Supporting Information for *Macromol. Rapid Commun.*, 2007, 28, 2217.

Synthesis of polyelectrolytes bearing phosphorylcholine moieties

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2-{2-[2-(2-N-tertButoxycarbonylamino-ethoxy)-ethoxy]-ethoxy}-ethylphosphorylcholine (BOCNH(EO)$_4$PC): the method described for BOC(EO)$_3$PC was applied to BOCNH(EO)$_4$OH (0.67 g, 2.29 mmol) as the starting material and afforded BOCNH(EO)$_4$PC as a white powder (0.59 g, 55 % yield).

^{1}H NMR (D$_2$□ □00 Mhz) :δ = 4.34 (br m, 2H, POC*H*$_2$CH$_2$N), 4.06 (br m, 2 H, POC*H*$_2$CH$_2$O), 3.81-3.68 (m, 8 H, C*H*$_2$OC*H*$_2$C*H*$_2$O, C*H*$_2$N(CH$_3$)$_3$), 3.62 (t, 2 H, *J* = 5.4 Hz, OC*H*$_2$CH$_2$N), 3.29 (t, 2 H, *J* = 5.4 Hz, C*H*$_2$N), 3.26 (s, 9H, N(C*H*$_3$)$_3$), 1.47 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (D$_2$□, 100 Mhz : δ = 158.8 (CO), 81.6 (*C*(CH$_3$)$_3$), 70.8 (d, *J* = 7.7 Hz, POCH$_2$*C*H$_2$O), 70.4, 70.3, 70.3, 70.1, (OC*H*$_2$*C*H$_2$), 66.7 (m, *C*H$_2$N(CH$_3$)$_3$) , 65.5 (d, *J* = 5.9 Hz, PO*CH*$_2$CH$_2$O), 60.1 (d, *J* = 5.1 Hz, POC*H*$_2$CH$_2$N), 54.7 (t, *J* = 3.9 Hz, N(*C*H$_3$)$_3$), 40.3 (*C*H$_2$N), 28.4 (C(*C*H$_3$)$_3$. IR (ATR) ν$_{max}$: 3365 , 3240 (ν NH), 2977 (ν CH$_3$), 2935 (ν$_{as}$ CH$_2$), 2874 (ν$_{as}$ CH$_2$), 1689 (amide I), 1522 (amide II), 1482 (δ$_{as}$ (CH$_3$)$_3$N$^+$), 1455, 1419, 1366 (δ CH$_3$), 1238, 1137, 1086 (ν$_s$ PO$_2^-$), 1058, 970, 953 (ν$_{as}$ (CH$_3$)$_3$N$^+$), 925, 875, 781 cm^{-1}.

PGA(EO)$_3$PC 35 :

^{1}H NMR (D$_2$□ 400 MHz) : δ = 4.34 (broad s, POC*H*$_2$CH$_2$N, NHC*H*CO), 4.05 (broad m, POC*H*$_2$CH$_2$O), 3.78-3.67 (m, C*H*$_2$OC*H*$_2$C*H*$_2$O, C*H*$_2$N(CH$_3$)$_3$), 3.63 (t, *J* = 5.6 Hz, OC*H*$_2$CH$_2$N), 3.40 (t, *J* = 5.6 Hz, C*H*$_2$N), 3.24 (s, N(C*H*$_3$)$_3$, 2.33 (broad s, C*H*$_2$CO), 2.07

(broad s, CHC*H*$_2$CH$_2$), 1.97 (broad s, CHC*H*$_2$CH$_2$). ^{13}C NMR (D_2O, 100 MHz) : δ = 180.6 (*C*O), 175.5 (*C*O), 174.2 (*C*O), 173.8 (*C*O), 70.7 (d, *J* = 7.7 Hz, POCH$_2$*C*H$_2$), 70.3, 70.1, 69.4, (OC*H*$_2$*C*H$_2$), 66.6 (m, *C*H$_2$N(CH$_3$)$_3$), 65.5 (d, *J* = 5.5, PO*C*H$_2$CH$_2$O), 60.1 (d, *J* = 4.5 Hz, POCH$_2$CH$_2$N), 54.6 (t, *J* = 3.7 Hz, N(*C*H$_3$)$_3$), 54.1 (*C*H), 53.7 (*C*H), 39.5 (*C*H$_2$N), 33.2 (*C*H$_2$CO), 32.4 (*C*H$_2$CO), 28.05 (CH*C*H$_2$CH$_2$), 27.8 (CH*C*H$_2$CH$_2$). IR (sol. D_2O) ν_{max} : 3406, 1697 (ν COO), 1645 (amide I), 1566 (amide II), 1458, 1404, 1366, 1086 (ν_s PO_2^-), 1064, 973, 953 (ν_{as} $(CH_3)_3N^+$), 799 cm^{-1}.

