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Post-polymerization functionalization of linear polyglycidol with diethyl vinylphosphonate

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Experimental

Materials

Bromotrimethylsilane (98 %, ABCR), potassium *tert*-butoxide (1 M solution in THF, Aldrich), *N*,*N*-Dimethylformamid abs., over molecular sieves (Aldrich), chloroform p.a. (VWR) and methanol p.a. (VWR) were used as received. Diethyl vinylphosphonate (95 + %, Aldrich) was stirred with calcium hydride for 24 h, distilled under reduced pressure and stored under nitrogen in a Schlenk flask. 3-Phenyl-1-propanol (3-PP) (≥ 98%, Fluka) was reacted with small amounts of sodium and distilled. Diglyme was distilled over sodium before use. Ethoxy ethyl glycidyl ether (EEGE) was synthesized from 2,3-epoxypropan-1-ol (glycidol) and ethyl vinyl ether according to *Fitton et al.*,[1]purified by distillation and stored under nitrogen atmosphere over molecular sieves (4 Å). The syntheses of Poly(ethoxy ethyl glycidyl ether) (P(EEGE)) **(1)**and polyglycidol (PG) **(2)** were perfomed according to *Hans et al*.[2]

All reactions were carried out in nitrogen atmosphere unless otherwise noted. Nitrogen (Linde 5.0) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

The results of the chemical analysis for P(EEGE)**(1)** and PG **(2)**are summarized in Table S1.

Table S1. Ratio of monomer to initiator adjusted in the feed, degree of polymerization (P_n) and molecular weight (M_n) determined by end group analysis (^{1}H NMR) and SEC data of linear P(EEGE)**(1)**and PG **(2)**.

polymer	[EEGE]/[3-PP]	P_n[a]	M_n[a] (g/mol)	M_n[b] (g/mol)	M_w/M_n[b]	yield / %
P(EEGE) (1)	20	22	3352	3000	1.19	100
PG (2)	---	--	1766	1800	1.12	75

[a] Degree of polymerization (P_n) and molecular weight (M_n) calculated from ^{1}H NMR. [b] Molecular weight and molecular weight distribution determined by size exclusion chromatography (SEC) in THF as eluent for P(EEGE) and DMF as eluent for PG. Narrow distributed poly(methyl methacrylate) standards and were used for calibration.

Measurements

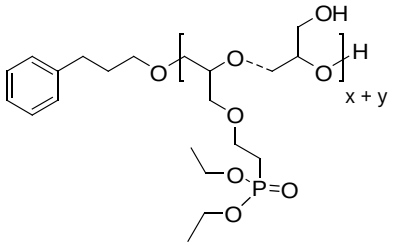
^{1}H NMR, ^{13}C NMR and proton decoupled ^{31}P NMR spectra (^{31}P{^{1}H}) were recorded on a Bruker DPX-400 FT-NMR spectrometer at 400 MHz and 101 MHz and 162 MHz, respectively. Deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) were used as solvents. TMS served as internal reference for $CDCl_3$.Spectra recorded in DMSO-$d_6$were referenced against the solvent signal (DMSO-d_6: δ (ppm) = 2.50). ^{31}P{^{1}H} NMR spectra were referenced against 85 % H_3PO_4 as external reference. The coupling constants J_{xy} are given in Hz.

Molecular weights (M_n and M_w) were determined by size exclusion chromatography (SEC). SEC analyses were carried out with THF, DMF or water as eluent. For THF SEC a high pressure liquid chromatography pump (ERC 6420) with a RI detector (WGE Dr. Bures ETA 2020) at 30 °C was used. The eluent was THF HPLC grade and a flow rate of 1.0 mL/min was used. Four columns with MZ SDplus gel were applied. Length of each column was 300 mm, diameter 8 mm and nominal pore widths were 50, 100, 1000, 10000 Å. The calibration was achieved with commercial poly(methyl methacrylate) standards. For DMF SEC a high pressure liquid chromatography pump (Bischoff HPLC Compact Pump) with a RI detector (Jasco RI-2031plus) at 30 °C was used. The eluent was DMF optigrade with 1 mg/mL LiBr and a flow rate of 1.0 mL/min was used. Three columns with PSS GRAM gel were applied. Length of each column was 300 mm, diameter 8 mm and nominal pore widths were 100, 1000, 3000 Å. Narrow distributed poly(methyl methacrylate) standards were used for calibration. Water SEC is using a high pressure liquid chromatography pump (Agilent Series 1100) with a RI detector (Optilab DSP) at 30 °C. The eluent was H_2O HPLC grade and a flow rate of 1.0 mL/min was used. Three columns with PSS SUPREMA gel were applied. Length of each column was 300 mm, diameter 8 mm and nominal pore widths were 30, 1000, 3000 Å. The calibration was achieved with commercial poly(ethylene glycol) standards.

