Supporting Information

Intermolecular Interaction of Polymer Brushes Containing Phosphorylcholine and Inverse- Phosphorylcholine

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S1. Preparation of monomers

S1-1. 2-(methacryloyloxy)ethyl phosphorylcholine (MPC)

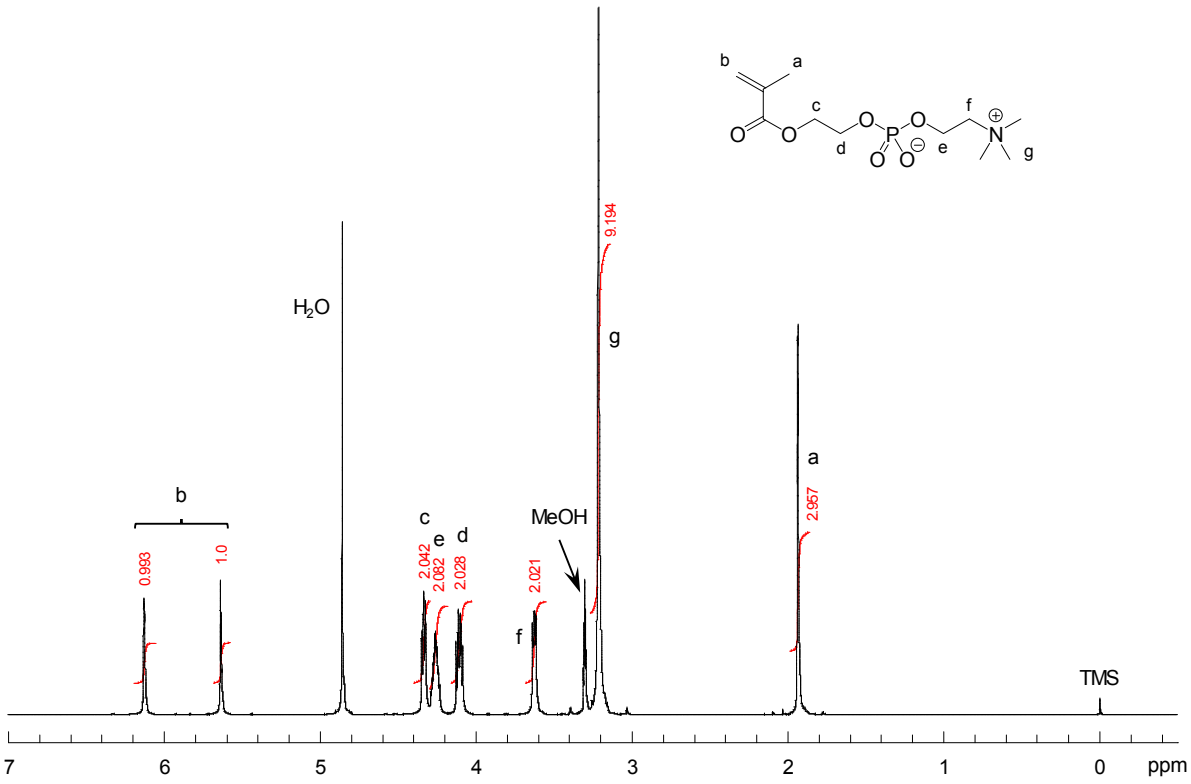

Figure S1-1. ^{1}H NMR spectrum of 2-(methacryloyloxy)ethyl phosphorylcholine in CD_3OD