PGA(EO)$_4$PC 16 : this compound is synthesized as described above for PGA(EO)$_3$PC with PGA (153 mg,1.01 mmol of monomer units) and BOCNH(EO)$_4$PC (179 mg,0.39 mmol, 0.38 equiv.) . PGA(EO)$_4$PC 16 is obtained as a white powder (150 mg, yield 71%): ^{1}H NMR (D_2O, 400 MHz) : δ = 4.33 (broad s, POC*H*$_2$CH$_2$N, NHC*H*CO), 4.03 (broad m, POC*H*$_2$CH$_2$O), 3. 80 – 3. 66 (m, C*H*$_2$OC*H*$_2$C*H*$_2$O, C*H*$_2$N(CH$_3$)$_3$), 3.61 (t, J = 5.58 Hz, OC*H*$_2$CH$_2$N), 3.39 (broad s, C*H*$_2$N), 3.22 (s, N(C*H*$_3$)$_3$), 2.37 (broad s, C*H*$_2$CO), 2.07 (broad s, CHC*H*$_2$CH$_2$), 1.97 (broad s, CHC*H*$_2$CH$_2$). ^{13}C NMR (D_2O, 100 MHz) : δ = 180.6 (CO), 175.5 (CO), 174.2 (CO), 173.8 (CO), 70.7 (d, J=7.63 Hz, POCH$_2$*C*H$_2$O), 70.3, 70.2, 70.1, 69.5 (O*C*H$_2$*C*H$_2$), 66.7 (m, *C*H$_2$N(CH$_3$)$_3$), 65.6 (d, J=5.41 Hz, PO*C*H$_2$CH$_2$O), 60.1 (d, *J* = 5.11 Hz, POC*H*$_2$CH$_2$N), 56.4 (broad s, *C*H), 54.7 (t, J=3.63 Hz, N(*C*H$_3$)$_3$), 39.6 (*C*H$_2$N), 32.4 (*C*H$_2$CO), 32.0 (*C*H$_2$CO), 26.2 (broad s, CH*C*H$_2$CH$_2$). IR (sol. D_2O) ν_{max} : 3406, 1697 (ν COO), 1644 (amide I), 1564 (amide II), 1482 (δ_{as} $(CH_3)_3N^+$), 1463, 1447, 1405, 1086 (ν_s PO_2^-), 1066, 972, 956 (ν_{as} $(CH_3)_3N^+$), 798 cm^{-1}.

PAA(EO)$_3$PC 25 : this compound is synthesized as described above for PGA(EO)$_3$PC 35 with PAA (77 mg, 1.06 mmol of monomer units) and BOCNH(EO)$_3$PC (110 mg, 0.27 mmol, 0.25 equiv.) as the starting materials. Pure PAA(EO)$_3$PC 25 is obtained as a white powder (126 mg, 82% yield). ^{1}H NMR (D_2O, 400 Mhz): δ = 4.32 (broad s, POC*H*$_2$CH$_2$N, CH$_2$C*H*),

4.03 (broad m, POCH_2CH_2O), 3. 79–3. 65 (m, CH_2OCH_2CH_2O, CH_2N(CH_3)$_3$), 3.60 (broad s), 3.37 (broad s, CH_2N), 3.23 (s, N(CH_3)$_3$), 2.22 (broad s), 2.08 (broad s), 1.74 (broad s), 1.57 (broad s), (CH_2CH). ^{13}C NMR (D_2O, 100 Mhz): δ = 182.0 (CO), 181.8 (CO), 177.3 (CO), 70.1 (d, *J* = 7.7 Hz, POCH$_2$*C*H$_2$O), 69.7, 69.5, 68.8, (O*C*H$_2$*C*H$_2$), 65.9 (m, *C*H$_2$N(CH$_3$)$_3$), 64.9 (d, *J* = 5.1 Hz, PO*C*H$_2$CH$_2$O), 59.4 (d, *J* = 4.8 Hz, POC*H*$_2$CH$_2$N), 54.0 (t, *J* = 3.3 Hz, N(*C*H$_3$)$_3$, 44.0 (broad s), 42.6 (broad s), 38.8 (broad s), 36.1 (broad s) (*C*H$_2$*C*H).