Results were evaluated using the PSS WinGPC Unity software.

Syntheses

Synthesis of linear poly[(glycidol-diethylphosphonatoethyl)-*co*-glycidol] P[(G^{DEPE})-*co*-G] (3d)



Polyglycidol **(2)** (0.579 g, 0.355 mmol) was dissolved in DMF (12 mL) and potassium *tert*-butoxide (0.35 mL of a 1 M solution in THF, 0.35 mmol) was added over 2 h using a syringe pump. Upon addition of the alkoxide, a small amount of insoluble coagulate was formed, which was identified as potassium salt of polyglycidol. The solution was stirred for 30 minutes at room temperature. The *tert*-butanol formed was removed by distillation. Diethyl vinylphosphonate (0.874 g, 5.328 mmol) was added and the mixture was stirred for 144 h at room temperature. The coagulate was removed by filtration and the product was dried in vacuum. The residue was redissolved in chloroform and precipitated in cold pentane. A brownish viscous liquid was obtained. **(3d)**Yield: 1.016 g (70 %).^{1}H NMR (DMSO-d_6): δ 1.23 (tr, 6H, $^{3}J_{HH}$ = 7.02 Hz, POCH$_2$C*H*$_3$), 1.78 (quin, 2H, $^{3}J_{HH}$ = 7.00 Hz, ArCH$_2$C*H*$_2$), 2.05 (dtr, 2H, $^{3}J_{HH}$ = 7.27 Hz,$^{2}J_{HP}$ = 18.3 Hz, CH$_2$OCH$_2$C*H*$_2$P), 2.61 (tr, 2H, $^{3}J_{HH}$ = 7.66 Hz, ArC*H*$_2$), 3.20-3.75 (m, 14H, ArCH$_2$CH$_2$C*H*$_2$, OC*H*$_2$C*H*(C*H*$_2$OH)O, OC*H*$_2$C*H*(C*H*$_2$OC*H*$_2$CH$_2$P)O), 3.88-4.10 (m, 4H, POC*H*$_2$CH$_3$), 4.57 (br s, OCH$_2$CH(CH$_2$O*H*)O), 7.13-7.23 (m, 3H, Ar), 7.23-7.33 (m, 2H, Ar). ^{13}C NMR (DMSO-d_6): δ 16.2 (d, $^{3}J_{CP}$ = 5.8 Hz, POCH$_2$C*H*$_3$), 26.0 (d, $^{1}J_{CP}$ = 137 Hz, CH$_2$OCH$_2$C*H*$_2$P), 31.0 (ArCH$_2$C*H*$_2$), 31.6 (ArC*H*$_2$), 61.0, (PO*C*H$_2$CH$_3$, OCH$_2$CH(*C*H$_2$OH)O), 64.8 (CH(CH$_2$O*C*H$_2$CH$_2$P)O), 69.2-70.2 (ArCH$_2$CH$_2$*C*H$_2$, O*C*H$_2$CH(*C*H$_2$OCH$_2$CH$_2$P)O, OCH$_2$CH(*C*H$_2$OH)O), 78.1, 78.2 (OCH$_2$*C*H(CH$_2$OCH$_2$CH$_2$P)O), 80.1, 80.2 (OCH$_2$*C*H(CH$_2$OH)O), 125.7 (Ar), 128.3 (Ar), 141.2 (Ar). ^{31}P NMR (DMSO-d_6): δ 28.5.

The synthesis of P[(G^{DEPE})-*co*-G] (**3a,b,c**) was performed in analogy to **3d**. Reagent ratios, reaction conditions and yields obtained after purification are listed in Table S2. For analytical

data of the product see Table S3. The conversion of hydroxy groups vs. reaction time is shown in Figure S4.

Table S2. Synthesis of linear P[(G^{DEPE})-*co*-G]**(3a-d)**: Reagent ratios, reaction conditions and yields obtained after purification.

