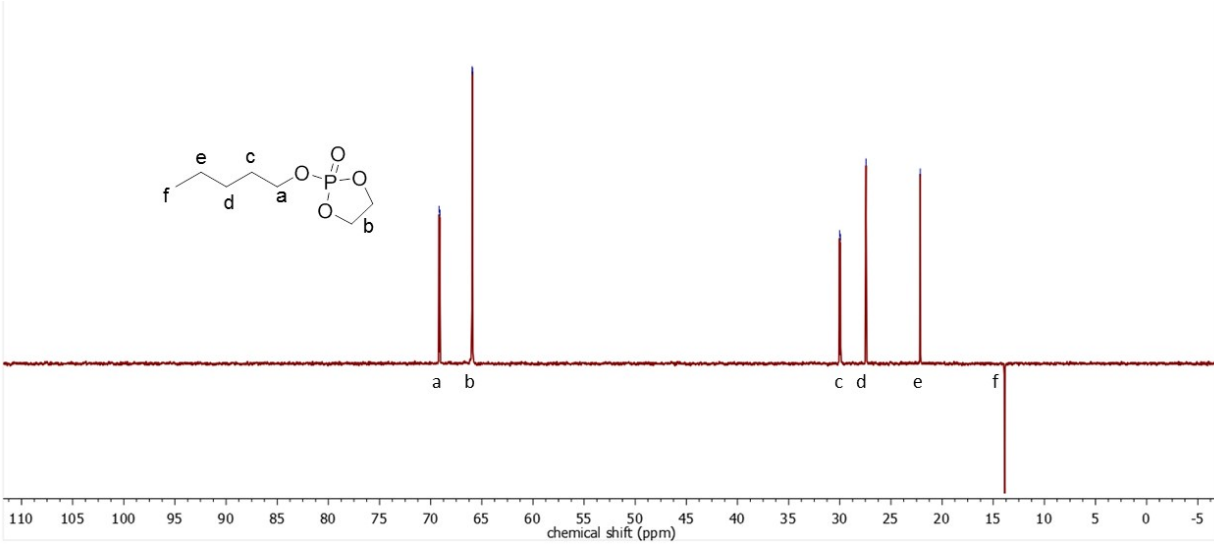


Figure S8. $^{13}C\{H\}$-DEPT NMR (76 MHz, $CDCl_3$) of **PEP** (**3**) at 298 K.

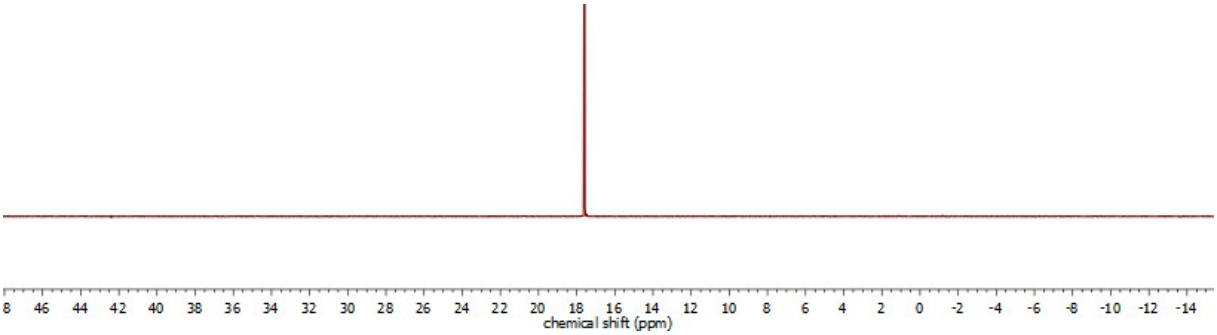


Figure S9. $^{31}P\{H\}$ NMR (121 MHz, $CDCl_3$) of **PEP** (**3**) at 298 K.

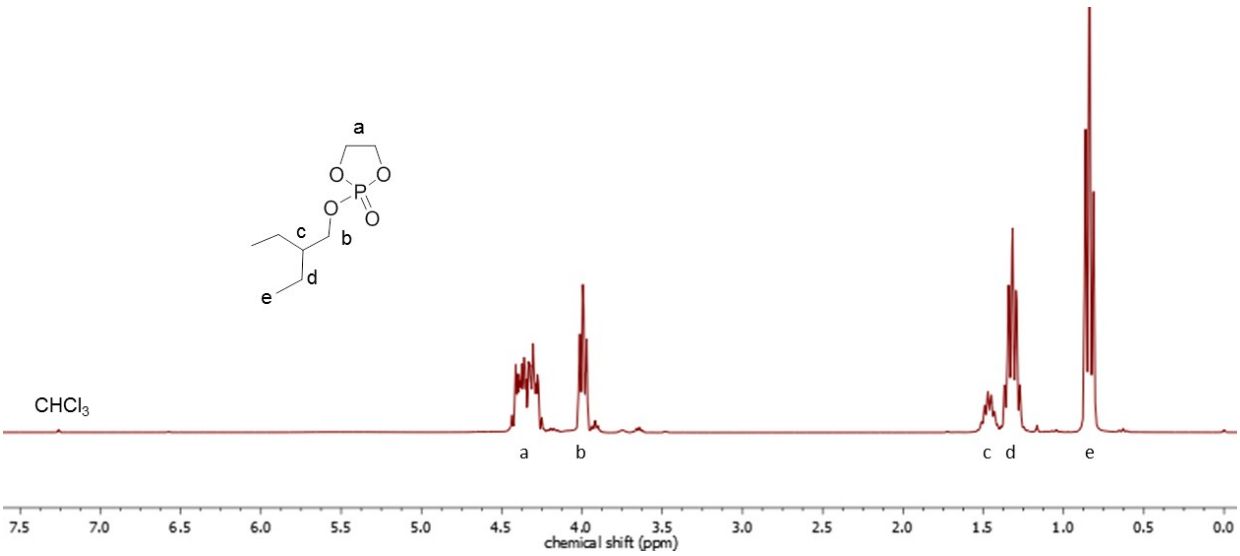


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) of **EBP** (**4**) at 298 K.

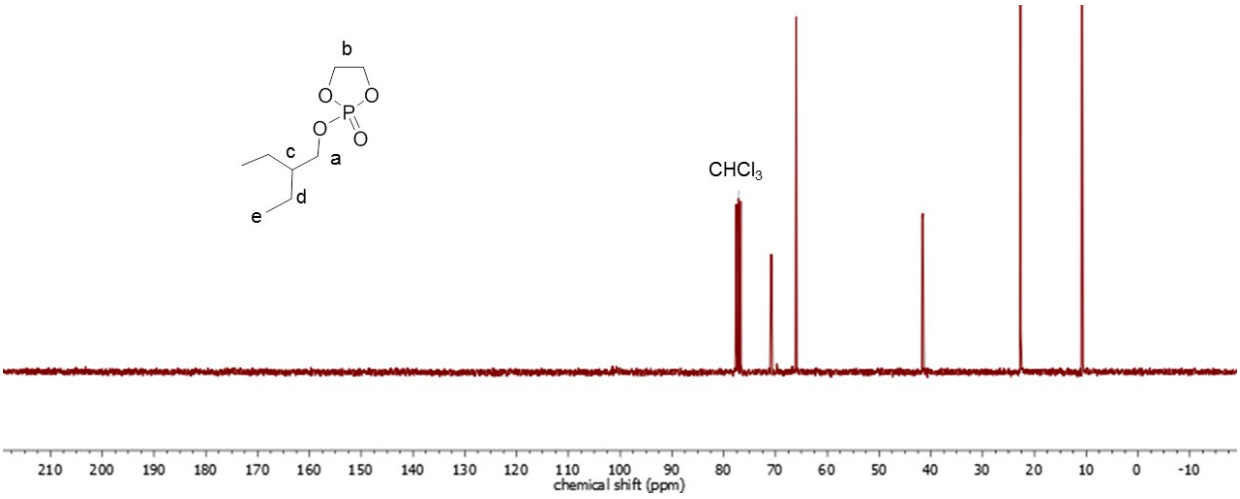


Figure S11. $^{13}C\{H\}$ NMR (76 MHz, $CDCl_3$) of **EBP** (**4**) at 298 K.

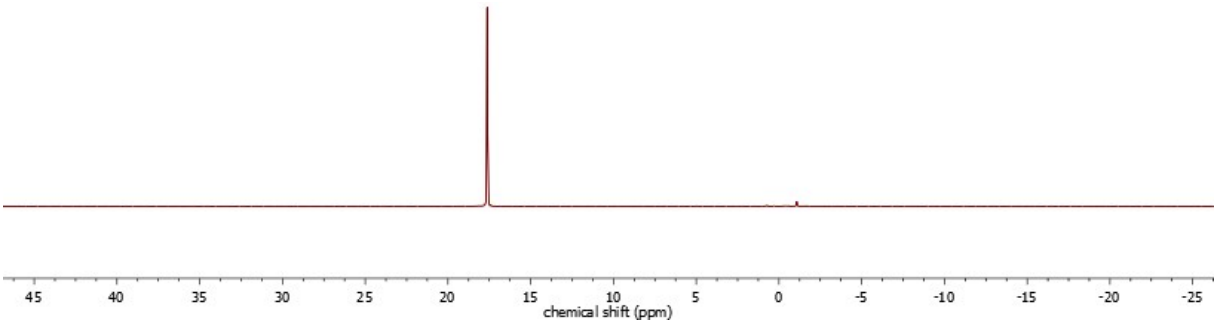


Figure S12. $^{31}P\{H\}$ NMR (121 MHz, $CDCl_3$) of **EBP** (**4**) at 298 K.

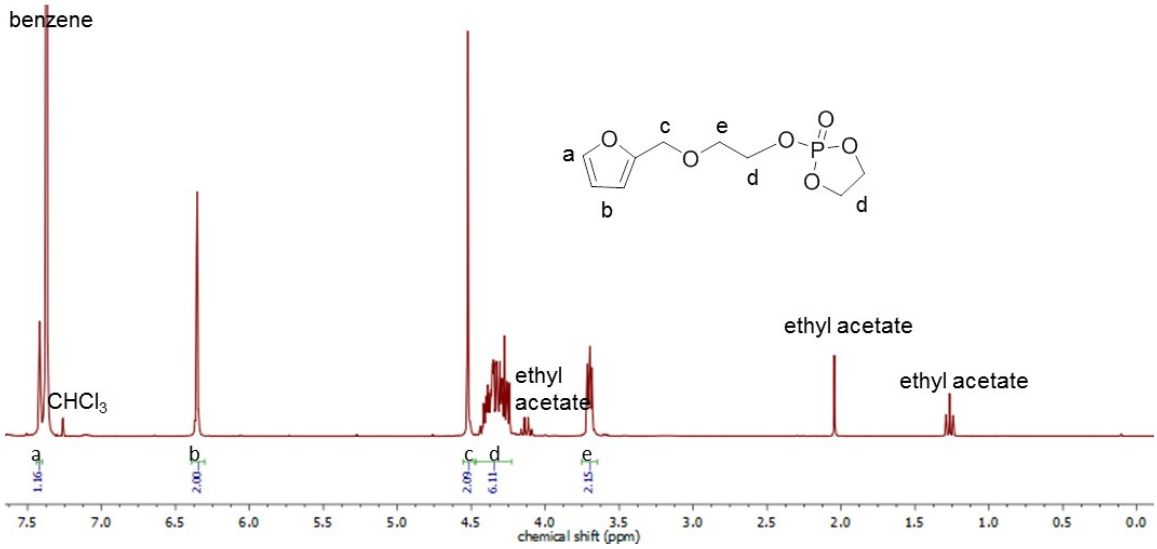


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) of **FEP** (**5**) at 298 K.

