Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for the Manuscript Entitled *Allyl Group-Containing Polyvinylphosphonates as a Flexible Platform for the Selective Introduction of Functional Groups via Polymer-Analogous Transformations*†

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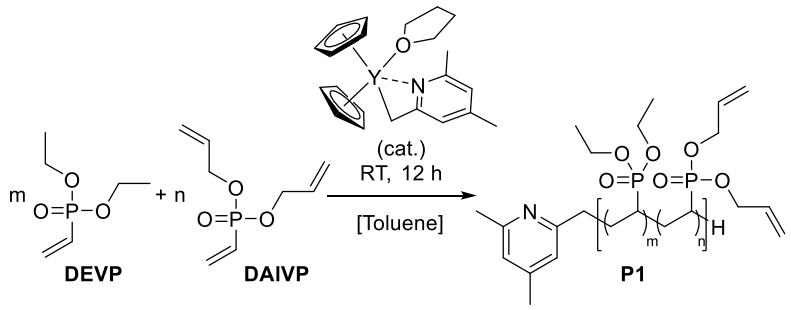
1 Polymerization of DEVP and DAlVP to P(DEVP-*co*-DAlVP) P1



^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.22 – 6.85 (m, $CH_{Ar,}$ 2H), 6.04 (s, CH_{Allyl}, 22H), 5.42 (d, ^{3}J = 16.9 Hz, CH_{Allyl}, 22H), 5.28 (s, CH_{Allyl}, 22H), 4.63 (s, $POCH_{2,Allyl}$, 44H), 4.18 (s, $PO\mathit{CH_2}$, 440H), 2.96 – 1.15 (m, polymer backbone, 363H), 1.38 (s, $POCH_2\mathit{CH_3}$, 660H).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3506 (br w), 2984 (m, ν_{C-H}), 2934 (m, ν_{C-H}), 2910 (m, ν_{C-H}), 1481 (w, δ_{C-H}), 1445 (m, δ_{C-H}), 1393 (m, δ_{C-H}), 1369 (w, δ_{C-H}), 1223 (st, $\nu_{P=O}$), 1164 (m, ν_{C-O}), 1098 (w), 1047 (w, ν_{P-O}), 1017 (st, ν_{P-O}), 952 (st), 780 (st).

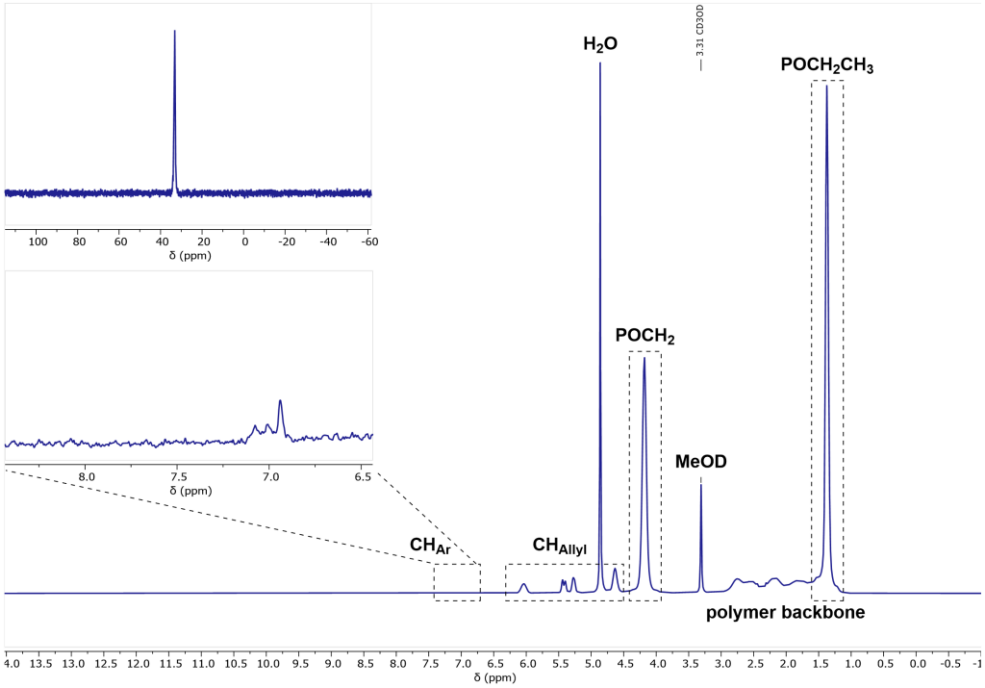


Fig. S1 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P1** in MeOD.

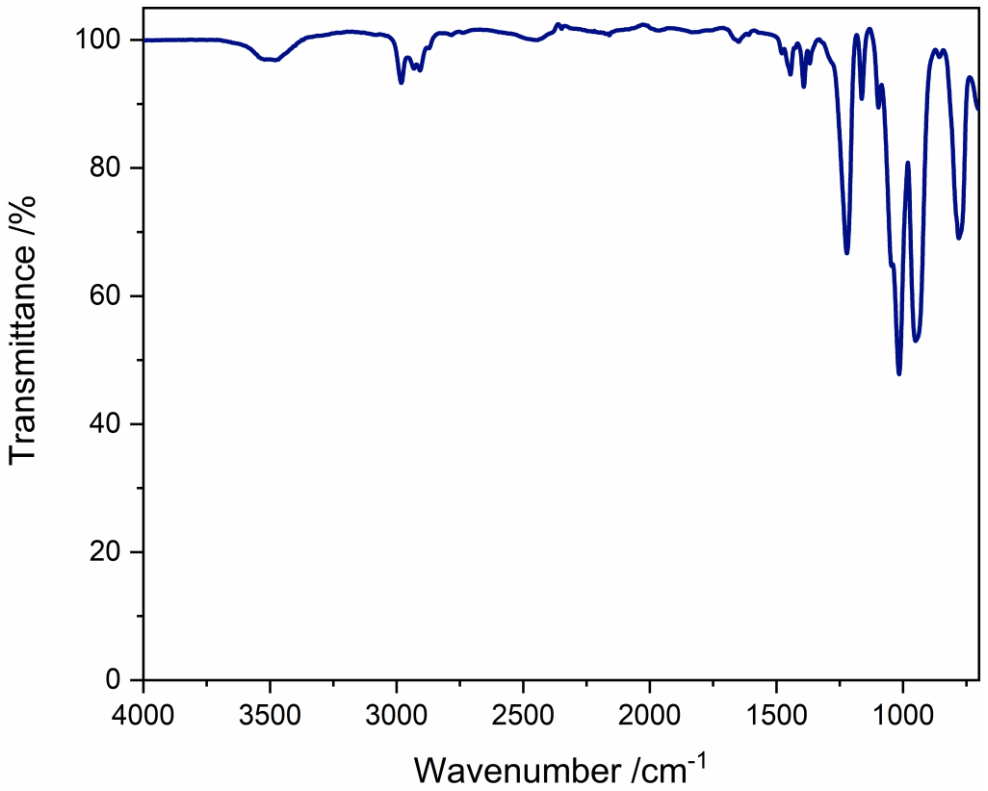


Fig. S2 IR spectrum of polymer **P1**.

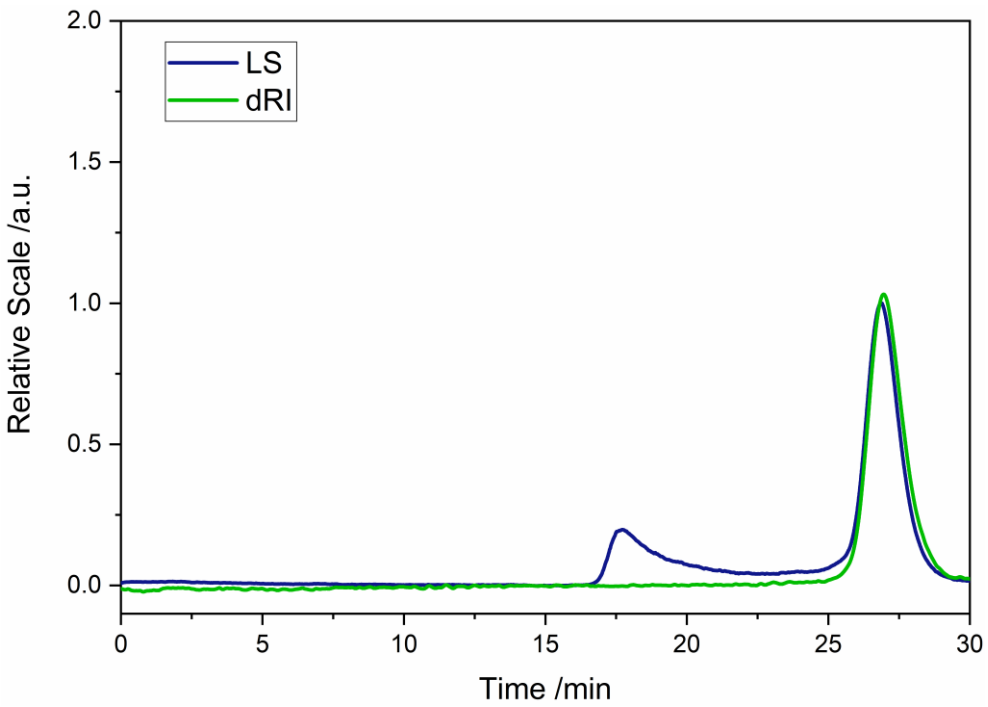
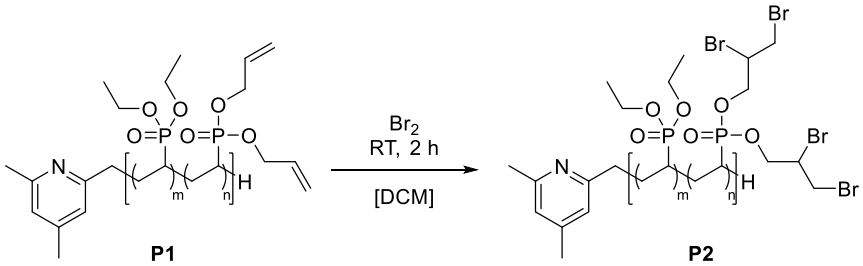


Fig. S3 GPC trace of polymer **P1** in THF/water measured via GPC-MALS.

2 Bromination and Follow-up Functionalizations

Bromination of P(DEVP-*co*-DAlVP) P1



^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.76 – 7.65 (m, CH_{Ar}), 7.61 (s, CH_{Ar}), 4.63 – 4.48 (m, PO*CH_2*CHBr), 4.20 (s, PO*CH_2*), 4.04 – 3.86 (m, CHBr, CH_2Br), 3.67 – 3.46 (m, CHBr, CH_2Br), 2.91 – 1.16 (m, polymer backbone), 1.38 (s, POCH$_2$*CH_3*).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.1.

IR (ATR): ῦ (cm^{-1}) = 3349 (br w), 2989 (m, ν_{C-H}), 2937 (m, ν_{C-H}), 2910 (m, ν_{C-H}), 1481 (w, δ_{C-H}), 1447 (m, δ_{C-H}), 1394 (m, δ_{C-H}), 1370 (w, δ_{C-H}), 1209 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1097 (w), 1043 (w, ν_{P-O}), 1022 (st, ν_{P-O}), 958 (st), 783 (st), 594 (w, ν_{C-Br}).

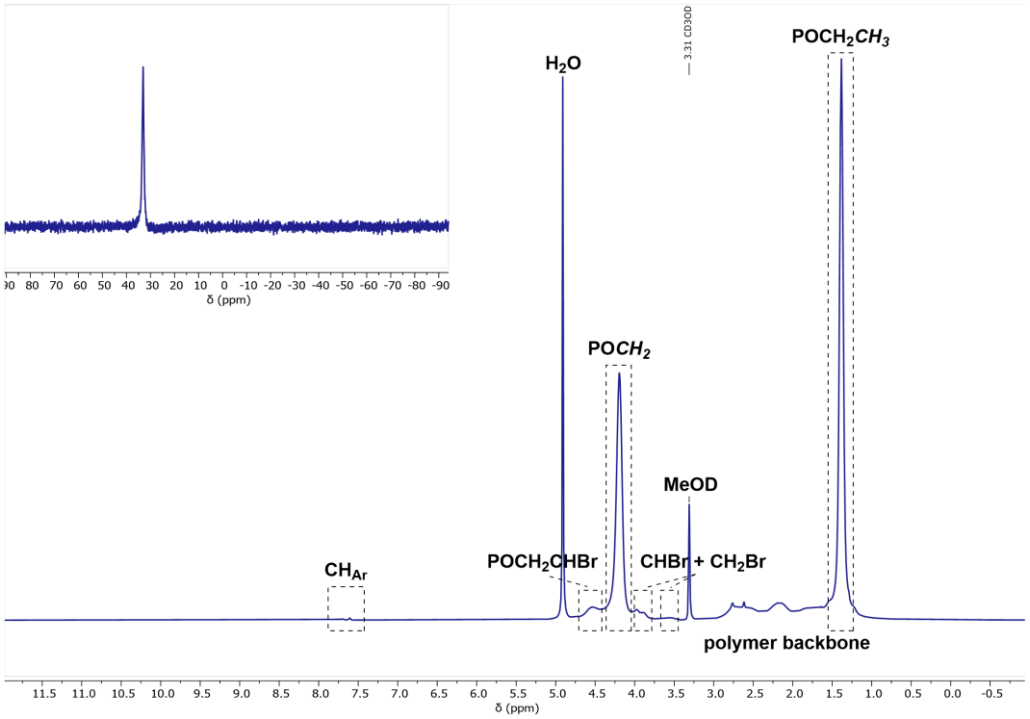


Fig. S4 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P2** in MeOD.

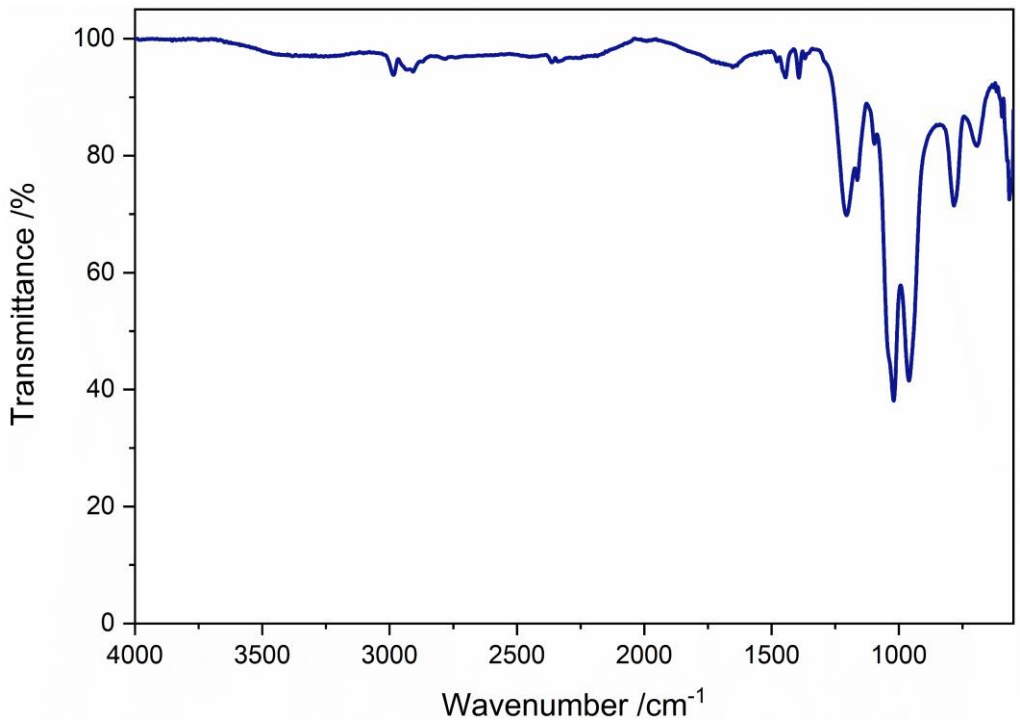


Fig. S5 IR spectrum of polymer **P2**.

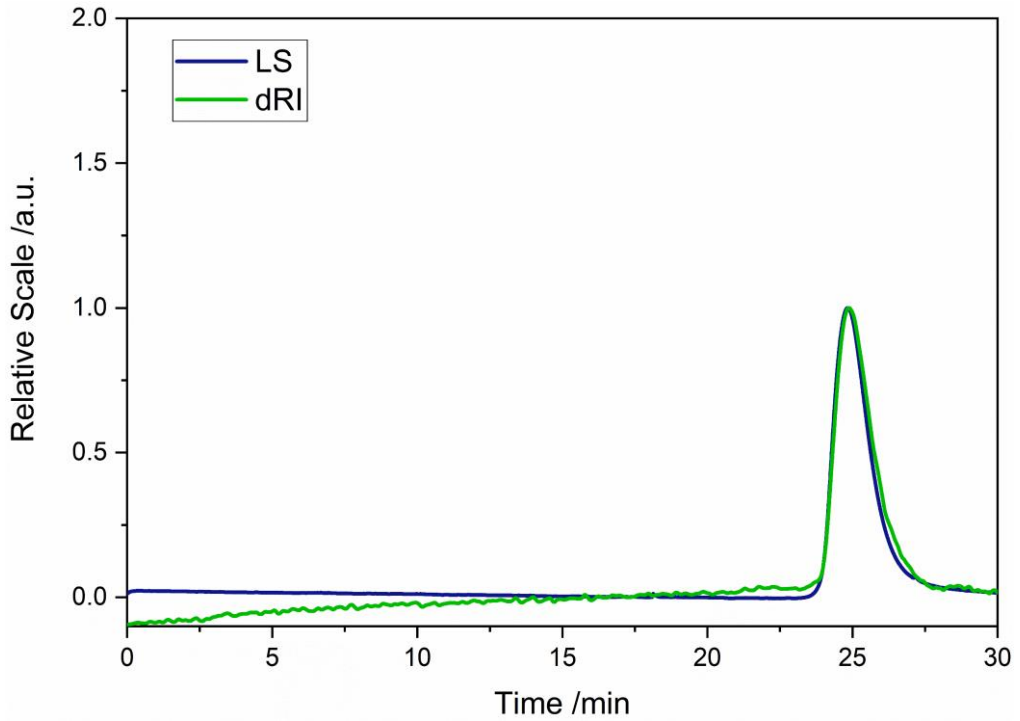
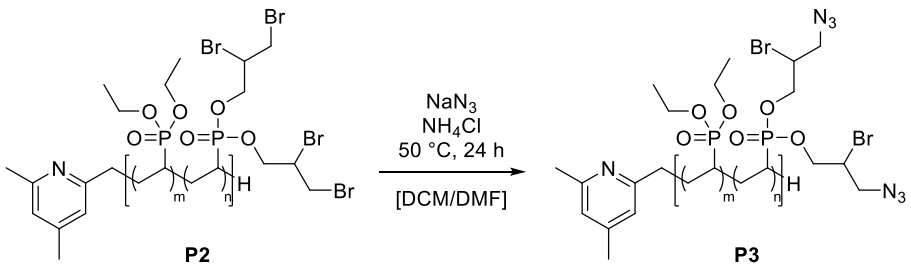


Fig. S6 GPC trace of polymer **P2** in THF/water measured via GPC-MALS.