Polymer	PG / g, (mmol)	KO^{t}Bu / [a] mL, (mmol)	DEVP / g, (mmol)	t / h	yield / [b] %
3a	0.384, (0.24)	0.08, (0.08)	0.193,(1.18)	96	94
3b	0.509, (0.31)	0.16, (0.16)	0.41, (2.50)	115	78
3c	0.477, (0.29)	0.19, (0.19)	0.480,(2.92)	144	84
3d	0.579, (0.36)	0.35, (0.35)	0.874,(5.33)	144	70

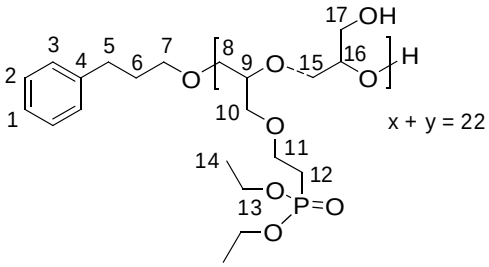
[a] 1 M solution in THF. 6.5 Mol.-% relative to the amount of DEVP. [b] Yield after purification by precipitation in cold pentane.

Table S3. Ratios of DEVP to hydroxy groups in the feed, degree of functionalization F (percentage of phosphonoethylation), number average molecular weights determined by ^{1}H NMR and SEC and molecular weight distribution of P[(G^{DEPE})-*co*-G] **(3a-d)**.

polymer	ratio [DEVP]/[OH]	F_{NMR} [a] (%)	$M_{n,\,NMR}$ [a] (g/mol)	$M_{n,\,SEC}$ [b] (g/mol)	$M_w/M_{n,SEC}$ [b]
3a	0.23	27	2751	3300	1.16
3b	0.36	32	2915	3600	1.17
3c	0.45	50	3572	4000	1.20
3d	0.68	64	4064	4000	1.15

[a] According to ^{1}H NMR analysis. Deviation from the adjusted ratio due to integration error. [b] Molecular weight and molecular weight distribution determined by size exclusion chromatography (SEC) using narrow distributed poly(methyl methacrylate) standards and DMF as eluent.

Formula used for the calculation of the degree of functionalization F by ^{1}H NMR analysis:



$$F(\%) = \frac{\frac{5 \cdot I(12)}{2 \cdot I(1,2,3)} \cdot 100}{x + y}$$

I (*a*): Intensity of the signal *a*. Assignment based on the structure shown above.

x+y: Total number of repeating units

In Figure S1 the conversion of hydroxy groups within polyglycidol is plotted against the reaction time.

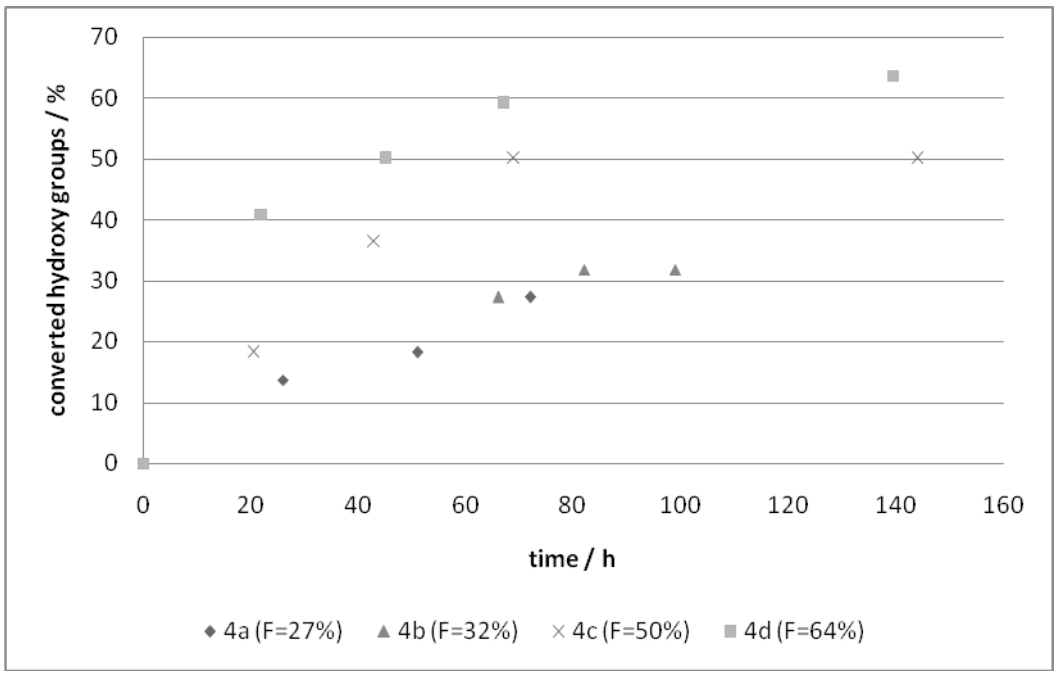


Figure S1. Phosphonoethylation of polyglycidol with DEVP: Conversion of hydroxy groups(in %) as a function of time for different reagent ratios (see Table S3).

