

Supporting Information

for

Multifunctional poly(phosphoester)s with two orthogonal protective groups

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Additional spectra and molecular weight data:

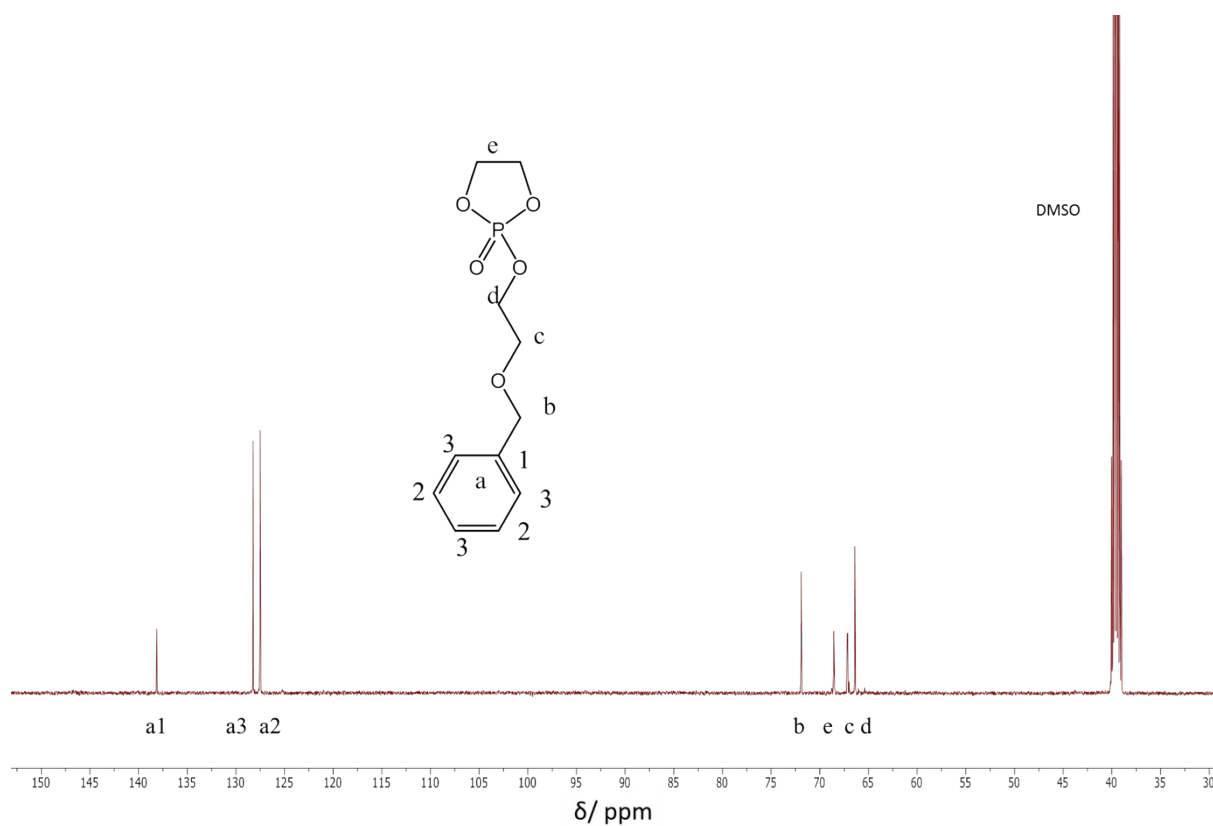


Figure S1: ^{13}C NMR spectrum of BnEEP (75 MHz, DMSO).

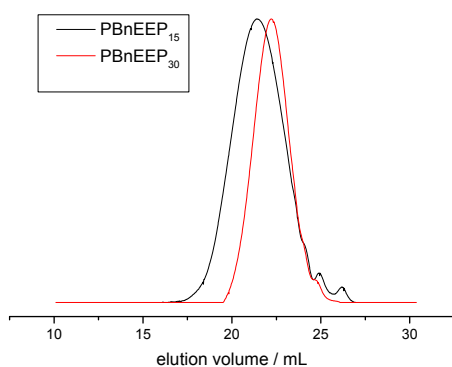


Figure S2: SEC elugrams of PBnEEP in THF (RI detection). The elugrams measured in THF indicates the formation of a polymer with a monomodal molecular weight distribution. However, for PBnEEP₁₅ also small oligomers at higher elution volumes are detected.

