Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Triazolinedione-"clicked" poly(phosphoester)s: Systematic adjustment of thermal properties

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Content

1. 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. Bromine, butyl isocyanate, phenyl isocyanate and potassium hydroxide, 3-buten-1-ol, 10-undecen-1-ol, phenol, HCl (37%), tris(hydroxymethyl)phosphine (90%), catalyst Grubbs 1st generation were purchased from Sigma-Aldrich. $POCl_3$ (phosphoryl chloride, 99%), 1-chloronaphthalene, ethyl carbazate and aluminium oxide (neutral, for chromatography) were purchased from Acros Organics. 1,4-diazabicyclo[2.2.2]octane was purchased from TCI chemicals. Triethylamine (Et_3N, 99.5%) was purchased from Roth, dried with CaH_2, distilled and stored over molecular sieves.

2. Instrumentation and Characterization Techniques

For the poly(phosphoester)s, size exclusion chromatography (SEC) measurements were performed in THF with a PSS SecCurity system (Agilent Technologies 1260 Infinity). Sample injection was performed by a 1260-ALS autosampler (Waters) at 30 °C. SDV columns (PSS) with dimensions of 300 × 80 mm, 10 μm particle size, and pore sizes of 106, 104, and 500 Å were employed. The DRI Shodex RI-101 detector (ERC) and UV−vis 1260-VWD detector (Agilent) were used for detection. Calibration was achieved using PS standards provided by Polymer Standards Service. For nuclear magnetic resonance analysis 1H, 13C, and 31P NMR spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer. All spectra were measured in either d_6-DMSO or $CDCl_3$ at 298 K. The spectra were calibrated against the solvent signal ($CDCl_3$ (7.26 ppm) or d_6-DMSO (2.50 ppm)) and analyzed using MestReNova 8 from Mestrelab Research S.L. The thermal properties of the synthesized polymers have been measured by differential scanning calorimetry (DSC) on a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The glass

transition temperatures were determined from midpoints in the second heating using the STARe software of Mettler-Toledo. Thermogravimetric analysis (TGA*)* was performed using a Mettler-Toledo TGA/SDTA851e equipment. Samples (5 to 10 mg) were heated in a nitrogen atmosphere with a heating rate of 10 K min^{-1} going from 25°C to 800°C. For the analysis of the thermograms, the STARe software of Mettler-Toledo was used. All curves are blank corrected.

3. Synthetic Procedures

Representative Procedure for Monomer Synthesis: The monomers were synthesized according to literature[1]. To a stirred solution of $POCl_3$ (10.00 g, 65.22 mmol, 1 eq.) in 100 mL dry DCM a mixture of a 3-buten-1-ol (9.41 g, 130.44 mmol, 2 eq.) and Et_3N (13.20 g, 130.44 mmol, 2 eq.) in 20 mL dry DCM at 0°C was added dropwise. After 18 h, a mixture of dry ethanol (6.01 g, 130.44 mmol, 2 eq.) and Et_3N (13.20 g, 130.44 mmol, 2 eq.) in 20 mL dry DCM was added dropwise at 0°C. After 24 h, the solvent was concentrated, diethyl ether added and Et_3N*HCl as a white solid removed by filtration. Remaining di(but-3-en-1-yl) phosphorochloridate was removed by flushing the crude product over neutral Al_2O_3 with DCM to give the pure product, a clear oil.

*Di(but-3-en-1-yl) ethyl phosphate (**1**):* DCM/ethyl acetate = 10:1, R_f=0,53. Yield: 73% (11.15 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 5.83-5.70 (m, 2H, CH_2=C*H*-CH_2-CH_2-O-P), 5.14-5.04 (m, 4H, CH_2=CH-CH_2-CH_2-O-P), 4.13-4.01 (m, 6H, -CH_2-O-P), 2.45-2.37 (dd, 4H, CH_2=CH-CH_2-CH_2-O-P), 1.30 (t, 3H, CH_3-). ^{13}C NMR (176 MHz, $CDCl_3$): δ [ppm] 133.51 (CH_2=*C*H-CH_2-CH_2-O-P), 117.81 (*C*H_2=CH-CH_2-CH_2-O-P), 66.83 (CH_2=CH-CH_2-*C*H_2-O-P), 63.97 (-*C*H_2-O-P), 34.77 (CH_2=CH-*C*H_2-CH_2-O-P), 16.22 (-*C*H_3). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -1.03. ESI-MS: *m/z* 257.07 $[M + Na]^+$, 491.17 $[2M + Na]^+$

(calculated for $C_{10}H_{19}O_4P$: 234.10). FTIR (cm^{-1}): 3080, 2981, 2933, 2904, 1642, 1473, 1432, 1391, 1369, 1264 (P=O), 1165, 1013 (P-O-C), 988 (P-O-C), 914, 860, 799, 734, 701.

*Di(but-3-en-1-yl) phenyl phosphate (**2**):* Following the general procedure described above and using phenol instead of ethanol, **2** was obtained after column chromatography over silica using as eluent dichloromethane. DCM, R_f= 0.3. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.33−7.16 (m, 5H, *Ph*-O-P), 5.79−5.73 (m, 2H, CH_2=C*H*-CH_2-CH_2-O-P), 5.11-5.08 (m, 4H, C*H*$_2$=CH-CH_2-CH_2-O-P), 4.20−4.13 (m, 4H, -C*H*$_2$-O-P), 2.44−2.42 (m, 4H, CH_2=CH-C*H*$_2$-CH_2-O-P). ^{13}C NMR (176 MHz, $CDCl_3$): δ [ppm] 150.69, 150.65, 133.12, 129.70, 125.05, 120.04, 120.01, 117.91, 67.54, 67.50, 34.60, 34.56. ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] −6.40.

*Di(undecen-10-en-1-yl) phenyl phosphate (**3**):* Following the general procedure described above and using phenol instead of ethanol and 10-undecen-1-ol instead of 3-buten-1-ol, **3** was obtained after column chromatography over silica using as eluent dichloromethane. DCM, R_f=0.5. Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.32-7.16 (m, 5H, *Ph*-O-P), 5.83−5.77 (m, 2H, CH_2=C*H*-CH_2-), 5.00−4.91 (m, 4H, C*H*$_2$=CH-CH_2-),4.16−4.09 (m, 4H, -C*H*$_2$-O-P), 2.04−2.01 (m, 4H, CH_2=CH-*CH*$_2$-CH_2-), 1.69−1.65 (m, 4H, -*CH*$_2$-CH_2-O-P), 1.39−1.26 (m, 12H, - *CH*$_2$-). ^{13}C NMR (176 MHz, $CDCl_3$): δ [ppm] 150.98, 150.94, 139.29, 129.77, 125.02, 120.10, 114.27, 68.69, 68.66, 33.93, 30.37, 30.33, 29.55, 29.04. . ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] −6.11.

*General procedure for ADMET Polymerization (**C6-Et**, **C6-Ph**, **C20-Ph**):* The respective monomer, 3 mol% catalyst Grubbs 1st generation and ca. 50wt% 1-chloronaphthalene were mixed under argon atmosphere. Polymerization was carried out at reduced pressure to remove the evolving ethylene at 60-80°C for up to 72h until reaction was completed. Reaction progress was monitored with ^{1}H NMR spectroscopy and a spatula tip of additional catalyst added after measurement if necessary until reaction was completed. The

reaction was cooled down, 7 mL of DCM, ca. 10 mg of tris(hydroxymethyl)phosphine and 3 drops of Et_3N were added to deactivate the catalyst. After 1 h, 5 mL distilled water was added and the mixture was stirred overnight. The organic phase was extracted with aqueous HCl (5 wt%) and brine. The mixture was concentrated at reduced pressure and the polymer precipitated into hexane twice. Yields 50-90%.

C6-Et: ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 5.83-5.72 (m, CH_2=C*H*-CH_2-CH_2-O-P), 5.54-5.50 (m, -CH_2-C*H*=C*H*-CH_2-), 5.17-5.08 (m, C*H*$_2$=CH-CH_2-CH_2-O-P), 4.12-3.98 (m, -C*H*$_2$-O-P), 2.46-2.36 (m, CH_2=CH-C*H*$_2$-CH_2-O-P), 1.33 (t, CH_3-). ^{13}C NMR (176 MHz, $CDCl_3$): δ [ppm] 128.28, 127.31, 122.02, 67.07, 33.71, 16.34. ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -1.00.