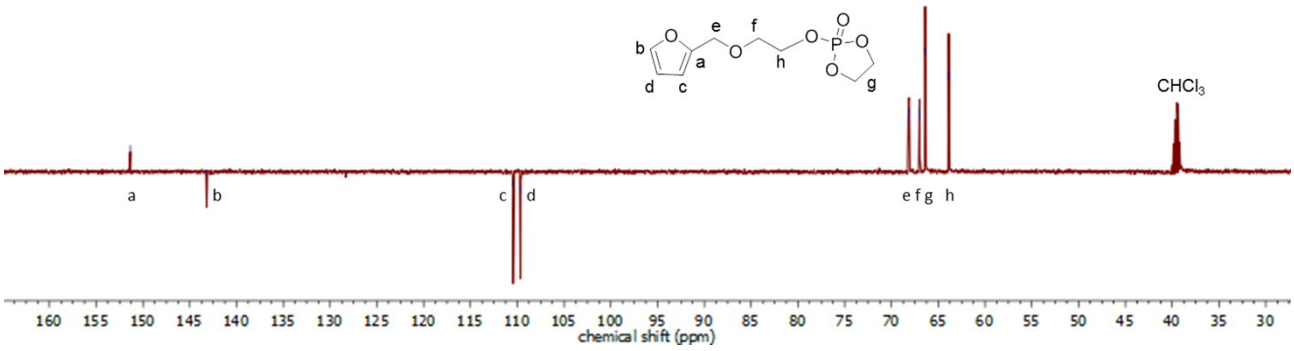


Figure S14. $^{13}C\{H\}$-DEPT NMR (126 MHz, $CDCl_3$) of **FEP** (**5**) at 298 K.

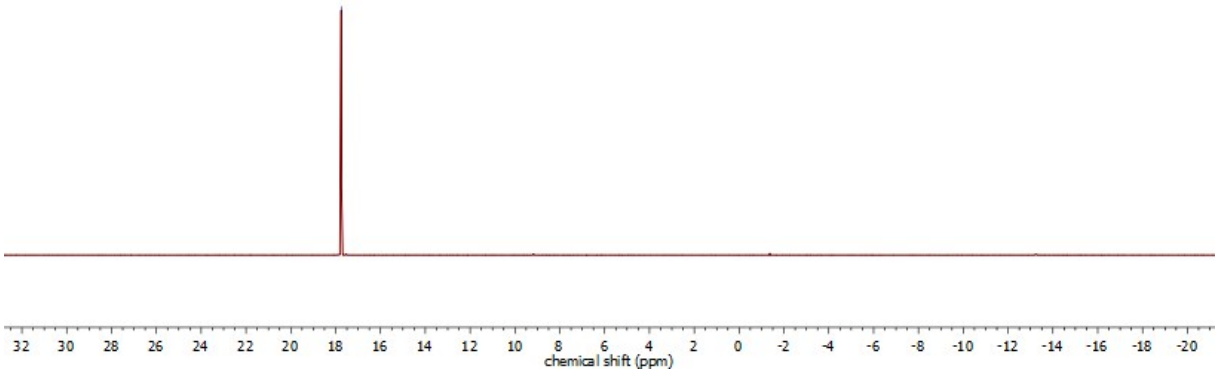


Figure S15. $^{31}P\{H\}$ NMR (202 MHz, $CDCl_3$) of **FEP** (**5**) at 298 K.

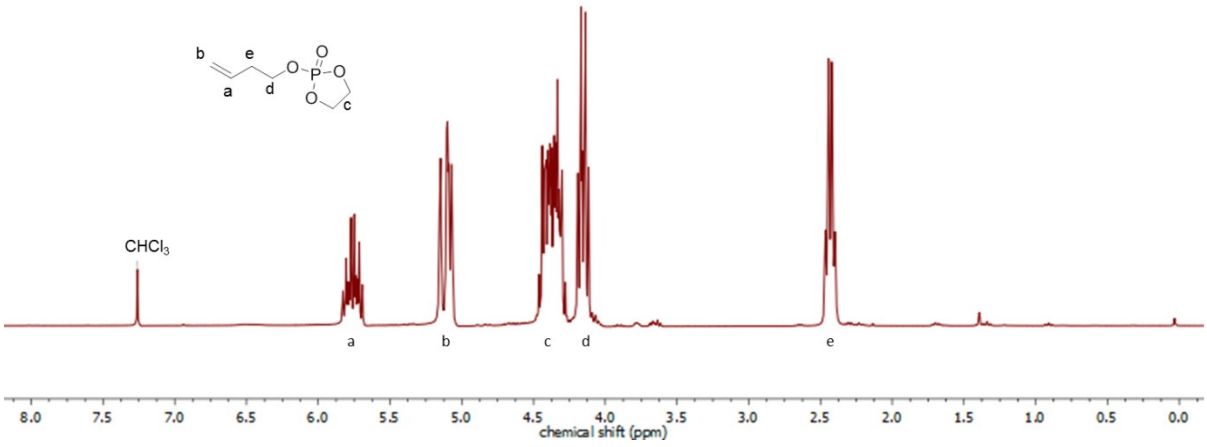


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) of **BuEP** (**6**) at 298 K.

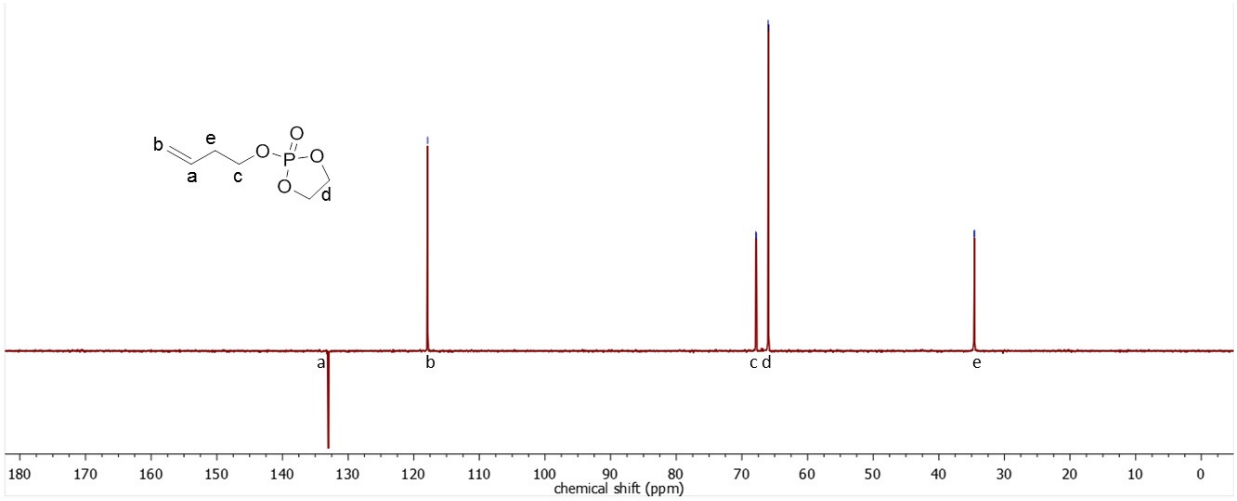


Figure S17. $^{13}C\{H\}$-DEPT NMR (76 MHz, $CDCl_3$) of **BuEP** (**6**) at 298 K.

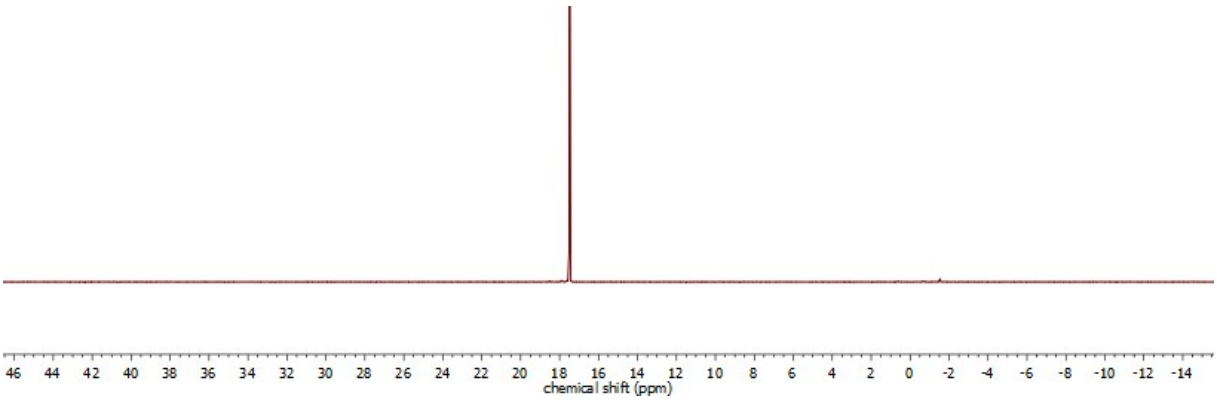


Figure S18. $^{31}P\{H\}$ NMR (121 MHz, $CDCl_3$) of **BuEP** (**6**) at 298 K.

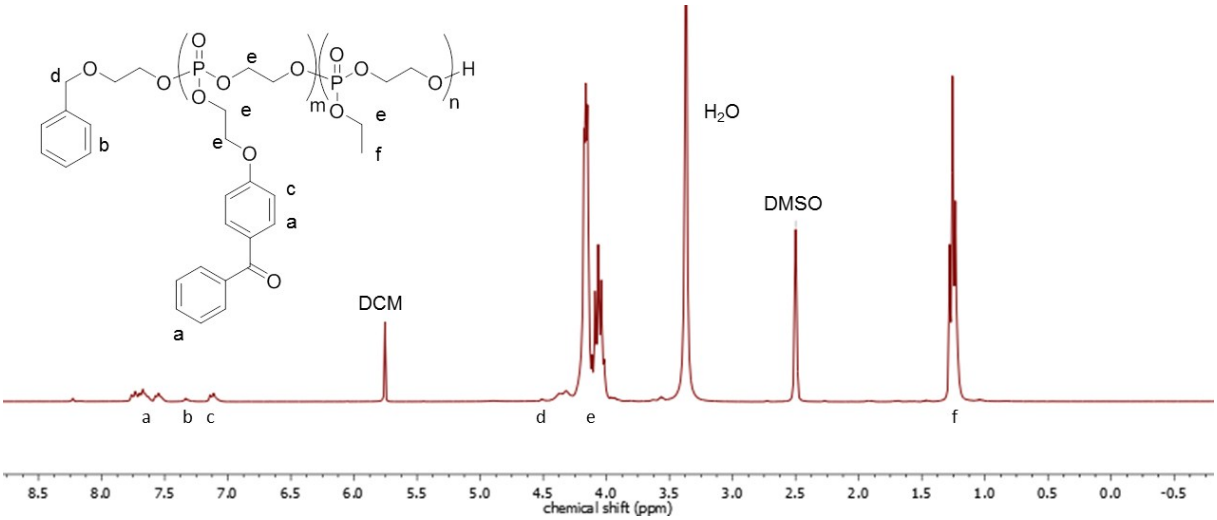


Figure S19. ^{1}H NMR (300 MHz, DMSO-d_6) of **P1** at 298K.

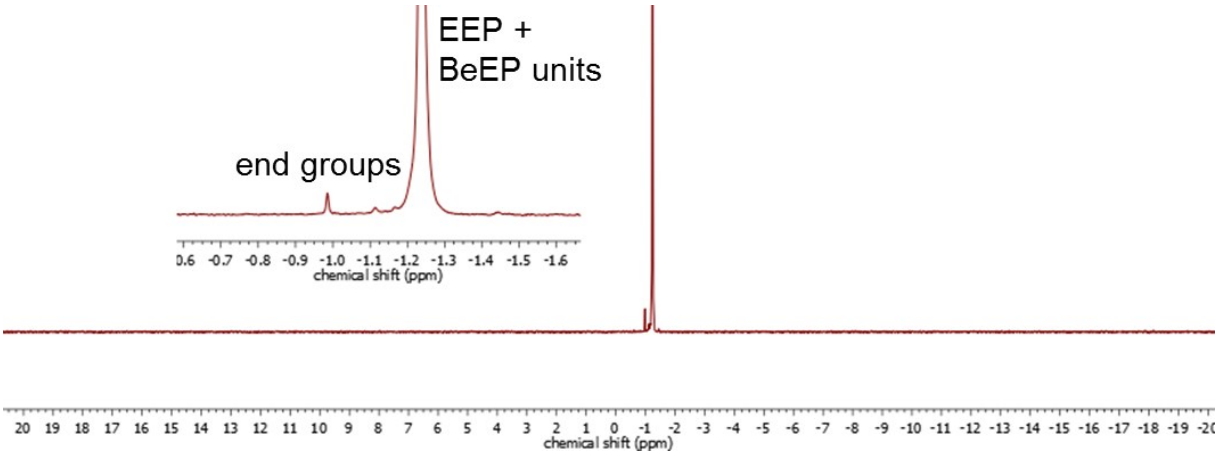


Figure S20. $^{31}P\{H\}$ NMR (121 MHz, DMSO-d_6) of **P1** at 298K.

