# Electronic supporting information

## *Polyglycidol-based metal adhesion promoters*

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**Synthesis of linear polyglycidol**

**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) and PG.

| 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) | 24 | 26 | 3801 | 3600 | 1.2 | 100 |
| PG | --- | --- | 1926 | 2600 | 1.2 | 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.

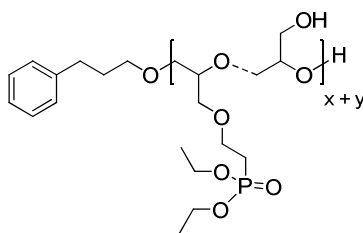**Oxa-Michael addition of PGs hydroxyl groups to DEVP – Synthesis of P(G$^{DEPE}_x$-$co$-G$_y$)**



**Table S2.** Synthesis of **P(G$^{DEPE}_x$-$co$-G$_y$)**: Reagent ratios, reaction times and yields obtained after purification.

| Polymer | PG$_{26}$ / g, (mmol) | KO$^t$Bu / [a] mL, (mmol) | DEVP / g, (mmol) | t / h | Yield / [b] % |
|---|---|---|---|---|---|
| **P(G$^{DEPE}_7$-$co$-G$_{19}$)** | 5.283, (2.743) | 1.78,(1.78) | 4.500, (27.43) | 66 | 83 |
| **P(G$^{DEPE}_8$-$co$-G$_{18}$)** | 4.770, (2.476) | 1.61, (1.61) | 4.065, (24.76) | 70 | 96 |
| **P(G$^{DEPE}_{10}$-$co$-G$_{16}$)** | 4.409, (2.289) | 1.48, (1.48) | 3.758, (22.89) | 64 | 87 |

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

**P(G$^{DEPE}_{10}$-$co$-G$_{16}$):** ^{1}H NMR (DMSO-$d_6$): δ 1.23 (tr, 6H, $^3J_{HH}$ = 6.95 Hz, POCH$_2$C$H_3$), 1.78 (quin, 2H, $^3J_{HH}$ = 6.89 Hz, ArCH$_2$C$H_2$), 2.05 (dtr, 2H, $^3J_{HH}$ = 7.12 Hz, $^2J_{HP}$ = 18.2 Hz, CH$_2$OCH$_2$C$H_2$P), 2.62 (tr, 2H, $^3J_{HH}$ = 7.60 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), 3.99 (quin, 4H, $^3J_{HH}$ = 6.85 Hz, POC$H_2$CH$_3$), 4.53 (br s, OCH$_2$CH(CH$_2$O$H$)O), 7.15-7.22 (m, 3H, Ar), 7.23-7.31 (m, 2H, Ar).

$^{13}$C NMR (DMSO-$d_6$): δ 16.2 (d, $^3J_{CP}$ = 5.8 Hz, POCH$_2$C$H_3$), 26.0 (d, $^1J_{CP}$ = 136.8 Hz, CH$_2$OCH$_2$C$H_2$P), 31.0 (ArCH$_2$C$H_2$), 31.6 (ArC$H_2$), 61.0, (d, $^2J_{CP}$ = 6.1 Hz, POC$H_2$CH$_3$, OCH$_2$CH(C$H_2$OH)O), 64.7 (CH(CH$_2$OC$H_2$CH$_2$P)O), 68.9-70.2 (ArCH$_2$CH$_2$C$H_2$, OC$H_2$CH(CH$_2$OCH$_2$CH$_2$P)O, OC$H_2$CH(C$H_2$OH)O), 78.0 (OCH$_2$C$H$(CH$_2$OCH$_2$CH$_2$P)O), 79.8-80.1 (OCH$_2$C$H$(CH$_2$OH)O), 125.6 (Ar), 128.2 (Ar), 141.7 (Ar). $^{31}$P NMR (DMSO-$d_6$): δ 28.6.