Conversion of Brominated Polyvinylphosphonate P2 with Sodium Azide



The brominated polyvinylphosphonate **P2** was dissolved in equal amounts of dichloromethane (4 mL per 100 mg of polymer) and *N*,*N*-dimethylformamide (4 mL per 100 mg of polymer) and treated with sodium azide (5.0 equiv. per C-Br bond). The reaction mixture was heated to 50 °C for 24 hours. Volatiles were then removed *in vacuo* and the residue was dissolved in deionized water. The polymer was dialysed against deionized water and freeze-dried from water.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 4.67 – 4.43 (m, non-converted PO*CH*$_2$CHBr), 4.19 (s, PO*CH*$_2$), 4.04 – 3.83 (m, non-converted CHBr), 3.03 – 1.13 (m, polymer backbone), 1.38 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.1.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3375 (br w), 2981 (m, ν_{C-H}), 2929 (m, ν_{C-H}), 1481 (w, δ_{C-H}), 2111 (m, $\nu_{N=N=N}$), 1648 (m), 1445 (m, δ_{C-H}), 1392 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1211 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1096 (w), 1041 (w, ν_{P-O}), 1019 (st, ν_{P-O}), 954 (st), 777 (st).

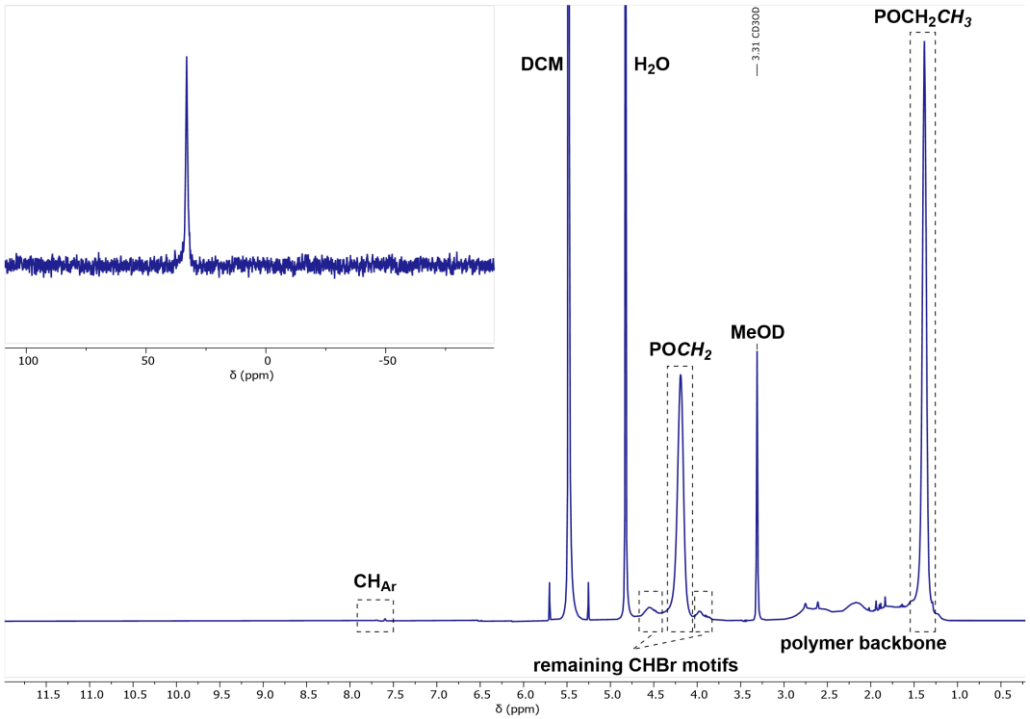


Fig. S7 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P3** in MeOD.

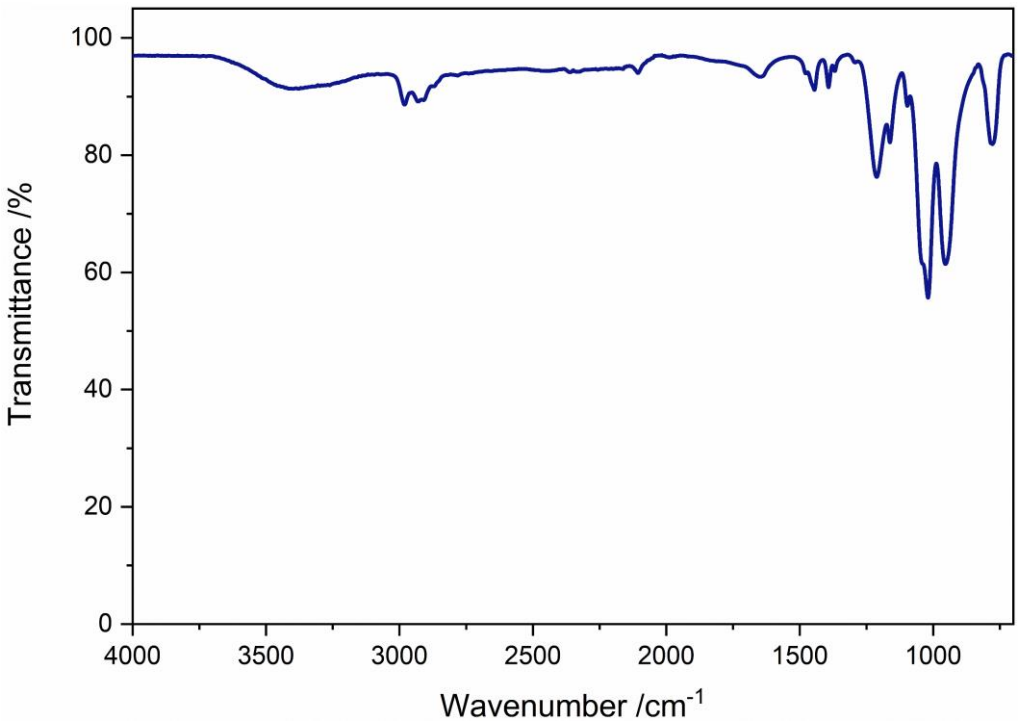
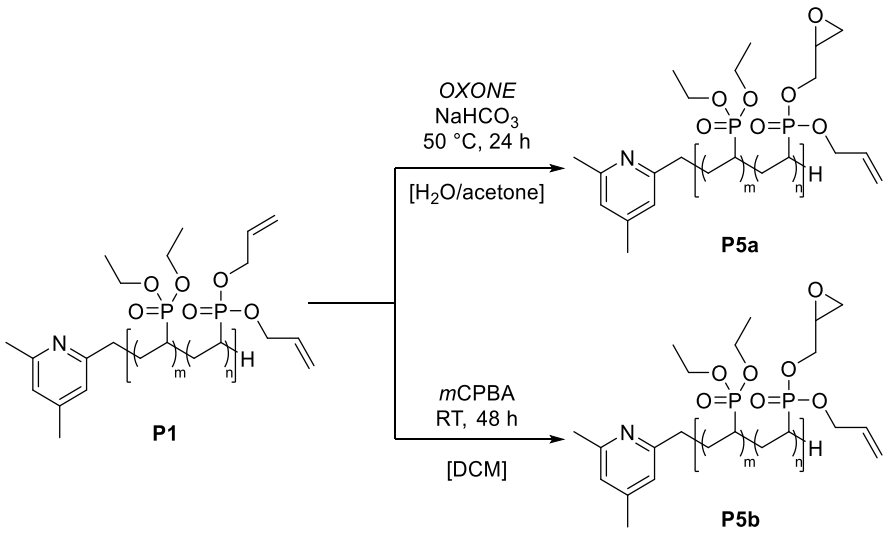


Fig. S8 IR spectrum of polymer **P3**.

3 Epoxydation Reactions and Follow-up Functionalizations

Epoxydation of P(DEVP-*co*-DAlVP) P1 with *OXONE* or *m*CPBA



The crude reaction solutions were used immediately for the follow-up functionalization reaction to prevent cross-linking of the epoxide groups.

Analytical data of polymer **P5a**

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.39 – 7.20 (m, CH_{Ar}), 6.04 (s, CH_{Allyl}), 5.42 (d, ^{3}J = 17.2 Hz, CH_{Allyl}), 5.27 (s, CH_{Allyl}), 4.65 (s, $POCH_{2,Allyl}$), 4.49 (s, $POCH_{2,Epxoide}$), 4.18 (s, $POCH_2$), 2.88 – 2.62 (m, $CH_{Epoxide}$), 2.98 – 1.08 (m, polymer backbone), 1.38 (s, $POCH_2CH_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.1.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3466 (br w), 2983 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2909 (m, ν_{C-H}), 1652 (m), 1478 (w, δ_{C-H}), 1446 (m, δ_{C-H}), 1394 (m, δ_{C-H}), 1370 (w, δ_{C-H}), 1217 (st, $\nu_{P=O}$), 1164 (m, ν_{C-O}), 1099 (w), 1043 (w, ν_{P-O}), 1015 (st, ν_{P-O}), 953 (st), 783 (st).

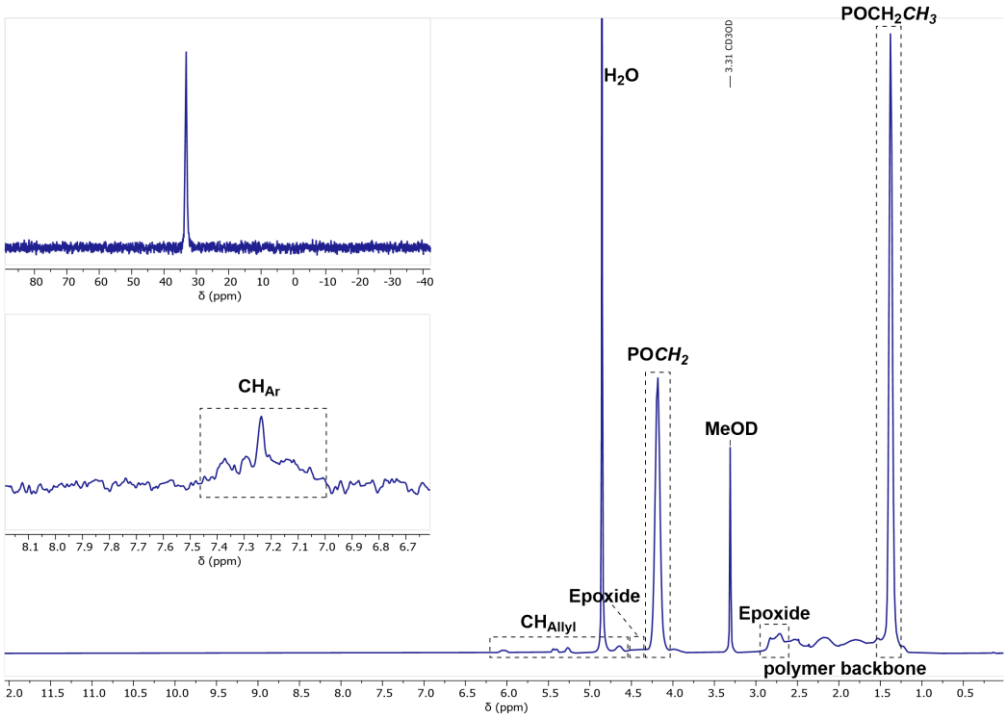


Fig. S9 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P5a** in MeOD.

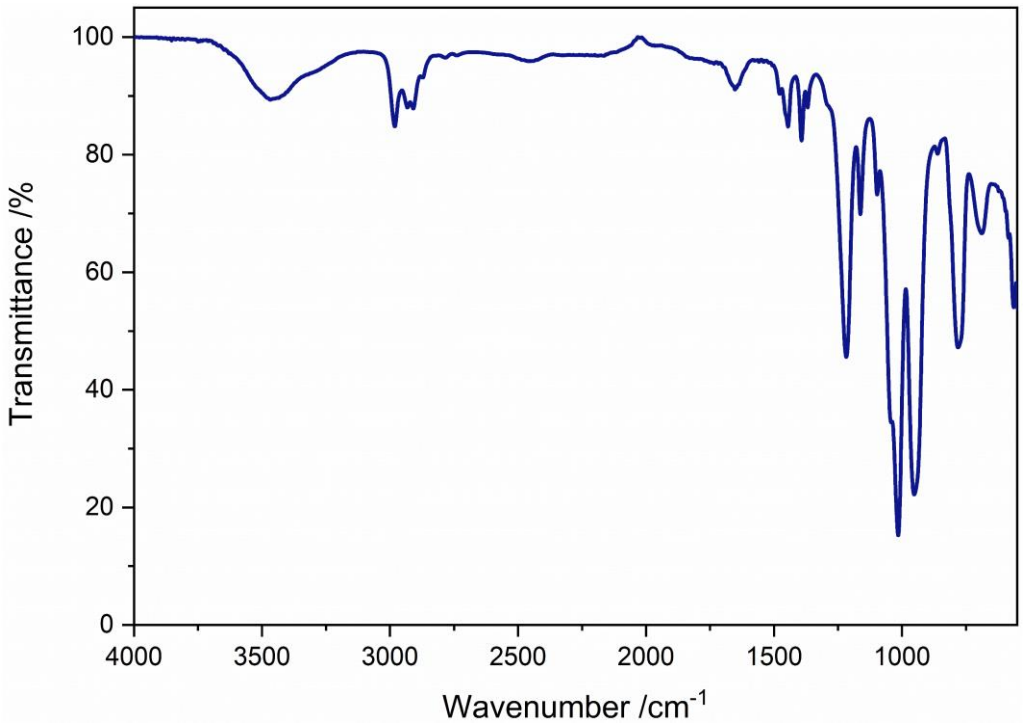


Fig. S10 IR spectrum of polymer **P5a**.

Analytical data of polymer **P5b**

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 6.04 (s, CH_{Allyl}), 5.42 (d, ^{3}J = 17.2 Hz, CH_{Allyl}), 5.27 (s, CH_{Allyl}), 4.64 (s, $POCH_{2,Allyl}$), 4.18 (s, $PO\mathit{CH_2}$), 2.88 – 2.67 (m, $CH_{Epoxide}$), 3.06 – 1.23 (m, polymer backbone), 1.38 (s, $POCH_2\mathit{CH_3}$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.1

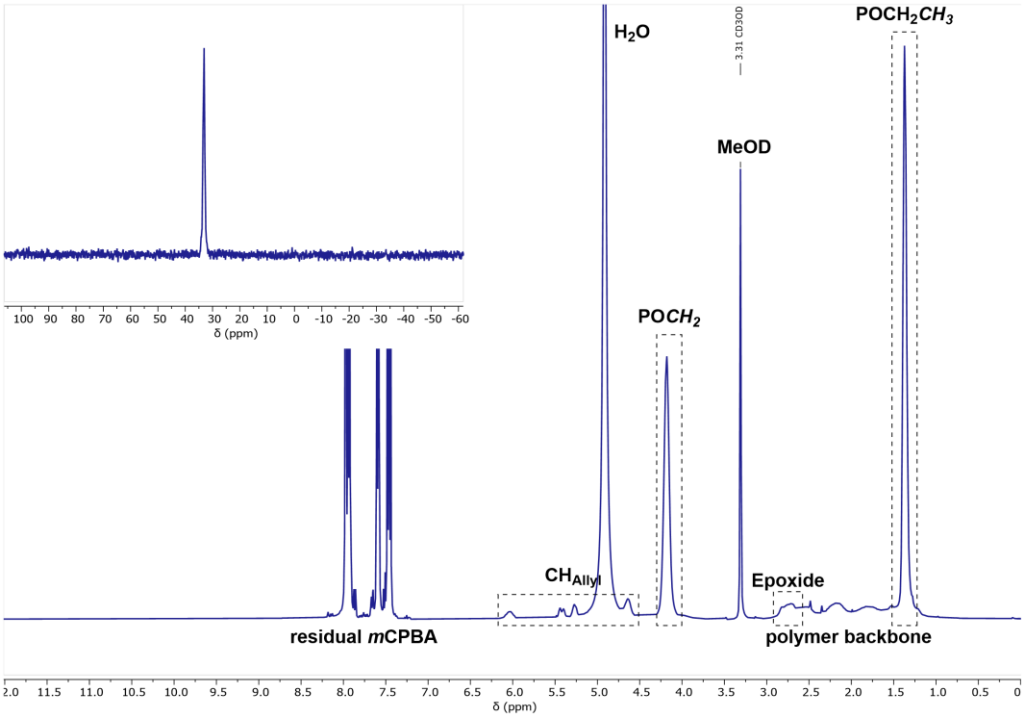
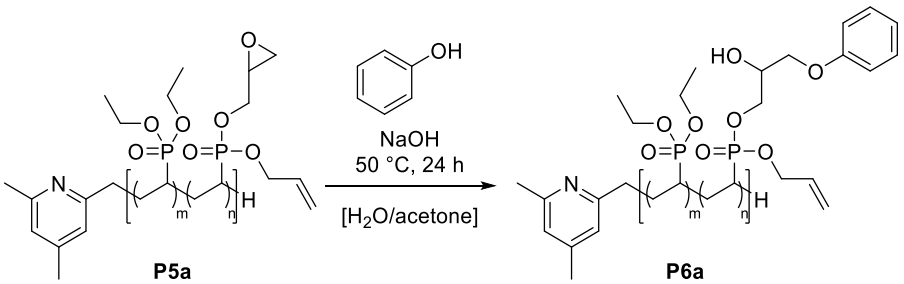


Fig. S11 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P5b** in MeOD.