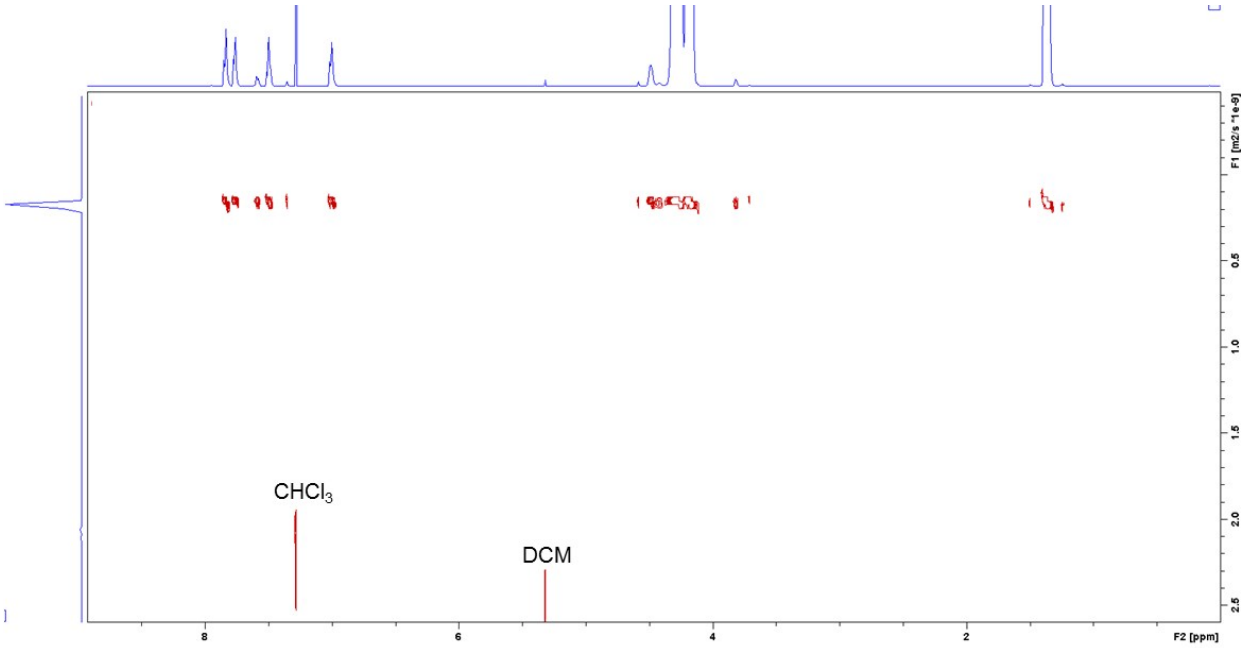


Figure S21. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P1** at 298K.

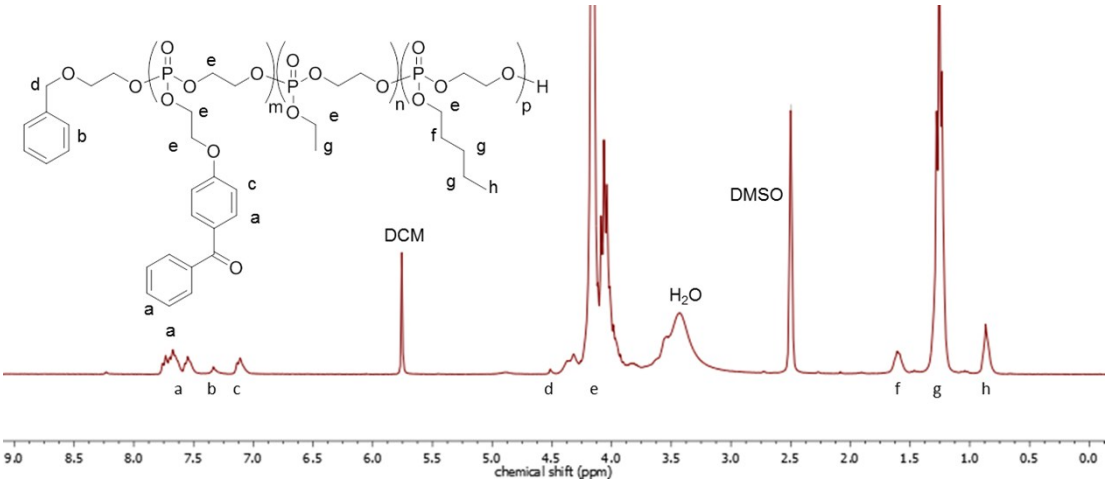


Figure S22. ^{1}H NMR (300 MHz, DMSO-d_6) of **P2** at 298K.

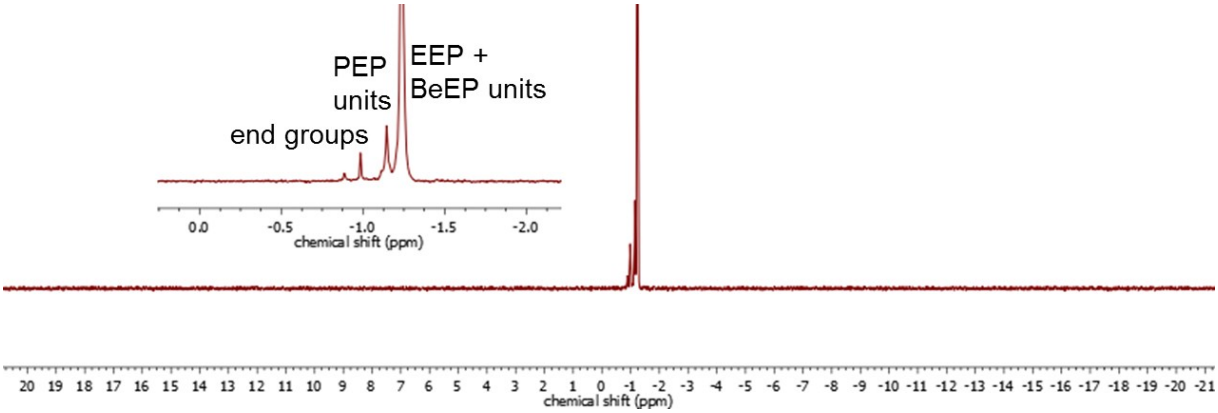


Figure S23. ^{31}P{H} NMR (121 MHz, DMSO-d_6) of **P2** at 298K.

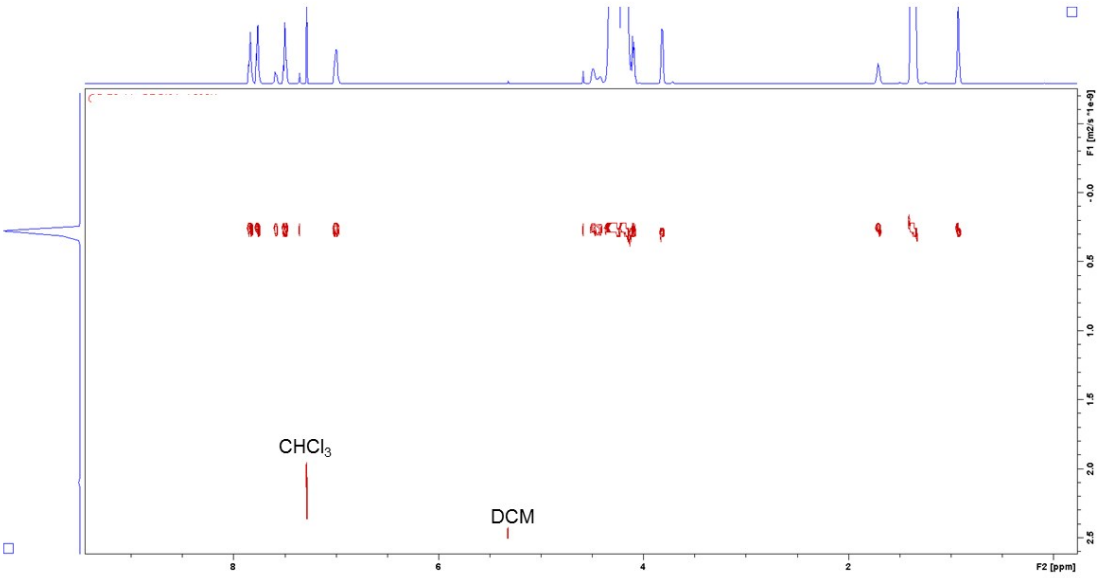


Figure S24. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P2** at 298 K.

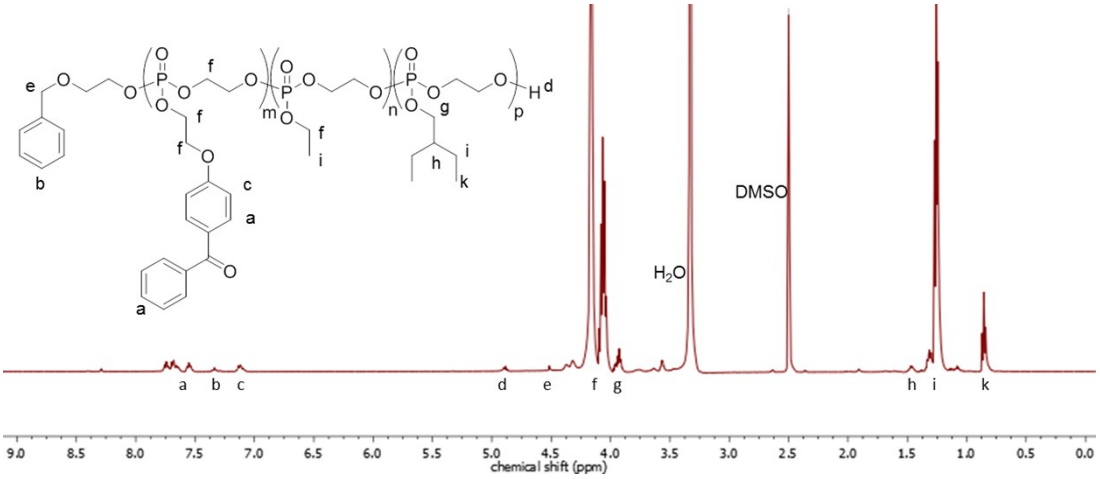


Figure S25. ^{1}H NMR (500 MHz, DMSO-d_6) of **P3** at 298K.

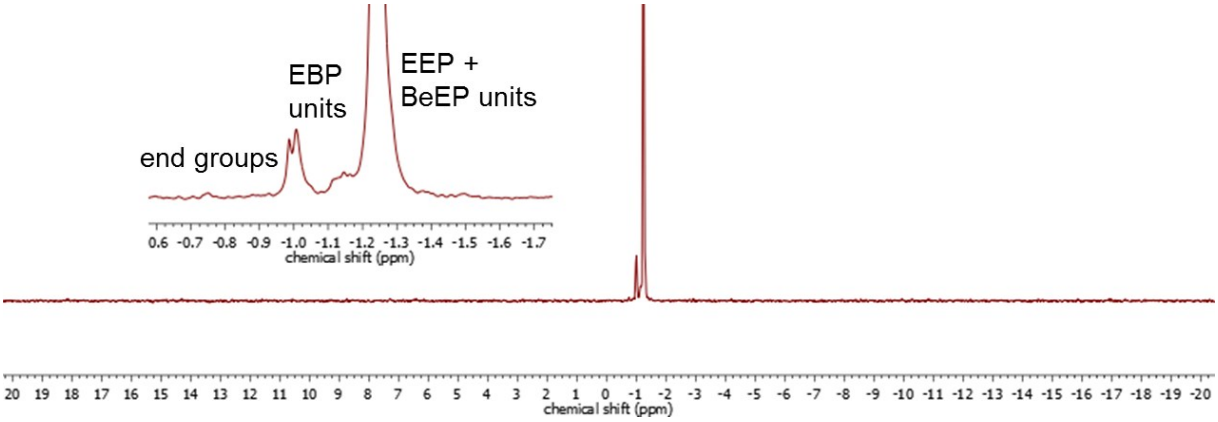


Figure S26. ^{31}P{H} NMR (202 MHz, DMSO-d_6) of **P3** at 298K.