C6-Ph: ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.36-7.12 (m, *Ph*-O-P), 5.80-5.71 (m, CH_2=C*H*-CH_2-CH_2-O-P), 5.56-5.38 (m, -CH_2-C*H*=C*H*-CH_2-), 5.15-5.06 (m, C*H*$_2$=CH-CH_2-CH_2-O-P), 4.20-4.06 (m, -C*H*$_2$-O-P), 2.46-2.25 (m, CH_2=CH-C*H*$_2$-CH_2-O-P). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.39.

C20-Ph: ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.36-7.13 (m, *Ph*-O-P), 5.40-5.30 (m, -CH_2-C*H*=C*H*-CH_2-), 4.16-4.09 (m, -C*H*$_2$-O-P), 1.99-1.92 (m, -CH=CH-*CH*$_2$-CH_2-), 1.69−1.62 (m, -*CH*$_2$-CH_2-O-P), 1.36−1.25 (m, 12H, - *CH*$_2$-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): -6.10.

Synthesis of TAD compounds:

DABCO-Br: In a 500 mL two-neck flask, 1,4-diazabicyclo[2.2.2]octane (6.73 g, 60.0 mmol, 1 eq.) was dissolved in chloroform (100 mL). In a next step, a solution of Br_2 (20.0 g, 0.125 mol, 2.1 eq.) in chloroform (100 mL) was added dropwise using an addition funnel. The resulting mixture was stirred under inert atmosphere for 1 hour. The yellow precipitate was

filtered off, washed with chloroform (50 mL) and dried overnight in a vacuum oven at 40 °C to obtain 23.3 g of yellow powder (14.8 mmol, 99%).

*4-phenyl-1,2,4-triazoline-3,5-dione (**Ph-TAD**):* A mixture of ethyl carbazate (10 g, 96.1 mmol, 1 eq.) and toluene (105 mL) was placed in a three neck flask (250 mL) and cooled in an ice bath. The flask was equipped with an addition funnel, containing 10.44 mL phenylisocyanate (96.1 mmol, 1 eq.), a mechanical stirrer and a bulb condenser. The mixture was put under inert atmosphere and the isocyanate was added slowly under vigorous stirring. After addition the mixture was stirred at room temperature for two hours, followed by 2 hours at 90°C. After cooling the reaction to room temperature, 4-phenyl-1-(ethoxycarbonyl) semicarbazide was filtered off and washed with toluene (96 %). Subsequently, the obtained 4-phenyl-1-(ethoxycarbonyl) semicarbazide (12.2 g, 60.0 mmol) was dissolved in 30 mL of an aqueous potassium hydroxide solution (4M) in a 50 mL flask under inert atmosphere. This mixture was refluxed for 1.5 hour (100°C), warm filtered, cooled to room temperature and acidified to pH 1 by addition of HCl. This mixture was cooled to room temperature to yield a white powder that was filtered off (95%). In a last step, a mixture of the just obtained 4-phenyl-1,2,4-triazolidine-3,5-dione (1 g, 5.64 mmol, 1 eq.), DABCO-Br (2 g, 1.27 mmol, 0.2 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate was concentrated in vacuo to obtain 4-phenyl-1,2,4-triazoline-3,5-dione (**Ph-TAD**) as dark red crystals (92%). The temperature of the cooling bath should not exceed 50°C due to the volatility of the obtained compound. ^{1}H-NMR (300 MHz, d_6-DMSO): δ [ppm] 7.60–7.45 (m, 5H, *Ar*-).

*4-butyl-1,2,4-triazoline-3,5-dione (**Bu-TAD**):* A mixture of ethyl carbazate (10 g, 96.1 mmol, 1 eq.) and toluene (105 mL) was placed in a three neck flask (250 mL) and cooled in an ice bath. The flask was equipped with an addition funnel, containing 10.8mL

butylisocyanate (96.1 mmol, 1 eq.), a mechanical stirrer and a bulb condenser. The mixture was put under inert atmosphere and the isocyanate was added slowly under vigorous stirring. After addition, the mixture was stirred at room temperature for two hours, followed by 2 hours at 90°C. After cooling the reaction to room temperature, 4-butyl-1-(ethoxycarbonyl) semicarbazide (96%) was filtered off and washed with toluene. In a 50 mL flask, 4-butyl-1-(ethoxycarbonyl) semicarbazide (12.2 g, 60.0 mmol) was dissolved in 30 mL of an aqueous potassium hydroxide solution (4M) under inert atmosphere. This mixture was refluxed for 1.5 hour (100°C), warm filtered, cooled to room temperature and acidified until pH 1 by addition of hydrogen chloride. This mixture was cooled to room temperature to yield 4-butyl-1,2,4-triazolidine-3,5-dione (62%) as a solid white powder, that was filtered off. A mixture of 4-butyl-1,2,4-triazolidine-3,5-dione (1 g, 6.36 mmol, 1 eq.), DABCO-Br (2 g, 1.27 mmol, 0.2 eq.) and dichloromethane (30 mL) was put in a flask (100 mL) under inert atmosphere and stirred for 2 hours at room temperature. The reaction mixture was filtered off, the residue washed with dichloromethane (2 × 30 mL) and the filtrate was concentrated in vacuo to obtain 4-butyl-1,2,4-triazoline-3,5-dione (72%). The temperature of the heating bath cannot exceed 50°C due to the volatility of the obtained compound. ^{1}H-NMR (300 MHz, d_6-DMSO): δ [ppm] 3.47 (t, 2H, N-C*H*$_2$-), 1.56 (m, 2H, N-CH$_2$-C*H*$_2$-), 1.30 (m, 2H, CH$_3$-C*H*$_2$-CH$_2$-), 0.88 (t, 3H, C*H*$_3$-(CH$_2$)$_3$-).

1-ethyl 2-phenyl hydrazine-1,2-dicarboxylate: The compound was synthesized according to literature.[2] 10.0 g of ethylcarbazate (96.1 mmol, 1 eq.) and 20.0 mL di-isopropylethylamine (DIPEA) (115 mmol, 1.2 eq) were solubilized in 100 mL dichloromethane under inert atmosphere. The reaction mixture was cooled with an ice bath and 12.1 mL phenyl chloroformate (96.1 mmol, 1 eq.) was added dropwise. After overnight stirring, the reaction mixture was extracted with 0.5M HCl solution (3 x 30.0 mL) and washed with 50.0 mL saturated NaCl-solution. The organic phase was dried on $MgSO_4$ and the

solvent was removed in vacuo to obtain 19.6 g 1-ethyl 2-phenyl hydrazine-1,2-dicarboxylate (87.4 mmol, 91 %). ^{1}H-NMR (300 MHz, d_6-DMSO): δ [ppm] 7.40 (t, 2H, aromatic), 7.25 (t, 1H, aromatic), 7.18 (d, 2H, aromatic), 6.85 (s (br), 1H, N*H*), 6.56 (s (br), 1H, N*H*), 4.27 (q, 2H, O-C*H*$_2$-CH$_3$), 1.32 (O-CH$_2$-C*H*$_3$).