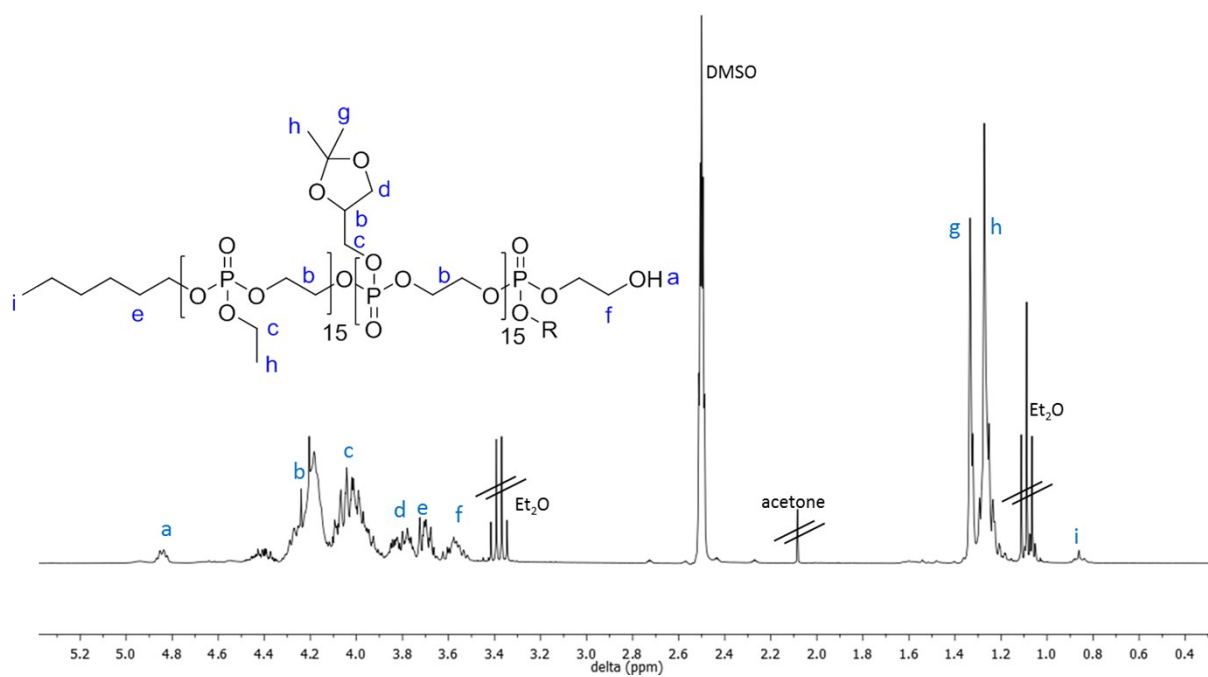


Figure S3: ^1H NMR of $\text{PEEP}_{15}\text{-co-PGEP}_{15}$ (300 MHz, $\text{DMSO-}d_6$, 298K).