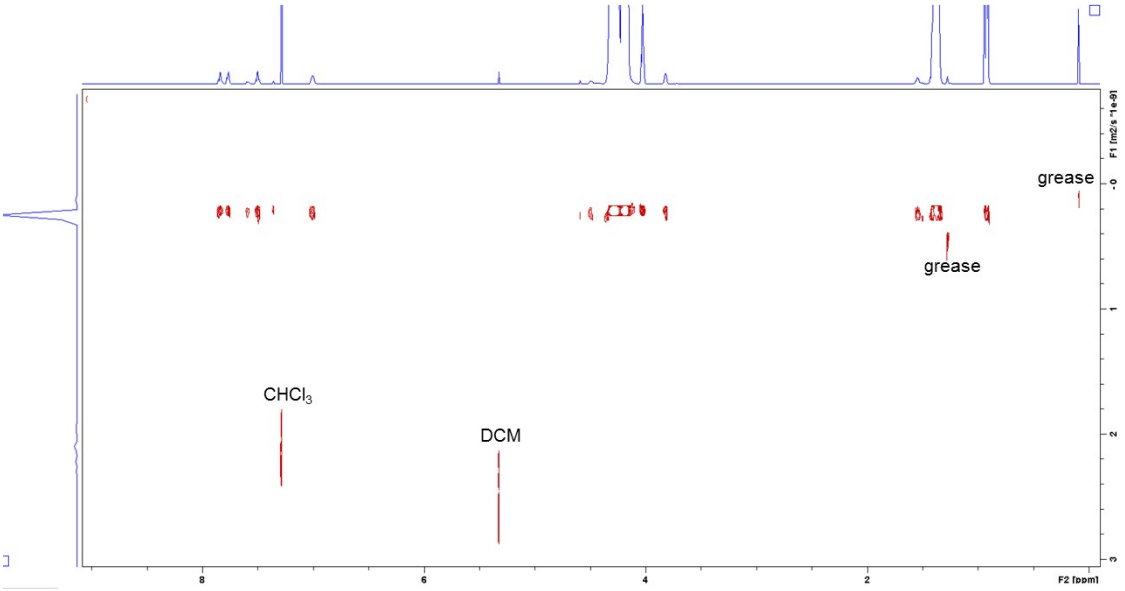


Figure S27. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P3** at 298 K.

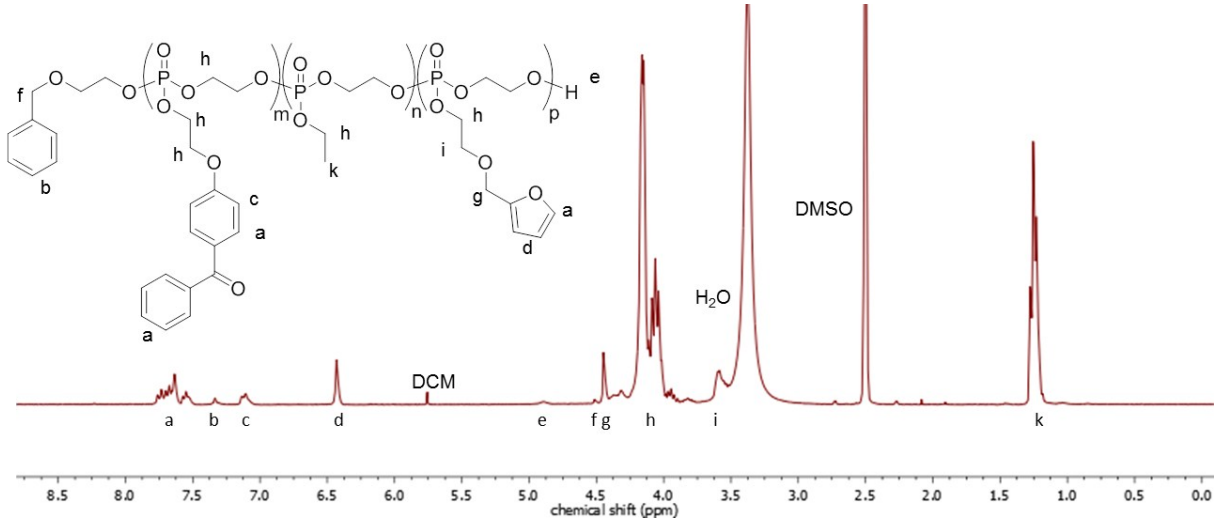


Figure S28. ^{1}H NMR (300 MHz, DMSO-d_6) of **P4** at 298K.

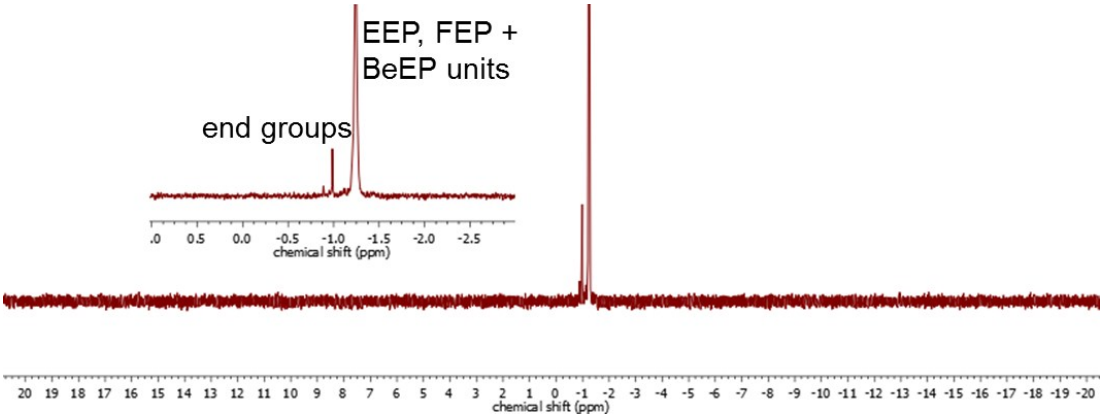


Figure S29. ^{31}P{H} NMR (121 MHz, DMSO-d_6) of **P4** at 298K.

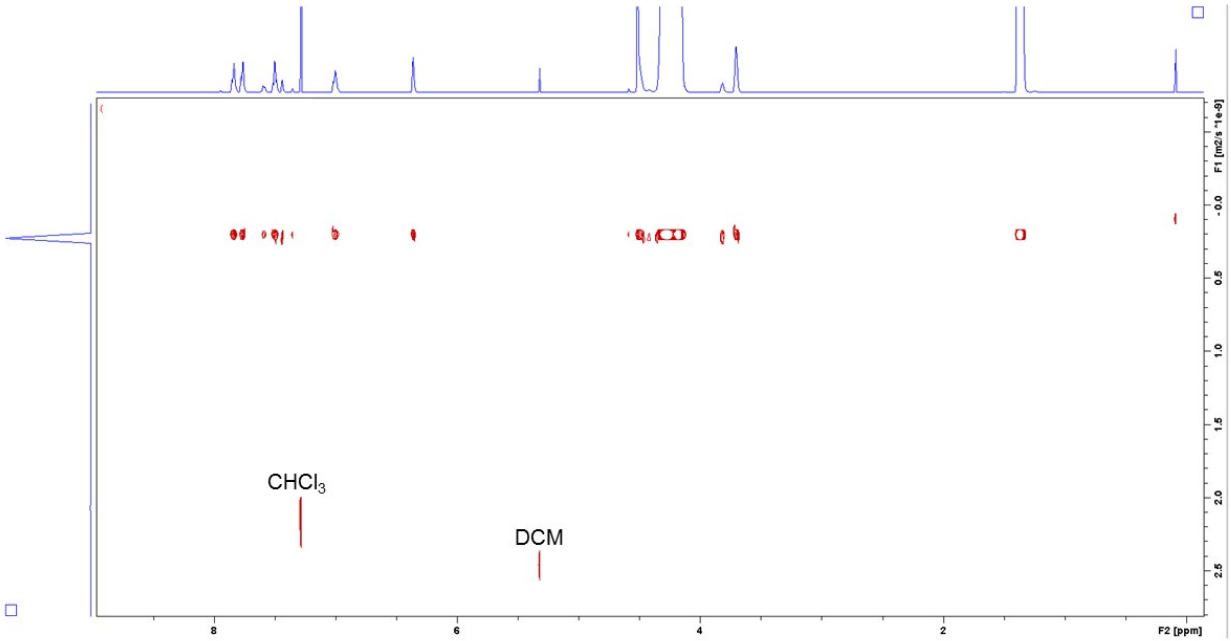


Figure S30. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P4** at 298 K.

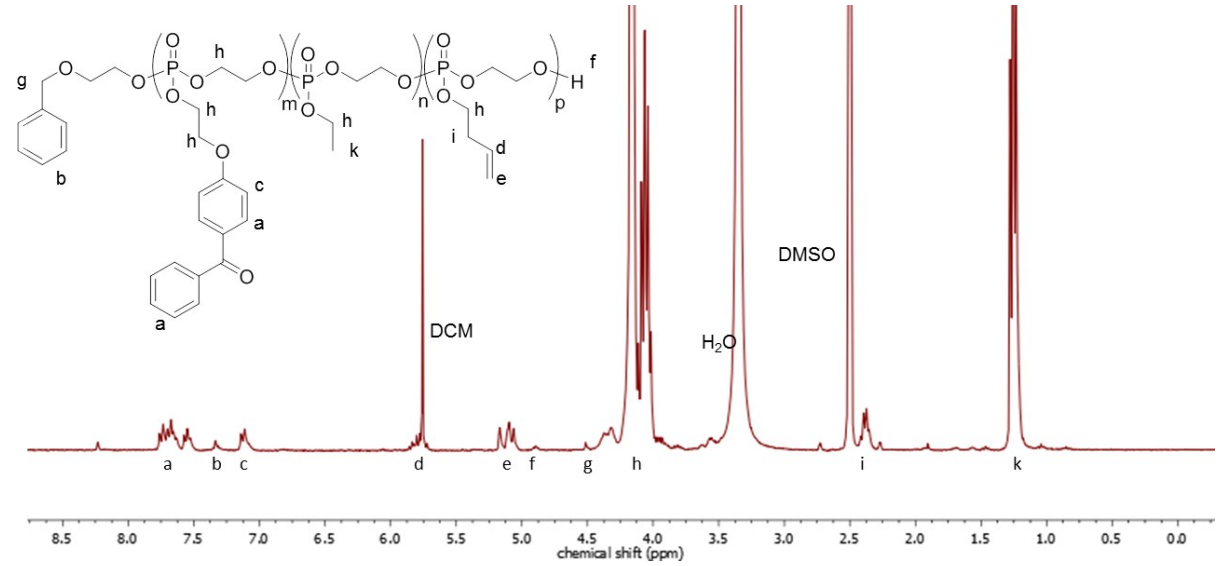


Figure S31. ^{1}H NMR (300 MHz, DMSO-d_6) of **P5** at 298K.

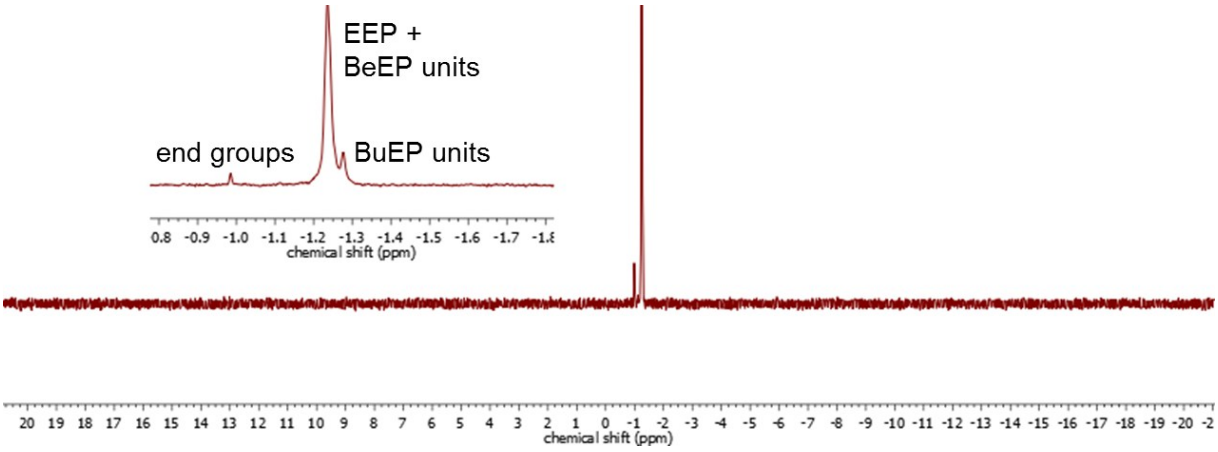


Figure S32. ^{31}P{H} NMR (121 MHz, DMSO-d_6) of **P5** at 298K.