*4-octyl-1,2,4-triazoline-3,5-dione (**Oct-TAD**):* In a 50 mL of acetonitrile, 1 mL (0.78 g, 6.03 mmol, 1 eq.) of octyl amine was added to 2.03 g ethylphenyl hydrazine dicarboxylate (9.05 mmol, 1 eq.) and this reaction mixture was stirred overnight at room temperature, after which the solvent was removed under reduced pressure. The product was purified via column chromatography (eluent EtOAc:Hexane 2:1), yielding 1.14g of pure semicarbazide (4.40 mmol, 73%). Subsequently, ring closure of the semicarbazide was performed in basic environment. The semicarbazide (1.14g, 4.40 mmol, 1 eq.) was solubilized in 30 mL of methanol and potassium carbonate (2.43 g, 17.60 mmol, 4 eq.) was added. The mixture was refluxed overnight, cooled to room temperature and acidified until pH 1 by addition of hydrogen chloride. The salts were filtered off and the solvent was removed in vacuo to yield 4-octyl-1,2,4-triazolidine-3,5-dione (0.84 g, 3.92 mmol, 89%) as a solid white powder. In the last step, 0.84 g of 4-octyl-1,2,4-triazolidine-3,5-dione was solubilized in dichloromethane (25 mL) and 1.23 g of DABCO-Br (0.78 mmol, 0.2 eq.) was added. This mixture was filtered off after one hour and the filtrate was concentrated in vacuo to yield 0.79 g of 4-octyl-1,2,4-triazoline-3,5-dione (3.72 mmol, 95%). 4-octyl-semicarbazide: ^{1}H-NMR (300 MHz, d_6-DMSO): δ [ppm] 8.70 (s, 1H, N*H*), 7.60 (s, 1H, N*H*), 6.27 (s, 1H, N*H*), 4.01 (q, 2H, O-C*H*$_2$-CH$_3$), 2.97 (q, 2H, NH-C*H*$_2$-CH$_2$-), 1.36 (quin, 2H, NH-CH$_2$-C*H*$_2$-), 1.24 (m, 10H, alkyl), 1.17 (t, 3H, O-CH$_2$-C*H*$_3$), 0.86 (t, 3H, -CH$_2$-CH$_2$-C*H*$_3$). 4-octyl-1,2,4-triazolidine-3,5-dione: ^{1}H-NMR (300 MHz, d_6-DMSO): δ [ppm] 10.00 (s, 2H, N*H*-N*H*), 3.33 (t, 2H, N-C*H*$_2$-CH$_2$-), 1.52 (quin, 2H, N-CH$_2$-C*H*$_2$-), 1.24 (m, 10H, alkyl), 0.86 (t, 3H, -CH$_2$-CH$_2$-C*H*$_3$). 4-octyl-

1,2,4-triazoline-3,5-dione: ^{1}H-NMR (300 MHz, d_6-DMSO): 3.45 (q, 2H, N-C*H*$_2$-CH$_2$-), 1.56 (quin, 2H, N-CH$_2$-C*H*$_2$-), 1.24 (m, 10H, alkyl), 0.86 (t, 3H, -CH$_2$-CH$_2$-C*H*$_3$).

General procedure for TAD functionalization of polymers: The polymers were solubilized in DCM (approx. 1ml) and 1 eq. of the corresponding TAD component, solubilized in ca. 0.5 mL DCM (Bu-TAD, Oct-TAD) or THF (Ph-TAD) was added in order to obtain full functionalisation. The reaction was stirred overnight to obtain full conversion and was precipitated in hexane. During reaction the colour changes from pink to colourless for C11-Ph or brownish for C4-Et and C4-Ph. After drying (overnight, vacuum, 40°C), a variation of glassy to sticky polymers was obtained in quantitative yields.

Table S1. Overview of amounts of polymers and TADs used for functionalization.

	C6-Ph	**C6-Et**	**C20-Ph**
Amount polymer	250 mg	100 mg	250 mg
Mass repeating unit	254,22 g/mol	206,17 g/mol	450,60 g/mol
n	0,9834 mmol	0,4850 mmol	0,5548 mmol
PhTAD	172 mg	127 mg	97 mg
Bu-TAD	152 mg	113 mg	86 mg
Oct-TAD	208 mg	154 mg	117 mg

C6-Et-Bu: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.35 (s, trans, -N-N*H*-C(=O)-), 10.01 (s, cis, -N-N*H*-C(=O)-), 5.77 (s, trans, -CH(N)-C*H*=C*H*-CH$_2$-), 5.51 (s, cis, -CH(N)-C*H*=C*H*-CH$_2$-), 4.61 (s, trans, -CH(N)-CH=CH-C*H*$_2$-O-P), 4.44 (s, -CH$_2$-C*H*(N)-CH=CH-), 4.10-3.88 (m, cis, -CH(N)-CH=CH-C*H*$_2$-O-P; m, -CH$_2$-C*H*$_2$-O-P; m, CH$_3$-C*H*$_2$-O-P), 2.31 (s, -C*H*$_2$-CH$_2$-O-P), 2.12-1.82 (m, CH$_3$-CH$_2$-CH$_2$-C*H*$_2$-N-), 1.59-1.44 (m, CH$_3$-CH$_2$-C*H*$_2$-CH$_2$-N-), 1.38-1.16 (m, CH$_3$-C*H*$_2$-CH$_2$-CH$_2$-N-; t, C*H*$_3$-CH$_2$-O-P), 0.92-0.77 (m, C*H*$_3$-CH$_2$-CH$_2$-CH$_2$-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -1.40.

C6-Et-Oct: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.54 (s, trans, -N-N*H*-C(=O)-), 10.21 (s, cis, -N-N*H*-C(=O)-), 5.86 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.59 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.67 (s, trans, -CH(N)-CH=CH-C*H_2*-O-P), 4.50 (s, -CH_2-C*H*(N)-CH=CH-), 4.24-3.92 (m, cis, -CH(N)-CH=CH-C*H_2*-O-P; m, -CH_2-C*H_2*-O-P; m, CH_3-C*H_2*-O-P), 2.29 (s, -C*H_2*-CH_2-O-P), 2.06-1.79 (m, CH_3-$(CH_2)_5$-CH_2-C*H_2*-N-), 1.47 (m, CH_3-$(CH_2)_5$-C*H_2*-CH_2-N-), 1.35-0.94 (m, CH_3-(C*H_2)$_5$*-CH_2-CH_2-N-; t, C*H_3*-CH_2-O-P), 0.83-0.58 (m, C*H_3*-$(CH_2)_5$-CH_2-CH_2-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -1.39.

C6-Et-Ph: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.46 (s, trans, -N-N*H*-C(=O)-), 9.79 (s, cis, -N-N*H*-C(=O)-), 7.67-7.34 (m, *Ph*-), 5.86 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.50 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.73 (s, trans, -CH(N)-CH=CH-C*H_2*-O-P), 4.48 (s, -CH_2-C*H*(N)-CH=CH-), 4.09-3.87 (m, cis, -CH(N)-CH=CH-C*H_2*-O-P; m, -CH_2-C*H_2*-O-P; m, CH_3-C*H_2*-O-P), 2.30 (s, -C*H_2*-CH_2-O-P), 1.22 (t, C*H_3*-CH_2-O-P). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -1.04.

C6-Ph-Bu: : ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.32 (s, trans, -N-N*H*-C(=O)-), 10.01 (s, cis, -N-N*H*-C(=O)-), 7.40-7.19 (m, *Ph*-), 5.76 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.44 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.58 (s, trans, -CH(N)-CH=CH-C*H_2*-O-P; s, -CH_2-C*H*(N)-CH=CH-), 4.05 (s, cis, -CH(N)-CH=CH-C*H_2*-O-P; s, -CH_2-C*H_2*-O-P), 2.28 (s, -C*H_2*-CH_2-O-P), 2.14-1.85 (m, CH_3-CH_2-CH_2-C*H_2*-N-), 1.57-1.39 (m, CH_3-CH_2-C*H_2*-CH_2-N-), 1.35-1.11 (m, CH_3-C*H_2*-CH_2-CH_2-N-), 0.95-0.70 (m, C*H_3*-CH_2-CH_2-CH_2-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.71.

C6-Ph-Oct: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.31 (s, trans, -N-N*H*-C(=O)-), 10.00 (s, cis, -N-N*H*-C(=O)-), 7.38-7.18 (m, *Ph*-), 5.75 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.43 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.57 (s, trans, -CH(N)-CH=CH-C*H_2*-O-P; s, -CH_2-C*H*(N)-CH=CH-), 4.08 (s, cis, -CH(N)-CH=CH-C*H_2*-O-P; s, -CH_2-C*H_2*-O-P), 2.28 (s, -C*H_2*-CH_2-O-P), 2.14-1.85 (m, CH_3-$(CH_2)_5$-CH_2-C*H_2*-N-), 1.63-1.40 (m, CH_3-$(CH_2)_5$-C*H_2*-CH_2-N-), 1.34-

1.06 (m, CH_3-(C*H*$_2$)$_5$-CH_2-CH_2-N-), 0.91-0.74 (m, C*H*$_3$-(CH_2)$_5$-CH_2-CH_2-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.72.