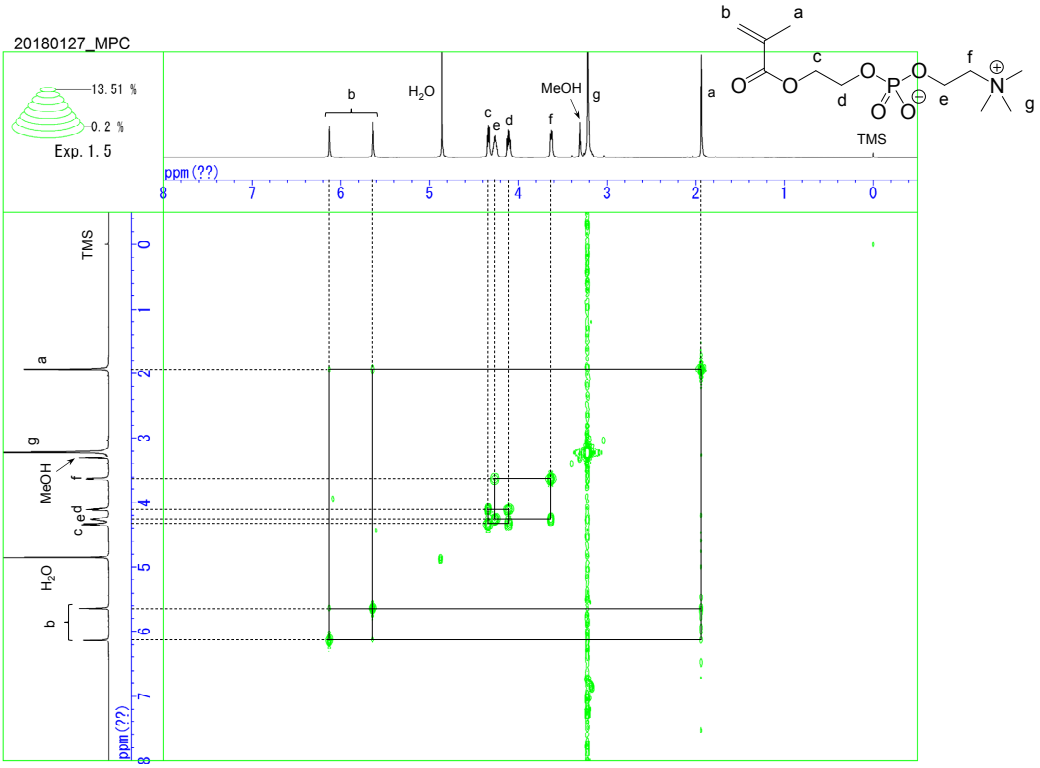

Figure S1-2. ^{1}H-^{1}H COSY spectrum of MPC in CD_3OD

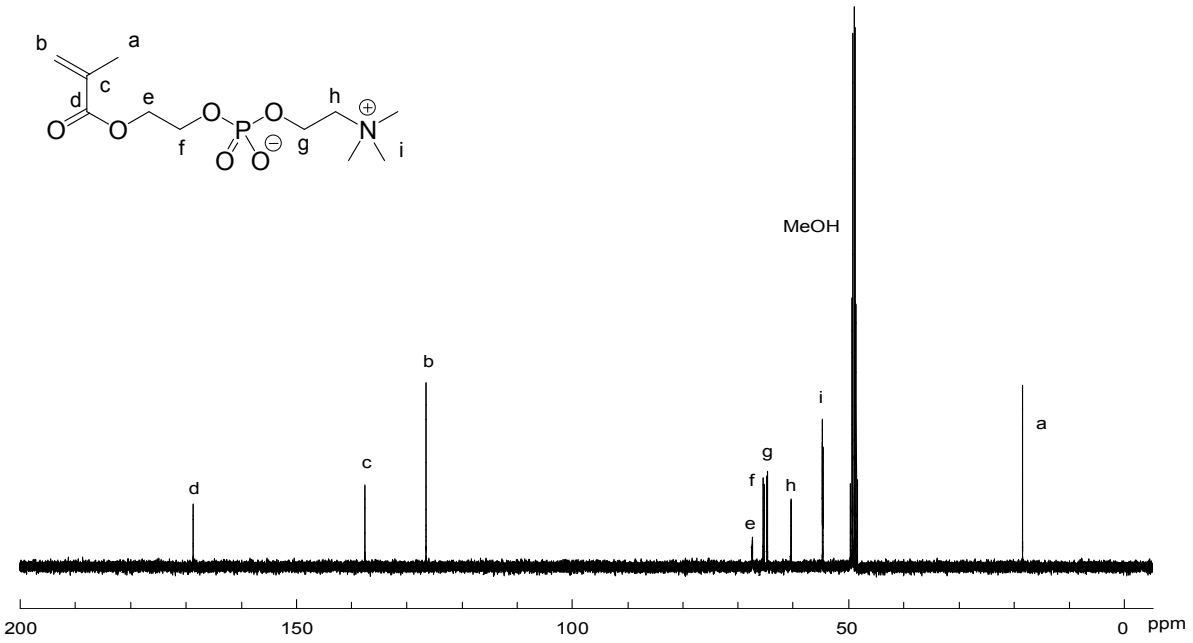

Figure S1-3. ^{13}C NMR spectrum of MPC in CD_3OD

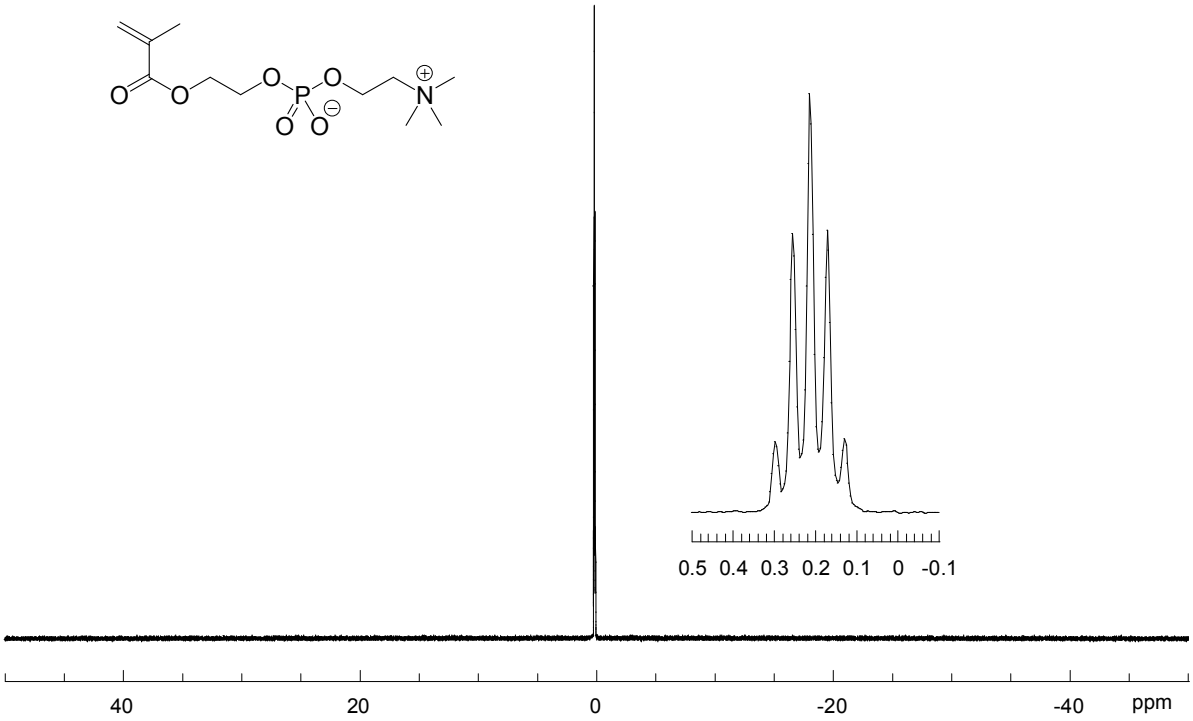

Figure S1-4. ^{31}P NMR spectrum of MPC in CD_3OD

S1-2. 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane (IOP)

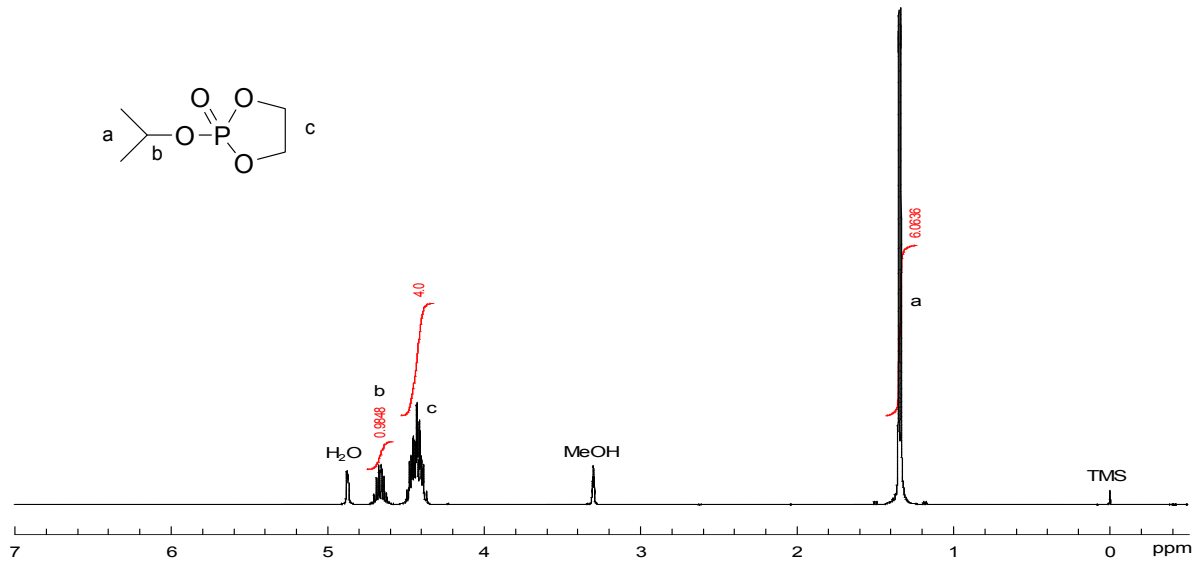

Figure S1-5. ^{1}H NMR spectrum of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane.

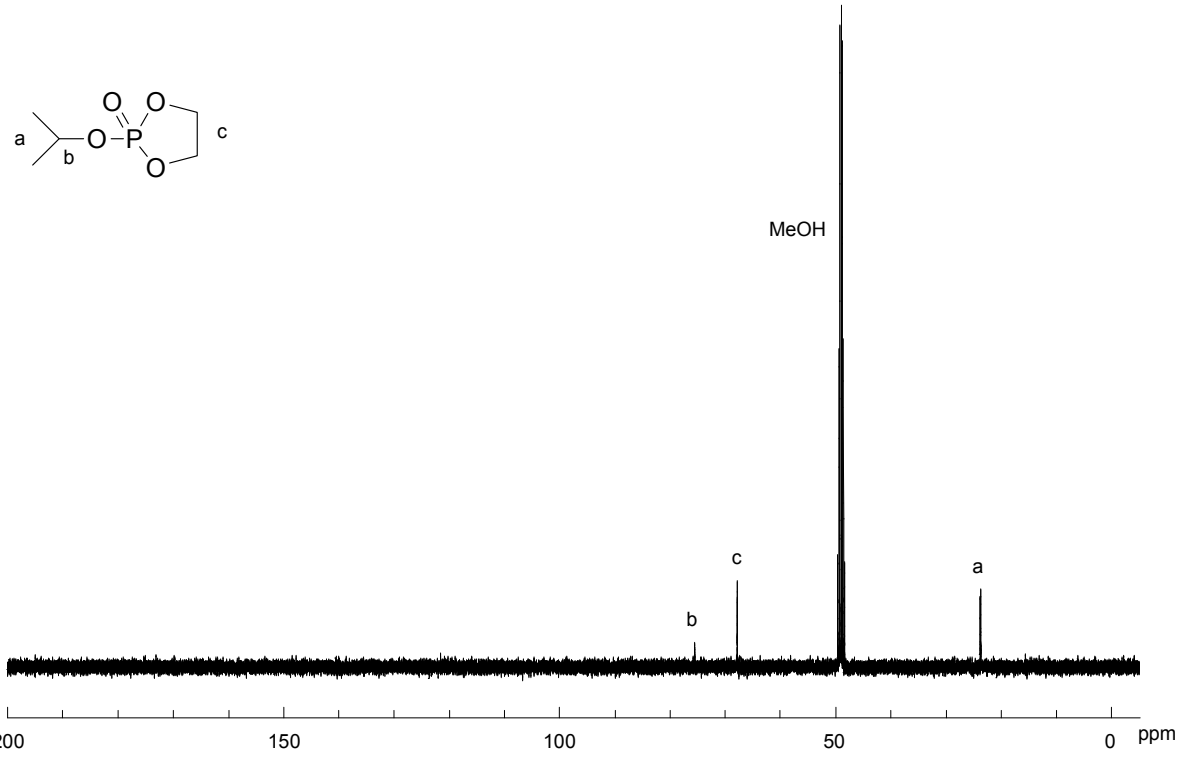

Figure S1-6. ^{13}C NMR spectrum of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane.

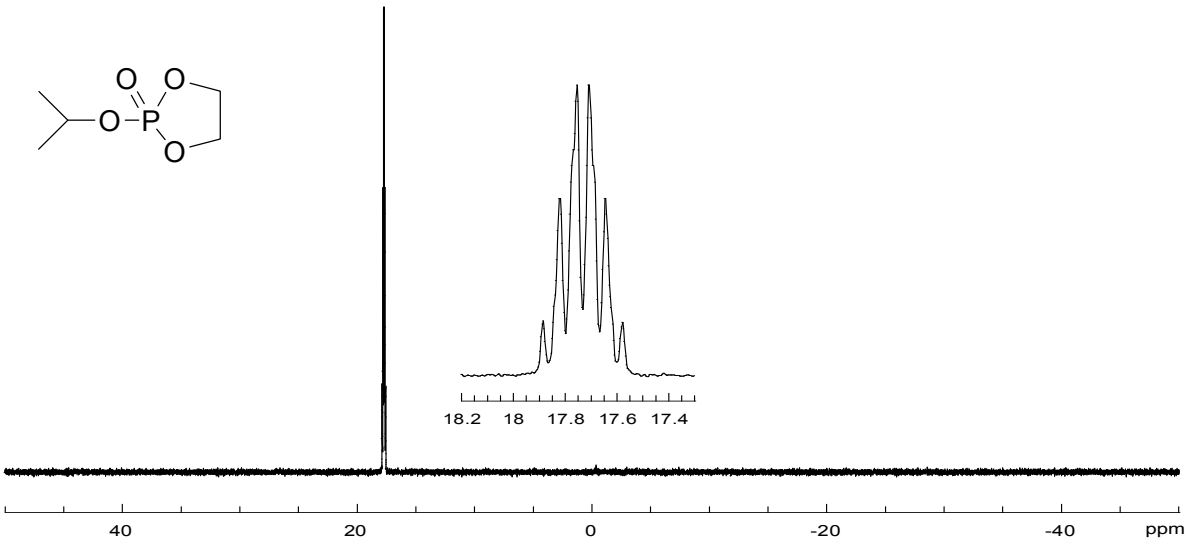

Figure S1-7. ^{31}P NMR spectrum of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane.