**Table S3.** Synthesis and characterization of **P(G$^{DEPE}_x$-$co$-G$_y$)**: Degree of functionalization with diethylphosphonatoethyl groups (G$^{DEPE}$; x, %), concentration of glycidol repeating units (G, y, %), number average molecular weights determined by $^1$H NMR, number average molecular weights by SEC and molecular weight distributions of **P(G$^{DEPE}_x$-$co$-G$_y$)**.

| P(G$^{DEPE}_x$-$co$-G$_y$) | G$^{DEPE}$ [a] x, (%) | G [a] y, (%) | M$_{n, NMR}$ [a] (g/mol) | M$_{n, SEC}$ [b] (g/mol) | M$_w$/M$_{n, SEC}$ [b] |
|---|---|---|---|---|---|
| P(G$^{DEPE}_7$-$co$-G$_{19}$) | 7, (26.9) | 19, (73.1) | 3075 | 3200 | 1.3 |
| P(G$^{DEPE}_8$-$co$-G$_{18}$) | 8, (30.8) | 16, (69.2) | 3239 | 3100 | 1.4 |
| P(G$^{DEPE}_{10}$-$co$-G$_{16}$) | 10, (38.5) | 16, (61.5) | 3567 | 3500 | 1.4 |

[a] According to $^1$H NMR analysis. [b] Molecular weight and molecular weight distribution determined by SEC using narrow distributed poly(methyl methacrylate) standards and DMF as eluent.

## Functionalization of P(G$^{DEPE}_x$-$co$-G$_y$)s with acrylates to P(G$^{DEPE}_x$-$co$-G$^{AC}_y$)

### Side-reactions at the electrophilic acrylic double bonds

The addition of bromide and/or chloride to the acrylic double bond during acylation and silylation, respectively, was evidenced by means of 2D H,H- and H,C-COSY NMR spectroscopy.
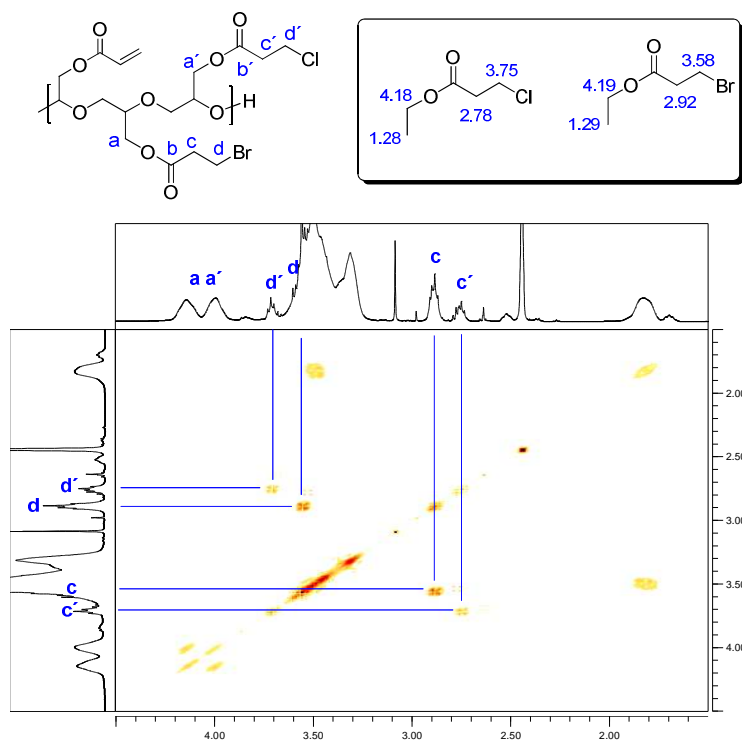
**Figure S1.** H,H-COSY NMR of **P(G<sup>PE</sup><sub>7</sub>-*co*-G<sup>AC</sup><sub>17</sub>) (VII<sup>PE</sup>)** after aqueous workup recorded in DMSO-$d_6$. For comparison, the chemical shifts of ethyl 3-chloropropanoate and ethyl 3-bromopropanoate are shown (they were simulated using ChemBioDraw software, version 11.0.1).
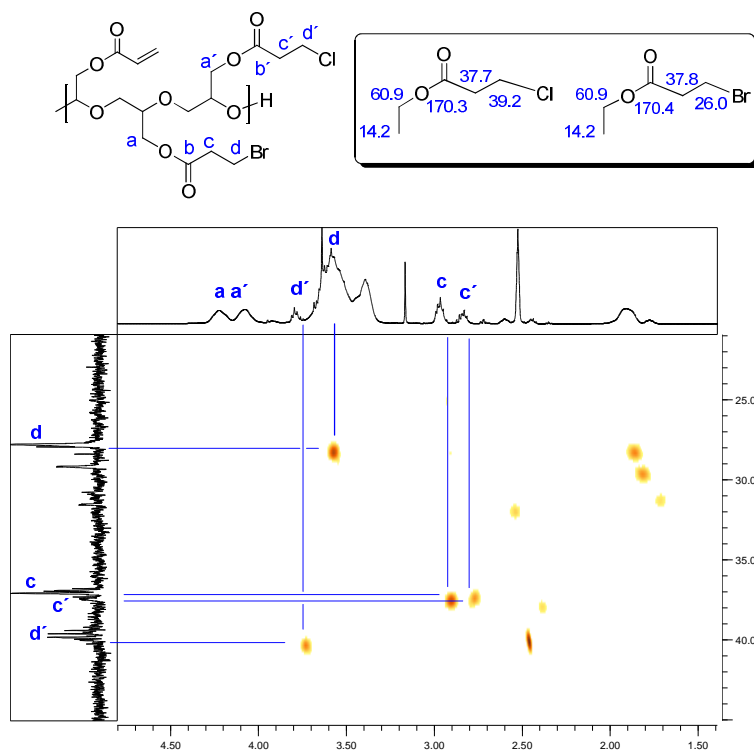