C6-Ph-Ph: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.79 (s, trans, -N-N*H*-C(=O)-), 10.45 (s, cis, -N-N*H*-C(=O)-), 7.60-7.18 (m, *Ph*-), 5.84 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.42 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.73 (s, trans, -CH(N)-CH=CH-C*H*$_2$-O-P), 4.61 (s, -CH_2-C*H*(N)-CH=CH-), 4.16 (s, cis, -CH(N)-CH=CH-C*H*$_2$-O-P), 4.04 (s, -CH_2-C*H*$_2$-O-P), 2.29 (s, -C*H*$_2$-CH_2-O-P). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.70.

C20-Ph-Bu: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.24 (s, trans, -N-N*H*-C(=O)-), 9.97 (s, cis, -N-N*H*-C(=O)-), 7.49-7.11 (m, *Ph*-), 5.57 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.35 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.28 (m, -CH_2-C*H*(N)-CH=CH-), 4.05 (m, -CH_2-C*H*$_2$-O-P), 1.92 (m, CH_3-CH_2-CH_2-C*H*$_2$-N-), 1.67-1.39 (m, CH_3-CH_2-C*H*$_2$-CH_2-N-; m, -C*H*$_2$-CH_2-O-P), 1.37-1.01 (m, CH_3-C*H*$_2$-CH_2-CH_2-N-; -CH_2- backbone), 0.83 (t, C*H*$_3$-CH_2-CH_2-CH_2-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.26.

C20-Ph-Oct: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.12 (s, trans, -N-N*H*-C(=O)-), 10.00 (s, cis, -N-N*H*-C(=O)-), 7.44-7.06 (m, *Ph*-), 5.54 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.36 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.21 (m, -CH_2-C*H*(N)-CH=CH-), 4.01 (m, -CH_2-C*H*$_2$-O-P), 1.88 (m, CH_3-(CH_2)$_5$-CH_2-C*H*$_2$-N-), 1.51 (m, CH_3-(CH_2)$_5$-C*H*$_2$-CH_2-N--; m, -C*H*$_2$-CH_2-O-P), 1.20-1.15 (m, CH_3-(*CH*$_2$)$_5$-CH_2-CH_2-N-; -CH_2- backbone), 0.83 (t, *CH*$_3$-(CH_2)$_5$-CH_2-CH_2-N-). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.25.

C20-Ph-Ph: ^{1}H NMR (300 MHz, d_6-DMSO): δ [ppm] 10.72 (s, trans, -N-N*H*-C(=O)-), 10.45 (s, cis, -N-N*H*-C(=O)-), 7.62-7.09 (m, *Ph*-), 5.65 (s, trans, -CH(N)-C*H*=C*H*-CH_2-), 5.49 (s, cis, -CH(N)-C*H*=C*H*-CH_2-), 4.40 (m, -CH_2-C*H*(N)-CH=CH-), 4.04 (m, -CH_2-C*H*$_2$-O-P), 1.96 (m, -CH(N)-CH=CH-C*H*$_2$-), 1.70 (m, -C*H*$_2$-CH_2-O-P), 1.55 (m, -CH_2- backbone), 0.1.21 (m, -CH_2- backbone). ^{31}P{H} NMR (283 MHz, $CDCl_3$): δ [ppm] -6.30.

4. NMR Spectra

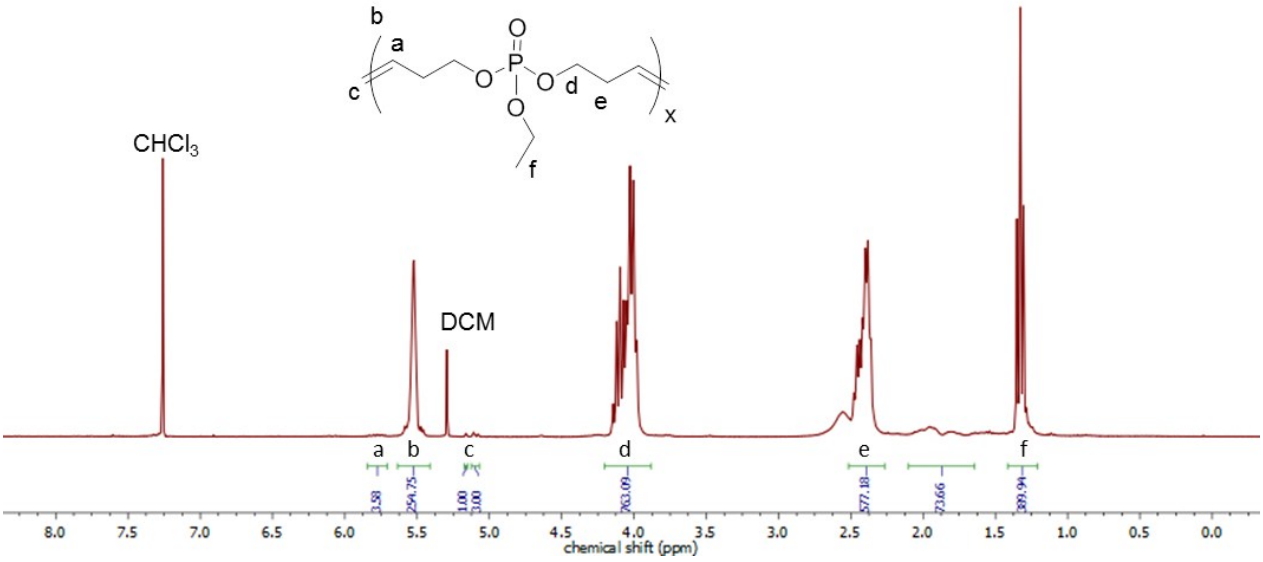

Figure S1: ^{1}H NMR (300 MHz, $CDCl_3$) of polymer **C6-Et**.

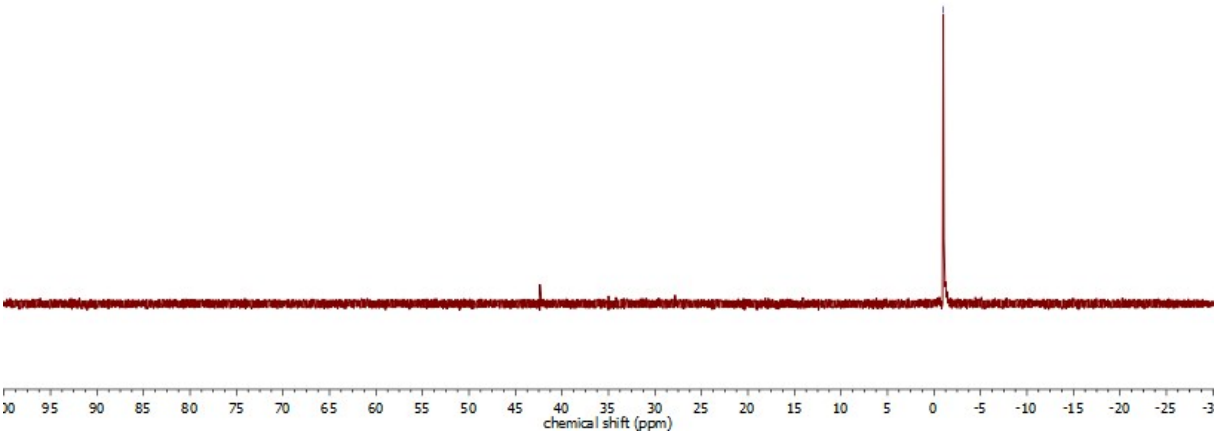

Figure S2: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymer **C6-Et**.