S1-3. 2-[2-(methacryloyl ethyl)dimethylammonio]ethyl isopropyl phosphate (MCP-iPr)

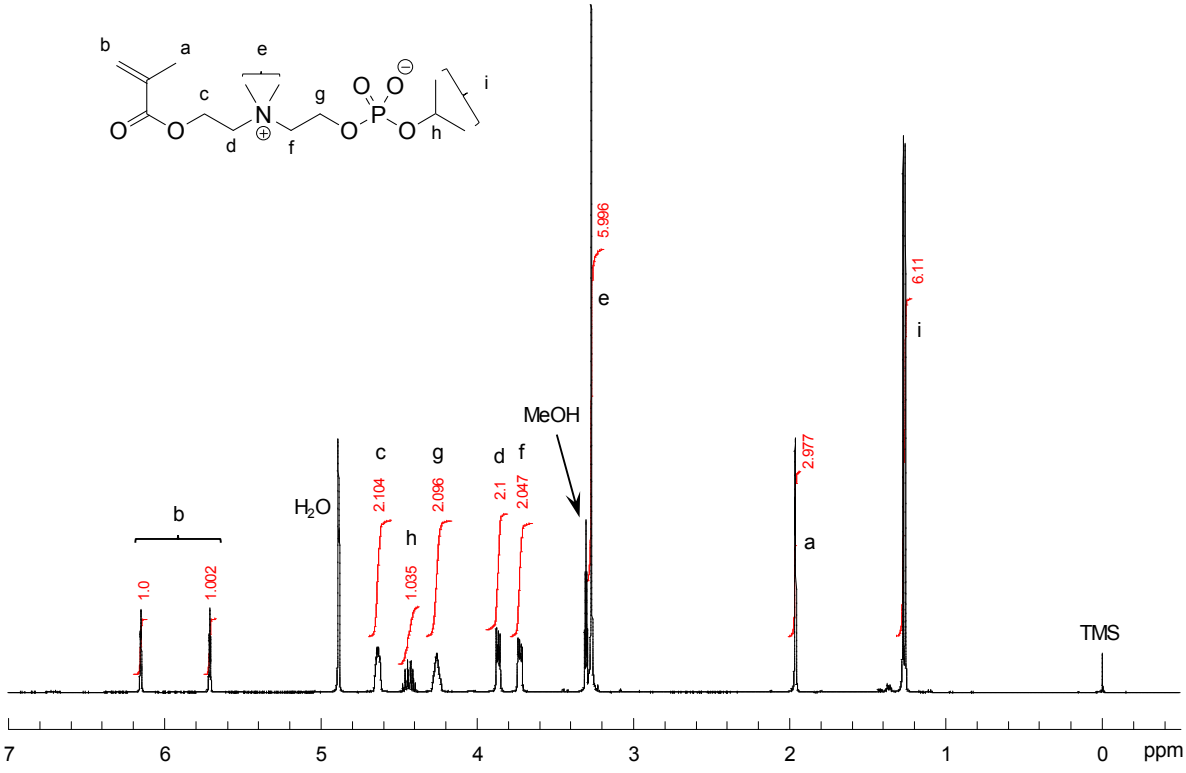

Figure S1-8. ^{1}H NMR spectrum of MCP-iPr in CD_3OD

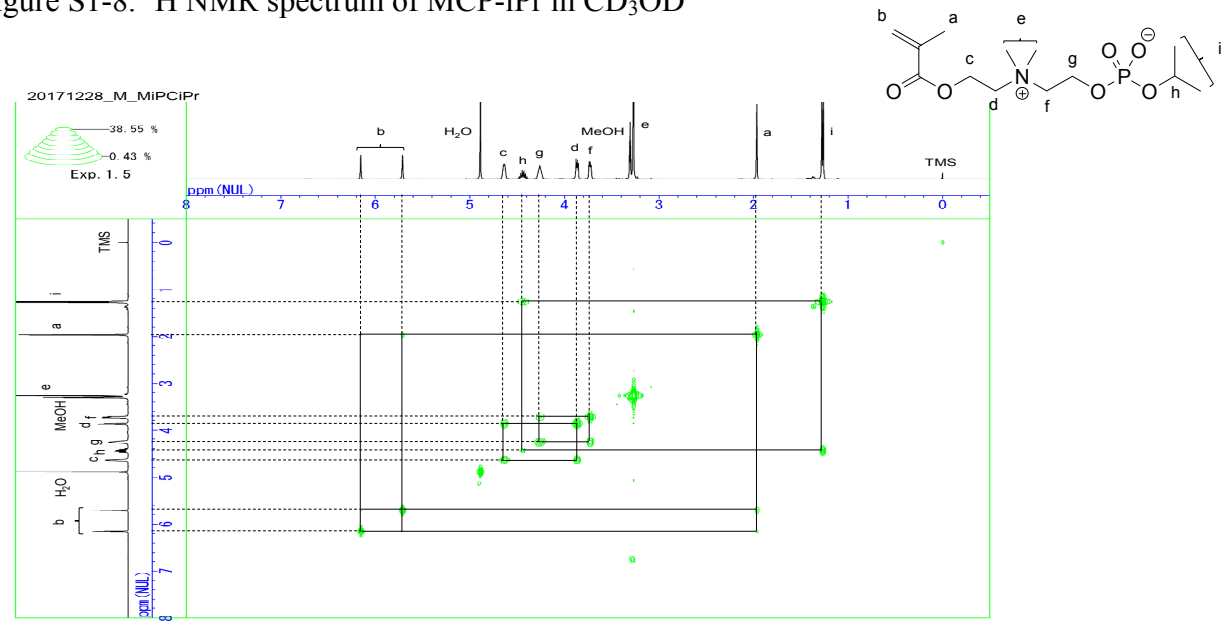

Figure S1-9. ^{1}H-^{1}H COSY spectrum of MCP-iPr in CD_3OD

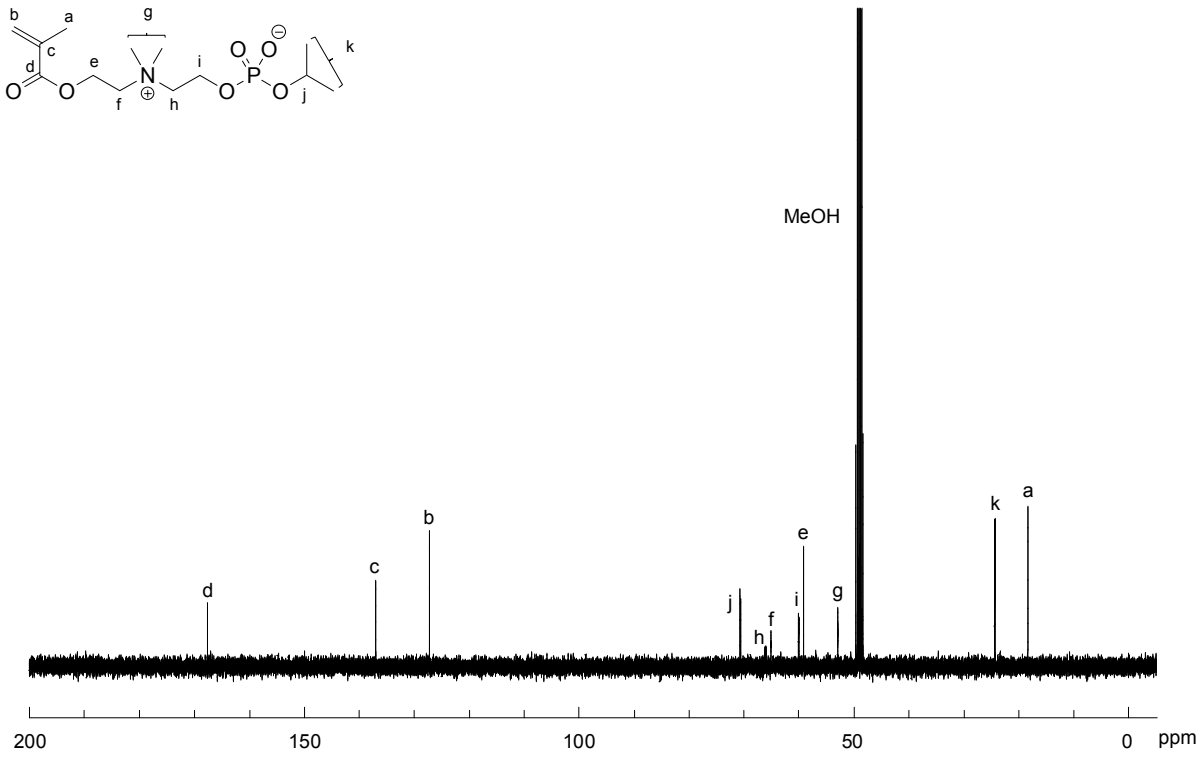

Figure S1-10. ^{13}C NMR spectrum of MCP-iPr in CD_3OD

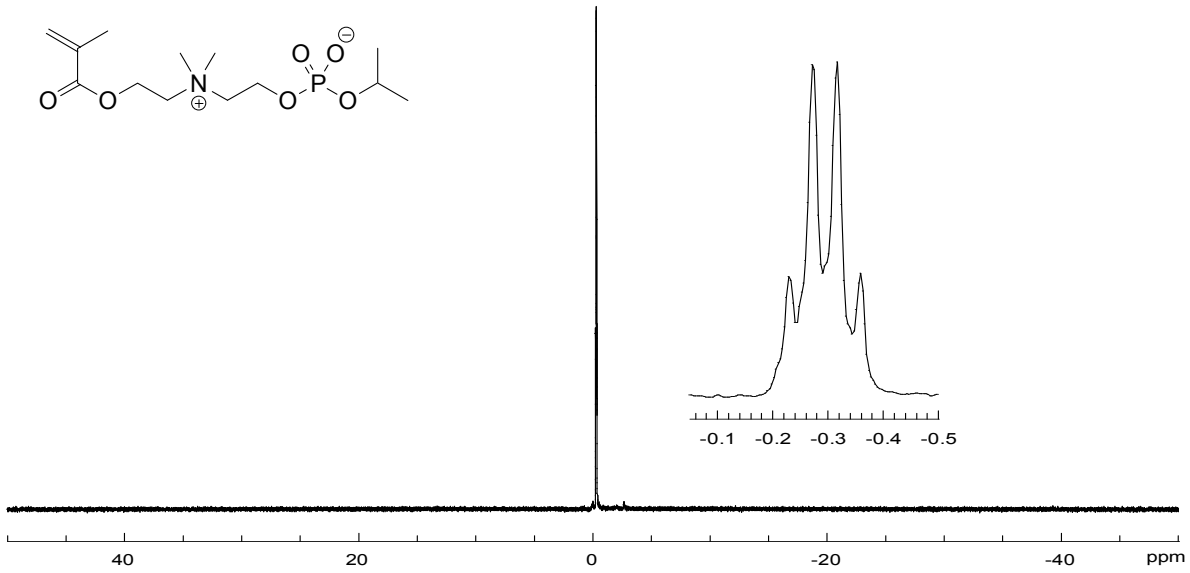