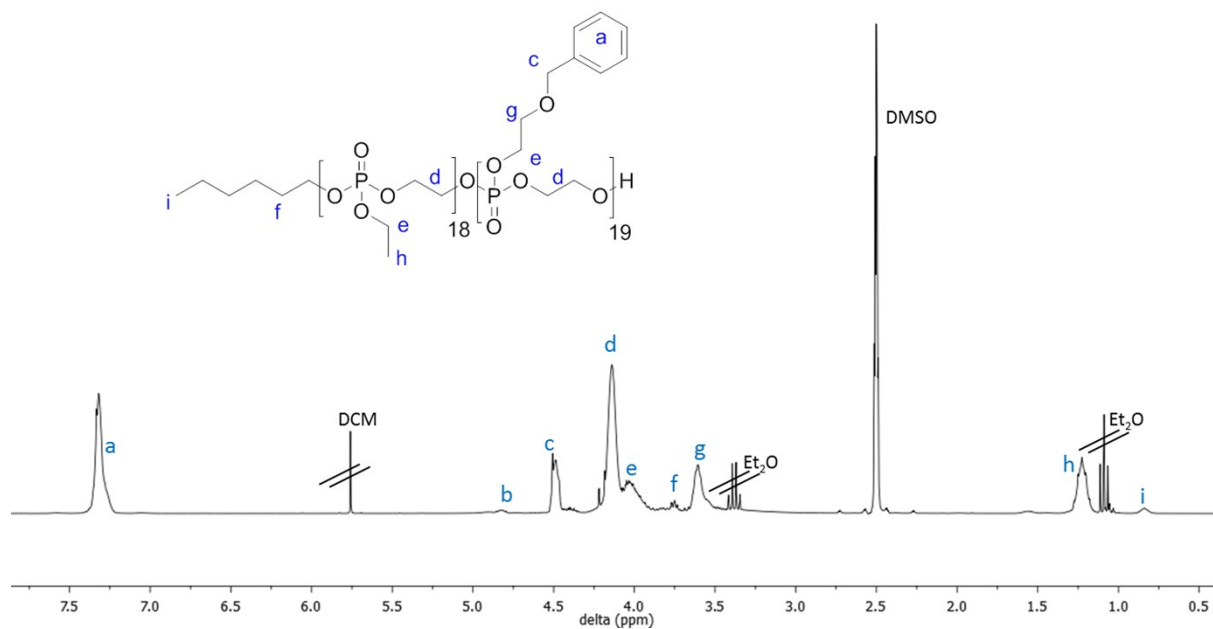


Figure S4: ^1H NMR of $\text{PEEP}_{18}\text{-co-PBnEEP}_{19}$ (300 MHz, $\text{DMSO-}d_6$, 298K).

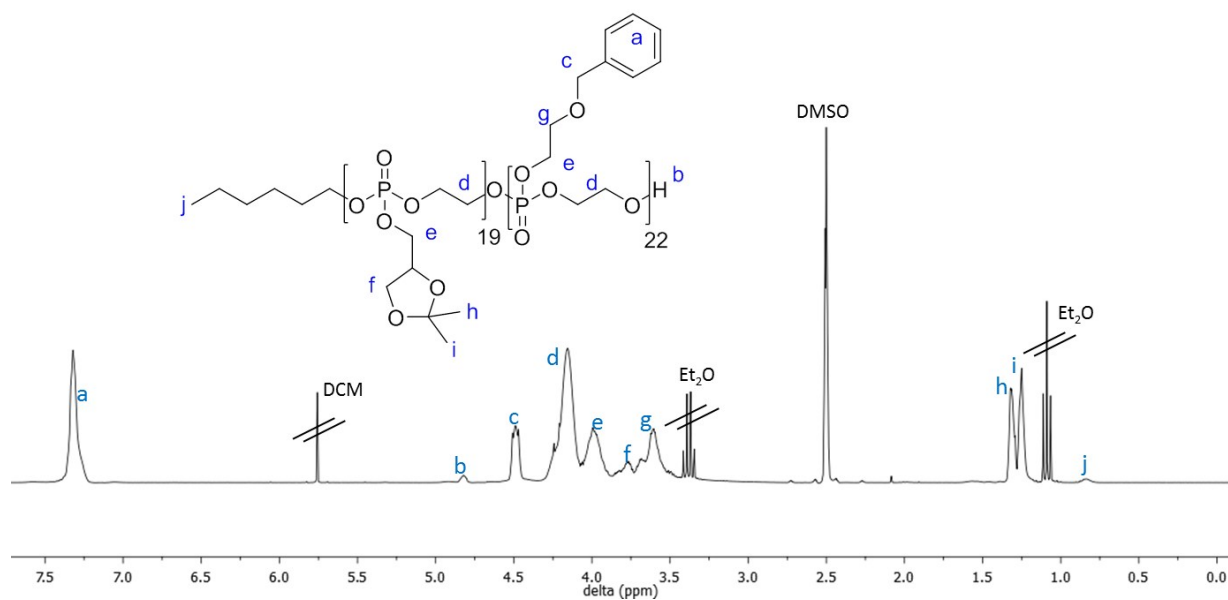


Figure S5: ^1H NMR spectrum of $\text{PBnEEP}_{22}\text{-co-PGEP}_{19}$ (300 MHz, $\text{DMSO-}d_6$, 298K).