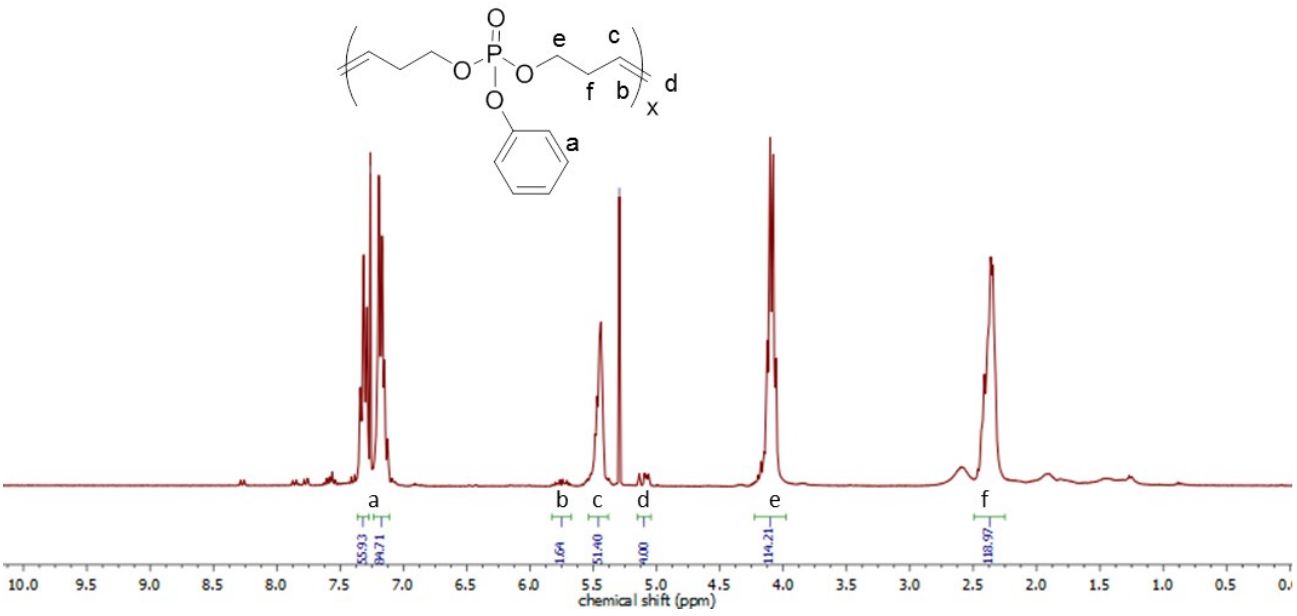

Figure S3: ^{1}H NMR (300 MHz, $CDCl_3$) of polymer **C6-Ph**.

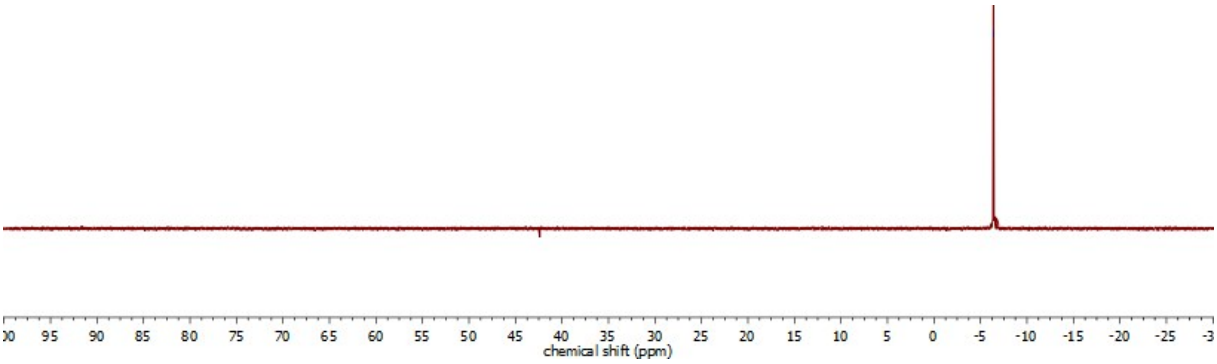

Figure S4: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymer **C6-Ph**.

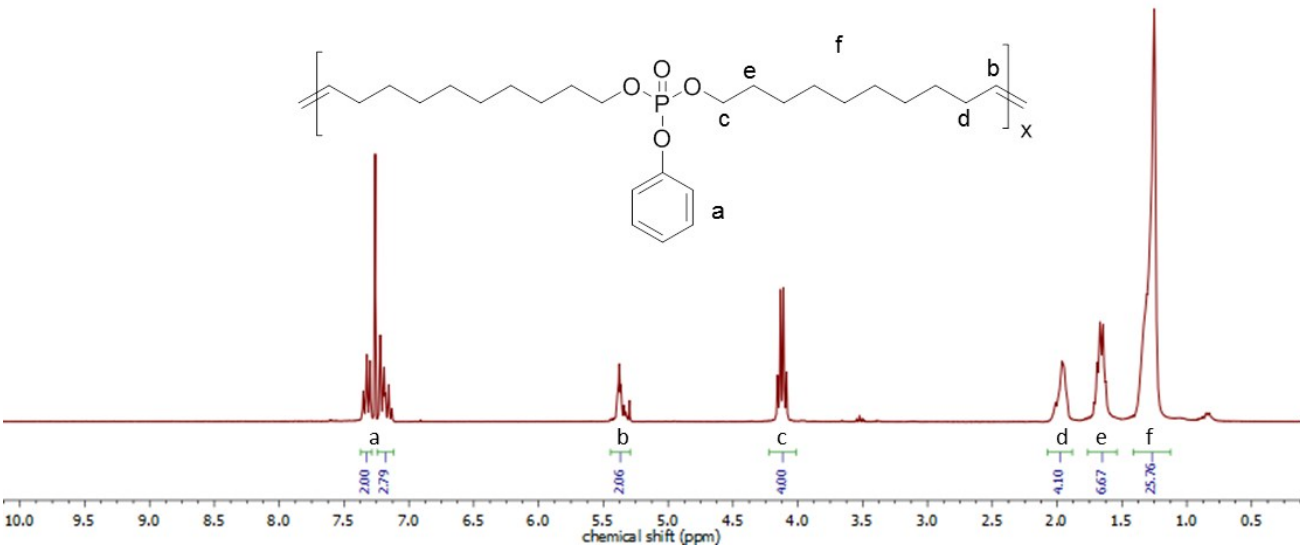

Figure S5: ^{1}H NMR (300 MHz, $CDCl_3$) of polymer **C20-Ph**.

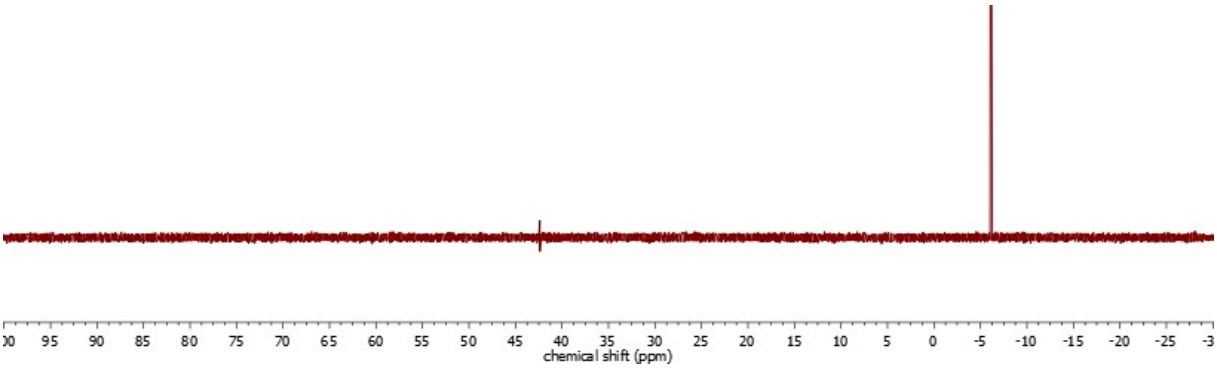

Figure S6: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymer **C20-Ph**.