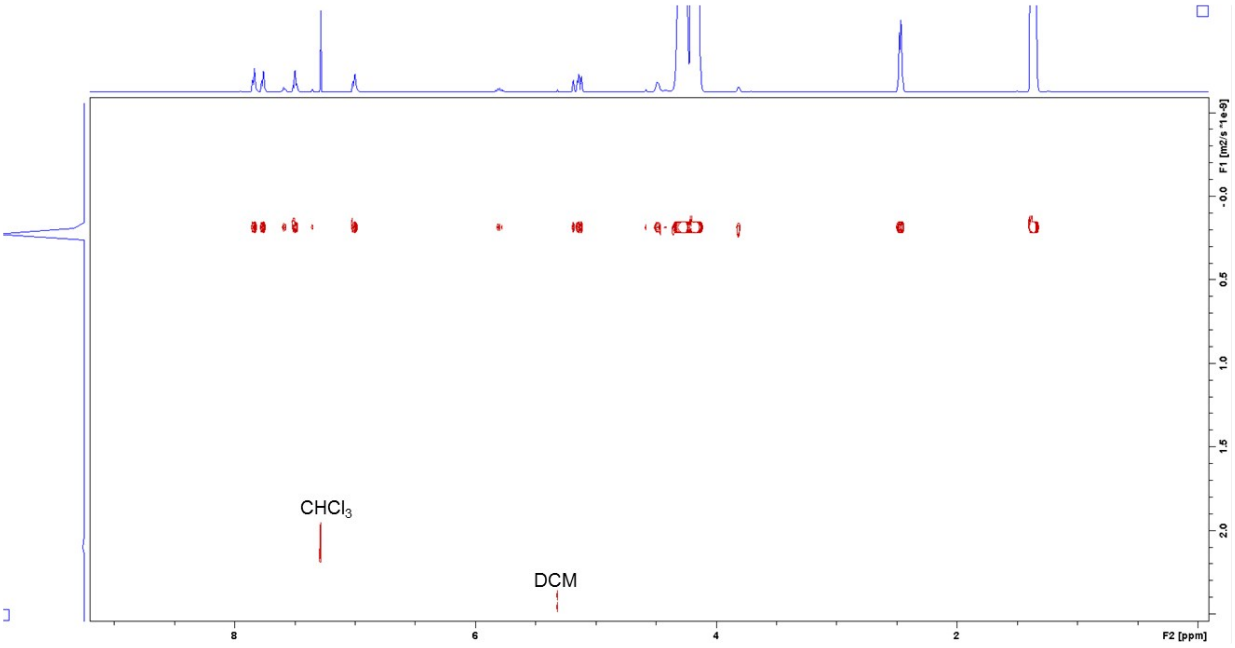


Figure S33. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P5** at 298 K.

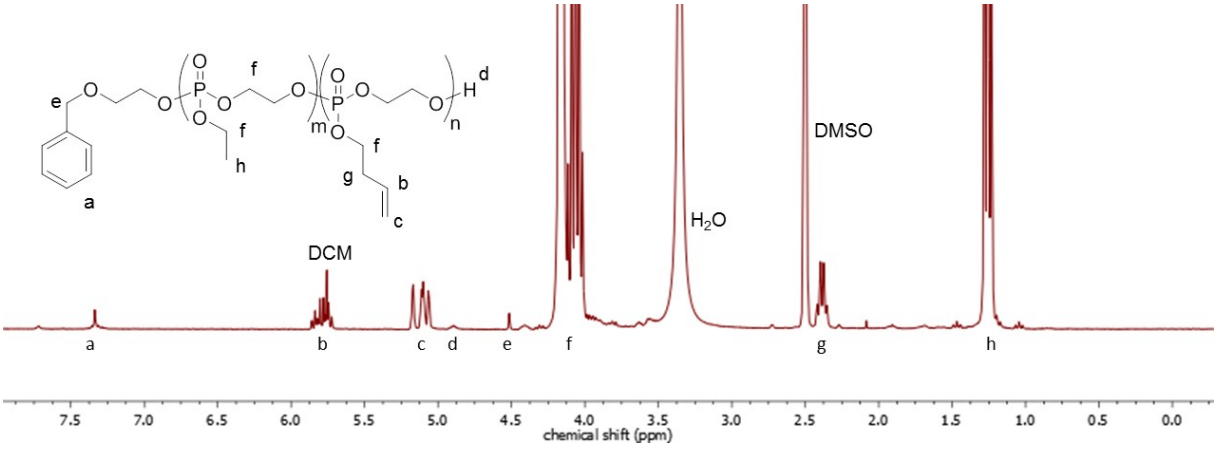


Figure S34. ^{1}H NMR (300 MHz, DMSO-d_6) of **P6** at 298K.

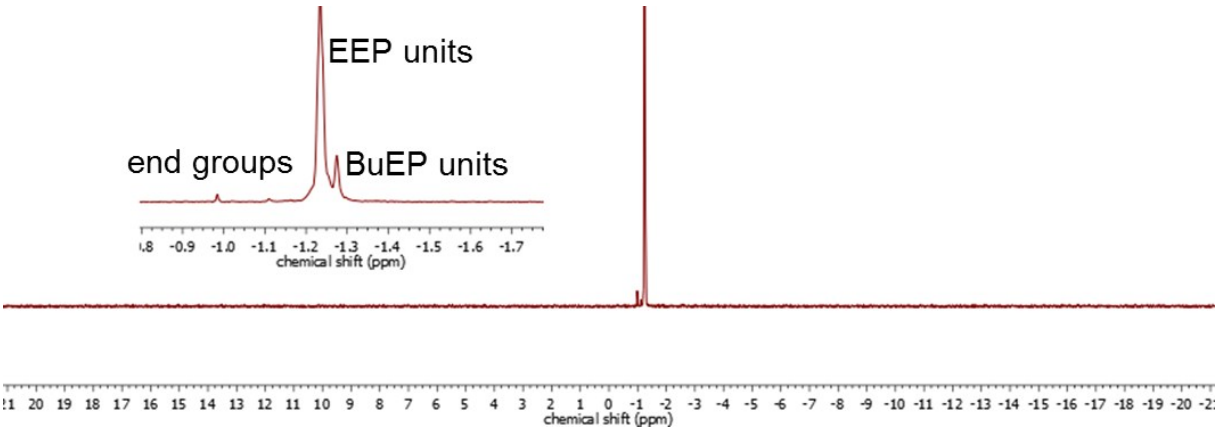


Figure S35. ^{31}P{H} NMR (121 MHz, DMSO-d_6) of **P6** at 298K.

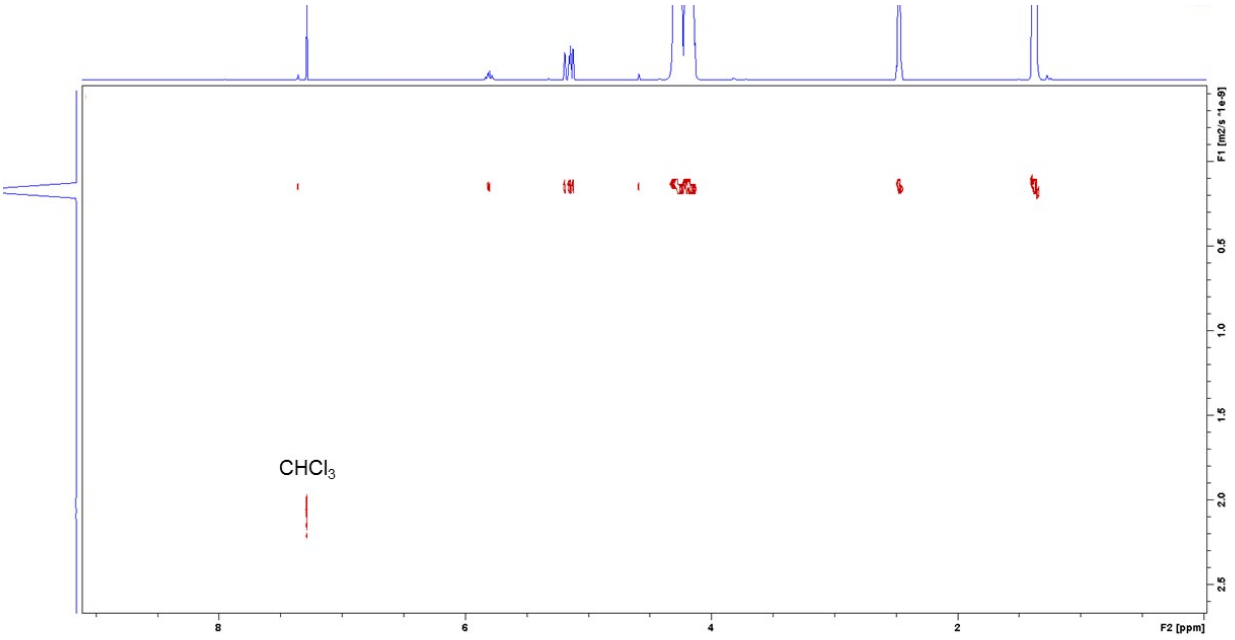


Figure S36. ^{1}H-DOSY (500 MHz, $CDCl_3$) of **P6** at 298 K.

b. IR spectra

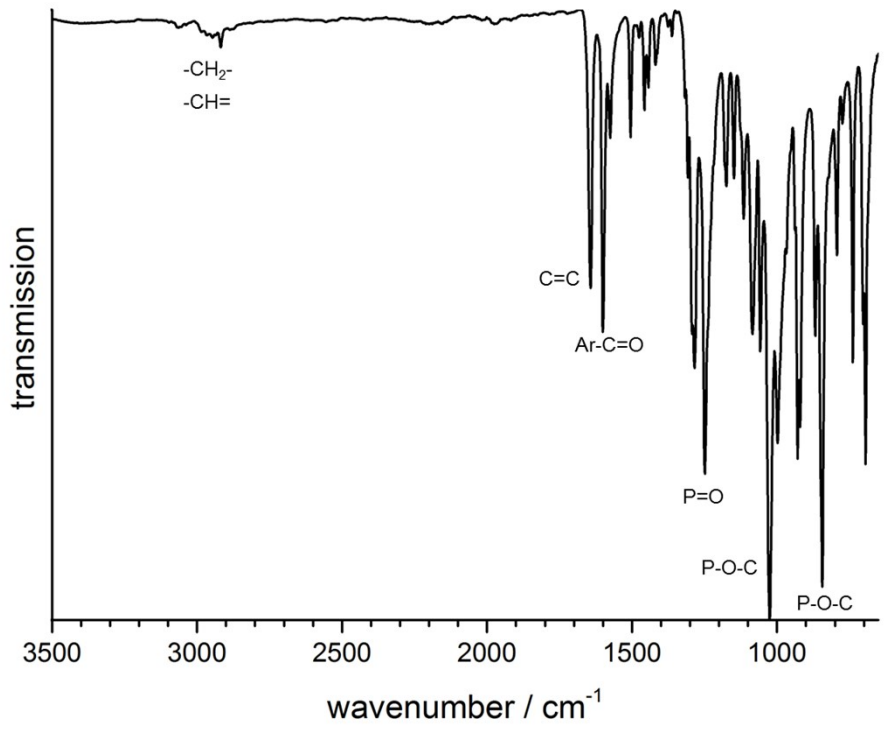


Figure S37. FT-IR spectrum of **BeEP** (**1**) at 298 K.

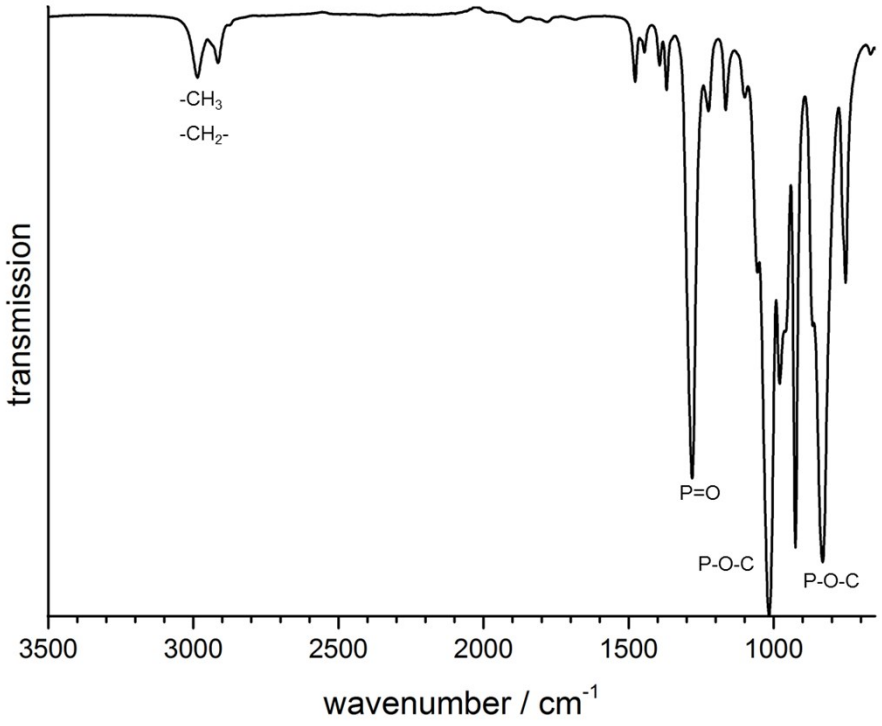


Figure S38. FT-IR spectrum of **EEP** (**2**) at 298 K.