Identification of diethyl-2-ethoxyethyl phosphonate as side-product after variation of the reaction conditions:

The P[(G^{DEPE})-co-G]s (**3a-d**) were purified by precipitation in cold pentane. In Figure S2the ^{1}H and ^{31}P NMR spectra of the mother liquor are shown for the addition of PG to DEVP in DMF as solvent catalyzed by **13 mole-% KO^{t}Bu at 70 °C**(These reaction conditions lead to increased coagulation and a broadening of the molecular weight distribution).Diethyl-2-ethoxyethyl phosphonate was found as side-product under this reaction condition.

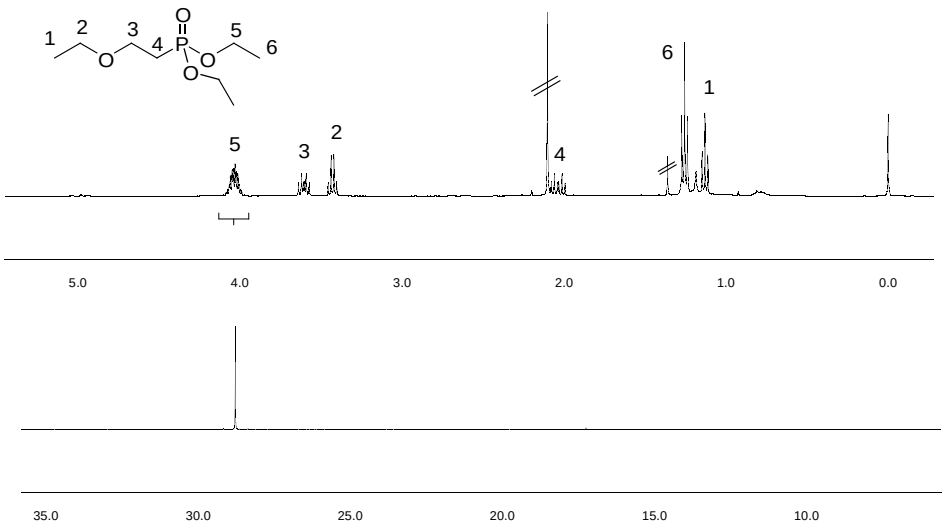
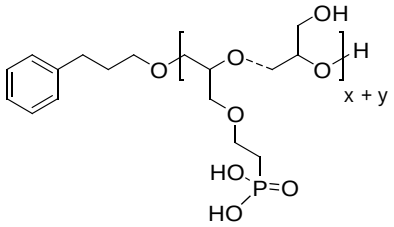


Figure S2. ^{1}H (top) and ^{31}P NMR spectrum (bottom) recorded in $CDCl_3$ of the pentane phase of a reaction performed at 70 °C with 13 Mole-% of the alkaline catalyst (*reaction is not included in this communication*).

^{1}H NMR ($CDCl_3$): δ 1.13 (tr, 3H, $^{3}J_{HH}$ = 7.02 Hz, C*H*$_3$CH$_2$OCH$_2$), 1.26 (tr, 6H, $^{3}J_{HH}$ = 7.07 Hz, POCH$_2$C*H*$_3$), 2.04 (dtr, 2H, $^{3}J_{HH}$ = 7.51 Hz, $^{2}J_{HP}$ = 18.7 Hz, CH$_2$OCH$_2$C*H*$_2$P), 3.43 (q, 2H, , $^{3}J_{HH}$ = 7.01 Hz CH$_3$C*H*$_2$OCH$_2$), 3.61 (dtr, 2H, $^{3}J_{HH}$ = 5.80 Hz, $^{2}J_{HP}$ = 11.6 Hz, CH$_2$OC*H*$_2$CH$_2$P), 3.96-4.13 (m, 4H, POC*H*$_2$CH$_3$).). ^{13}C NMR (DMSO-d_6): δ 15.2 (*C*H$_3$CH$_2$OCH$_2$), 16.4 (d, $^{3}J_{CP}$ = 6.1 Hz, POCH$_2$*C*H$_3$), 27.1 (d, $^{1}J_{CP}$ = 139 Hz, CH$_2$OCH$_2$*C*H$_2$P), 61.6 (d, $^{2}J_{CP}$ = 6.2 Hz, POC*H*$_2$CH$_3$), 64.4 (CH$_3$CH$_2$O*C*H$_2$), 66.3 (CH$_3$*C*H$_2$OCH$_2$). ^{31}P NMR (DMSO-d_6): δ 28.8.