PLLSuc(EO)$_3$PC 35:

^{1}H NMR (D_2□ 400 MHz) : δ = 4.33 (broad s, POC*H*$_2$CH$_2$N, CH$_2$C*H*), 4.05 (broad m, POC*H*$_2$CH$_2$O), 3. 78 -3. 67 (broad m, C*H*$_2$OC*H*$_2$C*H*$_2$O, C*H*$_2$N(CH$_3$)$_3$), 3.64 (t, *J* = 5.3 Hz, OCH$_2$CH$_2$N), 3.25 (s, N(C*H*$_3$)$_3$), 3.40 (t, *J* = 5.3 Hz, OCH$_2$CH$_2$NHCO), 3.17 (m, C*H*$_2$NHCO), 3.02 (t, *J* = 7.11 Hz, C*H*$_2$NH$_2$), 2.54 (broad s, COC*H*$_2$C*H*$_2$CO), 1.72 (broad m), (CH*C*H$_2$C*H*$_2$C*H*$_2$CH$_2$N), 1.49 (broad m). ^{13}C NMR (D_2□, 100MHz□ δ = 174.5 (*C*O), 173.7 (*C*O), 173.5 (*C*O), 70.1 (d, *J* = 7.8 Hz, OCH$_2$CH$_2$OP), 69.7, 69.4, 68.8, (O*C*H$_2$*C*H$_2$), 66.0 (m, *C*H$_2$N(CH$_3$)$_3$), 64.9 (d, *J* = 5.9 Hz, PO*C*H$_2$CH$_2$O), 59.4 (d, *J* = 4.78 Hz, POC*H*$_2$CH$_2$N), 54.0 (t, *J* = 3.81 Hz, N(*C*H$_3$)$_3$), 53.4 (*C*H), 39.2 (*C*H$_2$NH$_2$), 39.1 (*C*H$_2$NHCO), 39.0 (OCH$_2$*C*H$_2$NHCO), 31.2, 31.2, (CO*C*H$_2$*C*H$_2$CO), 30.6, 27.9, 26.5, 22.4, 22.2, (CH*C*H$_2$*C*H$_2$*C*H$_2$CH$_2$N).

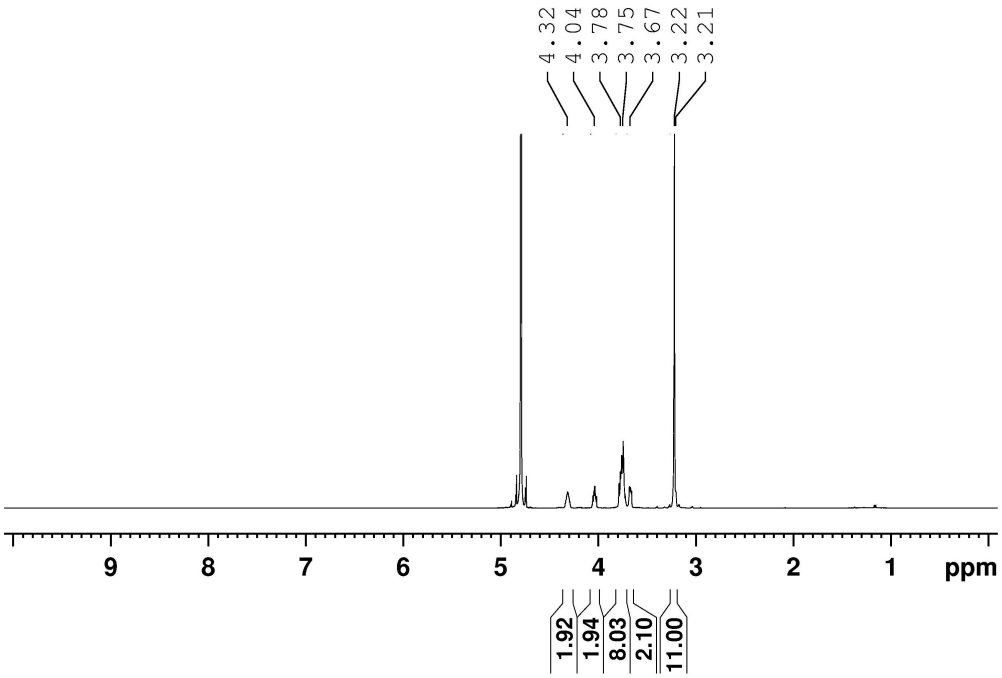

Figure S1. Spectrum of crude $PC(EO)_3NH_3Cl$.