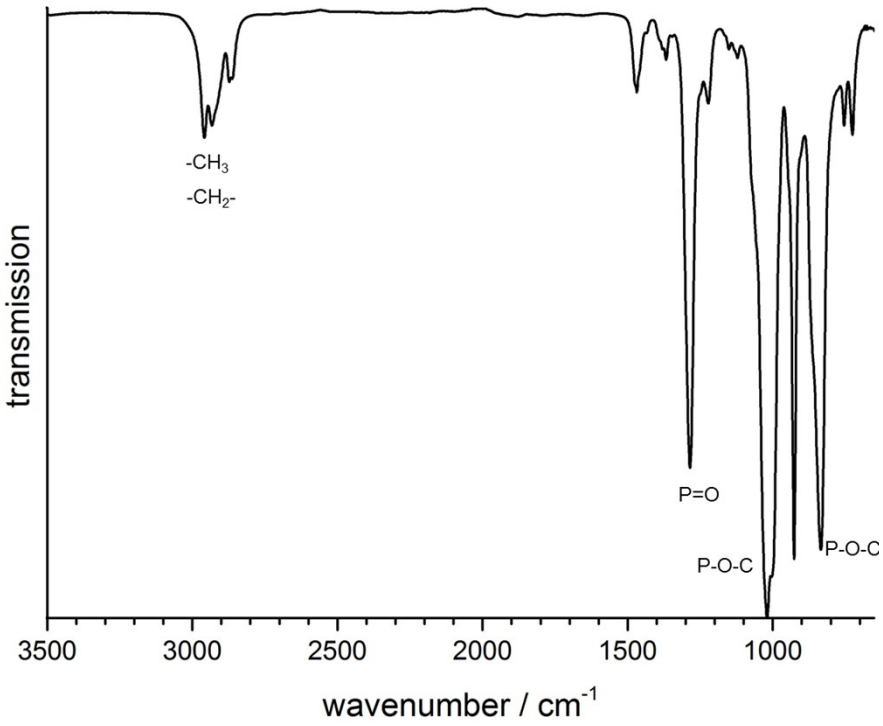


Figure S39. FT-IR spectrum of **PEP** (**3**) at 298 K.

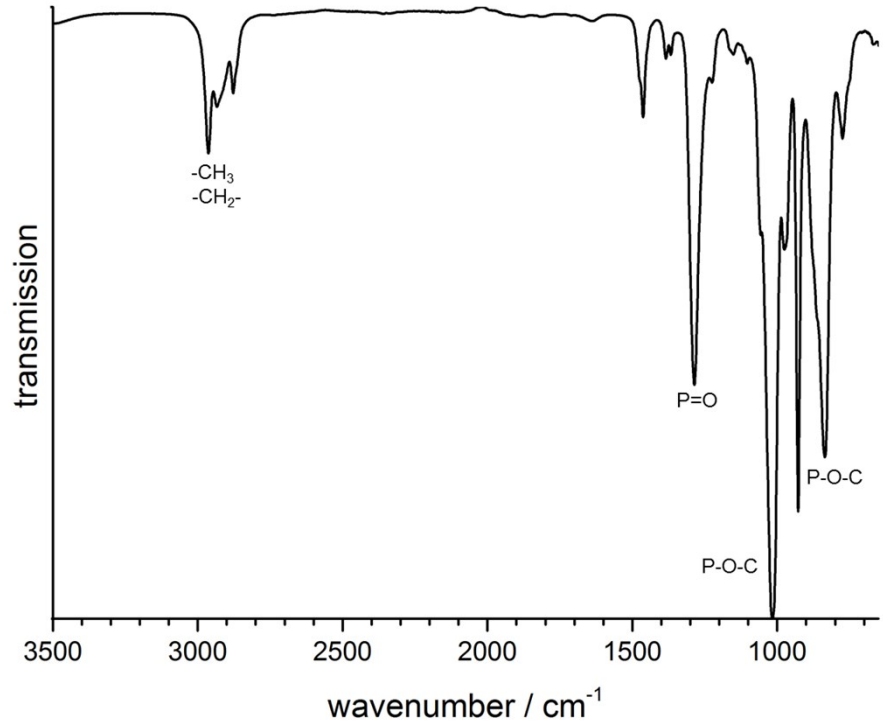


Figure S40. FT-IR spectrum of **EBP** (**4**) at 298 K.

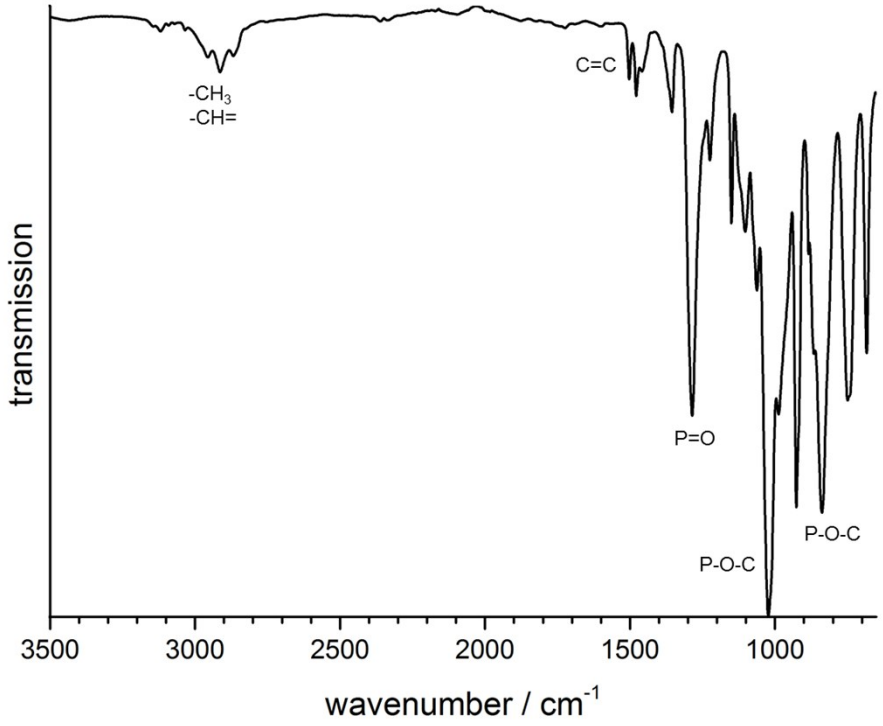


Figure S41. FT-IR spectrum of **FEP** (**5**) at 298 K.

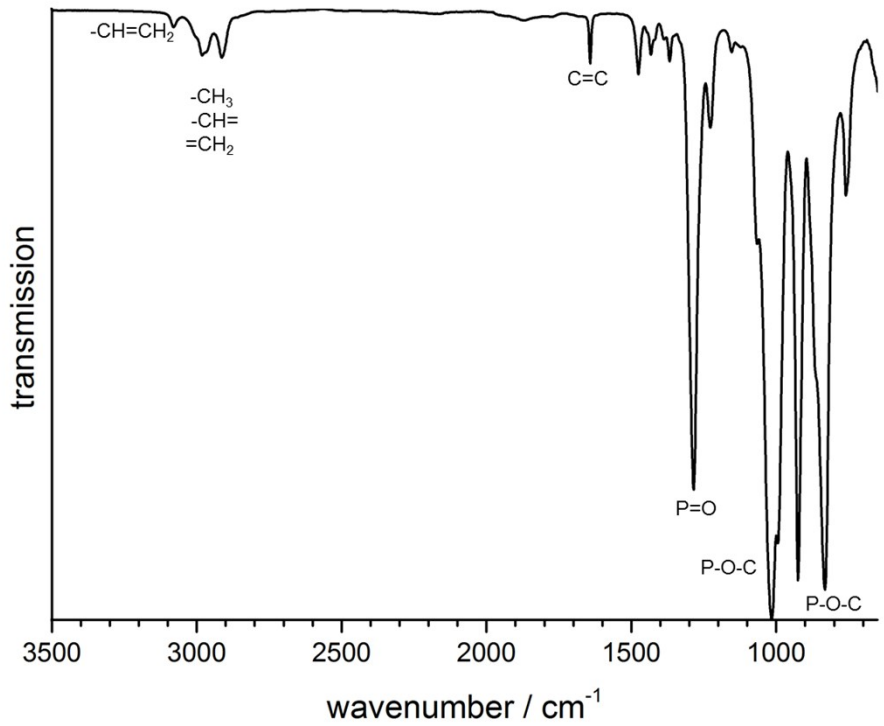


Figure S42. FT-IR spectrum of **BuEP** (**6**) at 298 K.

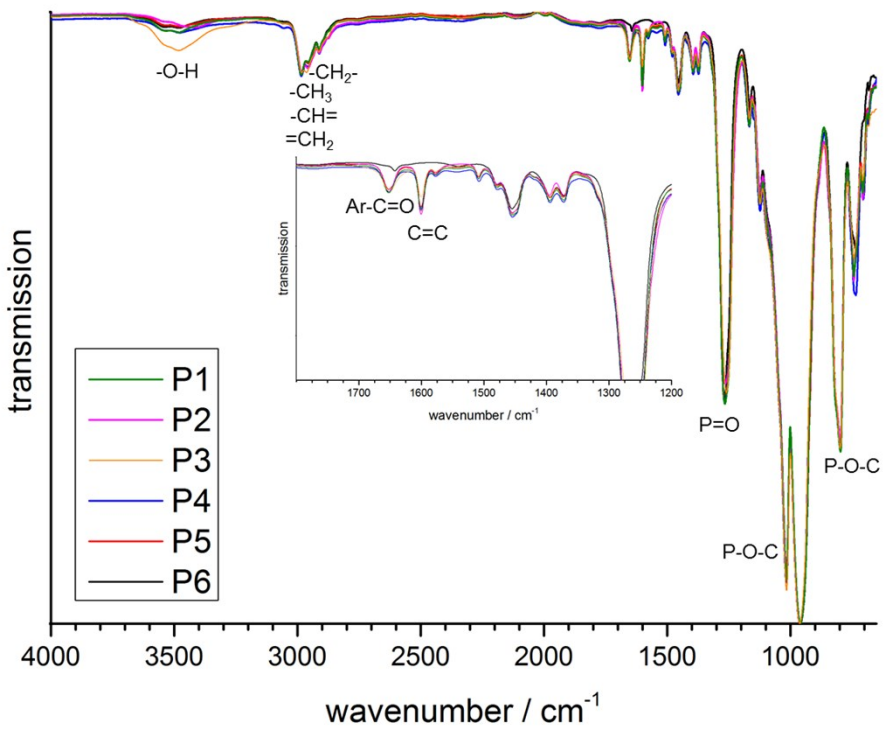


Figure S43. FT-IR spectra of polymers **P1-P6** at 298 K.