Ring-Opening of Polyvinylphosphonate P5a with Phenol (2)



The crude solution of **P5a** in acetone/water (approximately 100 mg per 10 mL solvent) was treated with a solution of phenol (**2**) (8.8 equiv. per epoxide, 500 µmol in 750 µL H_2O) and sodium hydroxide (9.0 equiv. per epoxide, 511 µmol per 750 µL H_2O) in deionized water. Hereafter, the mixture was stirred for 24 hours at 50 °C. The conversion of the epoxide groups was checked via ^{1}H-NMR spectroscopy and the solution was cooled to room temperature. Acetone was removed under reduced pressure and the aqueous phase was purified via dialysis against water for 48 hours. The product was yielded via lyophilization from water.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.32 – 7.20 (m, C$H_{Ar,meta}$, 15H), 7.02 – 6.87 (m, C$H_{Ar,ortho,}$ C$H_{Ar,para}$, 22H), 6.04 (s, $CH_{Allyl,}$), 5.42 (d, ^3J = 17.5 Hz, CH_{Allyl}), 5.23 (s, CH_{Allyl}), 4.63 (s, $POCH_{2,Allyl,}$ 9H), 4.18 (s, POCH_2, 475H), 2.91 – 1.14 (m, polymer backbone), 1.36 (s, $POCH_2CH_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.3.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3466 (br w), 2983 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2909 (m, ν_{C-H}), 1652 (m), 1600 (m, $\nu_{C=C}$), 1497 (m, $\nu_{C=C}$), 1481 (w, δ_{C-H}), 1445 (m, δ_{C-H}), 1393 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1216 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1097 (w), 1043 (w, ν_{P-O}), 1016 (st, ν_{P-O}), 952 (st), 780 (st).

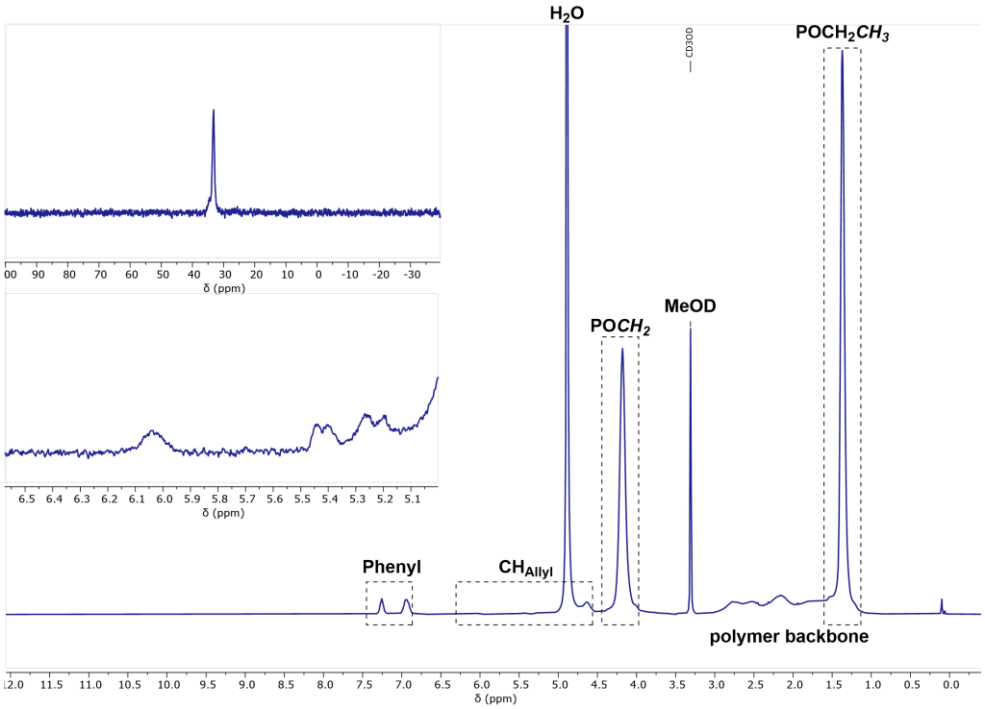


Fig. S12 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer conjugate **P6a** in MeOD.

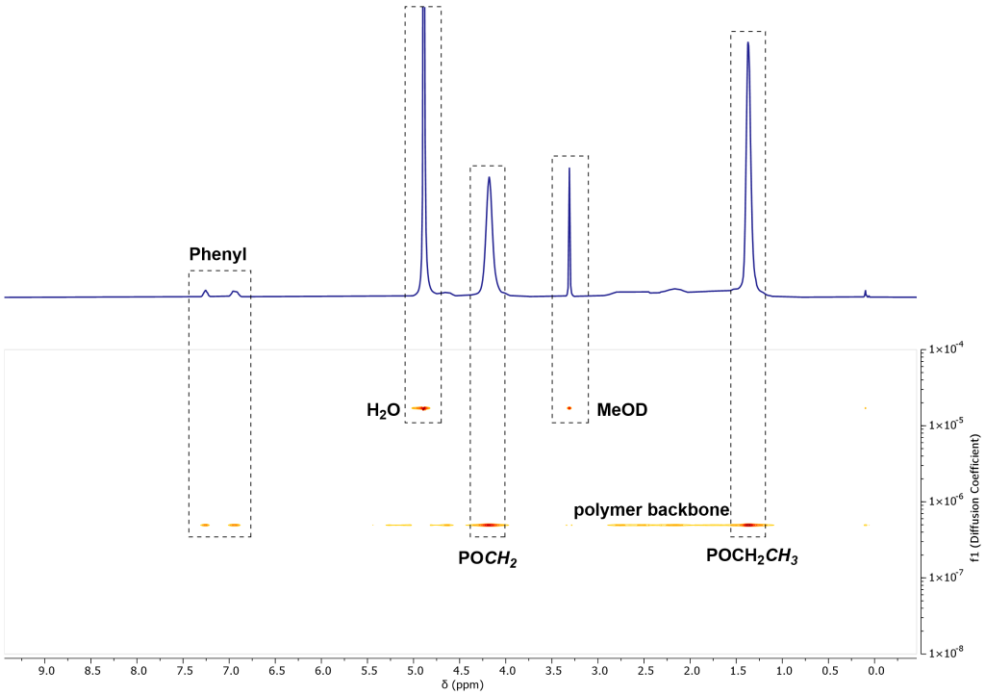


Fig. S13 DOSY spectrum of polymer **P6a** in MeOD.

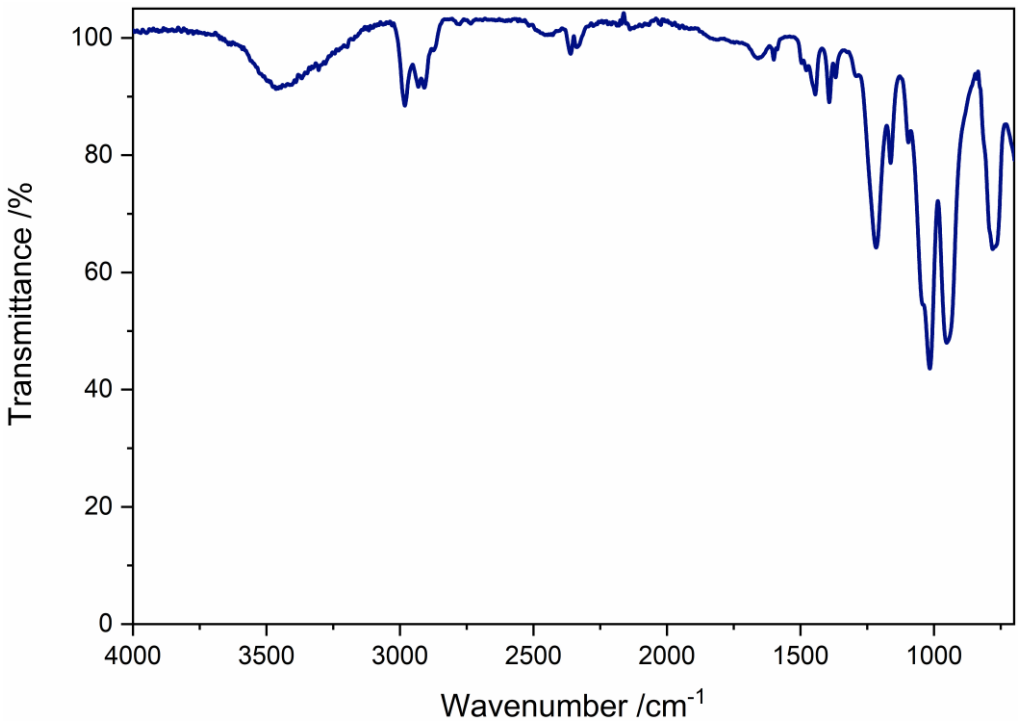


Fig. S14 IR spectrum of polymer conjugate **P6a**.

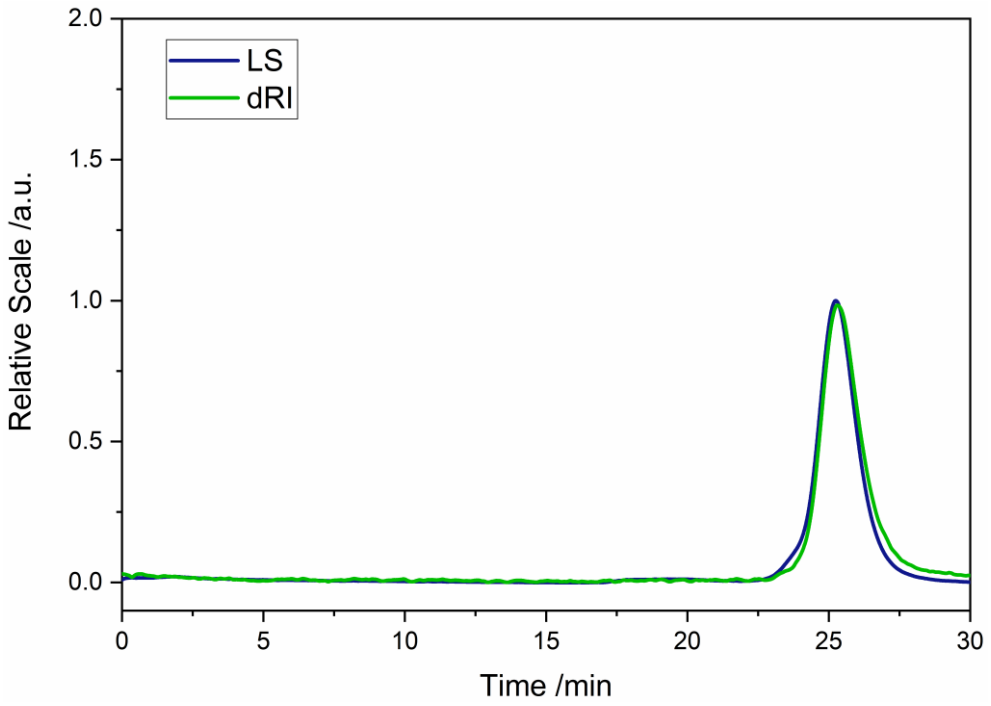
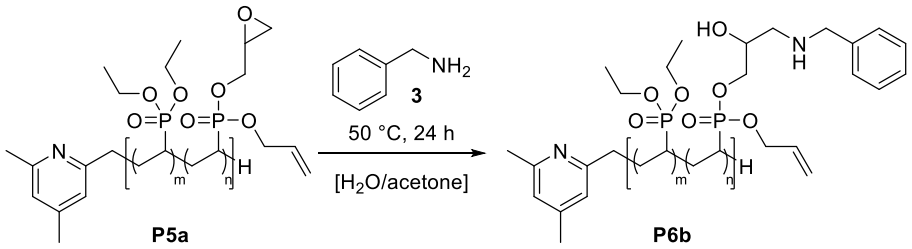


Fig. S15 GPC trace of polymer conjugate **P6a** in THF/water measured via GPC-MALS.

Ring-Opening of Polyvinylphosphonate P5a with Benzylamine (3)



The crude solution of polymer **P5a** in acetone/water (approximately 100 mg per 10 mL solvent) was treated with benzylamine (**3**) (8.5 equiv. per epoxide). Hereafter, the mixture was stirred for 24 hours at 50 °C. The conversion of the epoxide groups was checked via ^{1}H-NMR spectroscopy and the solution was cooled to room temperature. Acetone was removed under reduced pressure and the aqueous phase was purified via dialysis against water for 48 hours. Freeze-drying from water yielded polymer conjugate **P6b**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.77 – 7.07 (m, C*H*$_{Ar}$, 71H), 6.03 (s, CH$_{Allyl}$), 5.42 (d, ^{3}J = 17.1 Hz, CH$_{Allyl}$), 5.27 (s, CH$_{Allyl}$), 4.60 (s, POCH$_{2,Allyl}$, 13H), 4.18 (s, PO*CH*$_2$, 471H), 3.65 (s, C*H*$_2$NH), 2.97 – 1.08 (m, polymer backbone), 1.38 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.3.

IR (ATR): ῡ (cm^{-1}) = 3458 (br w), 2980 (m, ν$_{C-H}$), 2929 (m, ν$_{C-H}$), 2907 (m, ν$_{C-H}$), 1656 (m), 1496 (w, ν$_{C=C}$), 1477 (w, δ$_{C-H}$), 1446 (m, δ$_{C-H}$), 1393 (m, δ$_{C-H}$), 1368 (w, δ$_{C-H}$), 1220 (st, ν$_{P=O}$), 1163 (m, ν$_{C-O}$), 1096 (w), 1044 (w, ν$_{P-O}$), 1017 (st, ν$_{P-O}$), 950 (st), 787 (st).

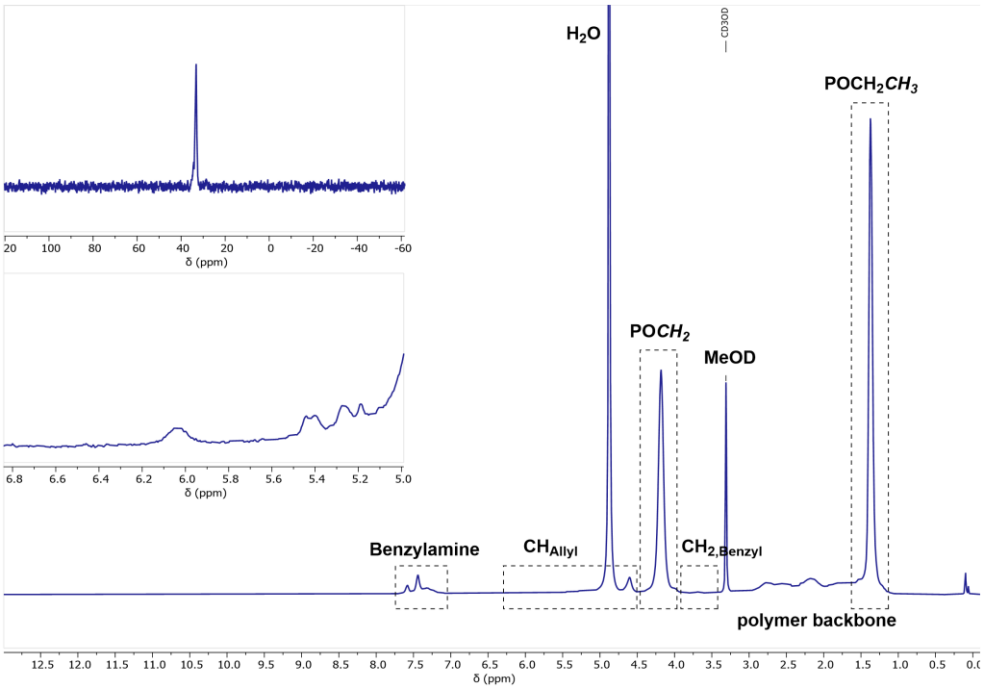


Fig. S16 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer conjugate **P6b** in MeOD.

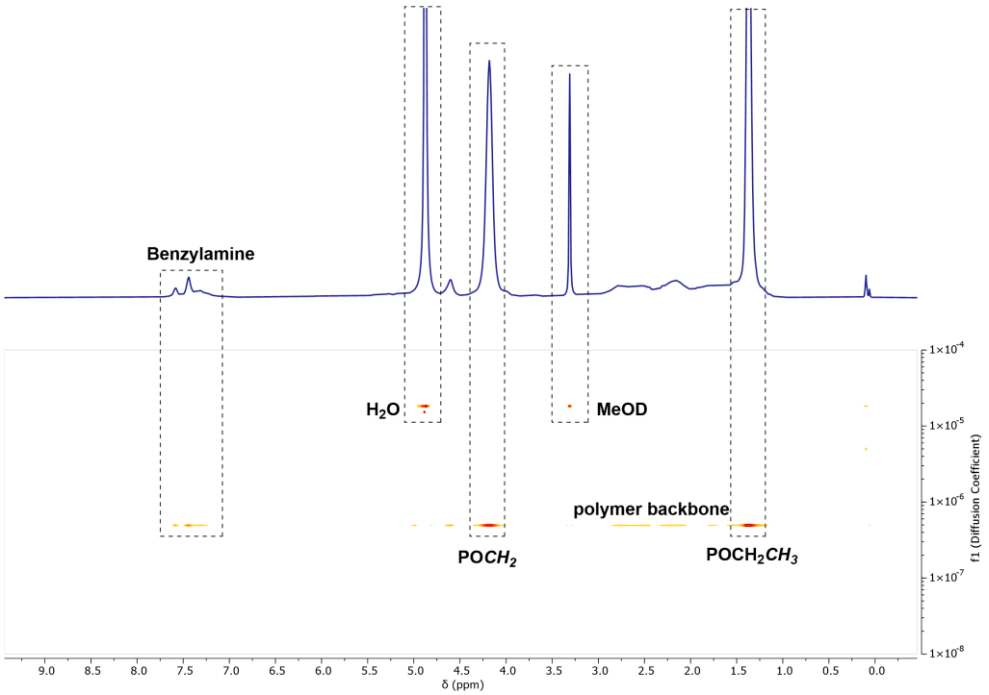


Fig. S17 DOSY spectrum of polymer **P6b** in MeOD.

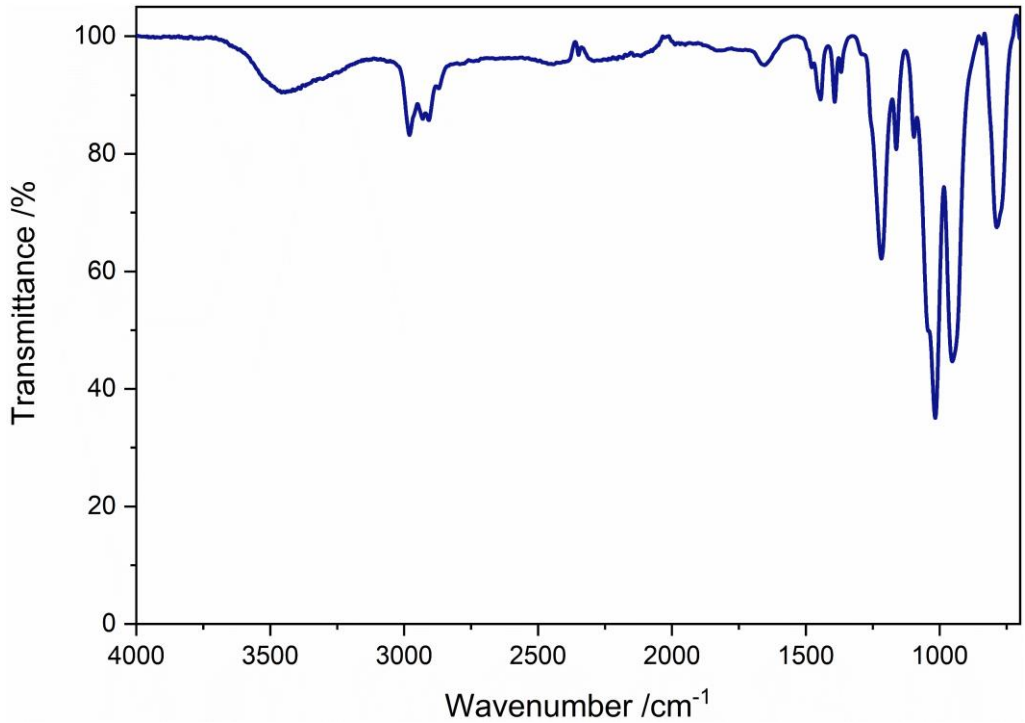


Fig. S18 IR spectrum of polymer conjugate **P6b**.