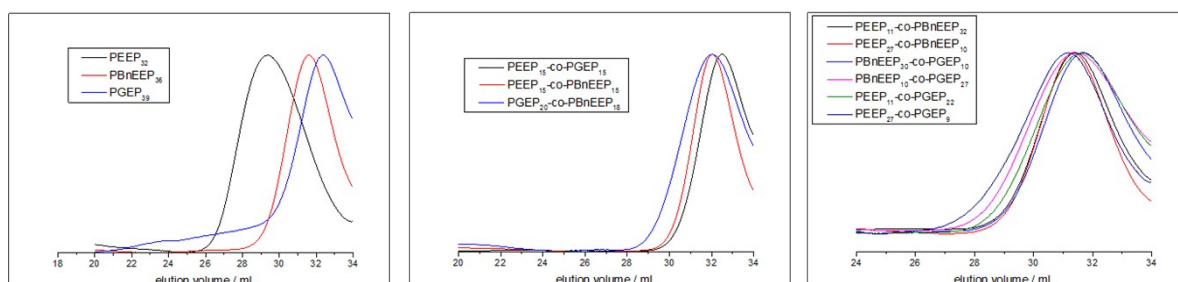


Figure S6: GPC elugrams of (co-)polymers (measured in THF, RI detection). All elugrams confirm previous results of a polymer formation with monomodal molecular weight distribution. Due to strong interactions of the polymers with the column-resin, high elution volumes were detected and determination of molecular weight is conducted by NMR. For the given method, a cut-off after 34 mL THF have passed the column is visible.

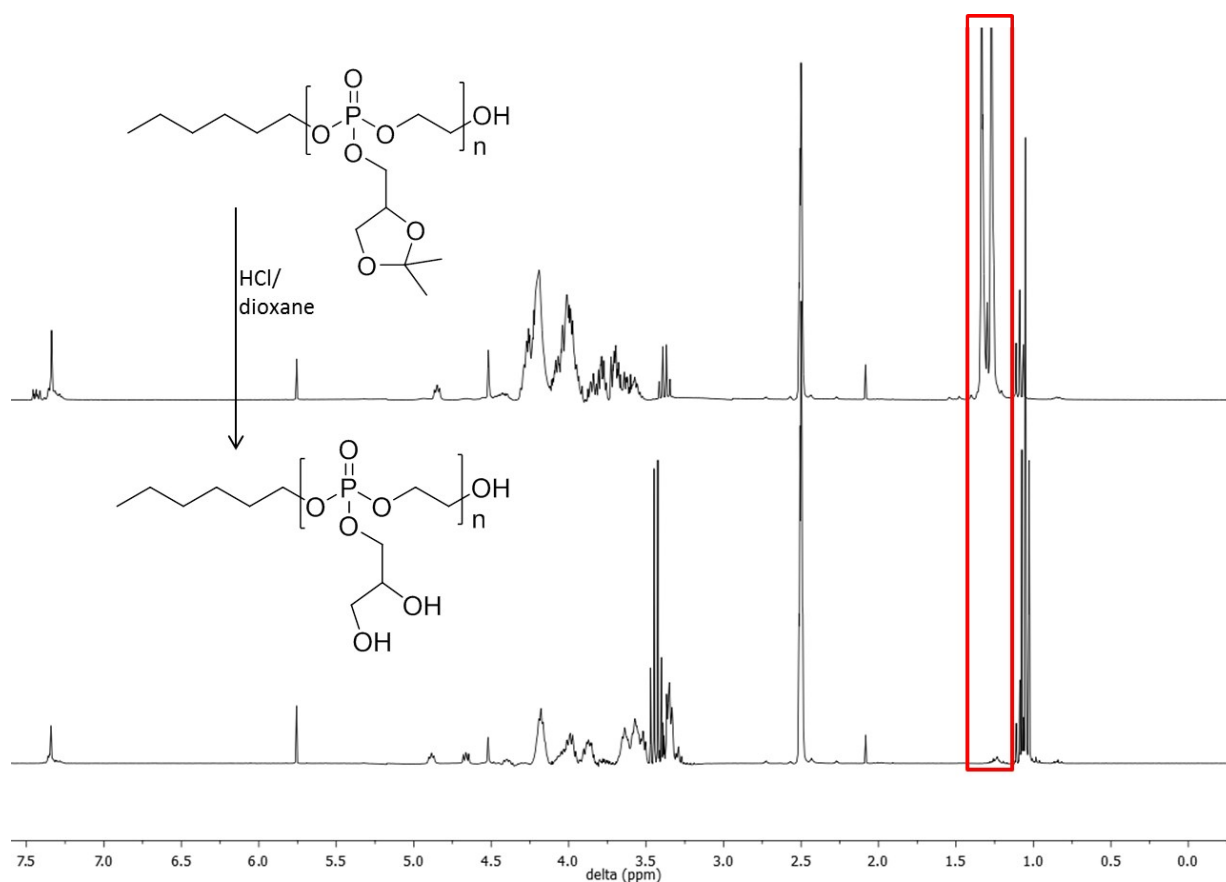


Figure S7: ^1H NMR of PGEP before (top) and after (bottom) acidic hydrolysis (300 MHz, $\text{DMSO}-d_6$, 298K).