Figure S1-11. ^{31}P NMR spectrum of MCP-iPr in CD_3OD

S1-4. 2-ethoxy-2-oxo-1,3,2-dioxaphospholane (EOP)

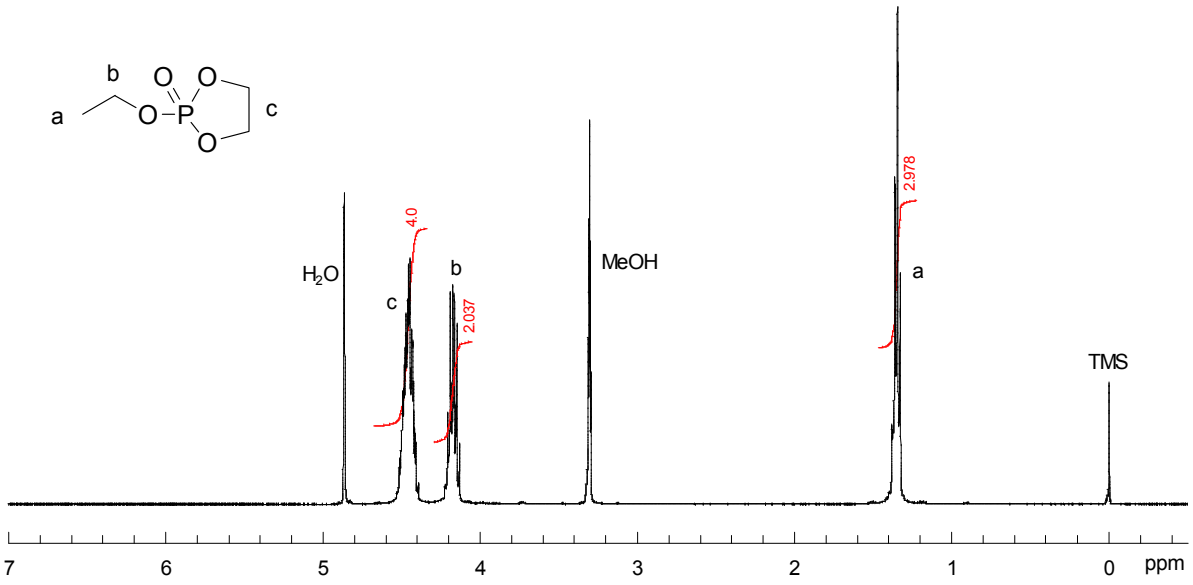

Figure S1-12. ^{1}H NMR spectrum of EOP in CD_3OD

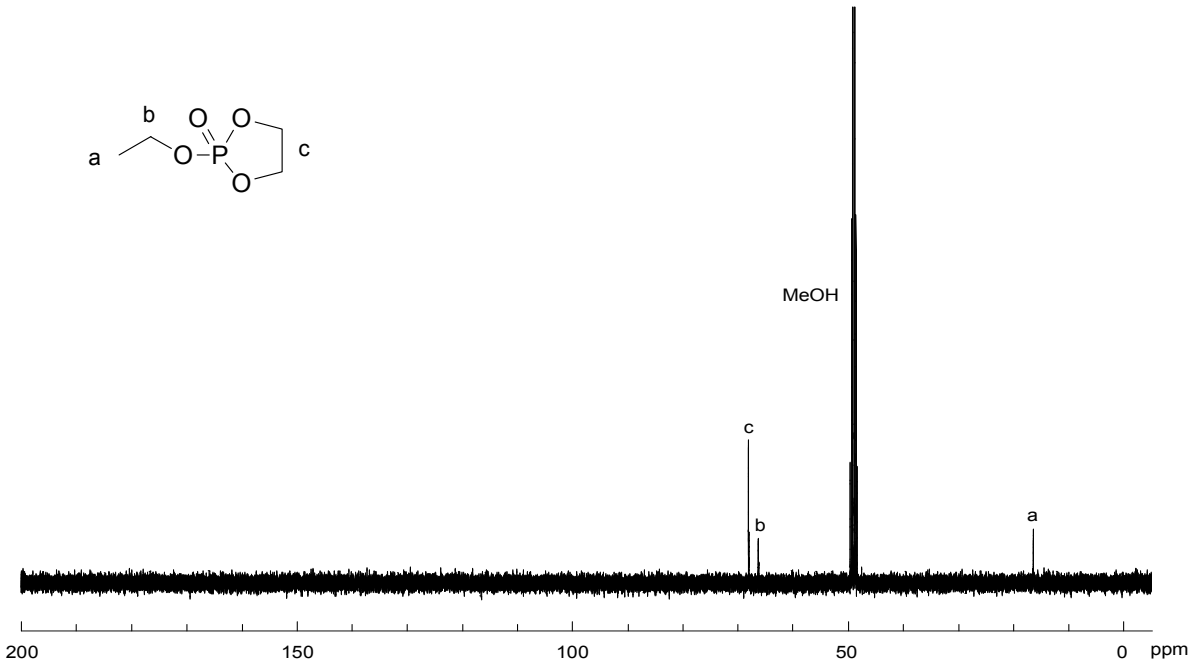

Figure S1-13. ^{13}C NMR spectrum of EOP in CD_3OD

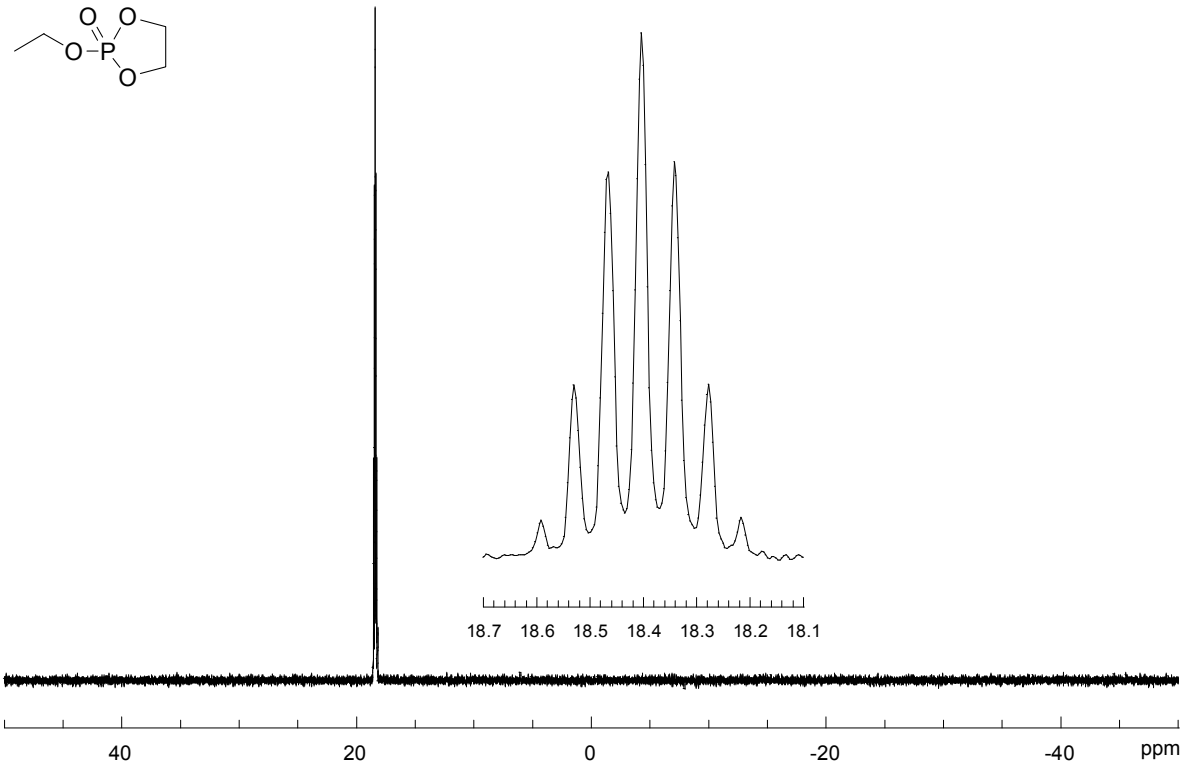

Figure S1-14. ^{31}P NMR spectrum of EOP in CD_3OD

S1-5. 2-[2-(methacryloyl ethyl)dimethylammonio]ethyl ethyl phosphate (MCP-Et)