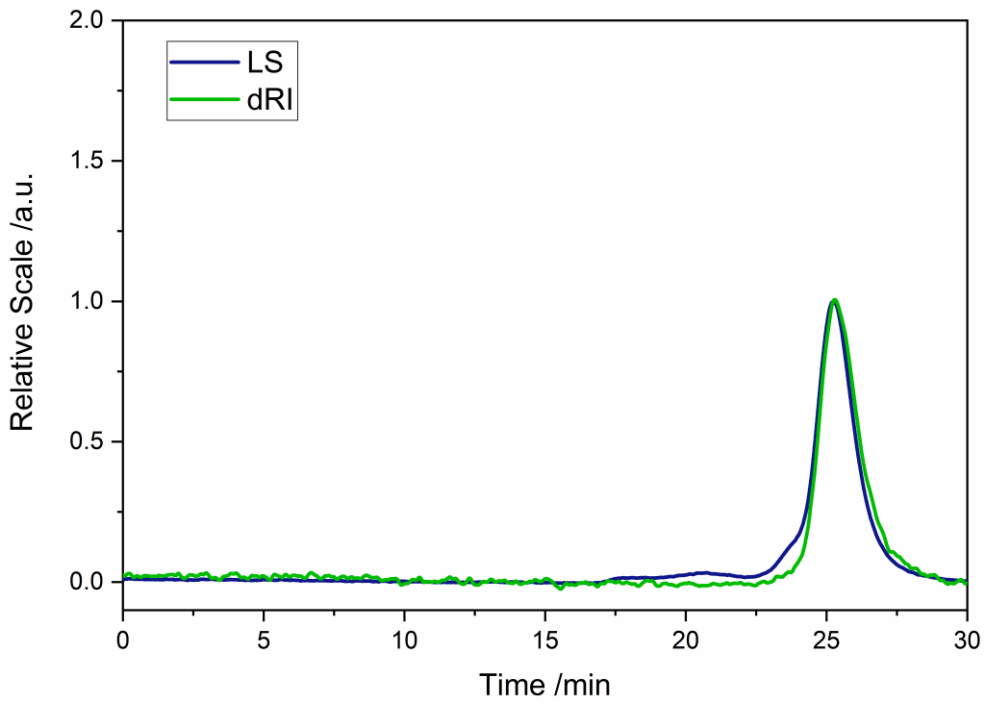
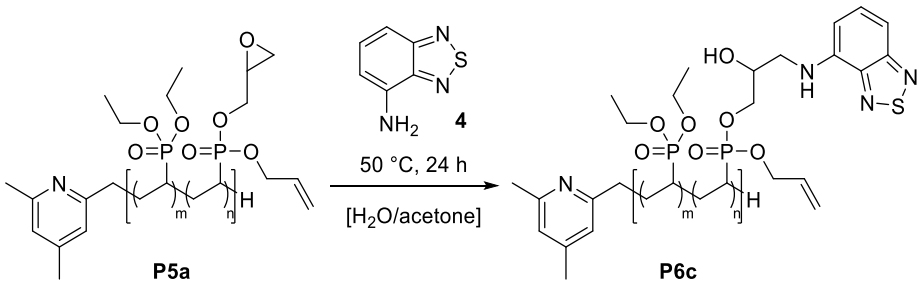


Fig. S19 GPC trace of polymer **P6b** in THF/water measured via GPC-MALS.

Ring-Opening of Polyvinylphosphonate P5a with 4-Amino-2,1,3-benzothiadiazole (4)



The crude solution containing polymer **P5a** in acetone/water (approximately 100 mg per 10 mL solvent) was treated with 4-amino-2,1,3-benzothiadiazole (**4**) (10 equiv. per epoxide). Hereafter, the mixture was stirred for 24 hours at 50 °C. The conversion of the epoxide groups was checked via ^{1}H-NMR spectroscopy and the solution was cooled to room temperature. Acetone was removed under reduced pressure and the remaining aqueous phase was purified via dialysis against water for 48 hours. Subsequent lyophilization from water yielded polymer conjugate **P6c**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.41 (d, ^{3}J = 7.9 Hz, C*H*CHCHCNH, 6H), 7.20 (d, ^{3}J = 8.7 Hz, CHC*H*CHCNH, 5H), 6.63 (d, ^{3}J = 7.7 Hz, CHCHC*H*CNH, 6H), 4.18 (s, PO*CH*$_2$, 484H), 2.88 – 1.16 (m, polymer backbone), 1.38 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3454 (br w), 2980 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2908 (m, ν_{C-H}), 1629 (m), 1556 (m, $\nu_{C=N}$), 1497 (w, $\nu_{C=C}$) 1479 (w, δ_{C-H}), 1444 (m, δ_{C-H}), 1390 (m, δ_{C-H}), 1367 (w, δ_{C-H}), 1217 (st, $\nu_{P=O}$), 1161 (m, ν_{C-O}), 1097 (w), 1045 (w, ν_{P-O}), 1016 (st, ν_{P-O}), 953 (st), 781 (st).

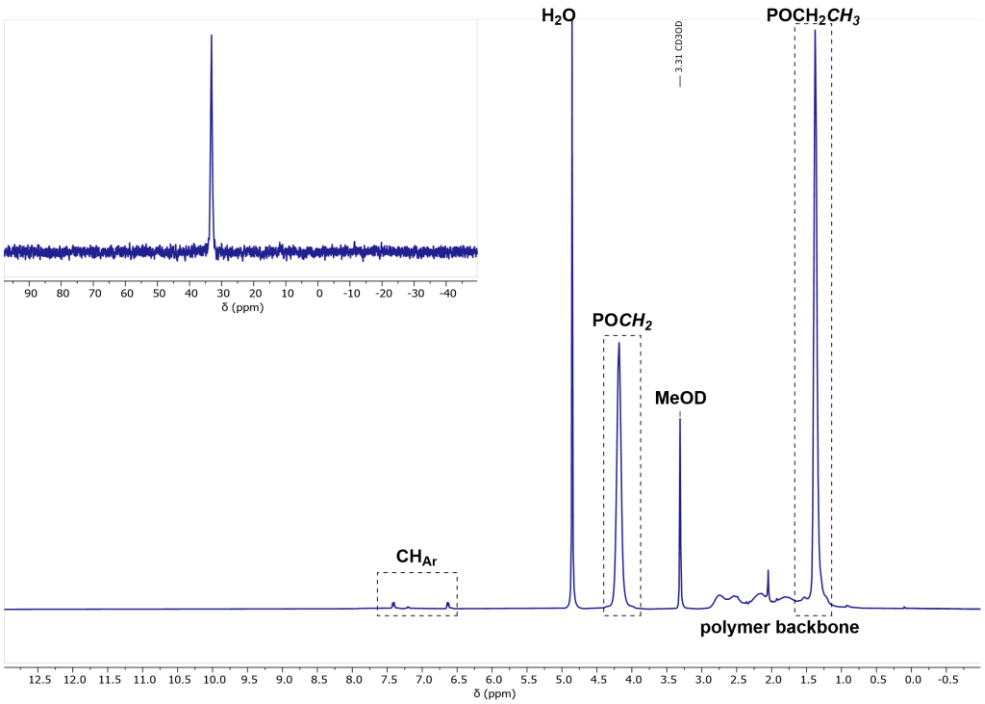


Fig. S20 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer conjugate **P6c** in MeOD.

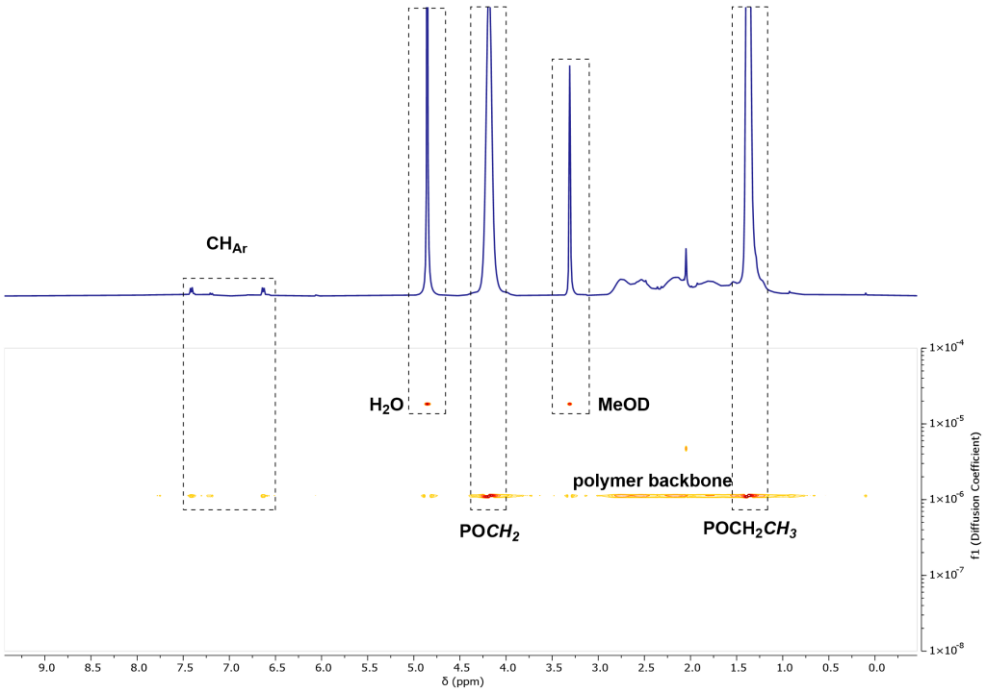


Fig. S21 DOSY spectrum of polymer **P6c** in MeOD.

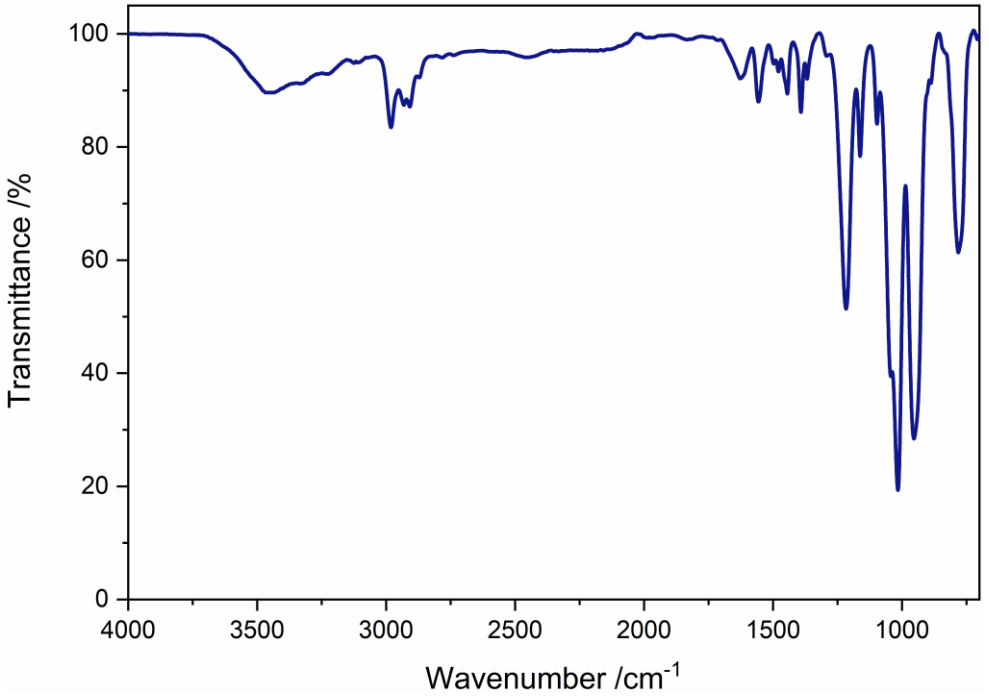


Fig. S22 IR spectrum of polymer conjugate **P6c**.

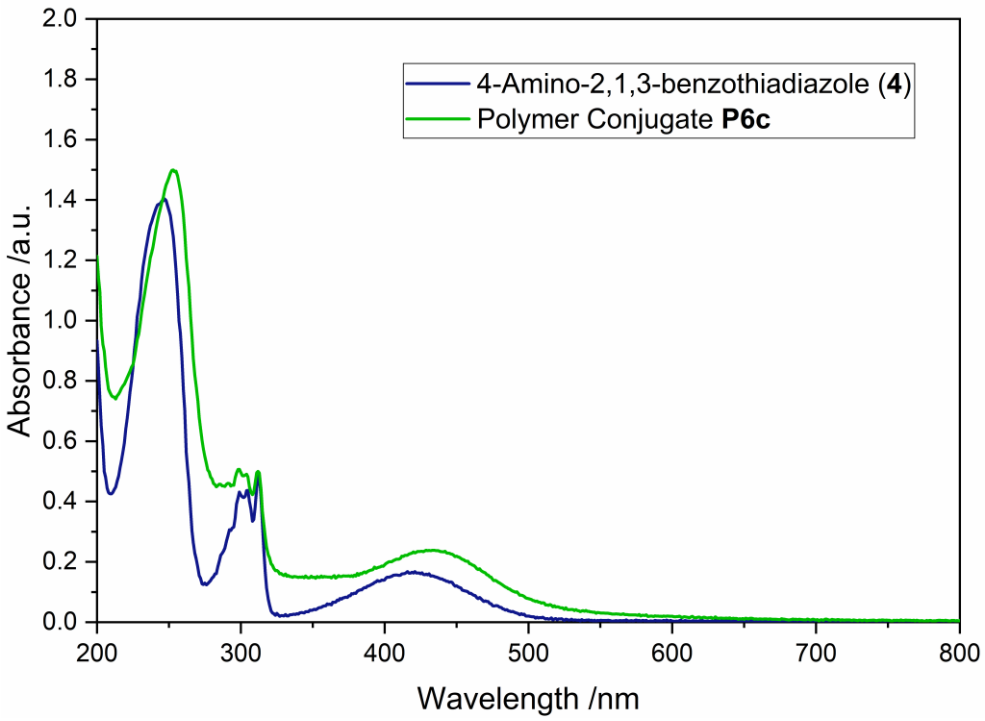


Fig. S23 UV/Vis spectrum of polymer conjugate **P6c** and 4-amino-2,1,3-benzpthiadiazole (**4**) in MeOH.

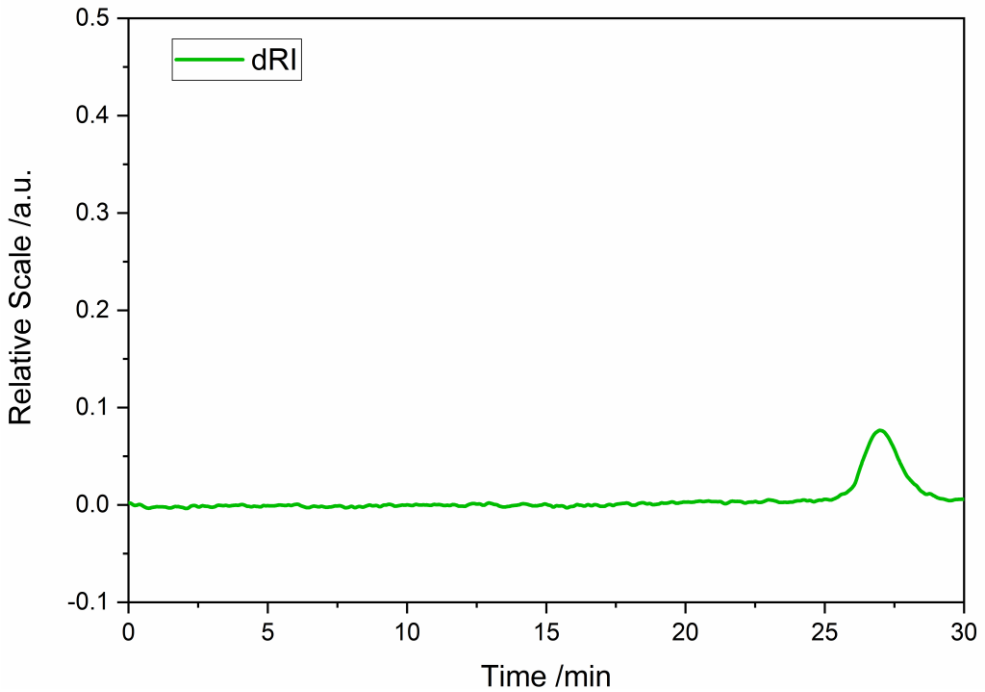
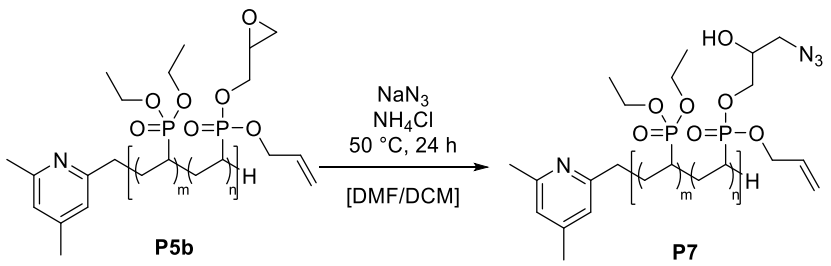


Fig. S24 GPC trace of polymer conjugate **P6c** in THF/water measured via GPC-MALS. Only the dRI trace is shown due to a strong interaction of the dye with MALS detector.