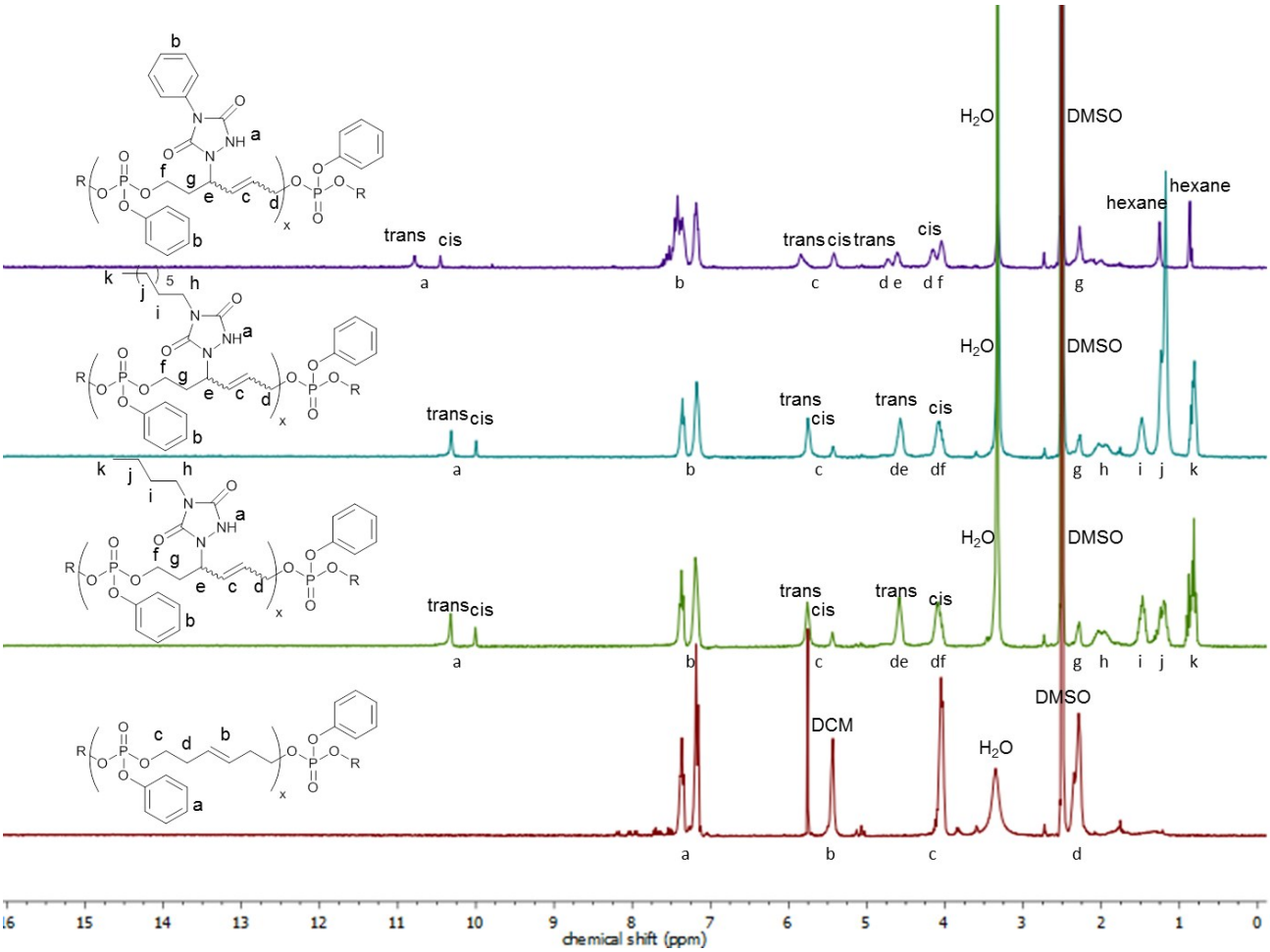

Figure S7: ^{1}H NMR (300 MHz, DMSO-d_6) of polymers **C6-Ph**, **C6-Ph-Bu**, **C6-Ph-Oct**, **C6-Ph-Ph**.

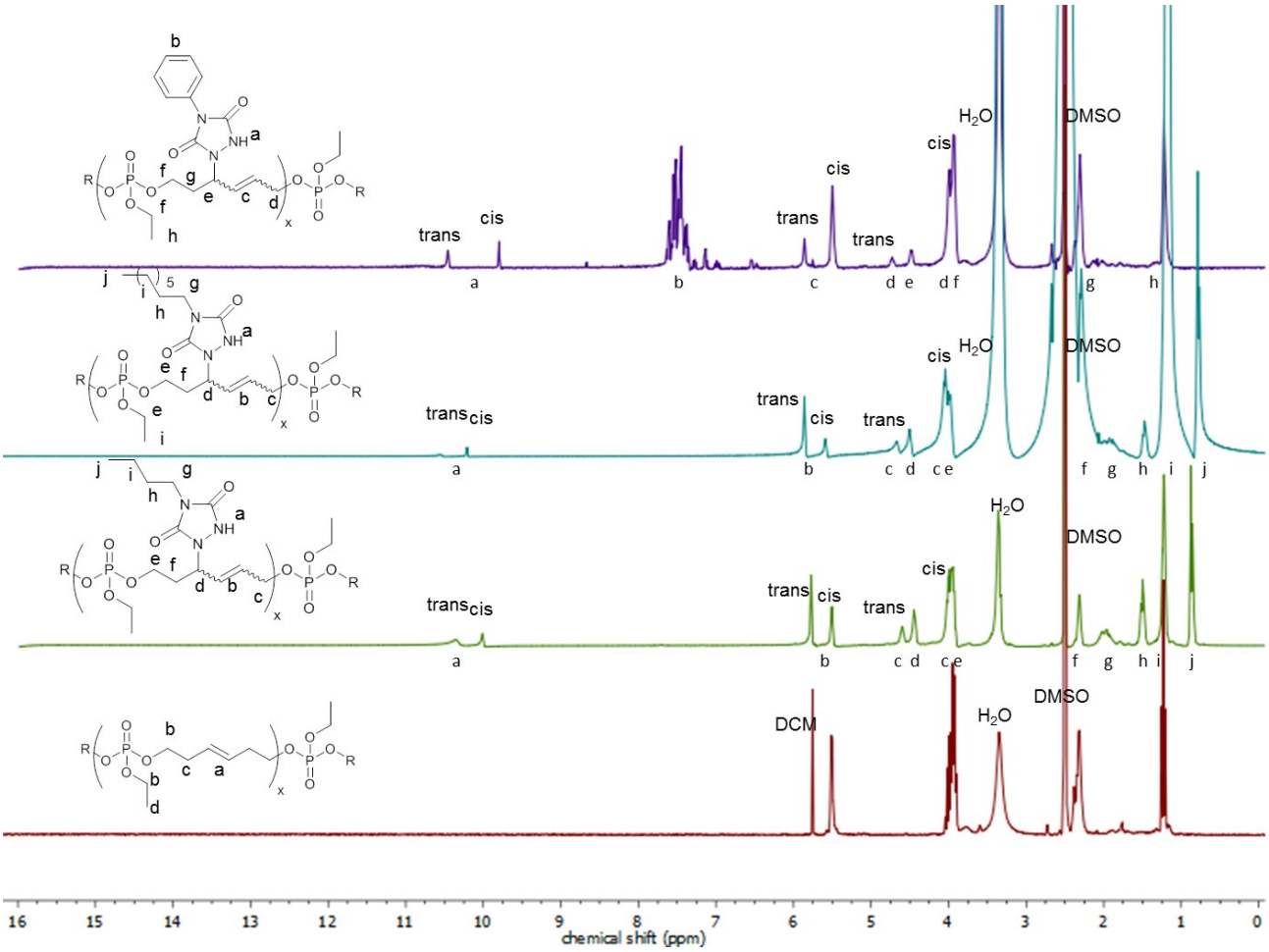

Figure S8: ^{1}H NMR (300 MHz, DMSO-d_6) of polymers **C6-Et**, **C6-Et-Bu**, **C6-Et-Oct**, **C6-Et-Ph**.