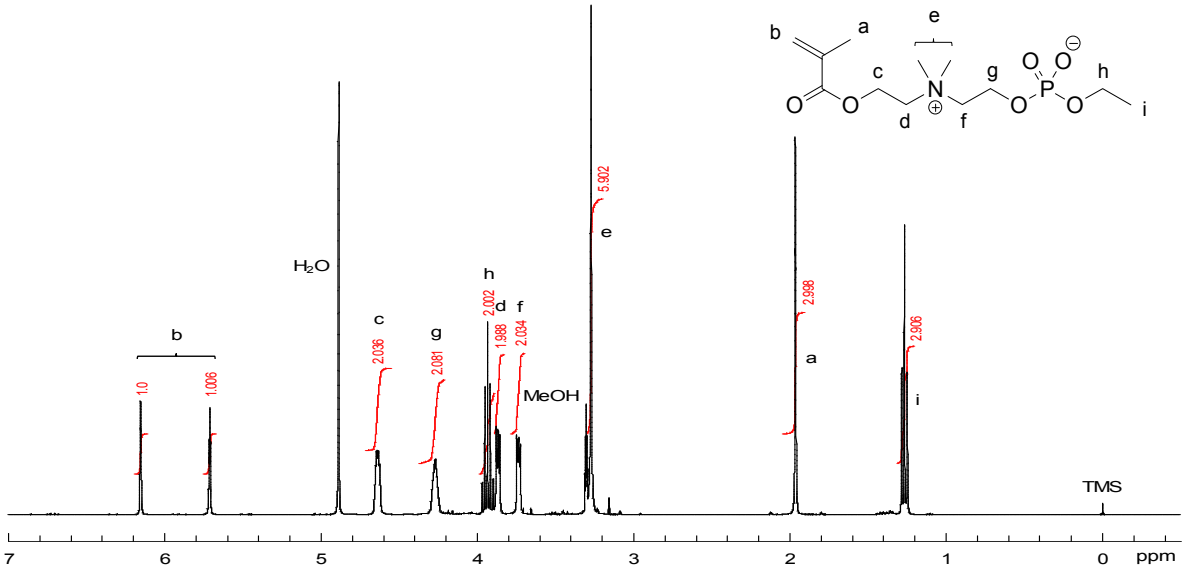

Figure S1-15. ^{1}H NMR spectrum of MCP-Et in CD_3OD

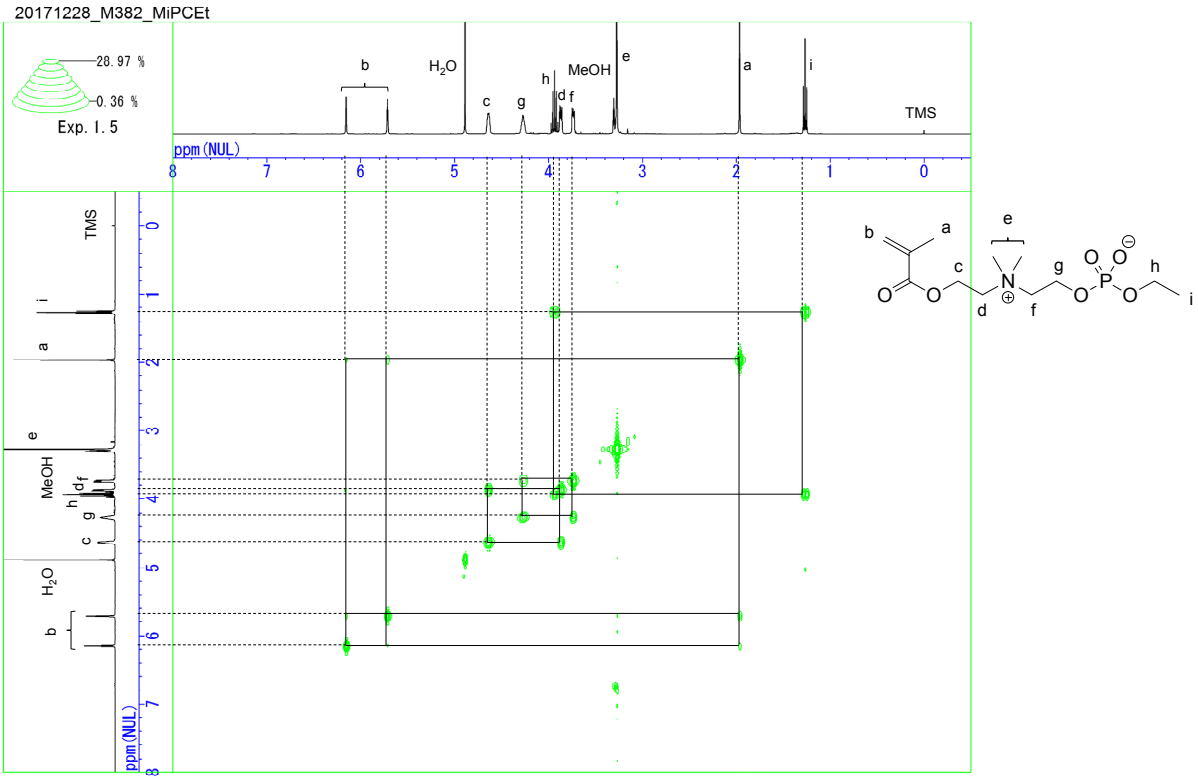

Figure S1-16. ^{1}H-^{1}H COSY spectrum of MCP-Et in CD_3OD

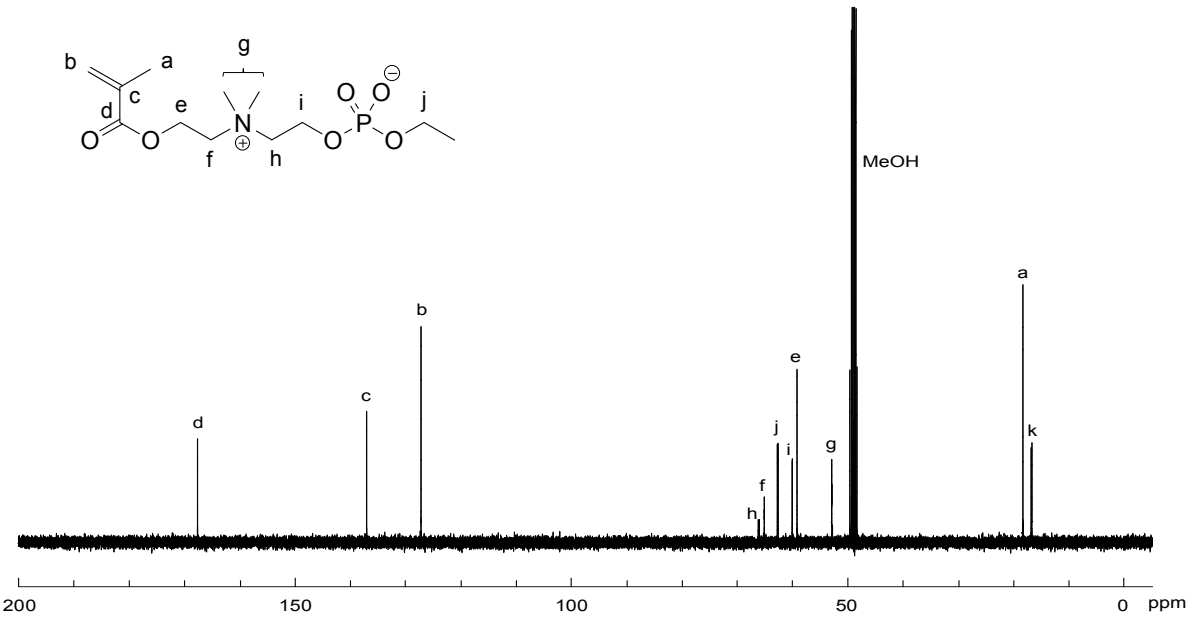

Figure S1-17. ^{13}C NMR spectrum of MCP-Et in CD_3OD

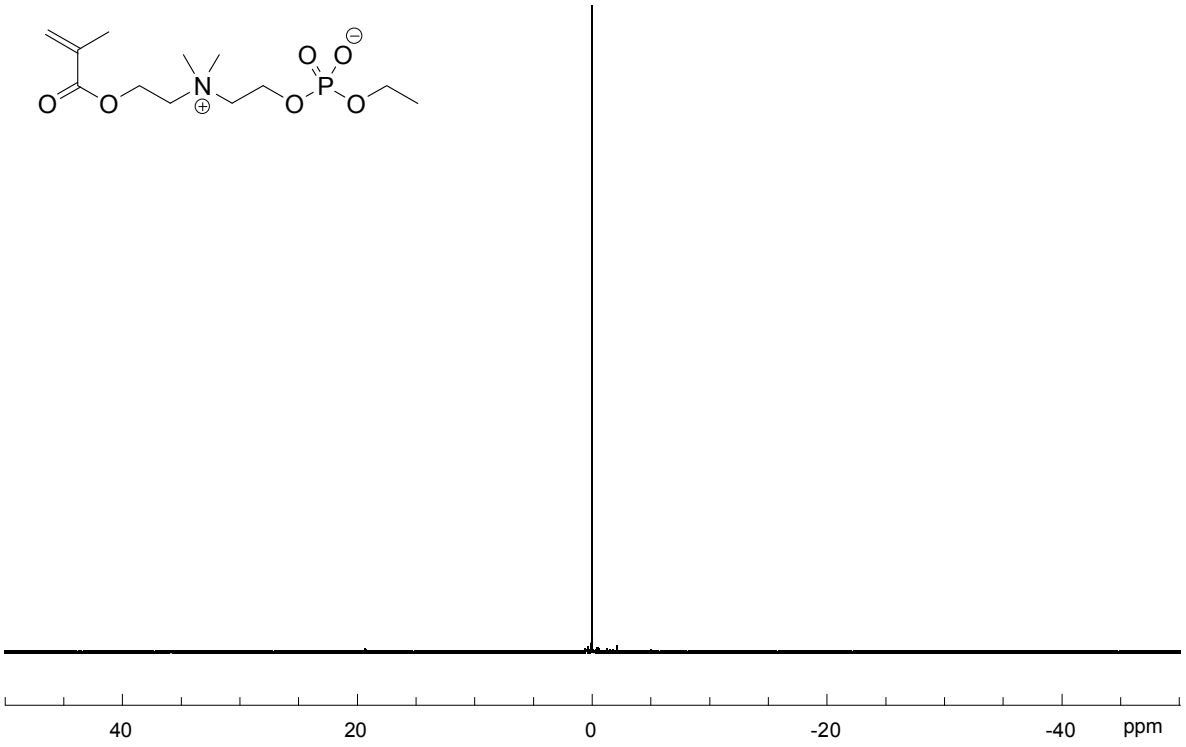

Figure S1-18. ^{31}P NMR spectrum of MCP-Et in CD_3OD