Kinetic measurements of copolymerizations

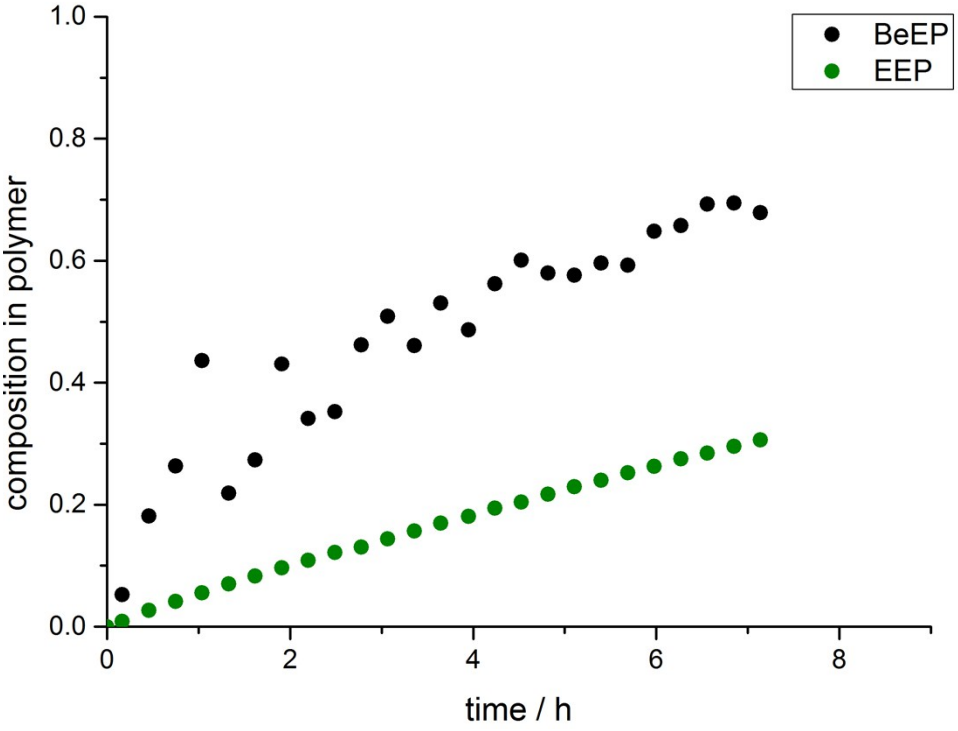


Figure S44. Simultaneous copolymerization: the monomer composition in polymer vs time (analog to polymer **P1**).

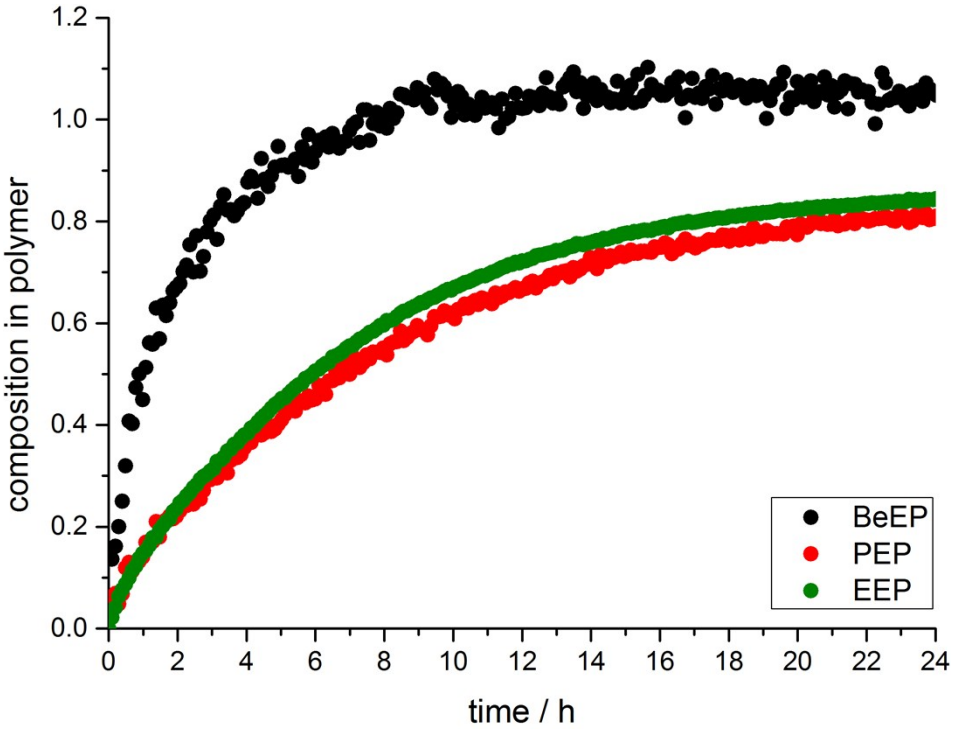


Figure S45. Simultaneous terpolymerization: the monomer composition in polymer vs time (analog to polymer **P2**).

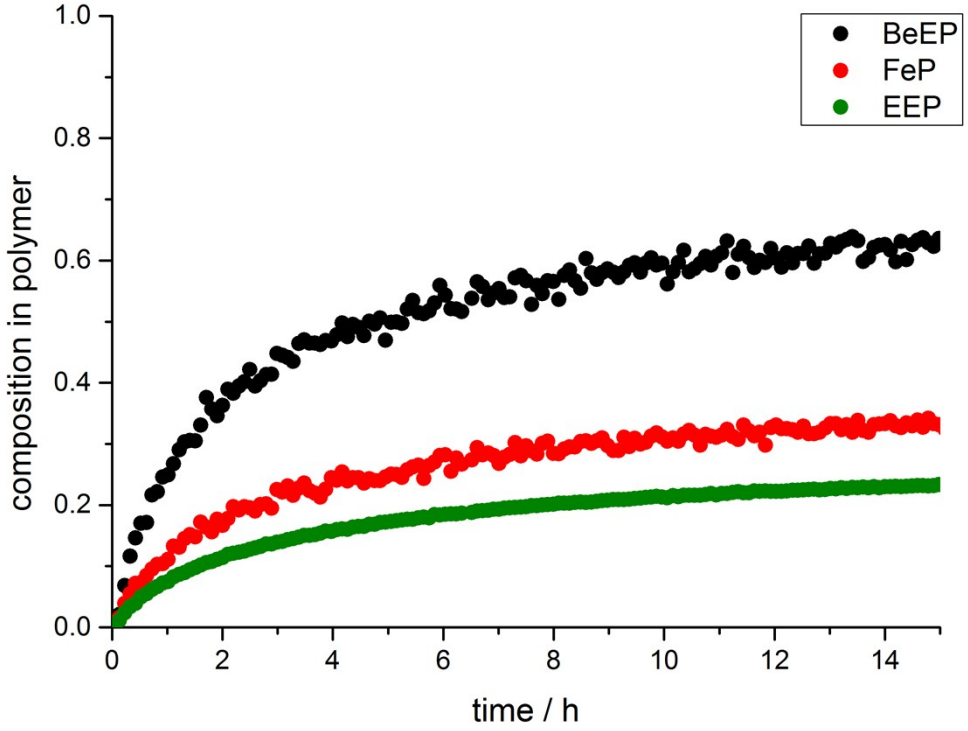
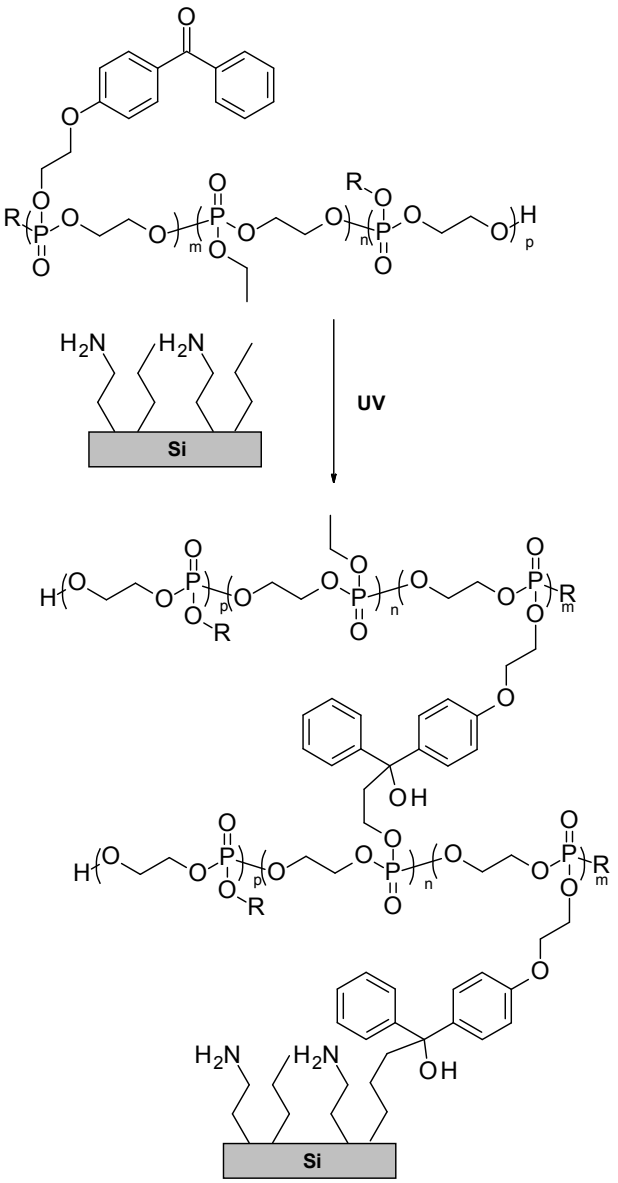


Figure S46. Simultaneous terpolymerization: the monomer composition in polymer vs time (analog to polymer **P5**).

Surface-attached gel formation and characterization



Scheme S1: Possible mechanism of attaching and crosslinking of the benzophenone-containing PPEs to the surface.

Table S1. Overview of layer thicknesses of PPE-networks of **P4** on silicon substrates in dependence of the concentration of used polymer solution.

polymer concentration / mg/mL	**layer thickness/nm**
50	199±2
30	61±1
20	54±1
10	24±1

Table S2. Contact angles of the polymer networks.

sample	**static / °**		**advancing / °**		**receding / °**	
	left	**right**	**left**	**right**	**left**	**right**
P2	20±1	21±0	21±4	22±4	11±1	10±1
P4	26±3	26±3	29±2	29±3	16±1	16±1
P5	26±1	25±1	34±3	35±3	8±1	8±1

Table S3. Layer thickness of PPE-networks made from **P2**, **P4,** and **P5** on silicon substrates with different ratios of propyl/amine groups. Films were coated from polymer solutions of 50 mg/mL in chloroform.

polymer	**ratio propyl:amine**	**number of layers**	**layer thickness /nm**
P2	5:1	1	56±1
P2	2:1	1	86±1
P2	1:1	1	104±1
P2	1:1	2	233±20
P2	1:1	3	327±7
P4	5:1	1	132±2
P4	2:1	1	173±1
P4	1:1	1	199±2
P4	1:1	2	321±2
P4	1:1	3	434±3

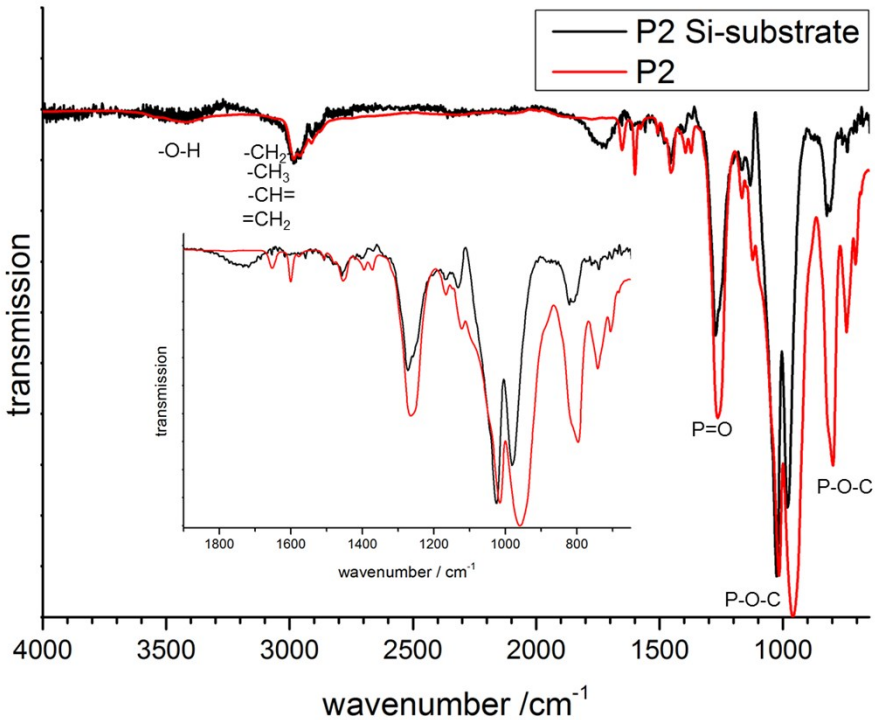


Figure S47. FT-IR spectra of **P2** and **P2** on Si-substrate.