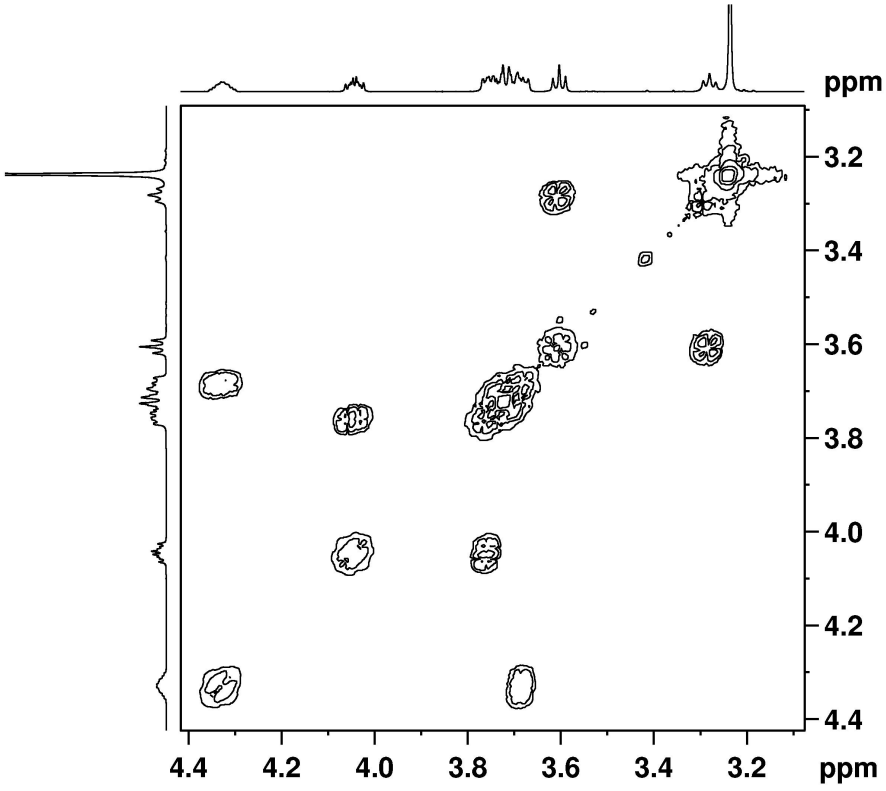

Figure S2. Section of the COSY spectrum of $BOCNH(EO)_3PC$.

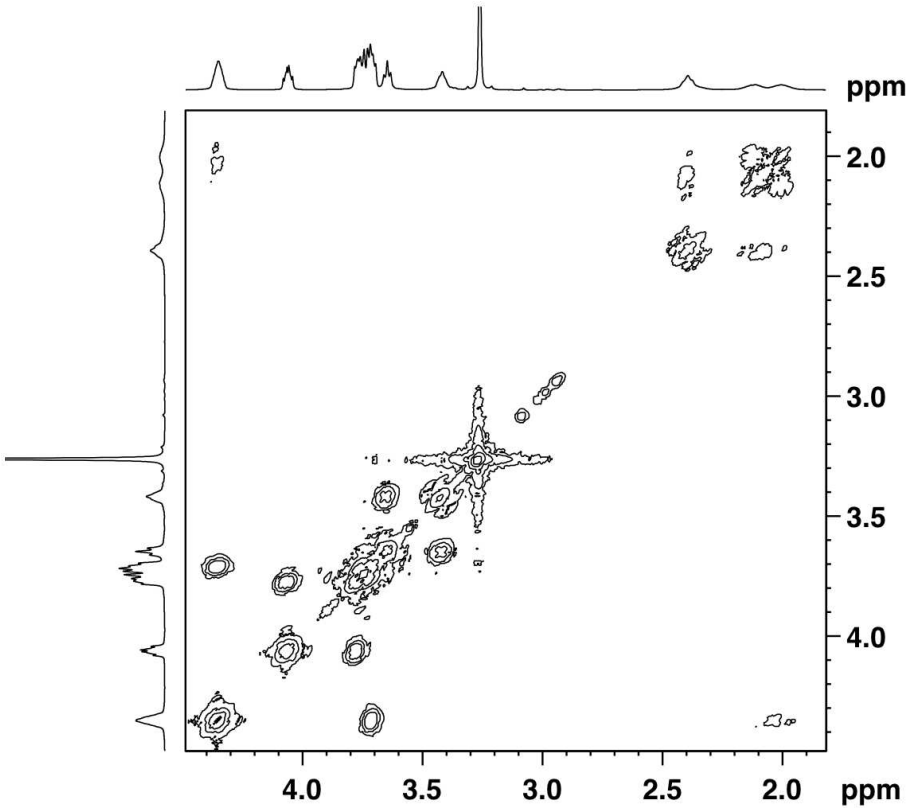

Figure S3a. COSY spectrum of PGA(EO)$_3$PC 80.