S1-6. 2-methoxyethoxy-2-oxo-1,3,2-dioxaphospholane (MEOP)

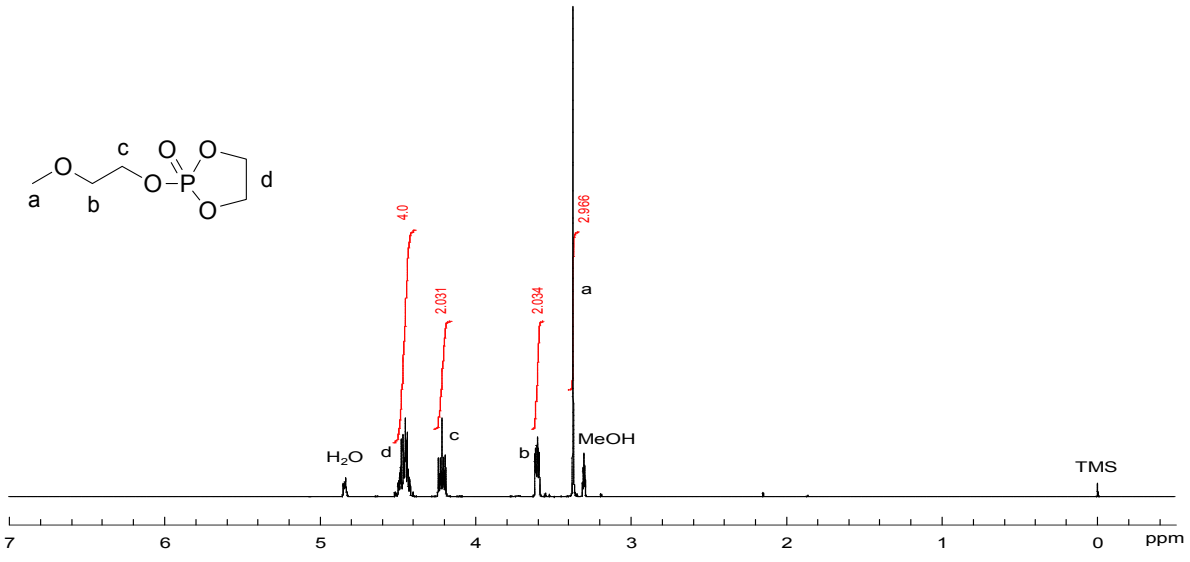

Figure S1-19. ^{1}H NMR spectrum of MEOP in CD_3OD

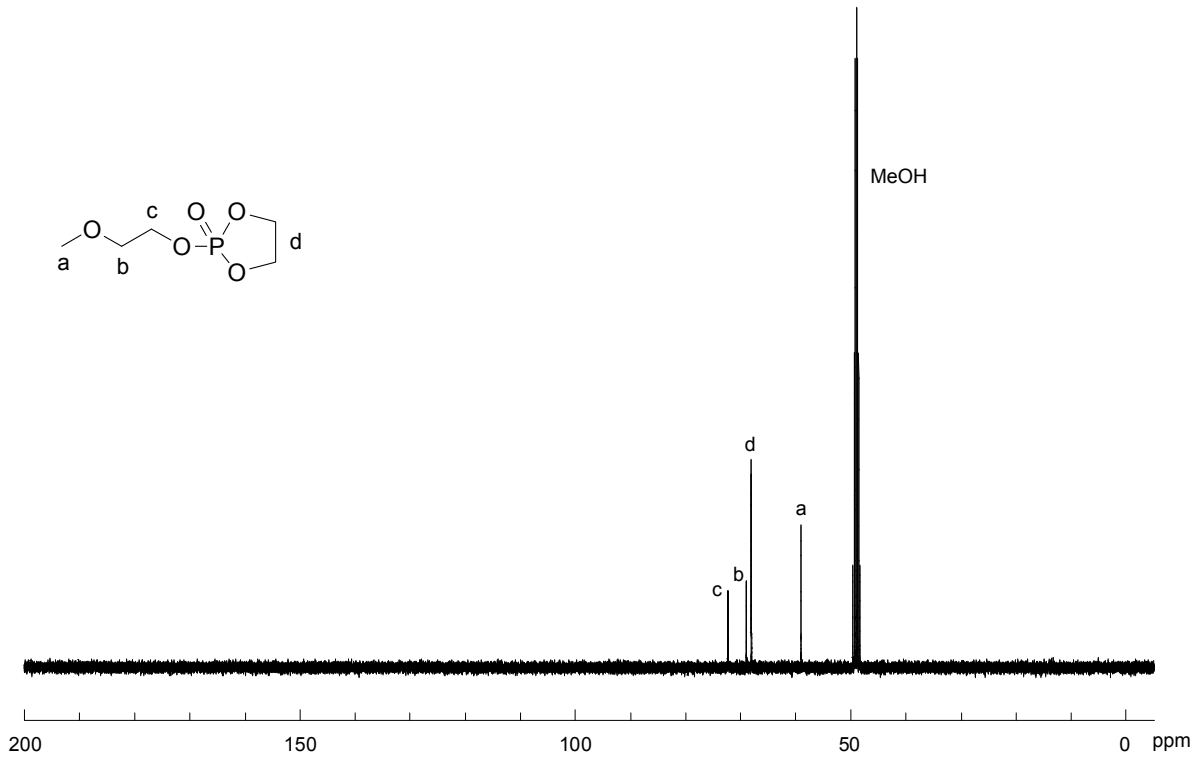

Figure S1-20. ^{13}C NMR spectrum of MEOP in CD_3OD

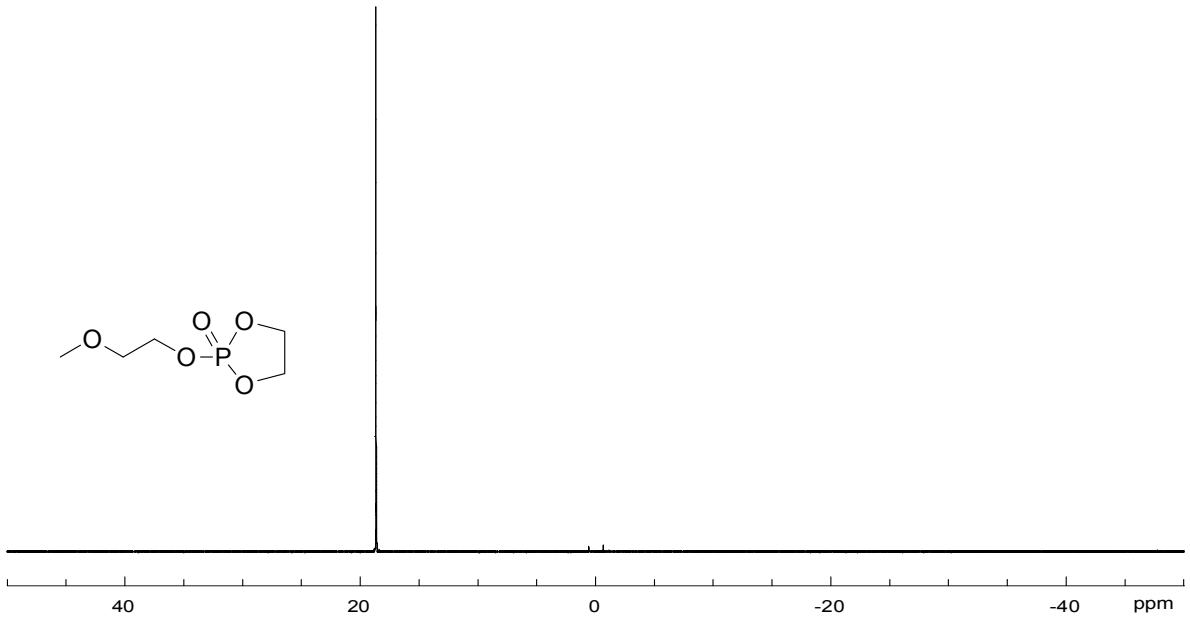

Figure S1-21. ^{31}P NMR spectrum of MEOP in CD_3OD

S1-7. 2-[2-(methacryloyl ethyl)dimethylammonio]ethyl methoxyethyl phosphate (MCP-MOE)