Ring-Opening of Polyvinylphosphonate P5b with Sodium Azide



The crude solution containing polymer **P5b** was concentrated to a volume of approximately 3.00 mL (100 mg polymer per 3.0 mL DCM) and diluted with *N*,*N*-dimethylformamide (3.00 mL). The solution was treated with sodium azide (9.0 equiv. per epoxide) and ammonium chloride (9.0 equiv. per epoxide). Hereafter, the mixture was stirred for 24 hours at 50 °C and the conversion of the epoxide groups was checked via ^{1}H-NMR spectroscopy, which substantiated a quantitative consumption of the polymer-bound epoxides. The solvent was removed under reduced pressure and the crude product was dialysed against water for 48 hours. Subsequently, lyophilization from water yielded polymer **P7**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 4.18 (s, PO*CH*$_2$, 440H), 2.88 – 1.16 (m, polymer backbone), 1.38 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): ῦ (cm^{-1}) = 3427 (br w), 2981 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2907 (m, ν_{C-H}), 2110 (m, $\nu_{N=N=N}$), 1713 (st), 1574 (m), 1477 (w, $\nu_{C=C}$) 1477 (w, δ_{C-H}), 1429 (m, δ_{C-H}), 1395 (m, δ_{C-H}), 1369 (w, δ_{C-H}), 1222 (st, $\nu_{P=O}$), 1193 (st), 1161 (m, ν_{C-O}), 1101 (w), 1047 (w, ν_{P-O}), 1017 (st, ν_{P-O}), 960 (st), 791 (m), 750 (st).

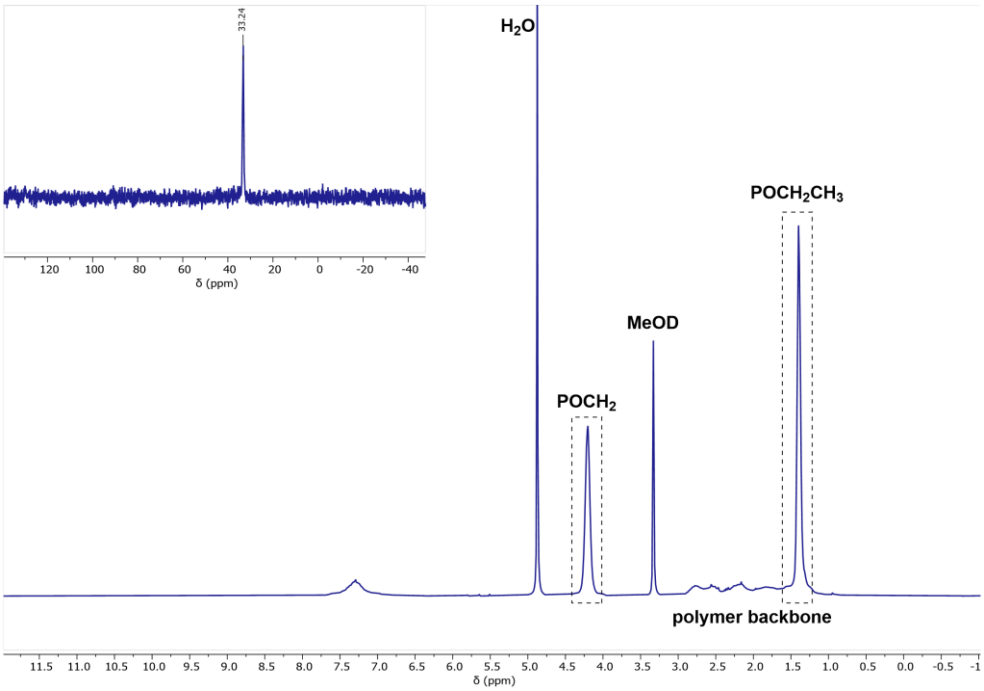


Fig. S25 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P7** in MeOD.

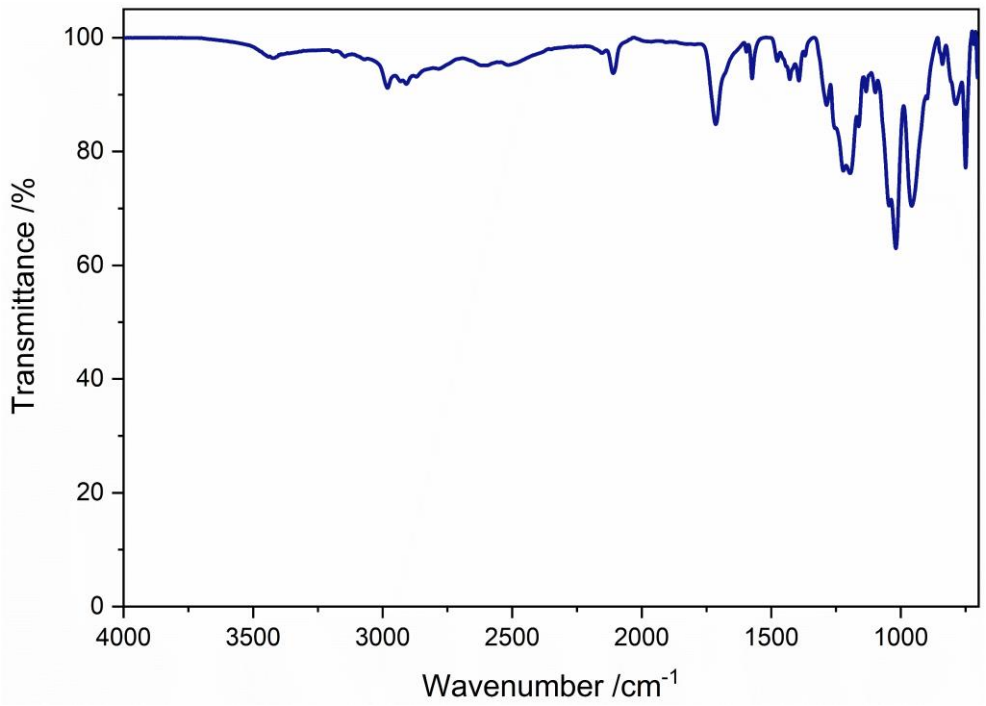


Fig. S26 IR spectrum of polymer **P7**.

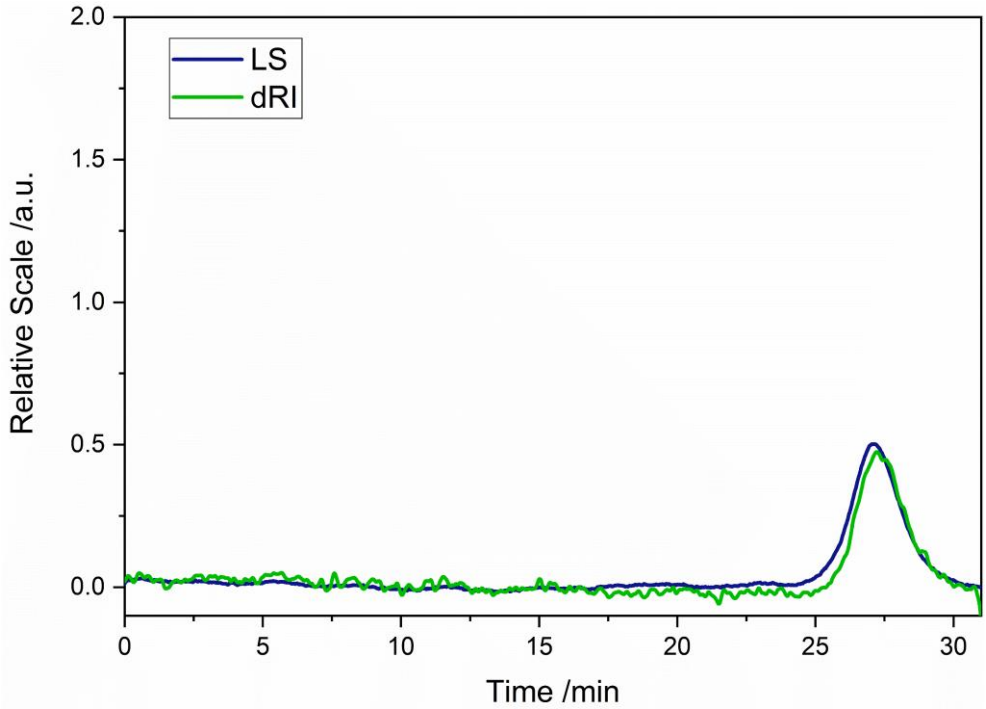
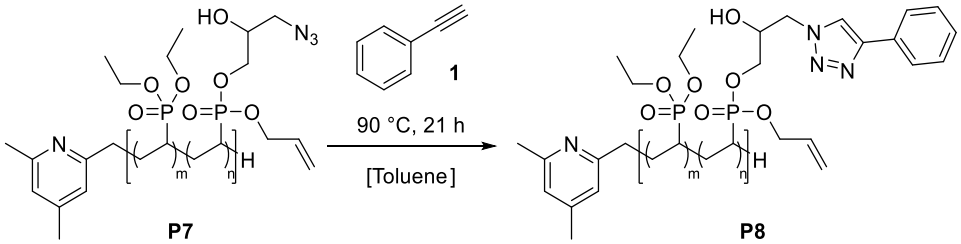


Fig. S27 GPC trace of polymer **P7** in THF/water measured via GPC-MALS.

Azide-Alkyne Click Coupling of Polyvinylphosphonate P7 with Phenylacetylene (1)



Polymer **P7** was dissolved in toluene (10 mg polymer per 1.0 mL solvent) and was treated with phenylacetylene (**1**) (8.0 equiv. per azide group; azide amount equal to epoxide amount in **P5b**). After heating to 90 °C, the reaction was stirred for 21 hours. ^{1}H- and DOSY-NMR spectroscopy was employed to check the outcome of the coupling reaction. Afterwards the polymer was washed with pentane to remove phenylacetylene and dialysed against water. Freeze-drying from water yielded conjugate **P8**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.99 – 7.07 (m, Phenyl, 65H), 6.03 (s, CH_{Allyl}), 5.42 (d, ^{3}J = 17.3 Hz, CH_{Allyl}), 5.26 (s, CH_{Allyl}), 4.63 (s, $POCH_{2,Allyl}$, 10H), 4.18 (s, $PO\mathit{CH_2}$, 474H), 3.00 – 0.78 (m, polymer backbone), 1.37 (s, $POCH_2\mathit{CH_3}$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): ῦ (cm^{-1}) = 3471 (br w), 2981 (m, ν_{C-H}), 2928 (m, ν_{C-H}), 2909 (m, ν_{C-H}), 1773 (m), 1713 (st), 1652 (br m), 1573 (w, $\nu_{C=C}$), 1480 (w, δ_{C-H}), 1444 (m, δ_{C-H}), 1392 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1216 (st, $\nu_{P=O}$), 1193 (st), 1162 (m, ν_{C-O}), 1097 (w), 1044 (w, ν_{P-O}), 1015 (st, ν_{P-O}), 951 (st), 778 (st).

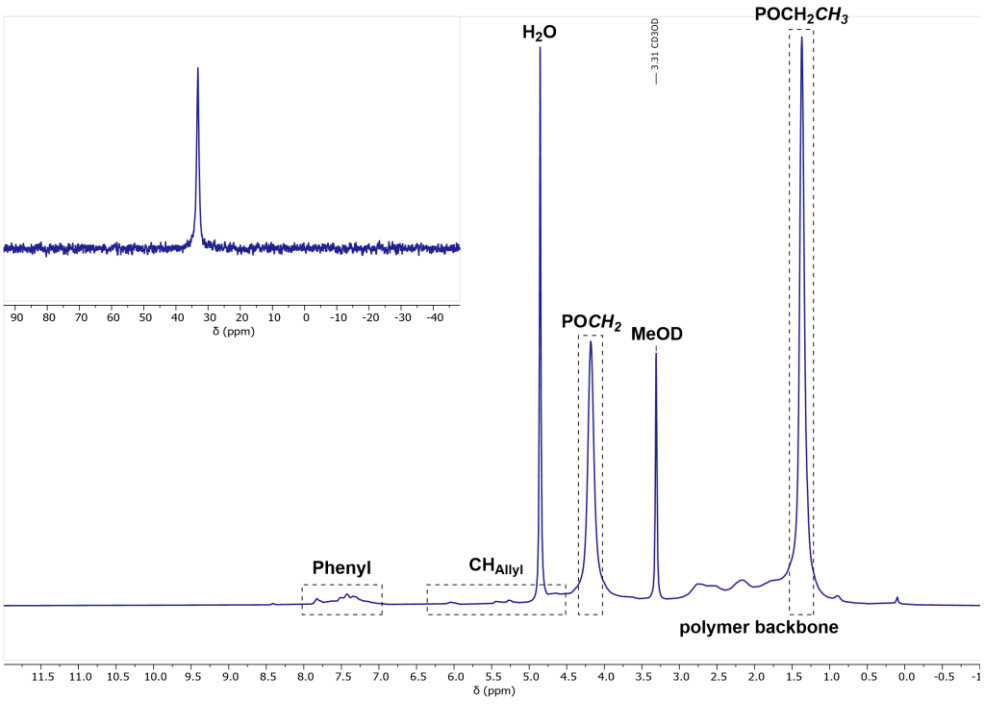


Fig. S28 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P8** in MeOD.

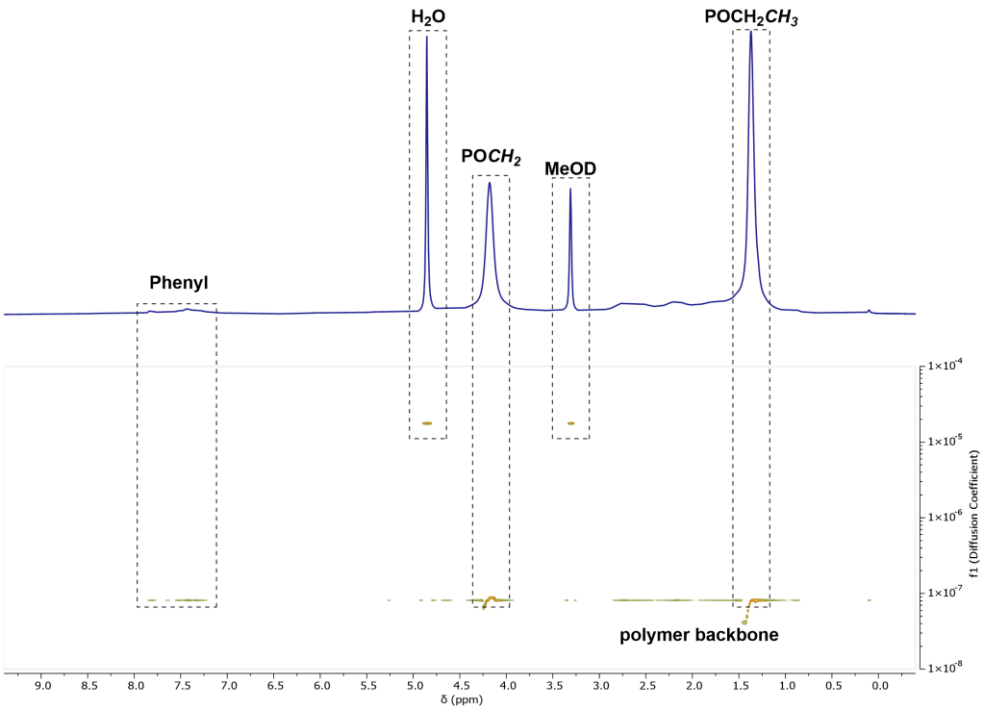


Fig. S29 DOSY spectrum of polymer **P8** in MeOD.

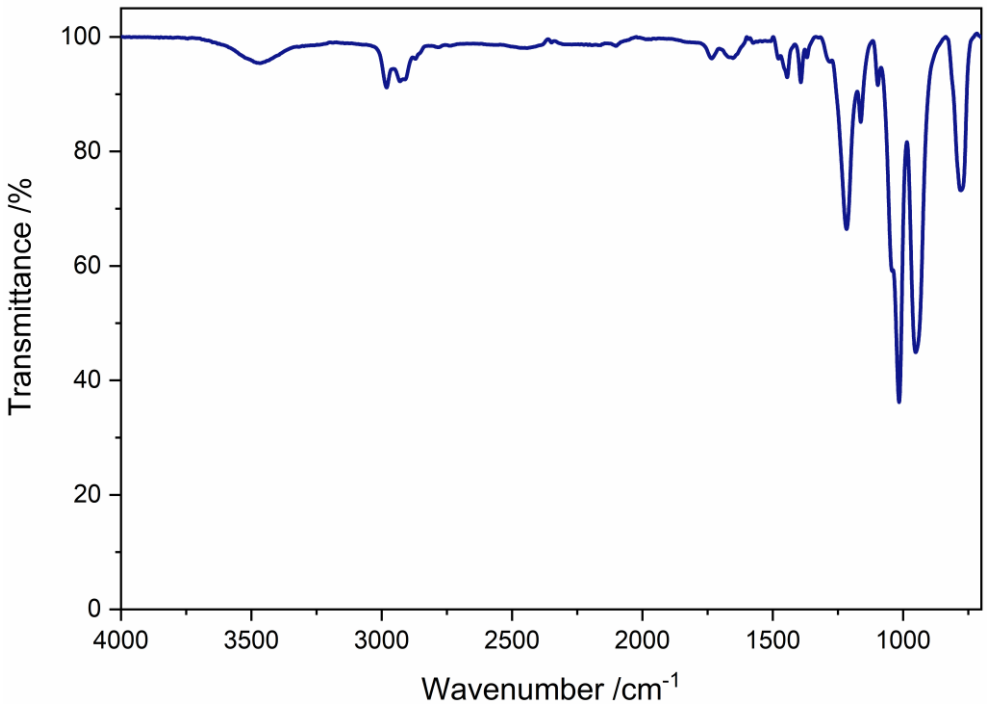


Fig. S30 IR spectrum of polymer **P8**.