Synthesis of linear poly[(glycidol-phosphonatoethyl)-*co*-glycidol]; P[(G^{PE})-*co*-G] (4d)



P[(G^{DEPE})-*co*-G] **(3d)** (0.495 g, 2.773 mmol, 1.774 mmolof phosphonate) was dissolved in chloroform and cooled to 0 °C. Four equivalents of bromotrimethylsilane (0.92 mL, 7.096 mmol) were added dropwise to the solution. After complete addition of the silylating agent, the ice bath was removed and the mixture was stirred for 117 h at room temperature. The solvent and other volatile byproducts were removed in vacuum. The residue obtained was dissolved in methanol (20 mL) and stirred for 24 h at room temperature. The solvent was removed by distillation and the product was taken up in water and purified by centrifugation. **(4d)**Yield: 0.359 g, (90 %). ^{1}H NMR (DMSO-d_6): δ 1.77 (quin, 2H, $^{3}J_{HH}$ = 6.92 Hz, $ArCH_2CH_2$), 1.90 (br s, 2H, $CH_2OCH_2CH_2P$), 2.60 (tr, 2H, $^{3}J_{HH}$ = 7.65 Hz, $ArCH_2$), 3.20-3.80 (m, 14H, $ArCH_2CH_2CH_2$, $OCH_2CH(CH_2OH)O$, $OCH_2CH(CH_2OCH_2CH_2P)O$), 5.62 (br s, 3H, $CH(CH_2OH)$, POH), 7.13-7.30 (m, 3H, Ar). ^{13}C NMR (DMSO-d_6): δ 28.6 (d, $^{1}J_{CP}$ = 134 Hz, $CH_2OCH_2CH_2P$), 31.6 ($ArCH_2$), 60.8, 60.9 ($OCH_2CH(CH_2OH)O$), 65.4 ($CH(CH_2OCH_2CH_2P)O$), 69.2-70.1 ($ArCH_2CH_2CH_2$, $OCH_2CH(CH_2OCH_2CH_2P)O$, $OCH_2CH(CH_2OH)O$), 78.0, 78.1 ($OCH_2CH(CH_2OCH_2CH_2P)O$), 80.1, 80.2 ($OCH_2CH(CH_2OH)O$), 125.7 (Ar), 128.3, 128.4 (Ar). *The signal for the quaternary carbon of the phenyl ring and the signal for $CH_2CH_2CH_2O$ could not be distinguished from the noise of the baseline.* ^{31}P NMR (DMSO-d_6): δ 23.9.

The synthesis of P[(G^{PE})-*co*-G] (**4a,b,c**) was performed in analogy to **4d**. Reagent ratios, reaction conditions and yields obtained after purification are listed in . For analytical data see .

Table S4. Synthesis of linear P[(G^{PE})-*co*-G]**(4a-d)**: Reagents, reaction times and yields.

Polymer	P(G^{DEPE}-*co*-G)/ g, (mmol, mmol phosphonate)	TMS-Br / mL, (mmol)	time / h	yield / %
4a	0.333, (2.802, 0.764)	0.40, (3.057)	98	92
4b	0.389, (3.080, 0.980)	0.51, (3.920)	120	95
4c	0.534, (3.420, 1.710)	0.56,(4.275)	86	94
4d	0.495, (2.773, 1.774)	0.92, (7.056)	117	90

Table S5. Synthesis of P[(G^{PE})-*co*-G] **(4a-d)**: Degree of functionalization and molecular weights determined from ^{1}H NMR and molecular weights and molecular weight distribution determined by SEC analysis.

polymer	F_{NMR}[a] (%)	$M_{n,\,NMR}$[a] (g/mol)	$M_{n,\,SEC}$[b] (g/mol)	$M_w/M_{n,SEC}$[b]
4a	27	2414	3000	1.25
4b	32	2522	3400	1.22
4c	50	2954	5400	1.18
4d	64	3278	4700	1.19

[a] According to ^{1}H NMR analysis. [b] Molecular weight and molecular weight distribution determined by SEC using narrow distributed poly(ethylene glycol) standards and water as eluent.