**Figure S2.** H,C-COSY NMR of **P(G<sup>PE</sup><sub>7</sub>-*co*-G<sup>AC</sup><sub>17</sub>) (VII<sup>PE</sup>)** after aqueous workup recorded in DMSO-$d_6$. For comparison, the chemical shifts of ethyl 3-chloropropanoate and ethyl 3-bromopropanoate are shown (they were simulated using the ChemBioDraw software, version 11.0.1).

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**$^{31}$P NMR spectra at different stages of the reaction of P(G$^{DEPE}_{10}$-*co*-G$^{Ac}_8$) (II$^{DEPE}$) to P(G$^{PE}_{10}$-*co*-G$^{Ac}_{12}$) (II$^{PE}$)**
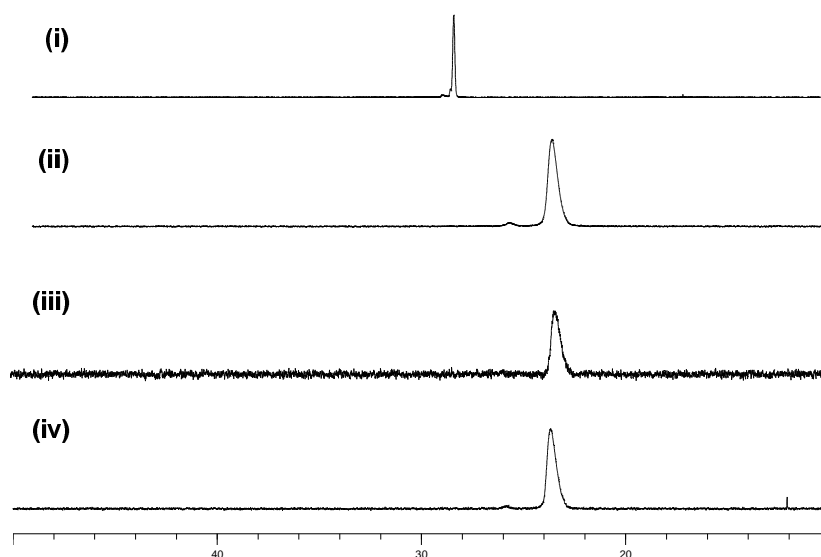


**Figure S3.** $^{31}$P NMR spectra of (II$^{DEPE}$) P(G$^{DEPE}_{10}$-*co*-G$^{AC}_8$) (i) and (II$^{PE}$) P(G$^{PE}_{10}$-*co*-G$^{AC}_{12}$) (iv) obtained after aqueous workup recorded in DMSO-$d_6$. (with (ii) silylated intermediate and (iii) P(G$^{PE}_{10}$-*co*-G$^{AC}_{12}$) after methanolysis.).