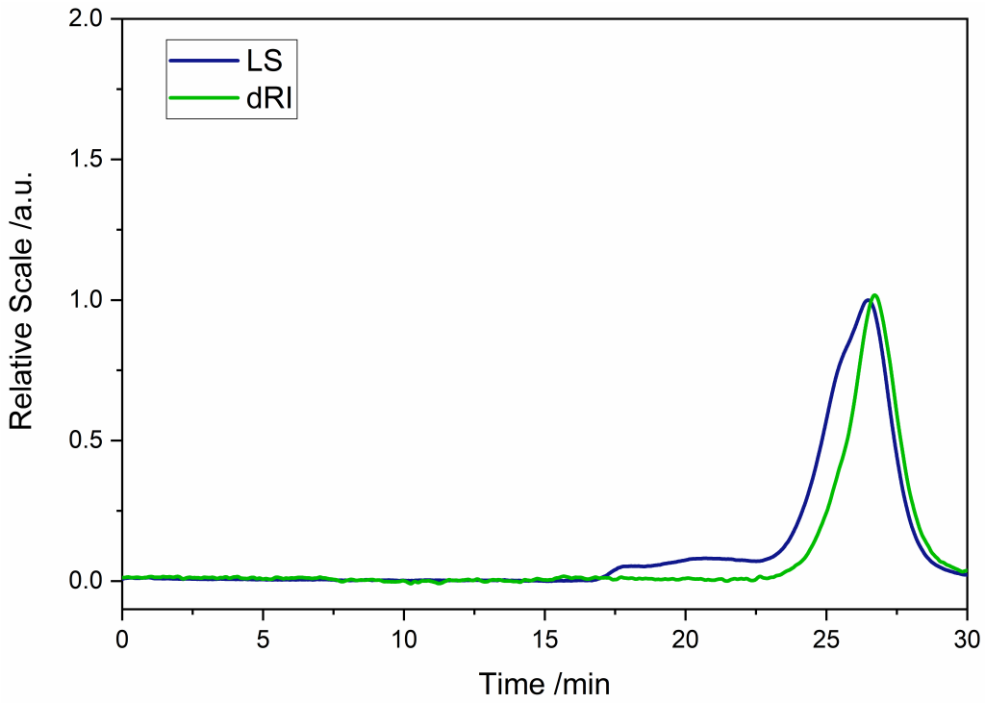
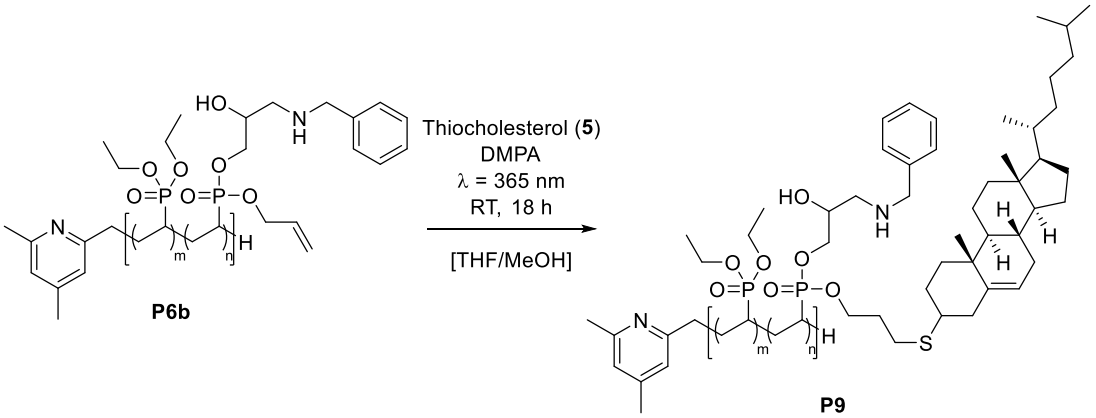


Fig. S31 GPC trace of polymer **P8** in THF/water measured via GPC-MALS.

4 Synthesis of Dual-Functionalized Polyvinylphosphonates

Follow-up Functionalization of P6b with Thiocholesterol (5) via Thiol-Ene Click Chemistry



Polymer **P6b** (100 mg per 10 mL solvent) was dissolved in a mixture of THF/water (5/1). This solution was treated with thiocholesterol (**5**) (4.0 equiv. per remaining allyl group) and catalytic amounts of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone. The reaction mixture was degassed (drawing vacuum and refilling with argon; 15 iterations) and irradiated at λ = 365 nm for 18 hours at room temperature. The consumption of the allyl groups was monitored by ^{1}H-NMR spectroscopy. Volatiles were then removed *in vacuo* and the crude polymer was washed several times with pentane to remove excess thiocholesterol, when the quantitative conversion of the allyl groups was observed via NMR. Hereafter, the conjugate was purified by dialysis against water and freeze-dried to yield substrate **P9**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 7.70 – 7.11 (m, benzylamine, 71H), 5.39 (s, CH_{Chol}), 4.18 (s, POCH_2, 484H), 2.91 – 1.14 (m, polymer backbone), 1.38 (s, POCH$_2$$CH_3$), 1.03 (s, $CH_{3,Chol}$), 0.95 (d, ^{3}J = 6.2 Hz, $CH_{3,Chol}$), 0.88 (d, ^{3}J = 6.6 Hz, 2 x $CH_{3,Chol}$), 0.72 (s, $CH_{3,Chol,}$ 13H).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

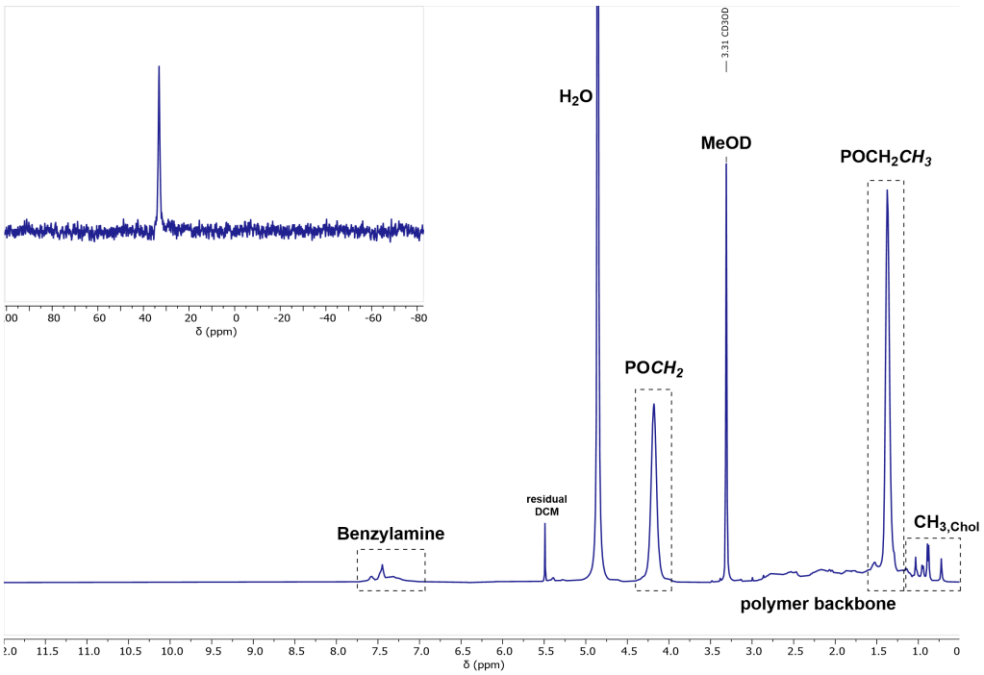


Fig. S32 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P9** in MeOD.

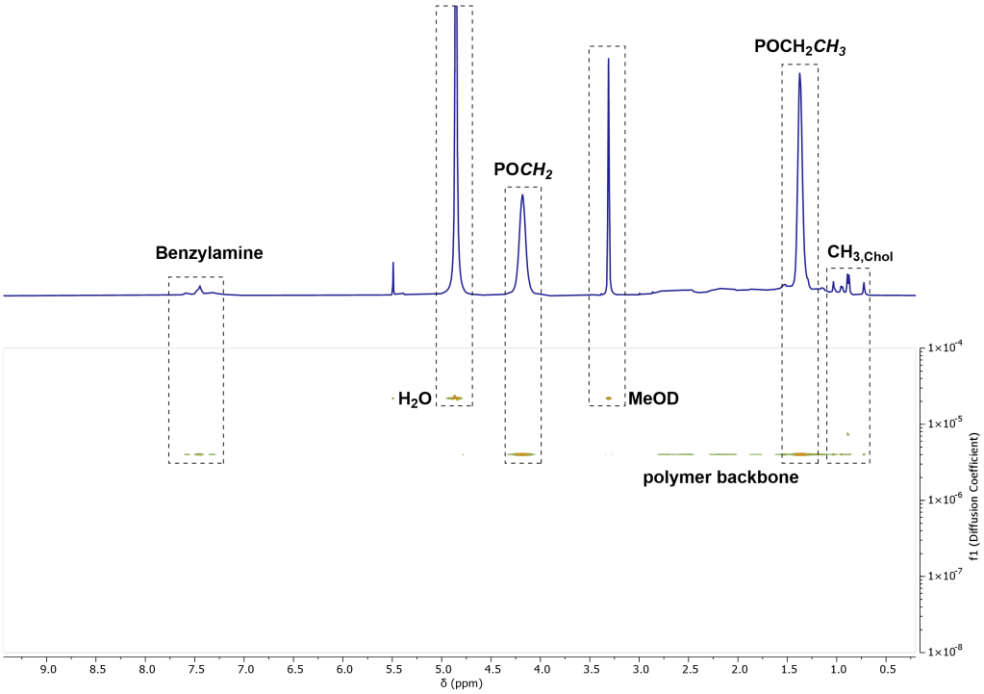
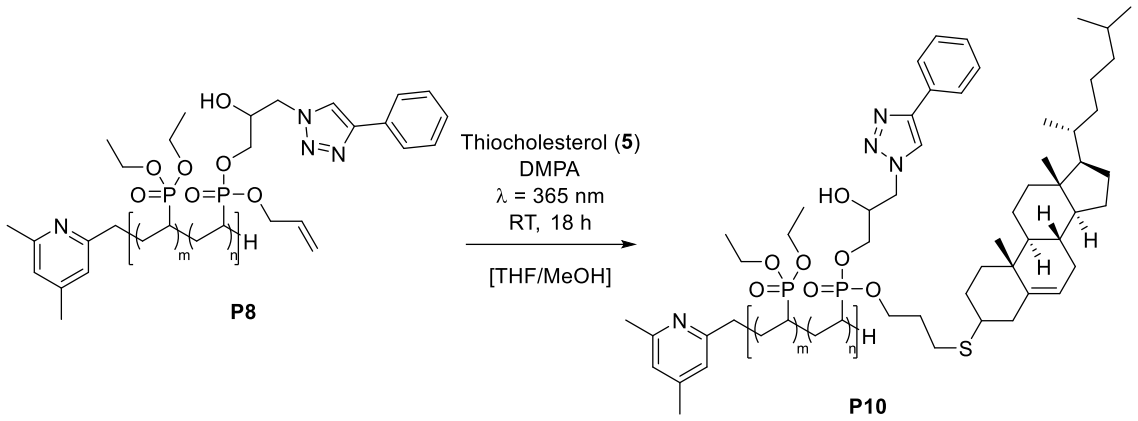


Fig. S33 DOSY spectrum of **P9** in MeOD.

Follow-up Functionalization of P8 with Thiocholesterol (5) via Thiol-Ene Click Chemistry



Polymer **P8** (100 mg per 10 mL solvent) was dissolved in a mixture of THF/water (5/1). This solution was treated with thiocholesterol (**5**) (4.0 equiv. per remaining allyl group) and catalytic amounts of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone. The reaction mixture was degassed (drawing vacuum and refilling with argon; 15 iterations) and irradiated at λ = 365 nm for 18 hours at room temperature. The consumption of the allyl groups was monitored by ^{1}H-NMR spectroscopy. Volatiles were then removed *in vacuo* and the crude polymer was washed several times with pentane to remove excess thiocholesterol, when the quantitative conversion of the allyl groups was observed by NMR. Hereafter, the conjugate was purified by dialysis against water and lyophilized to yield substrate **P10**.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 8.16 – 6.89 (m, Phenyl, 65H), 4.18 (s, POCH_2, 484H), 2.96 – 1.11 (m, polymer backbone), 1.38 (s, POCH$_2CH_3$), 0.95 (d, ^{3}J = 6.4 Hz, $CH_{3,Chol}$), 0.88 (d, ^{3}J = 6.5 Hz, 2 x $CH_{3,Chol}$), 0.72 (s, $CH_{3,Chol}$, 11H).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

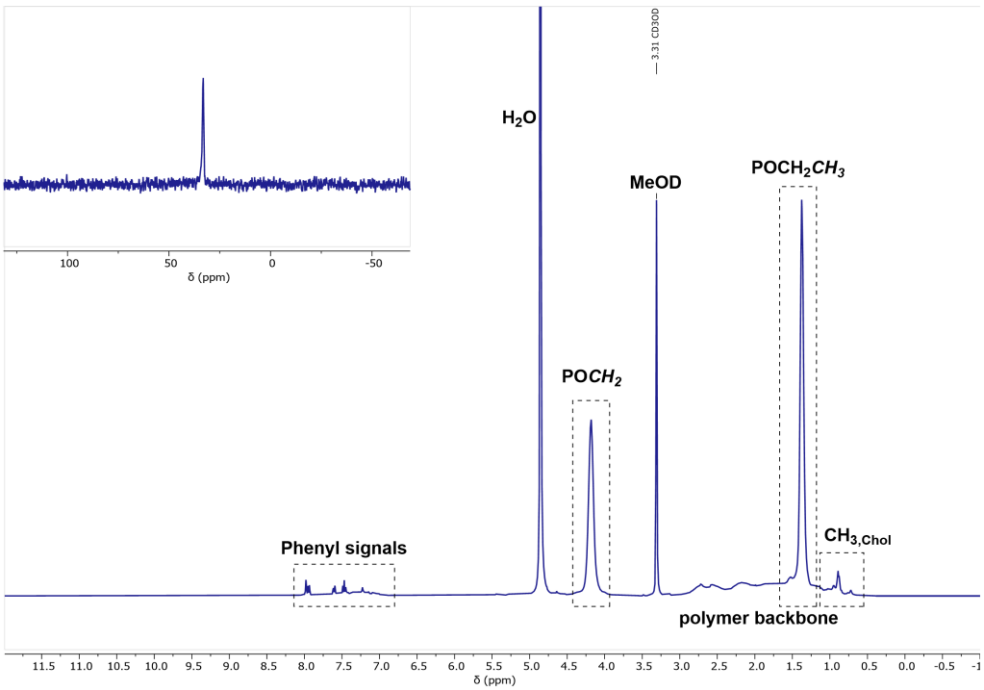


Fig. S34 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P10** in MeOD.

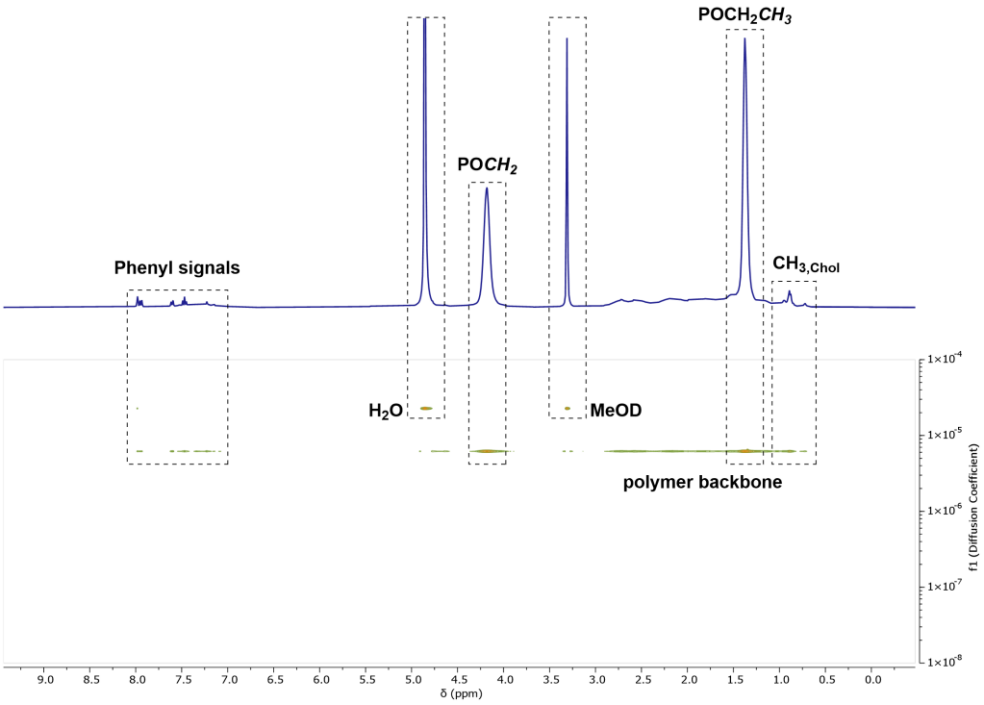
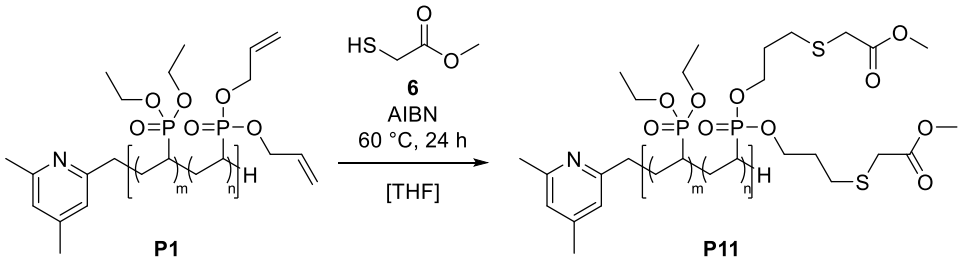


Fig. S35 DOSY spectrum of **P10** in MeOD.

5 Introduction of Hydrazone Linkages in P(DEVP-*co*-DAlVP) P1

Thiol-Ene Coupling of Methyl Thioglycolate (6) with P(DEVP-*co*-DAlVP) P1



Polyvinylphosphonate **P1** (500 mg, 25.0 µmol) was dissolved in THF (30 mL) in a pressurizable schlenk flask. Methyl thioglycolate (**6**) (236 µL, 2.64 mmol, 5.00 equiv. per allyl group) and catalytic amounts of azobisisobutyronitrile were added and the solution was degassed via repeated evacuation and filling with argon (20 iterations). The mixture was heated to 60 °C and stirred for 24 hours at this temperature. After this time period ^{1}H-HMR spectroscopy confirmed the quantitative conversion of the allyl groups. The solvent was removed *in vacuo*, the residue was dissolved in deionized water, and the aqueous solution was purified by dialysis against deionized water. After replacing the dialysate after two and four hours, the mixture was dialysed against water for additional 20 hours and the polymer-containing solution was freeze-dried to yield **P11** as a colourless solid.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 4.18 (br s, PO*CH*$_2$), 3.71 (s, methyl ester), 2.82 (s, SCH$_2$(C=O), CH$_2$S), 2.96 – 1.07 (m, polymer backbone), 2.04 (s,), 1.38 (br s, POCH$_2$*CH*$_3$).