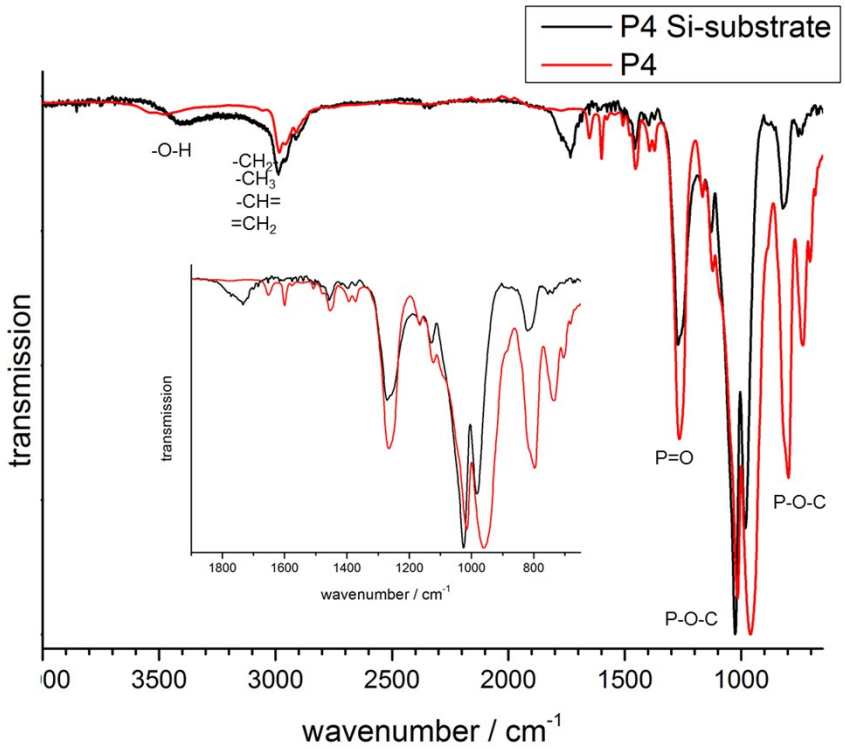


Figure S48. FT-IR spectra of **P4** and **P4** on Si-substrate.

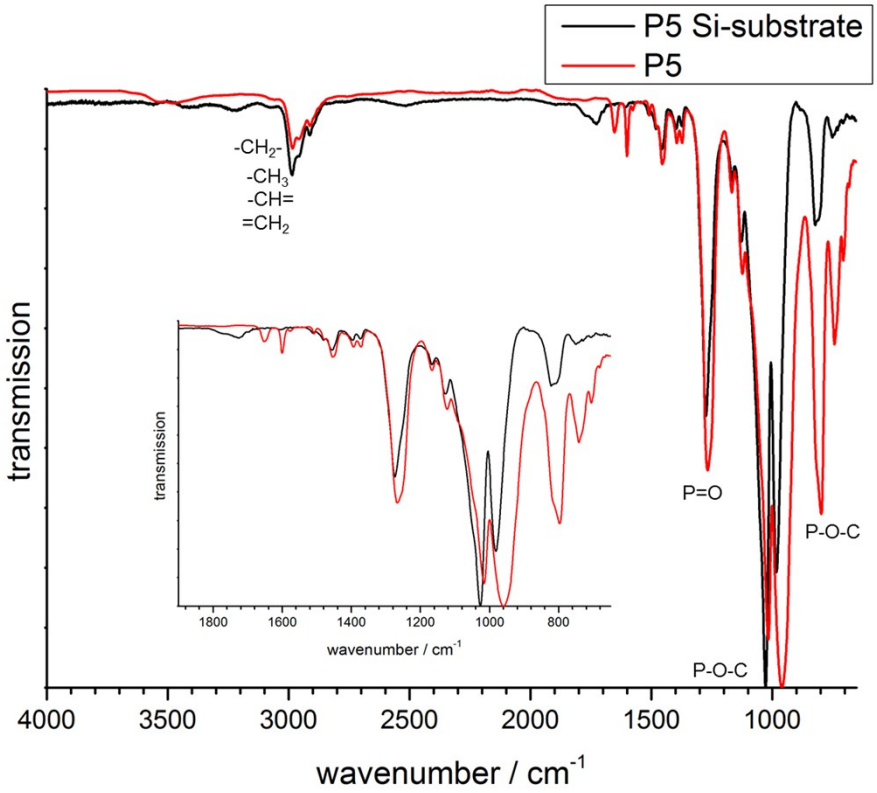


Figure S49. FT-IR spectra of **P5** and **P5** on Si-substrate.

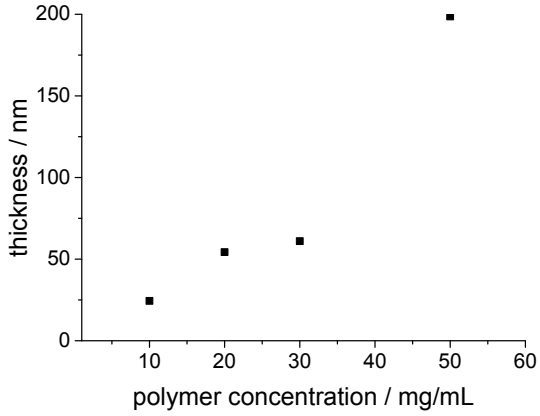


Figure S50 P4 spin-coated onto silicon substrates: "Master curve" of layer thickness vs. concentration of polymer solution.

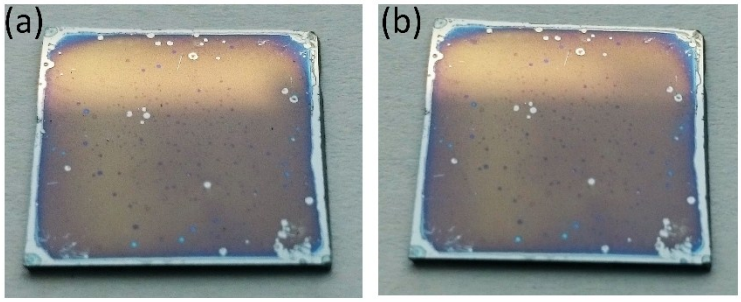


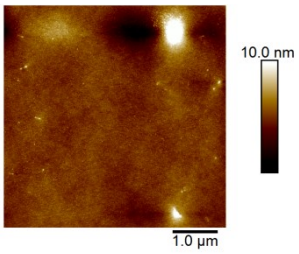
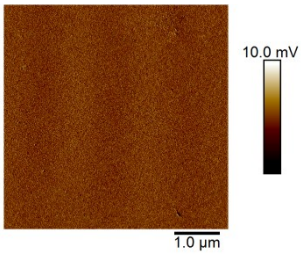
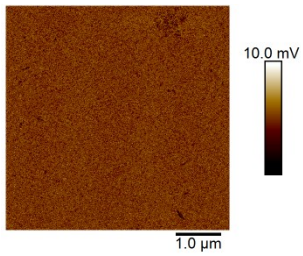
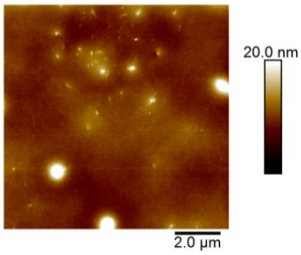
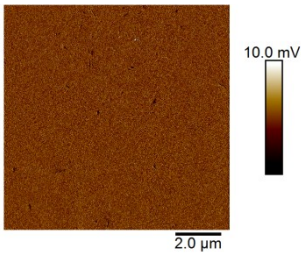
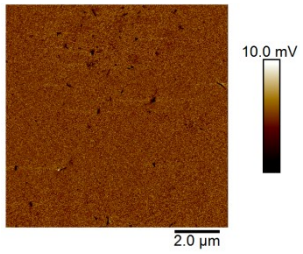
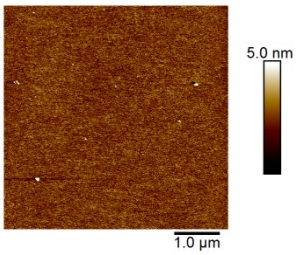
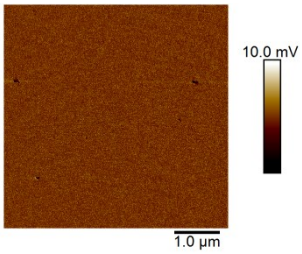
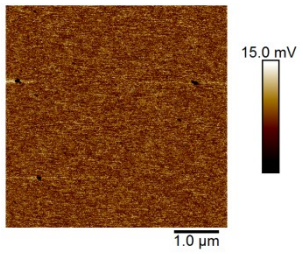
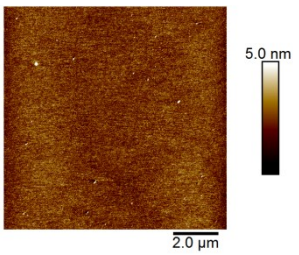
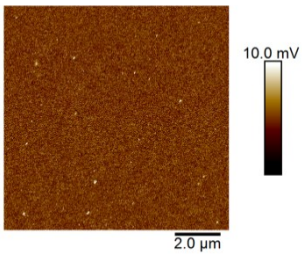
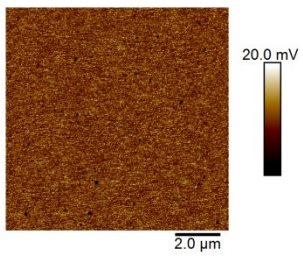
Figure S51: Fotographs of the PPE films before and after treatment with a tape strip. For better visibility, a film with dewetting defects was taken for the experiment. The picture demonstrates qualitatively that the polymer network is still present after this treatment. Ellipsometry data (Table S4) demonstrates that only a thin layer of polymer was removed with the tape.

Table S4: Film thickness before and after the Tape Test.

Sample name	Thickness	Thickness after Tape Test
P2	78 nm	74 nm

Figure S52: Representative AFM images (height, inphase, quadrature) of **P4** and **P5** films.

	Height	**Inphase**	**Quadratur**

P4	 10.0 nm 1.0 µm	 10.0 mV 1.0 µm	 10.0 mV 1.0 µm
	 20.0 nm 2.0 µm	 10.0 mV 2.0 µm	 10.0 mV 2.0 µm
P5	 5.0 nm 1.0 µm	 10.0 mV 1.0 µm	 15.0 mV 1.0 µm
	 5.0 nm 2.0 µm	 10.0 mV 2.0 µm	 20.0 mV 2.0 µm

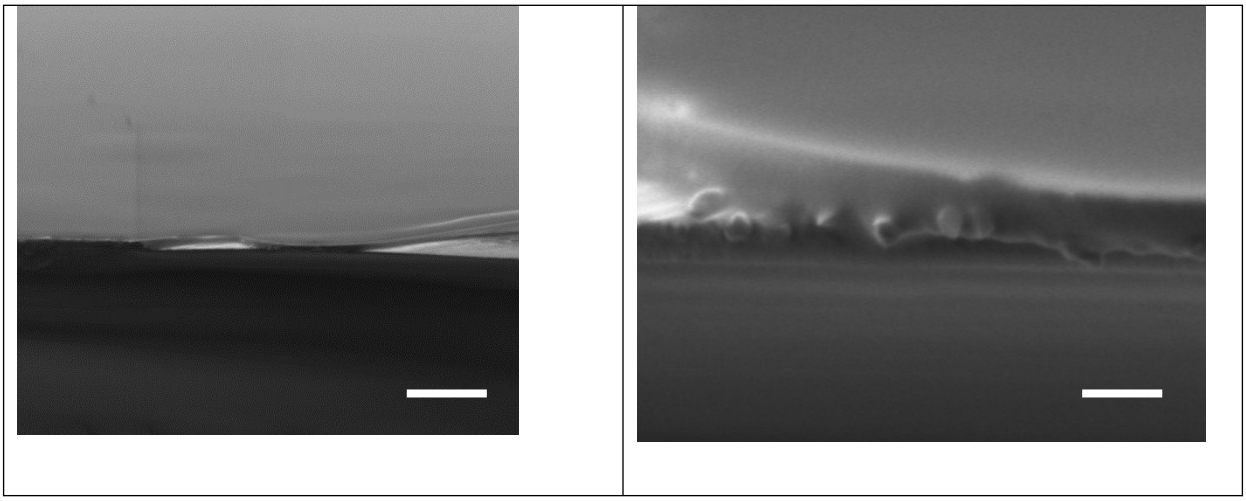


Figure S53: Representative scanning electron microscopy (SEM) images of **P2** after freeze-fracture. The wafer was broken and the cross-section was imaged, indicating a dense polymer layer with no discernible internal structure (scale bar = 2 μm and 200 nm).