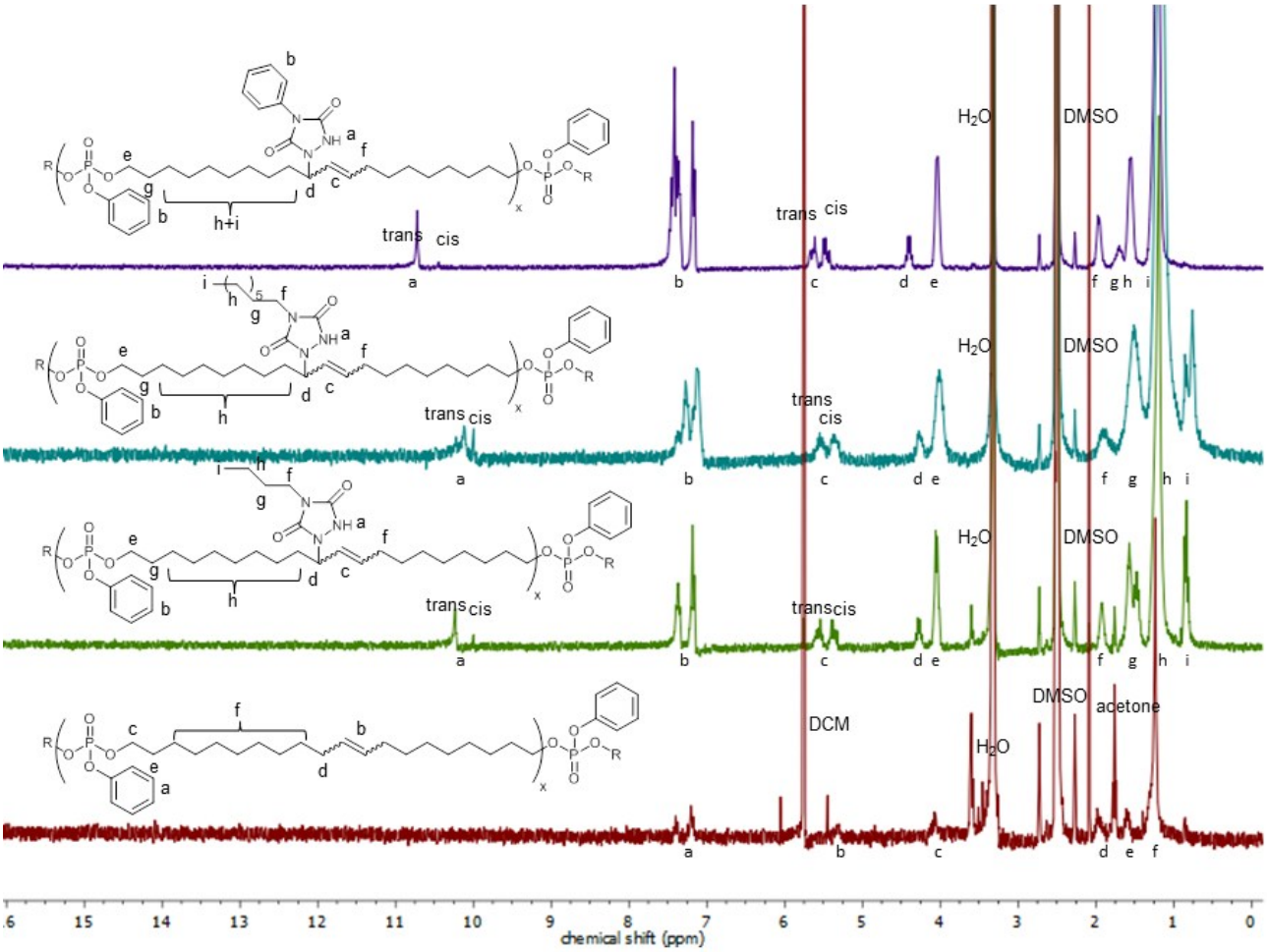

Figure S9: ^{1}H NMR (300 MHz, DMSO-d_6) of polymers **C20-Ph**, **C20-Ph-Bu**, **C20-Ph-Oct**, **C20-Ph-Ph**.

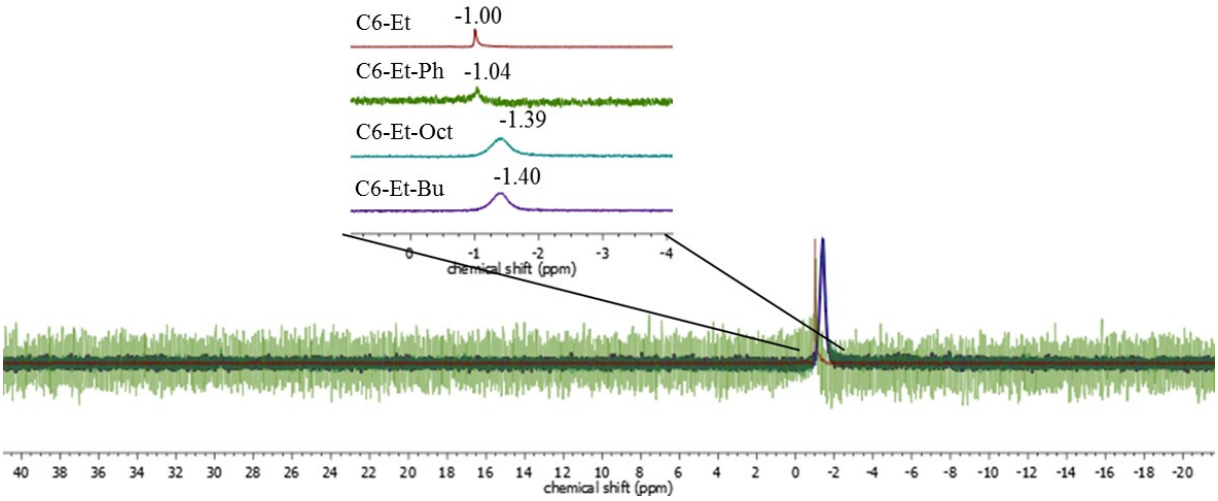

Figure S10: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymers **C6-Et**, **C6-Et-Bu**, **C6-Et-Oct**, **C6-Et-Ph**.

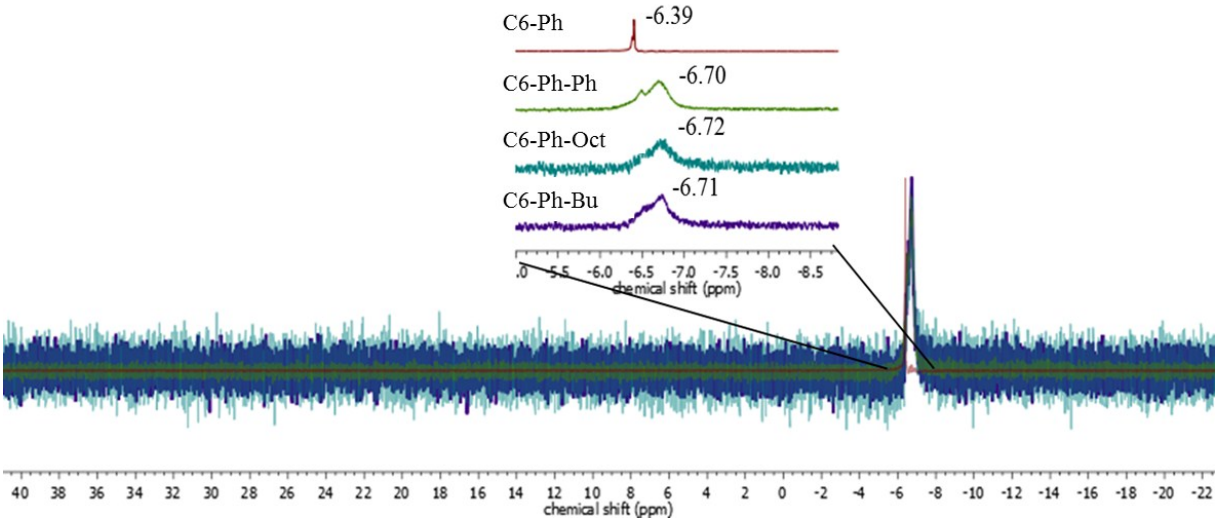

Figure S11: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymers **C6-Ph**, **C6-Ph-Bu**, **C6-Ph-Oct**, **C6-Ph-Ph**.