Comparison of (i) with (ii) shows quantitative conversion of the DEPE groups to the phosphonic acids. The water which is contained in the DMSO-$d_6$ used for NMR analysis causes hydrolysis of the silylated intermediate (ii). This is the reason for identical chemical shifts of (ii), (iii) and (iv). The phosphonic acids are stable in the aqueous environment, because no additional signals are observed in spectrum (iv).

**Application of optimized P(G$^{PE}_x$-*co*-G$^{AC}_y$) adhesion promoters**

**Table S4.** Analysis of polymer microstructure before silylation, number average molecular weights determined by $^1$H NMR and SEC and molecular weight distribution of **P(G$^{DEPE}$-*co*-G$^{AC}$) (VIII$^{DEPE}$)** and **(IX$^{DEPE}$)**.

| Entry | Polymer microstructure | $M_{n, NMR}$ [a] (g/mol) | $M_{n, SEC}$ [b] (g/mol) | $M_w/M_{n, SEC}$ [b] |
|---|---|---|---|---|
| (VIII$^{DEPE}$) | P(G$^{DEPE}_8$-*co*-G$^{AC}_{12}$) | 3900 | 3800 | 1.3 |
| (IX$^{DEPE}$) | P(G$^{DEPE}_{10}$-*co*-G$^{AC}_{11}$) | 4173 | 4000 | 1.3 |

[a] According to $^1$H NMR analysis. [b] Molecular weight and molecular weight distribution determined by size exclusion chromatography (SEC) using narrow distributed poly(methyl methacrylate) standards and DMF as eluent.
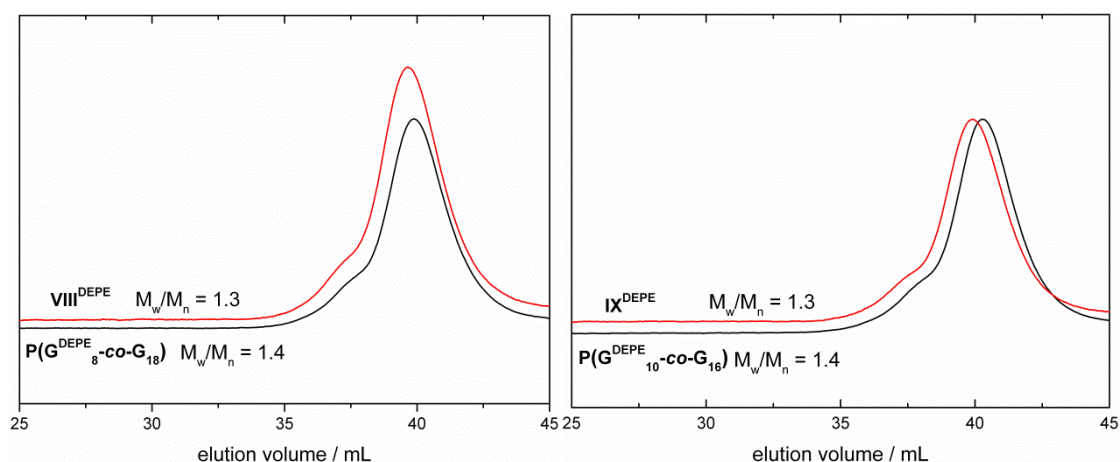
**Figure S4.** SEC traces of **VIII$^{DEPE}$** and **IX$^{DEPE}$** before silylation. Left: SEC traces of **P(G$^{DEPE}_8$-*co*-G$^{AC}_{12}$)** (**VIII$^{DEPE}$**) in comparison to **P(G$^{DEPE}_8$-*co*-G$_{18}$)**. Right: SEC traces of **P(G$^{DEPE}_{10}$-*co*-G$^{AC}_{11}$)** (**IX$^{DEPE}$**) compared to **P(G$^{DEPE}_{10}$-*co*-G$_{16}$)**. DMF was used as eluent and narrow distributed PMMA was used for calibration.