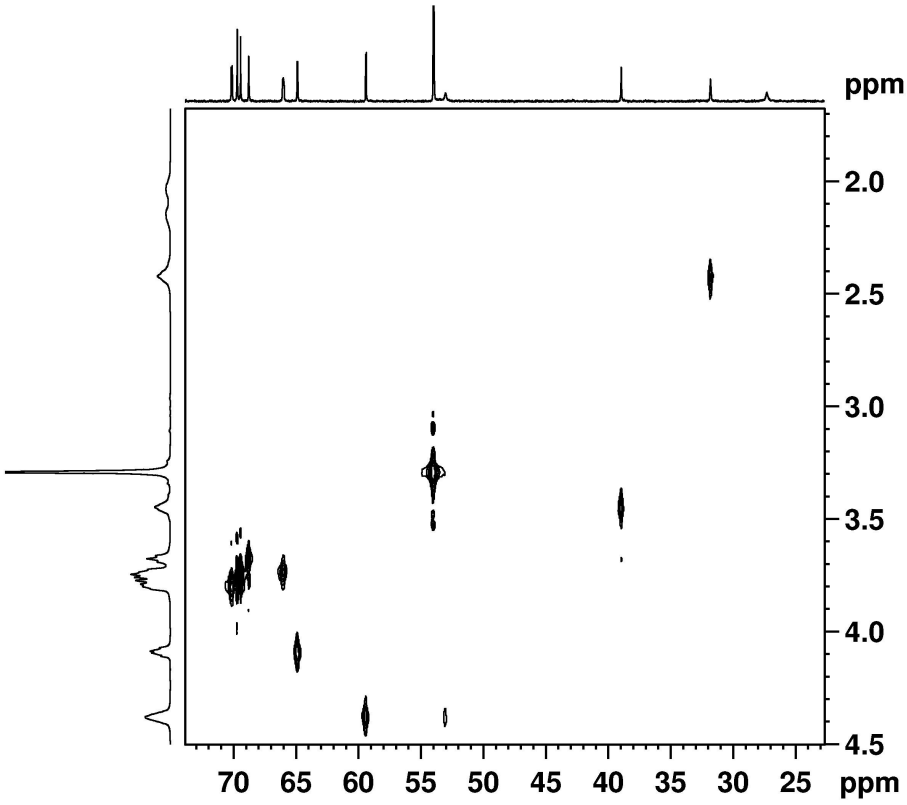

Figure S3b. ^{1}H-^{13}C correlation spectrum of PGA(EO)$_3$PC 80

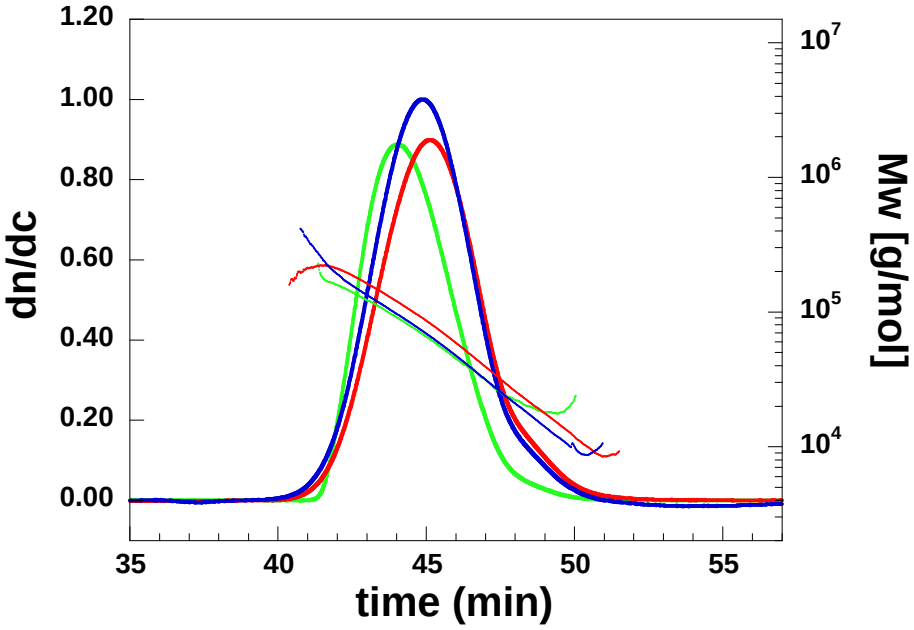

Figure S4. SEC measurements. Green: PGA; blue PGA$(EO)_4$PC 16; red: PGA$(EO)_3$PC 35.