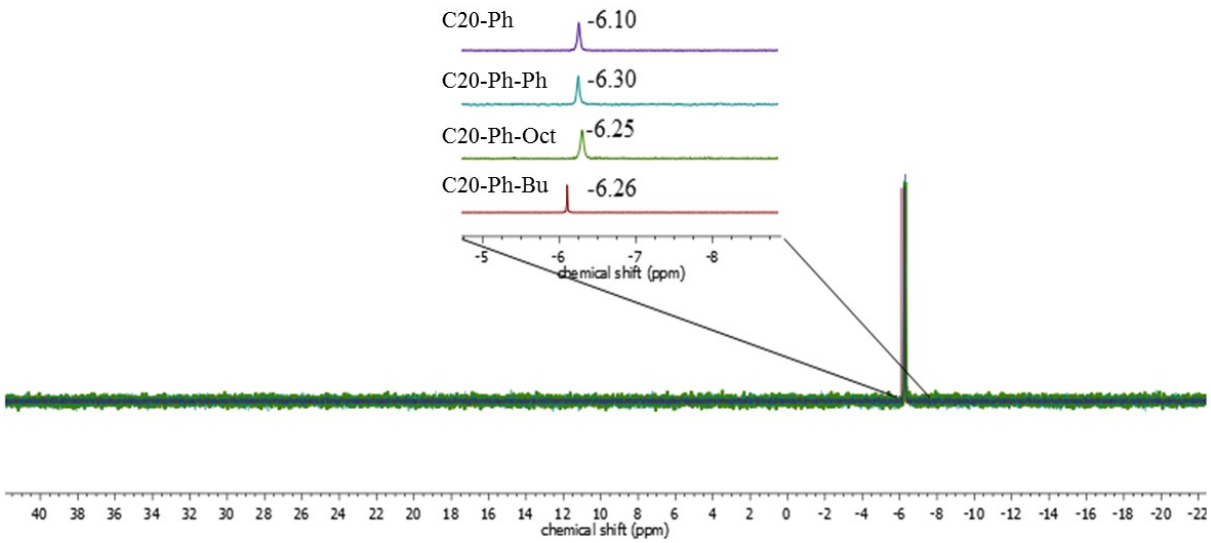

Figure S12: ^{31}P {H}NMR (283 MHz, $CDCl_3$) of polymers **C20-Ph**, **C20-Ph-Bu**, **C20-Ph-Oct**, **C20-Ph-Ph**.

5. Size Exclusion Chromatography

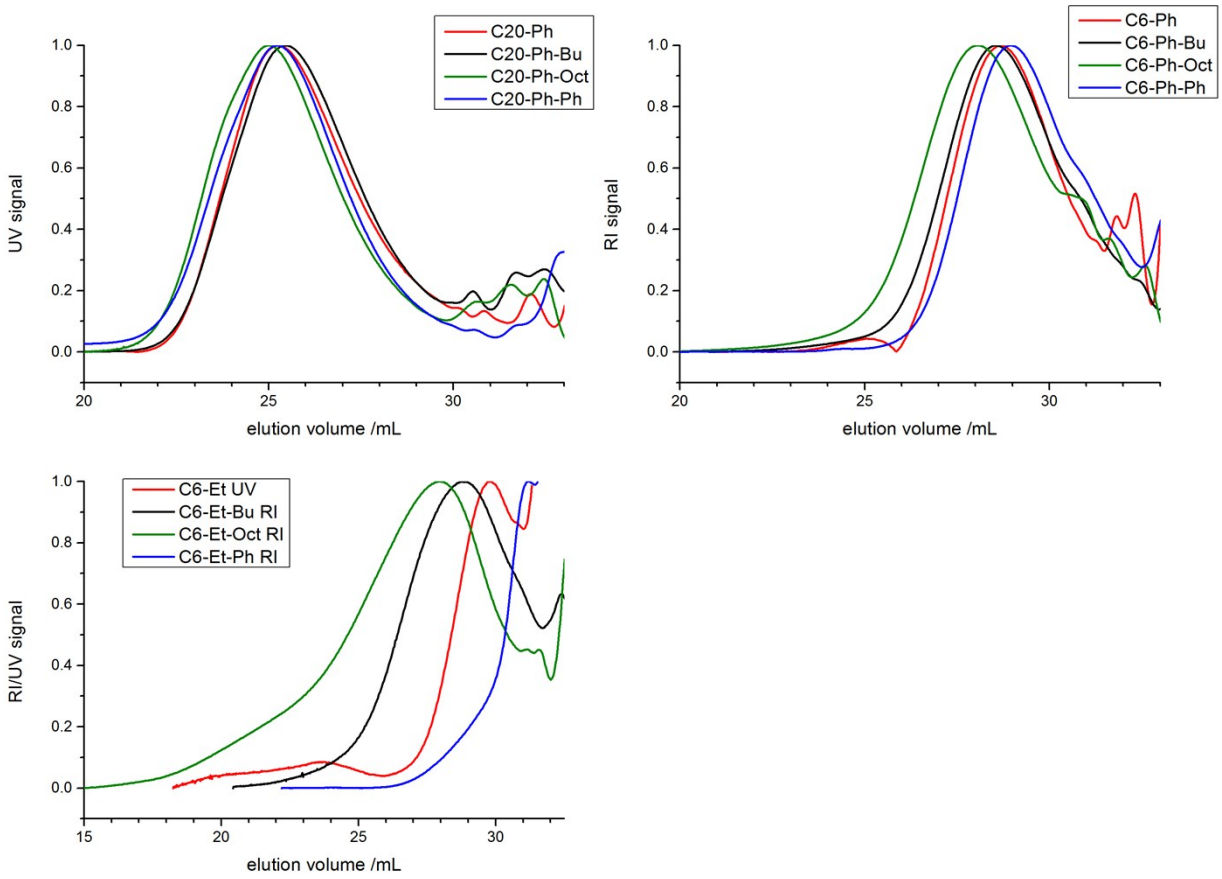

Figure S13: SEC curves of all polymers and functionalized polymers, in THF with UV-signal for **C20-Ph**, RI-signal for **C6-Ph** and UV or RI-signal for **C6-Et**.

Table S2: Overview of SEC results.

sample	signal	M_n / g/mol	M_w / g/mol	$Đ$	V_{max} / mL
C20-Ph	UV	10,100	22,400	2.21	25.26
C20-Ph-Bu	UV	11,000	21,800	1.99	25.45
C20-Ph-Oct	UV	14,500	28,500	1.97	25.01
C20-Ph-Ph	UV	12,800	28,200	2.20	25.24
C6-Ph	RI	2,300	4,300	1.84	28.68
C6-Ph-Bu	RI	2,300	4,700	2.00	28.54
C6-Ph-Oct	RI	4,200	8,100	1.95	28.06
C6-Ph-Ph	RI	2,000	3,600	1.83	28.96
C6-Et	UV	1,700	2,500	1.46	29.83
C6-Et-Bu	RI	3,300	7,500	2.22	28.83
C6-Et-Oct	RI	4,500	10,600	2.35	27.99
C6-Et-Ph	RI	1,000	1,700	1.66	31.22

6. TGA

Table S3. Overview of TGA results.

sample	wt% P_{th}	wt% N_{th}	T_{onset} (95 wt%) /°C	T_{max} /°C	Char Yield (wt%) at 700°C
C6-Et	**15.02**	**-**	**230.5**	**257**	**29**
C6-Et-Bu	**8.57**	**11.63**	**225**	**242**	**26**
C6-Et-Oct	**7.42**	**10.07**	**232**	**247**	**22**
C6-Et-Ph	**8.12**	**11.02**	**231**	**281**	**29**
C6-Ph	**12.18**	**-**	**221.5**	**236**	**28**
C6-Ph-Bu	**7.57**	**10.26**	**223**	**~275**	**34**
C6-Ph-Oct	**6.65**	**9.03**	**228**	**~310**	**29**
C6-Ph-Ph	**7.21**	**9.79**	**223**	**~310**	**39**
C20-Ph	**6.87**	**-**	**290.5**	**295**	**13**
C20-Ph-Bu	**5.11**	**6.94**	**261.5**	**272**	**9**
C20-Ph-Oct	**4.68**	**6.35**	**268**	**273**	**10**
C20-Ph-Ph	**4.95**	**6.72**	**263**	**267**	**16**

7. References

1. Marsico, F.; Wagner, M.; Landfester, K.; Wurm, F. R., *Macromolecules* **2012,** *45* (21), 8511-8518.
2. Breton, G. W.; Turlington, M., *Tetrahedron Letters* **2014,** *55* (33), 4661-4663.