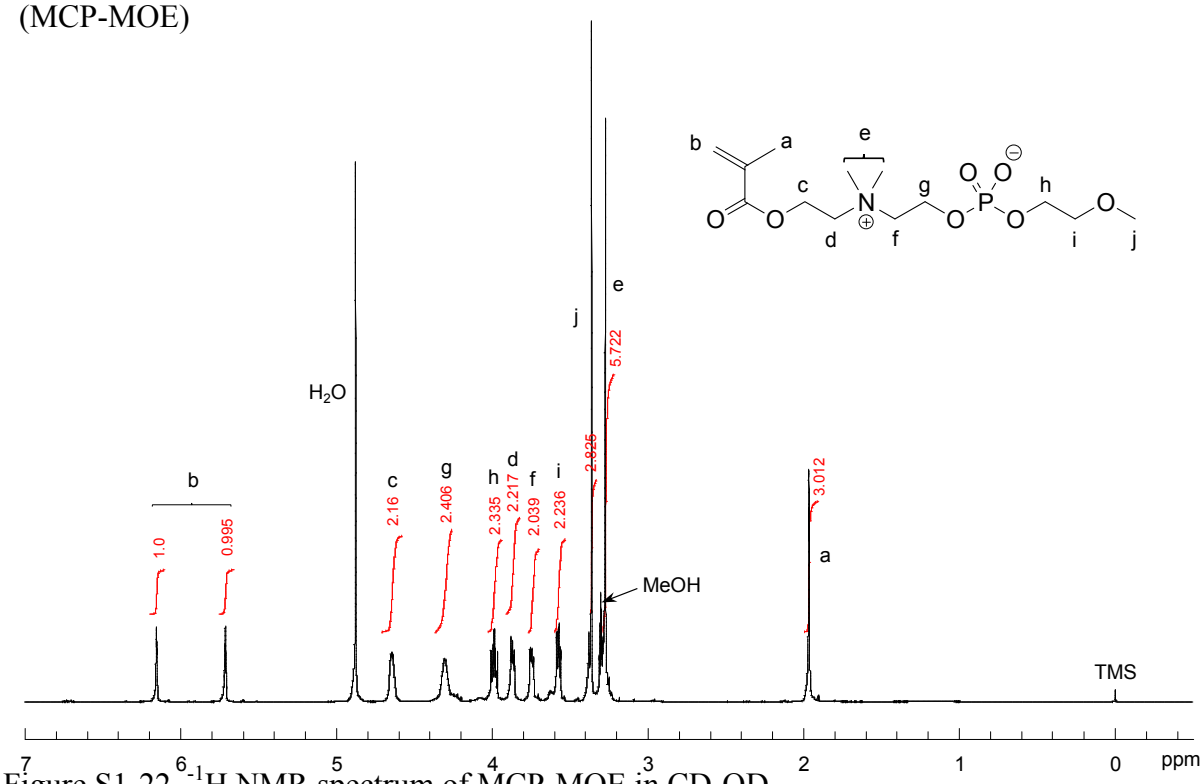

Figure S1-22. $^{-1}$H NMR spectrum of MCP-MOE in CD_3OD

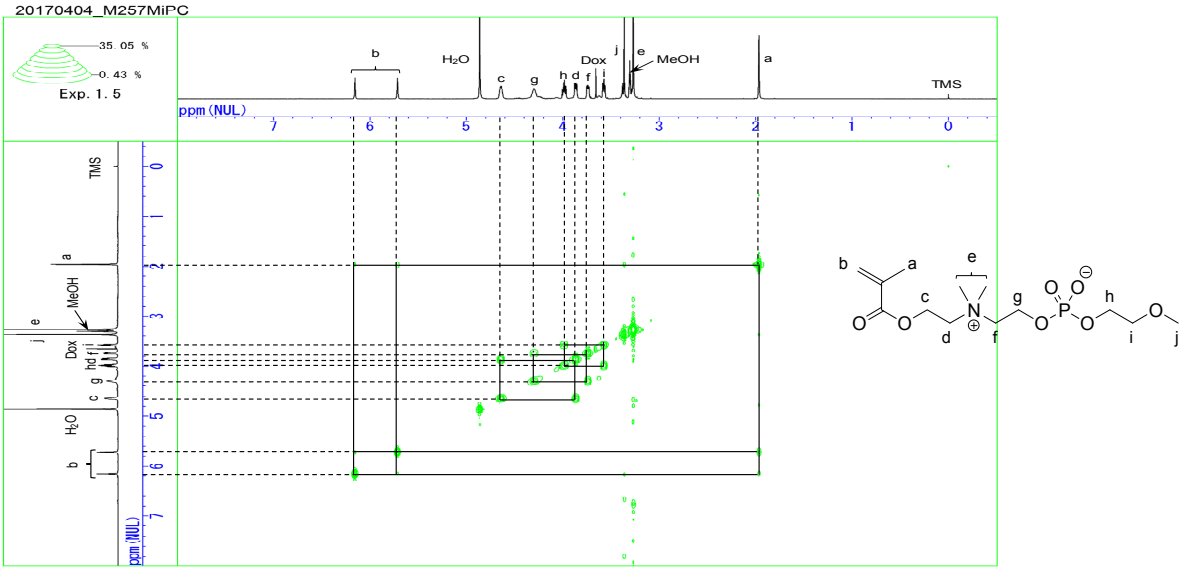

Figure S1-23. $^{-1}$H-^{1}H COSY spectrum of MCP-MOE in CD_3OD

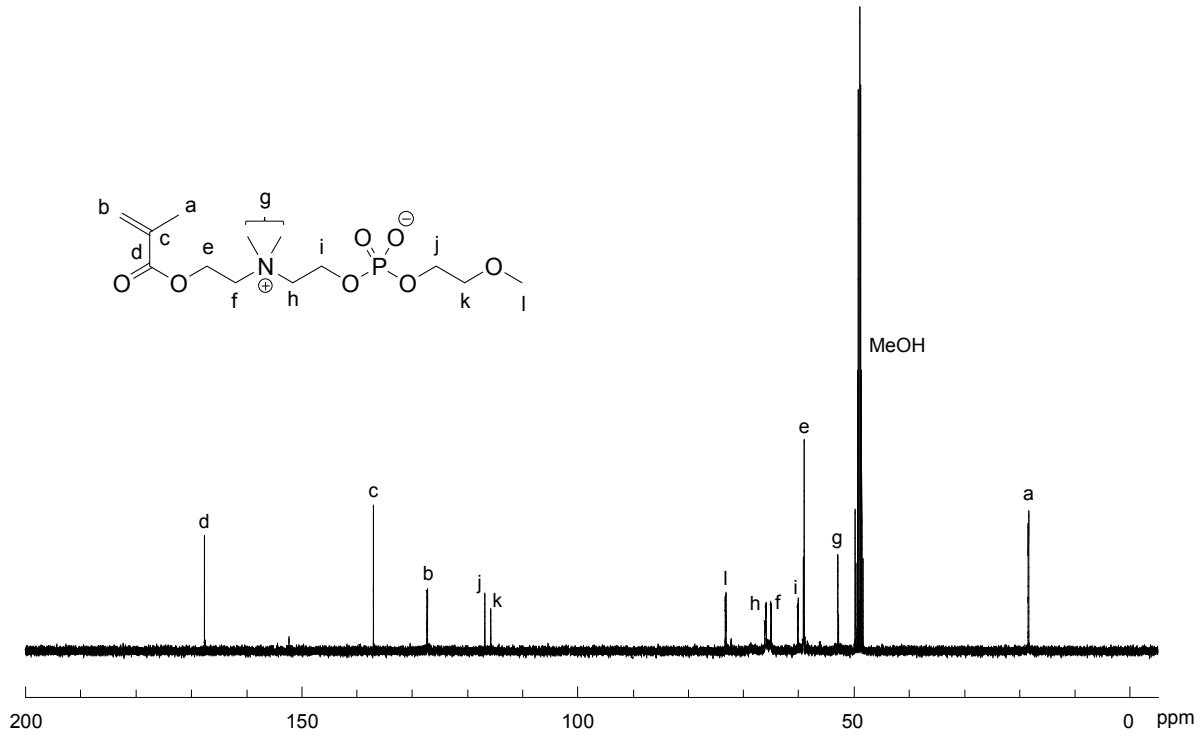

Figure S1-24. ^{13}C NMR spectrum of MCP-MOE in CD_3OD

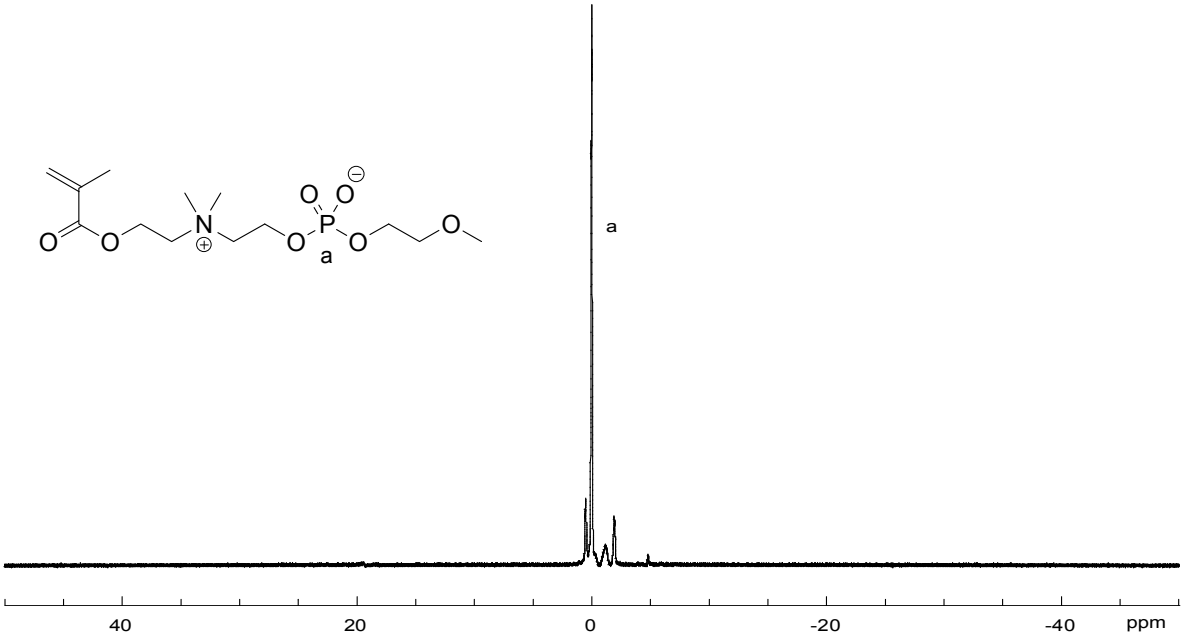

Figure S1-25. ^{31}P NMR spectrum of MCP-MOE in CD_3OD

S1-7. 2-methoxy-2-oxo-1,3,2-dioxaphospholane (MOP)