Figure S3shows the comparison of ^{31}P NMR spectra of P[(G^{DEPE}-*co*-G)] **(3d)**and P[(G^{PE}-*co*-G)]**(4d)**.

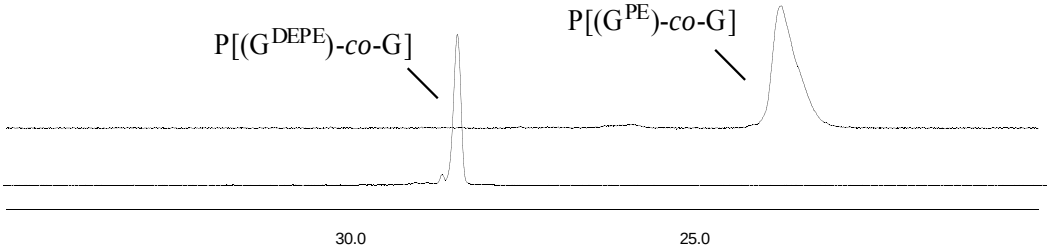


Figure S3. Comparison of ^{31}P NMR spectra of P[(G^{DEPE}-*co*-G)] and P[(G^{PE}-*co*-G)] recorded in DMSO-d_6.

A comparison of the ^{13}C NMR spectra of PG, P[(G^{DEPE}-*co*-G)] **(3d)**and P[(G^{PE}-*co*-G)] **(4d)**is shown in Figure S4.

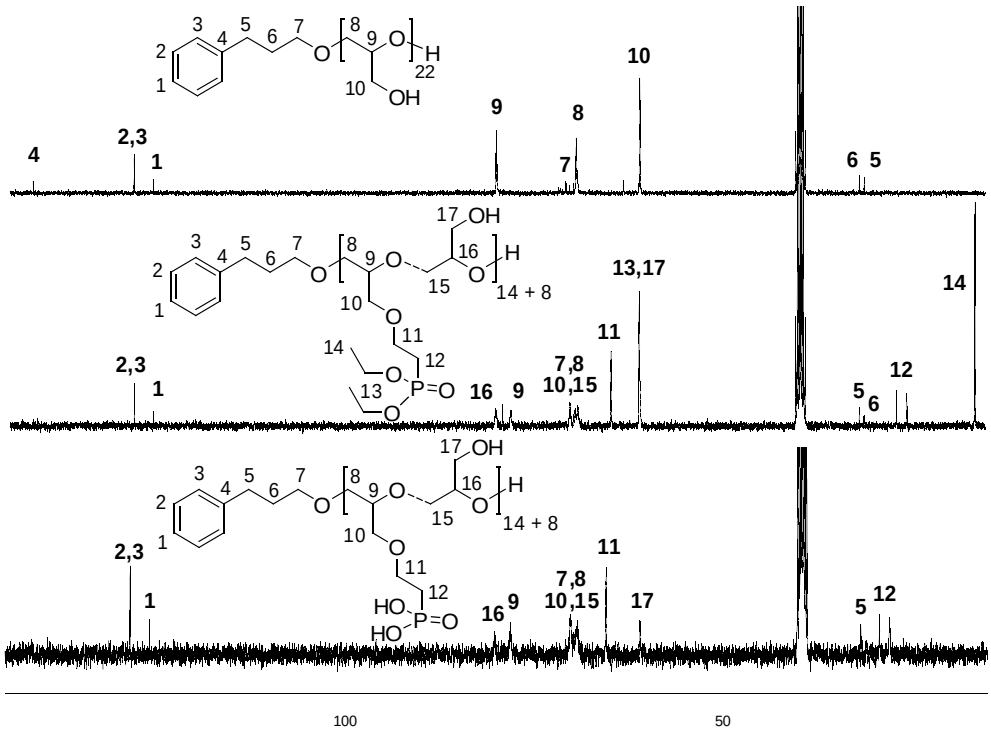


Figure S4. Comparison of ^{13}C NMR spectra of PG (top), P[(G^{DEPE}-*co*-G)] (middle) and P[(G^{PE}-*co*-G)] (bottom) recorded in DMSO-d_6.

References

1 A. O. Fitton, J. Hill, D. E. Jane, R. Millar, *Synthesis-Stuttgart,* 1987, **12**, 1140.

[2] M. Hans, P. Gasteier, H. Keul, M. Moeller, *Macromolecules,* 2006, **39**, 3184.