^{13}C-NMR (126 MHz, MeOD, 300 K): δ (ppm) = 172.6 (s, C=O), 65.9 (s, POCH$_2$), 63.5 (s, POCH$_2$), 52.8 (s, OCH$_3$), 33.8 (s, CH$_2$), 34.4 – 28.5 (m, polymer backbone), 31.1 (s, CH$_2$), 29.6 (s, CH$_2$), 17.2 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): ῡ (cm^{-1}) = 3472 (br w), 2980 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2909 (m, ν_{C-H}), 1736 (m, $\nu_{C=O}$), 1477 (w, δ_{C-H}), 1443 (m, δ_{C-H}), 1392 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1219 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1097 (w), 1043 (w, ν_{P-O}), 1015 (st, ν_{P-O}), 952 (st), 781 (st).

EA: calculated*: C 43.24 H 7.75 N 0.06 S 2.53
found: C 43.34 H 7.82 N 0.12 S 2.47
*with 1.5 wt-% residual water after freeze-drying

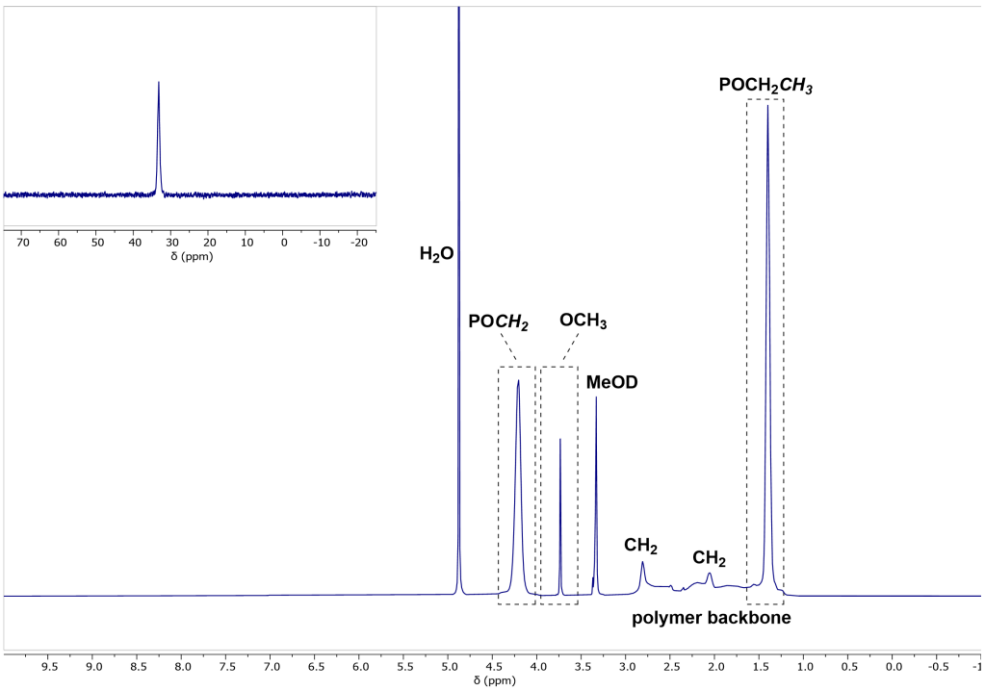


Fig. S36 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P11** in MeOD.

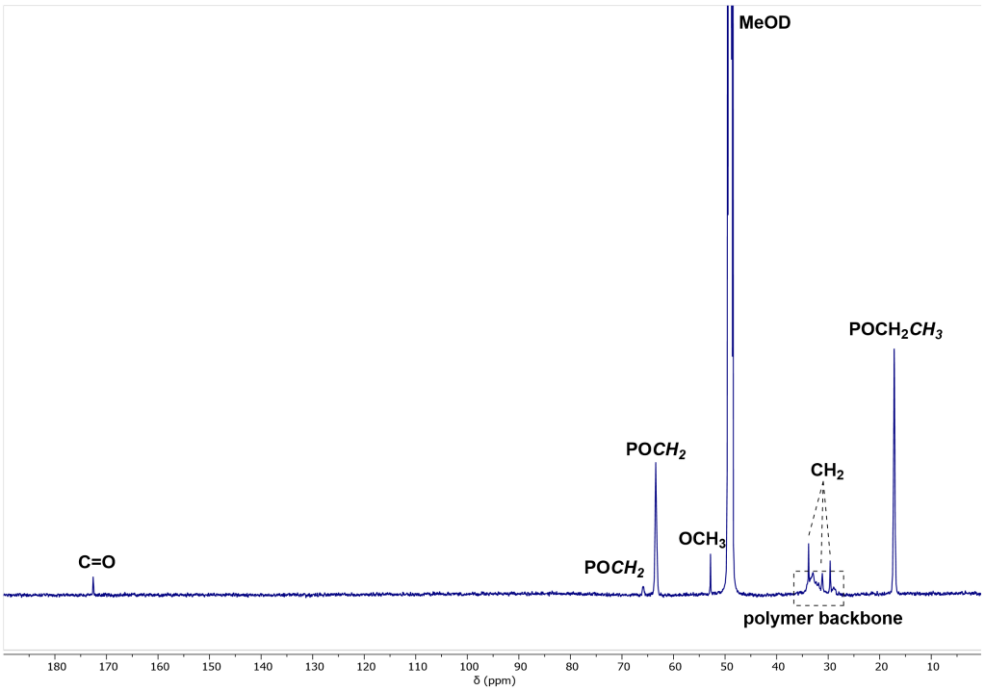


Fig. S37 ^{13}C-NMR spectrum of polymer **P11** in MeOD.

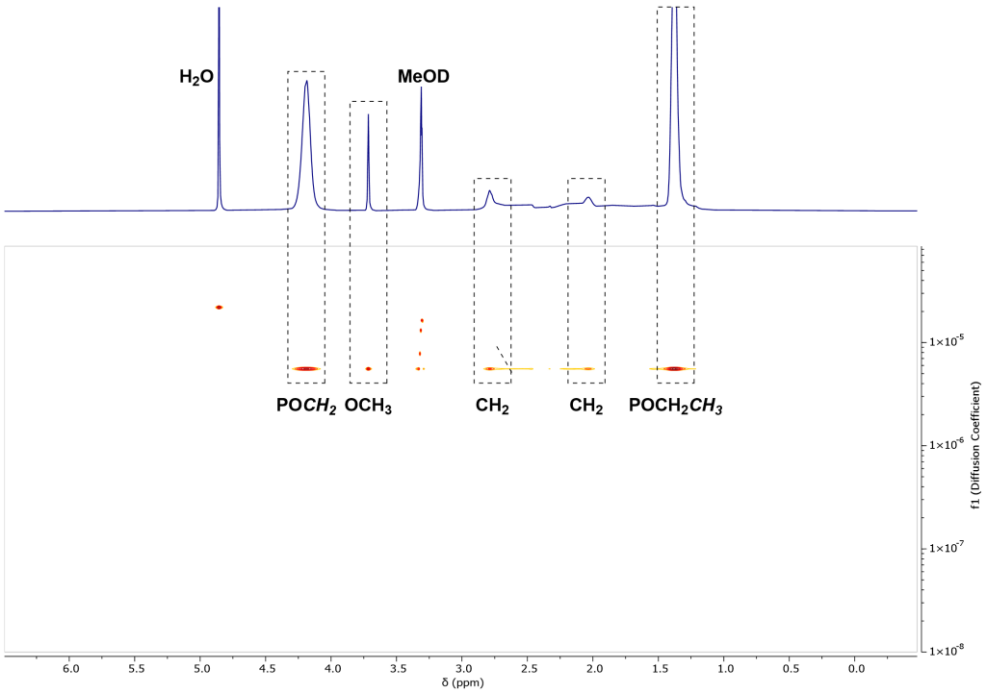


Fig. S38 DOSY-NMR of polymer **P11** in MeOD.

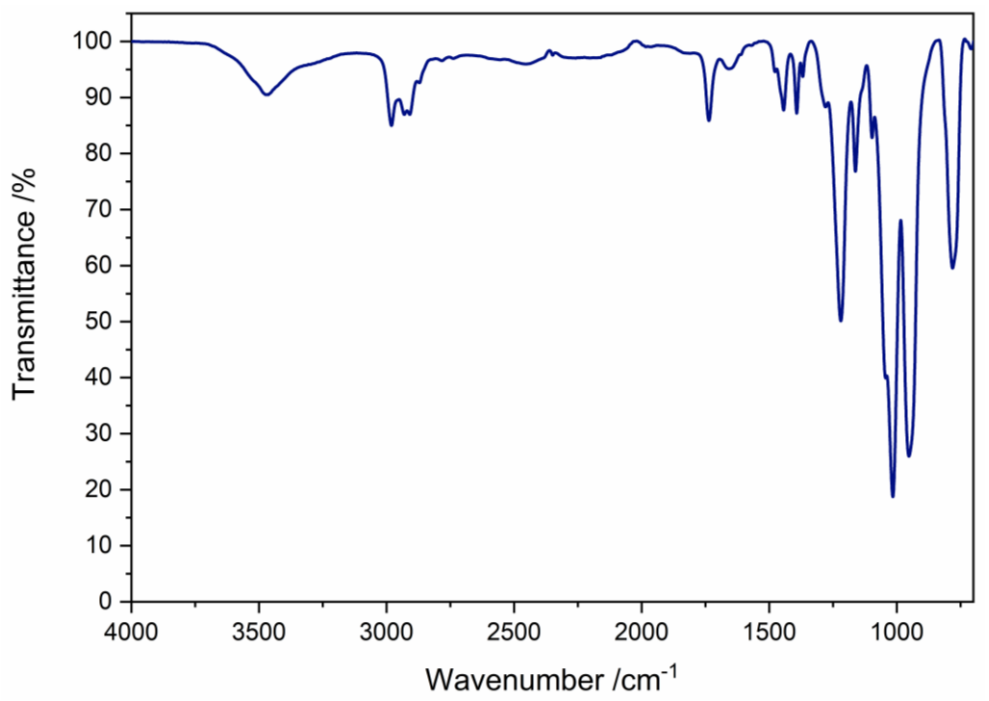
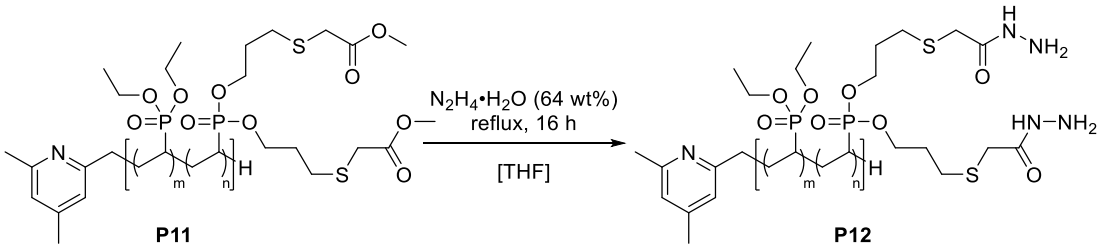


Fig. S39 IR spectrum of polymer **P11**.

Formation of Hydrazide P12



Under an argon atmosphere 300 mg of the thiol-ene adduct **P11** (13.5 µmol) were dissolved in absolute THF (30 mL) and treated with hydrazine-hydrate (700 µL, 14.3 mmol, 50.0 equiv. per ester). The mixture was refluxed for 24 hours and the quantitative conversion of the ester was confirmed by ^{1}H-NMR spectroscopy. Hereafter, the volatiles were removed *in vacuo* using an external cooling trap. Excess hydrazine was rendered harmless by addition of diluted hydrogen peroxide. The polymeric residue was dissolved in deionized water and purified by dialysis for 24 hours. The polymer-containing solution was lyophilized to yield hydrazide **P12** as a colourless solid.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 4.18 (br s, PO*CH*$_2$), 3.20 (s, SCH$_2$(C=O)), 2.76 (s, CH$_2$S), 2.96 – 1.16 (m, polymer backbone), 1.99 (s, CH$_2$), 1.38 (br s, POCH$_2$*CH*$_3$).

^{13}C-NMR (126 MHz, MeOD, 300 K): δ (ppm) = 171.6 (s, C=O), 66.1 (s, PO*CH*$_2$), 63.5 (s, PO*CH*$_2$), 34.1 (s, CH$_2$), 31.6 (s, CH$_2$), 35.0 – 28.2 (m, polymer backbone), 29.6 (s, CH$_2$), 17.2 (s, POCH$_2$*CH*$_3$).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): ῡ (cm^{-1}) = 3411 (br m), 2981 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2910 (m, ν_{C-H}), 1660 (m, $\nu_{C=O}$), 1478 (w, δ_{C-H}), 1444 (m, δ_{C-H}), 1392 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1212 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1096 (w), 1041 (w, ν_{P-O}), 1014 (st, ν_{P-O}), 954 (st), 783 (st).

EA: calculated*: C 42.25 H 7.86 N 2.27 S 2.53
found C 41.74 H 7.79 N 2.04 S 2.42
*with 3.0 wt-% residual water after freeze-drying

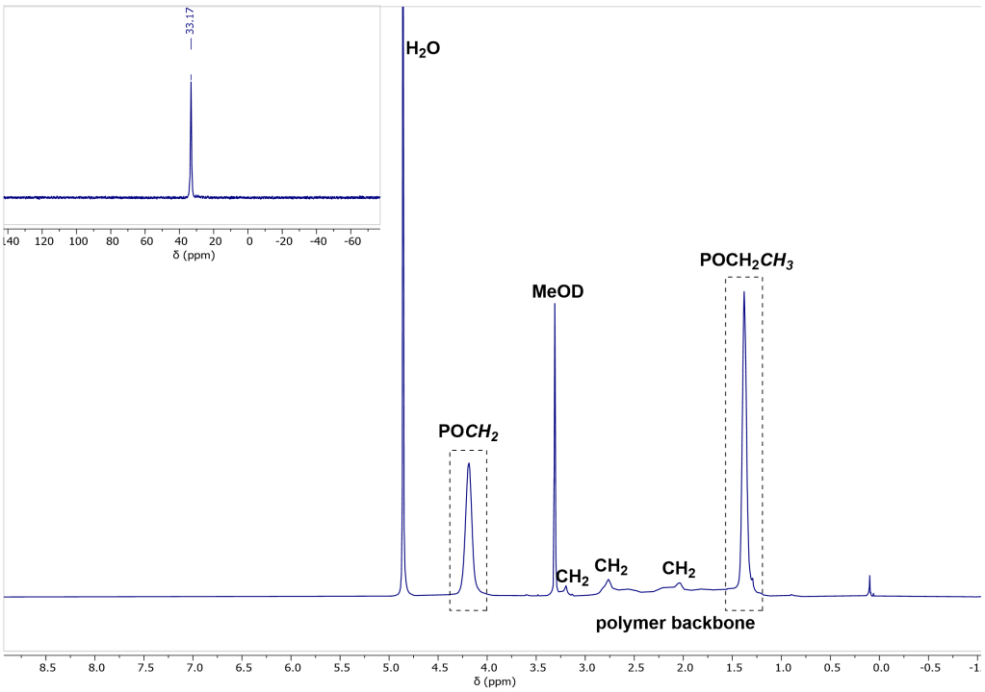


Fig. S40 ^{1}H- and zoom of ^{31}P-NMR spectrum of polymer **P12** in MeOD.

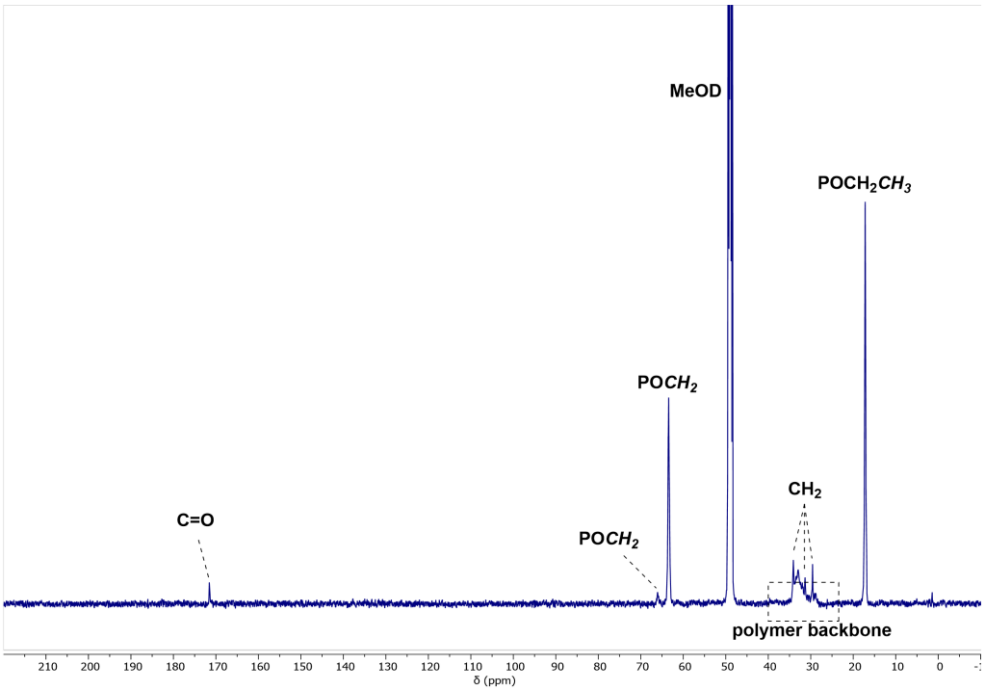


Fig. S41 ^{13}C-NMR spectrum of polymer **P12** in MeOD.

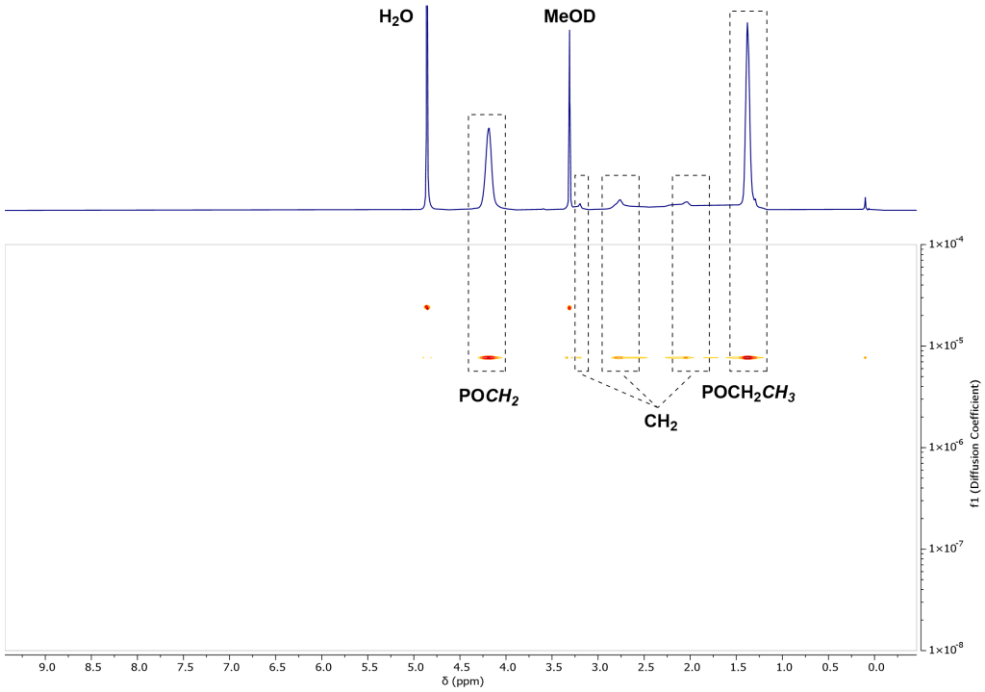


Fig. S42 DOSY-NMR of polymer **P12** in MeOD.