**Table S5.** Polymer microstructure of **P(G$^{PE}_x$-*co*-G$^{AC}_y$)** (**VIII$^{PE}$**) and (**IX$^{PE}$**) and number average molecular weights determined by $^1$H NMR.

| Entry | Polymer microstructure | $M_{n, NMR}$[a] (g/mol) | $M_{n, SEC}$[b] (g/mol) | $M_w/M_n,$ SEC[b] |
|---|---|---|---|---|
| (**VIII$^{PE}$**) | **P(G$^{PE}_8$-*co*-G$^{AC}_{18}$)** | 3888 | *n.d.* | *n.d.* |
| (**IX$^{PE}$**) | **P(G$^{PE}_{10}$-*co*-G$^{AC}_{16}$)** | 3782 | *n.d.* | *n.d.* |

*n.d.*: Not determined, due to hydrolytic instability of the products.
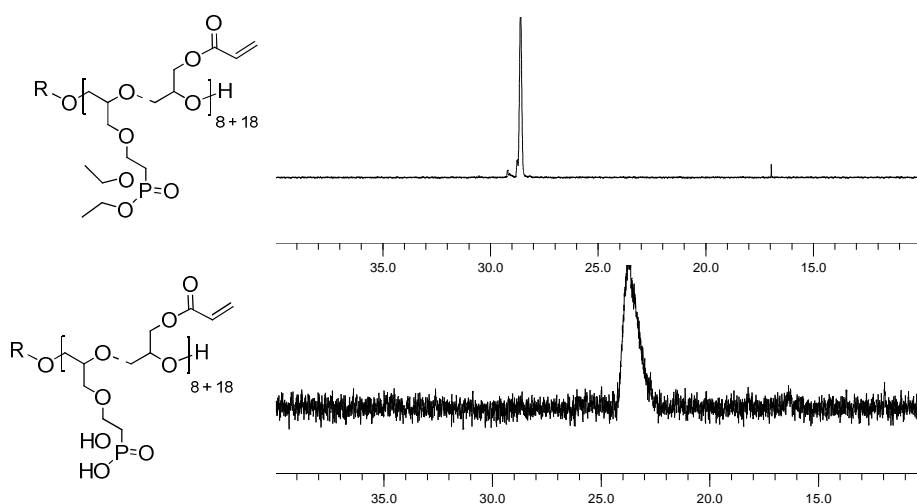


**Figure S5.** $^{31}$P NMR analysis of **P(G$^{DEPE}_8$-*co*-G$_{18}$)** (*top*) and **P(G$^{PE}_8$-*co*-G$^{AC}_{18}$)** (*bottom*) recorded in DMSO-$d_6$.

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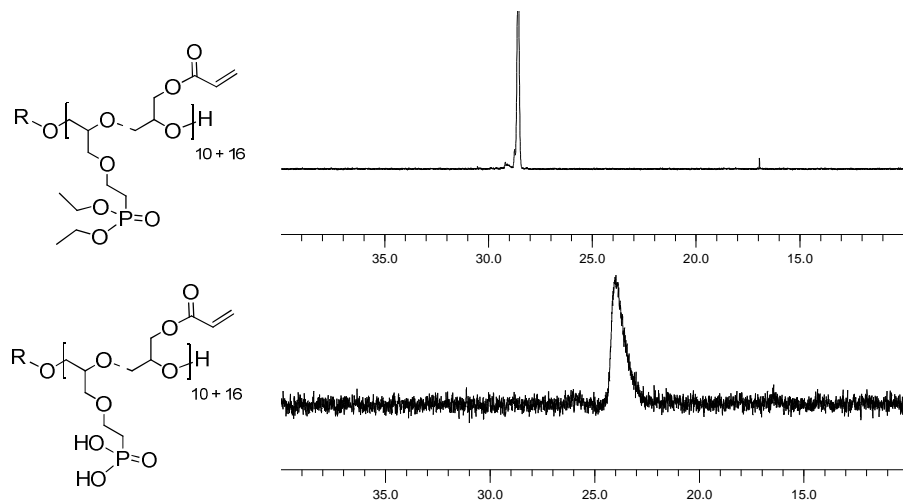
**Figure S6.** $^{31}$P NMR analysis of **P(G$^{DEPE}_{10}$-*co*-G$_{16}$)** (*top*) and **P(G$^{PE}_{10}$-*co*-G$^{AC}_{16}$)** (*bottom*) recorded in DMSO-$d_6$.