Table S1: Polymerization results of BnEEP under different conditions

#	initiator	cat	solvent	c	T/°C	time	M/I	M _n (GPC)	Đ	yield/%
1.1	1	5mol%TBD	DCM	1.76	0	15min	15	1200	1.24	26
1.2	1	10mol%TBD	DCM	1.76	0	2h	15	1000	1.17	~40
1.3	1	10mol%TBD	DCM	1.76	0	2h	30	1100	1.15	~40
1.4	2	5mol%TBD	Bulk		0	2h	15	1400	1.41	80
1.5	2	5mol%TBD	Bulk		0	2h	30	2100	1.53	40
1.6	2	5eq DBU	DCM	4	RT	17.75h	15	1300	1.81	100
1.7	2	5eq DBU	DCM	4	RT	17.75	30	1500	1.30	87
1.8	2	5eq DBU	Toluene	4	50	20min	15	1500	1.45	100
1.9	2	5eq DBU	Toluene	4	50	20min	30	1400	1.27	88
1.10	3	5eq DBU	Toluene	4	40	19min	15	1300	1.45	100
1.11	3	5eq DBU	Toluene	4	40	22min	30	1400	1.21	85
1.12	3	5eq DBU	Toluene	4	40	20min	15	1500	1.34	98
1.13	3	5eq DBU	Toluene	4	40	30min	30	1500	1.26	97
1.14	2	Sn(Oct)2	Bulk		90	2h	15	700	1.18	39
1.15	2	Sn(Oct)2	Bulk		90	5.75h	15	1400	1.08	78
1.16	2	Sn(Oct)2	Bulk		90	4.67h	15	1000	1.21	78
1.17	2	Sn(Oct)2	Bulk		90	4.67h	30	1000	1.23	77
1.18	3	Sn(Oct)2	Bulk		90	6h	15	1200	1.18	70
1.19	3	Sn(Oct)2	Bulk		90	6.25h	30	1200	1.26	~74
1.20	4	Sn(Oct)2	Bulk		90	6h	15	800	1.31	97
1.21	5	Sn(Oct)2	Bulk		90	6h	15	1000	1.36	75
1.22	5	Sn(Oct)2	Bulk		90	21h	90	1100	1.56	60
1.23	5	Sn(Oct)2	bulk		90	21h	150	1000	1.60	29

Table S2: composition of synthesized (co-)polymers

entry	N(EEP)	N(BnEEP)	N(GEP)	N(EEP)/ NMR	N(HEEP)/ NMR	N(GEP)/ NMR	Đ	Reaction time
2.1	40	-	-	32	-	-	1.58	2h
2.2	-	-	40	-	-	39	1.62	6h
2.3	-	40	-	-	36	-	1.57	16.3h
2.4	20	-	20	15	-	15	1.61	4.75h
2.5	20	20	-	15	15	-	1.91	6h
2.6	20	20	-	18	19	-	1.50	19.25h
2.7	-	20	20	-	18	15	2.47	14.5
2.8	-	20	20	-	22	19	1.56	19h
2.9	-	30	10	-	24	7	2.54	14.5h
2.10	-	30	10	-	30	10	1.60	19.3h
2.11	-	10	30	-	9	23	2.13	14.5h
2.12	-	10	30	-	10	27	1.72	19.17h
2.13	10	30	-	11	34	-	2.39	14.5h
2.14	10	30	-	11	32	-	1.47	19.25h
2.15	30	10	-	20	9	-	1.81	3.5h
2.16	30	10	-	27	10	-	1.34	19.25h
2.17	30	-	10	26	-	10	2.75	4.17h

2.18	30	-	10	27	-	9	1.72	18.25h
2.19	10	-	30	6	-	23	1.93	5h
2.20	10	-	30	11	-	22	1.66	18.25h

Table S3: glass-transition temperature of different homo-and co-polymers determined by DSC

Polymer-composition	glass-transition temperature in °C
P(EEP) ₃₂	-62
P(HEEP) ₃₆	-39
P(GEP) ₃₉	-35
P(EEP ₁₈ -co-HEEP ₁₉)	-45
P(EEP ₁₁ -co-HEEP ₃₂)	-46
P(EEP ₂₇ -co-HEEP ₁₀)	-52
P(GEP ₁₉ -co-HEEP ₂₂)	-34
P(GEP ₂₇ -co-HEEP ₁₀)	-38
P(GEP ₁₀ -co-HEEP ₃₀)	-47
P(EEP ₁₅ -co-GEP ₁₅)	-45
P(EEP ₁₁ -co-GEP ₂₂)	-40
P(EEP ₂₇ -co-GEP ₉)	-46