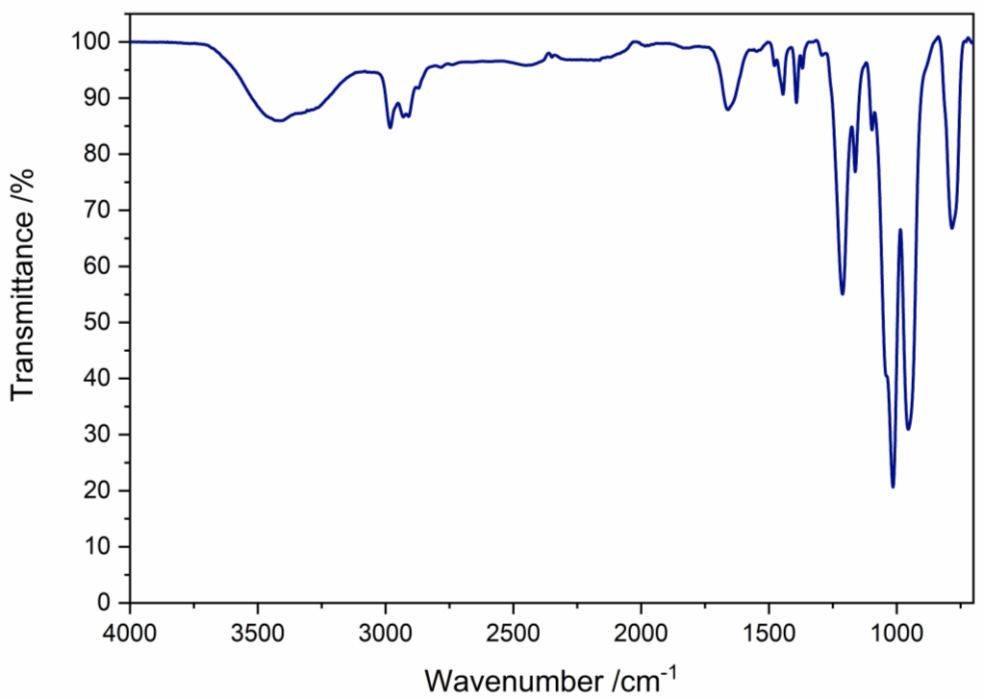
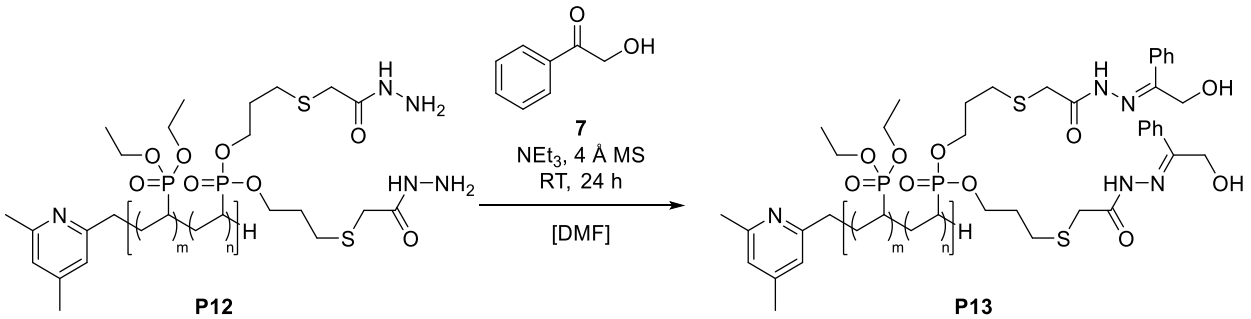


Fig. S43 IR spectrum of polymer **P12**.

Formation of Hydrazone P13



Under an argon atmosphere hydrazide **P12** (150 mg, 6.74 µmol) was dissolved in anhydrous DMF (6.0 mL) and treated with triethylamine (50 µL, 142 µmol, 2.50 equiv. per hydrazide motif) and 2-hydroxyacetophenone (**7**) (48.2 mg, 142 µmol, 2.50 equiv. per hydrazide motif). In the presence of molecular sieves (4 Å) the solution was stirred at room temperature. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy and the reaction was stopped after 24 hours. Remains of the molecular sieves were filtrated off, volatiles were removed in high vacuum, and the yellowish residue was dissolved in deionized water. The hydrazone adduct was purified by dialysis against deionized water for 24 hours. Lyophilization of the aqueous polymer solution yielded compound **P13** as a yellow solid.

^{1}H-NMR (400 MHz, MeOD, 300 K): δ (ppm) = 8.55 (s, $NH_{Hydrazone}$), 8.28 – 6.84 (m, Ph), 4.18 (s, $POCH_2$), 3.99 (s, CH_2OH), 3.19 (s, CH_2), 2.76 (s, CH_2), 2.04 (s, CH_2), 2.94 – 1.06 (m, polymer backbone), 1.37 (s, $POCH_2CH_3$).

^{13}C-NMR (126 MHz, MeOD, 300 K) δ (ppm) = 169.9 (s, C=O), 157.9 (s, C=N), 134.4 (s, C_{Ar}), 133.3 (s, C_{Ar}), 129.9 (s, C_{Ar}), 128.7 (s, C_{Ar}), 65.8 (weak s, PO*CH_2*), 63.5 (s, PO*CH_2*), 33.1 (s, CH_2), 30.8 (s, CH_2), 35.6 – 27.8 (m, polymer backbone), 23.7 (s, CH_2), 17.2 (s, $POCH_2$*CH_3*).

^{31}P-NMR (203 MHz, MeOD, 300 K): δ (ppm) = 33.2.

IR (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3407 (br m), 2980 (m, ν_{C-H}), 2927 (m, ν_{C-H}), 1680 (m, $\nu_{C=N}$), 1595 (m, $\nu_{C=O}$), 1478 (w, δ_{C-H}), 1444 (m, δ_{C-H}), 1391 (m, δ_{C-H}), 1368 (w, δ_{C-H}), 1215 (st, $\nu_{P=O}$), 1162 (m, ν_{C-O}), 1096 (w), 1043 (w, ν_{P-O}), 1018 (st, ν_{P-O}), 957 (st), 783 (st).

UV/Vis (MeOH): λ_{max} [nm] ($\varepsilon \times 10^3$ [L mol^{-1} cm^{-1}]) = 300 (5.2).

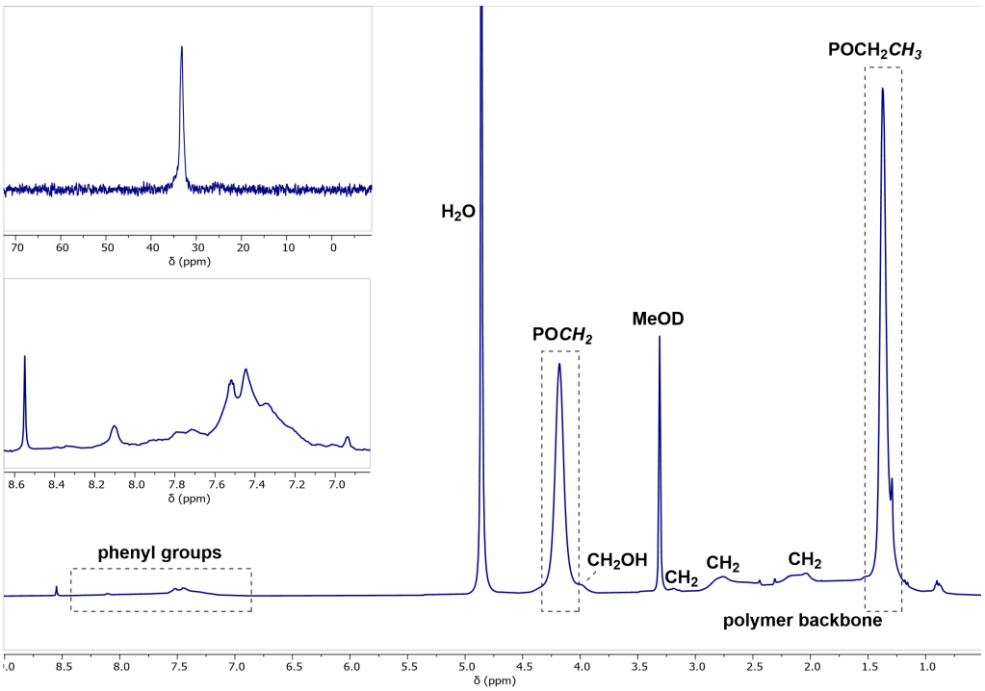


Fig. S44 ^{1}H-NMR, zoom of the aromatic region and ^{31}P-NMR spectrum of polymer **P13** in MeOD.

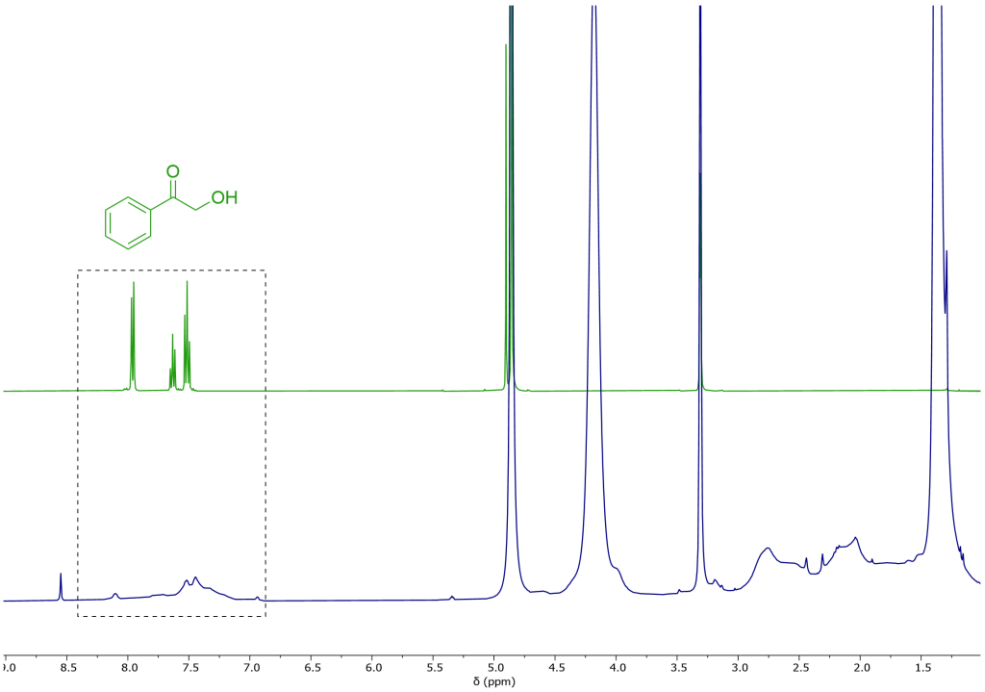


Fig. S45 NMR comparison of 2-hydroxyacetophenon (**7**) and polymer **P13** in MeOD.

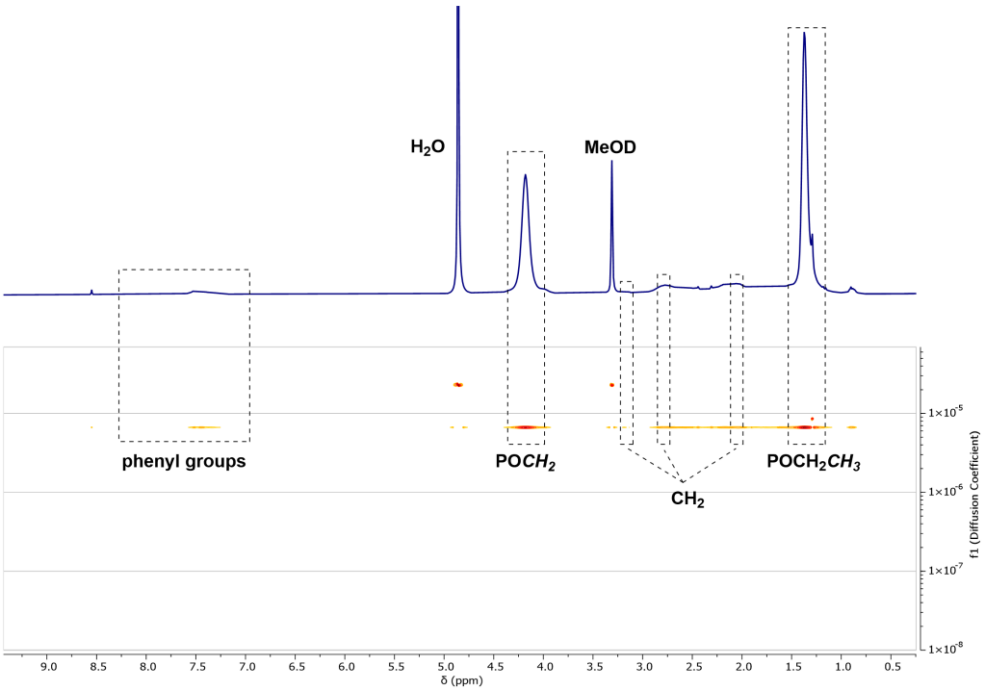


Fig. S46 DOSY-NMR of polymer **P13** in MeOD.

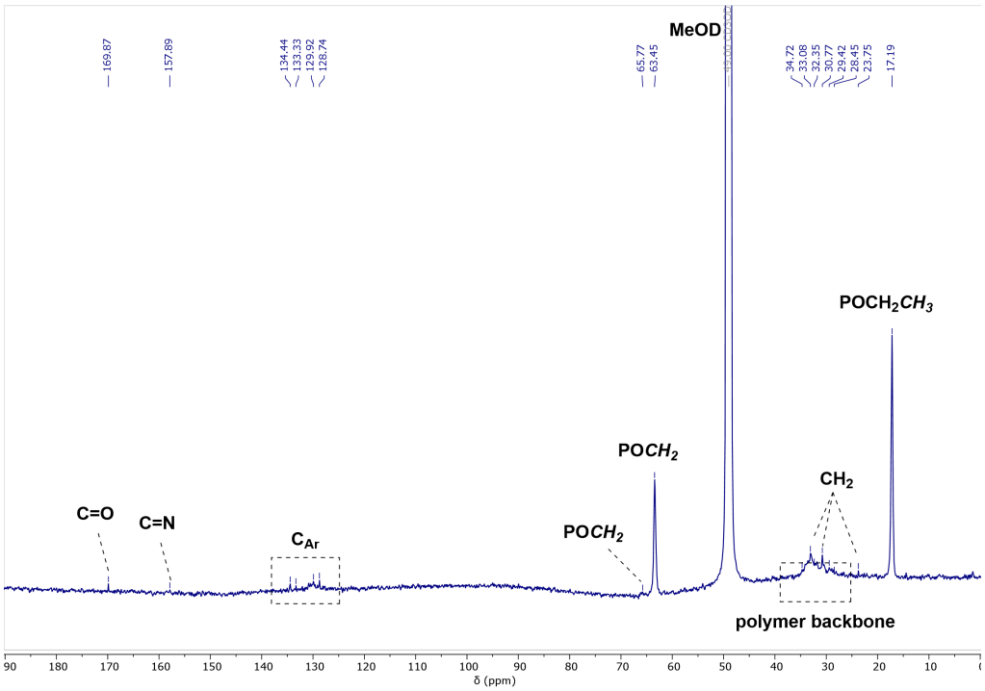


Fig. S47 ^{13}C-NMR of polymer **P13** in MeOD.

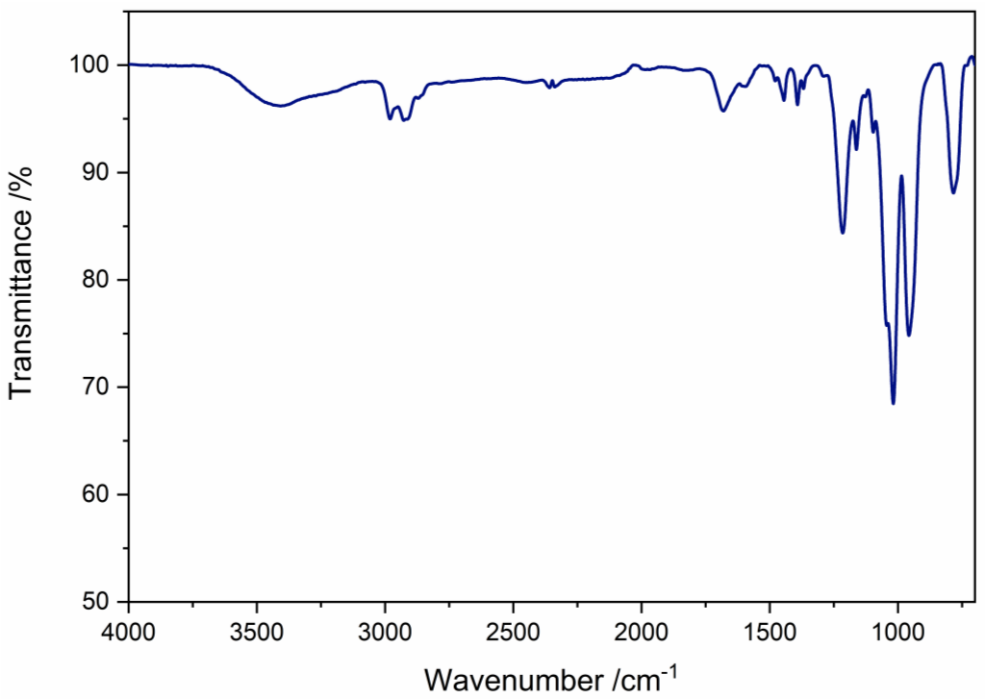


Fig. S48 IR spectrum of polymer **P13**.