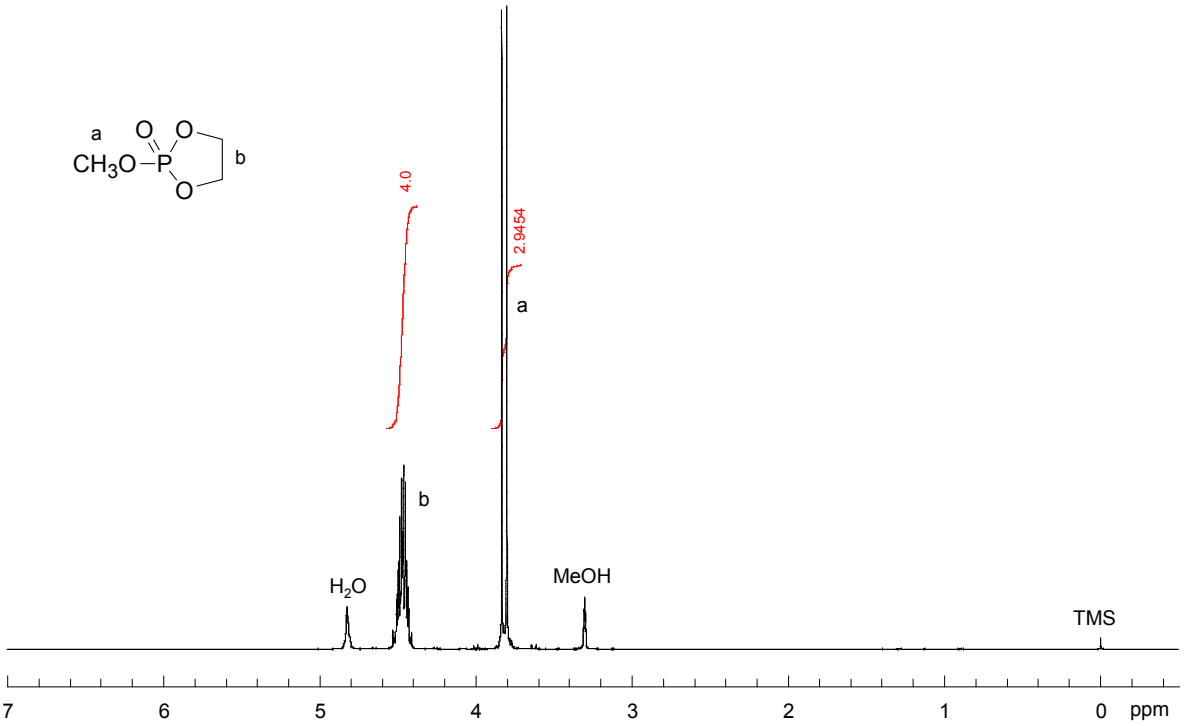

Figure S1-26. ^{1}H NMR spectrum of 2-methoxy-2-oxo-1,3,2-dioxaphospholane (MOP)

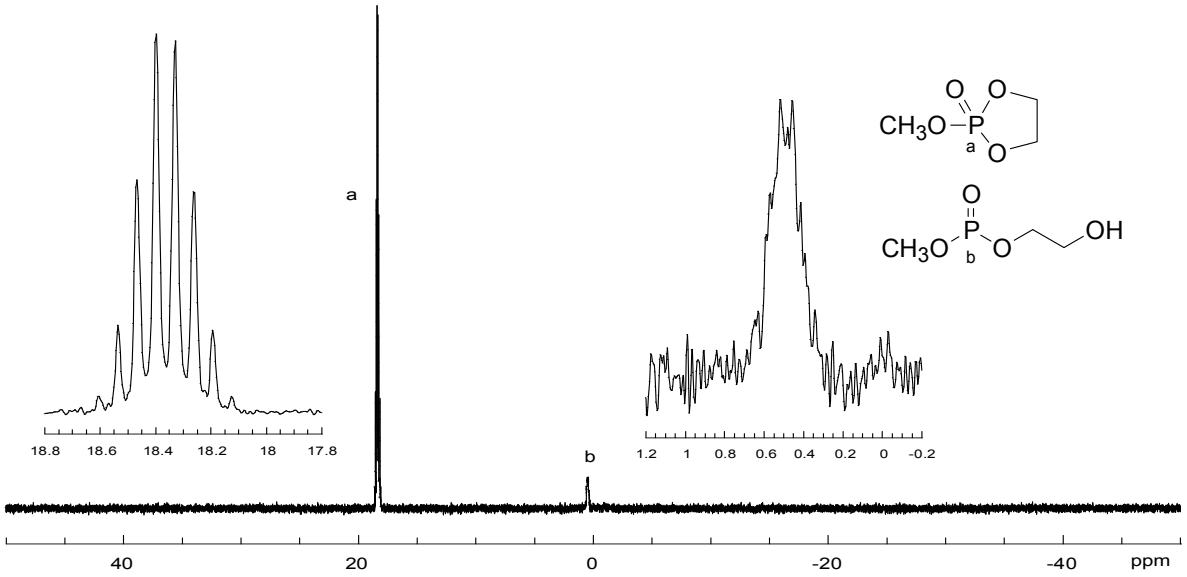

Figure S1-27. ^{31}P NMR spectrum of MOP and byproduct

S1-8. Polymerization of MPC, MCP-MOE, MCP-iPr, and MPC-ME

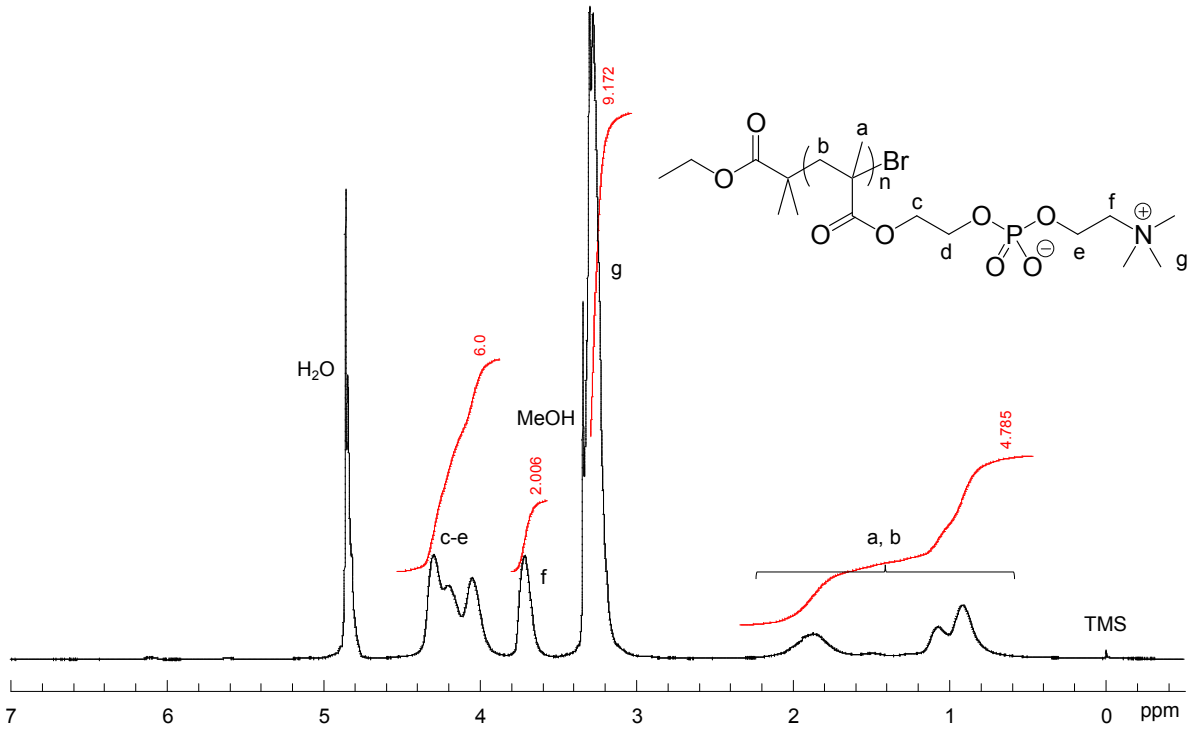

Figure S1-28. ^{1}H NMR spectrum of poly(MPC) in CD_3OD.

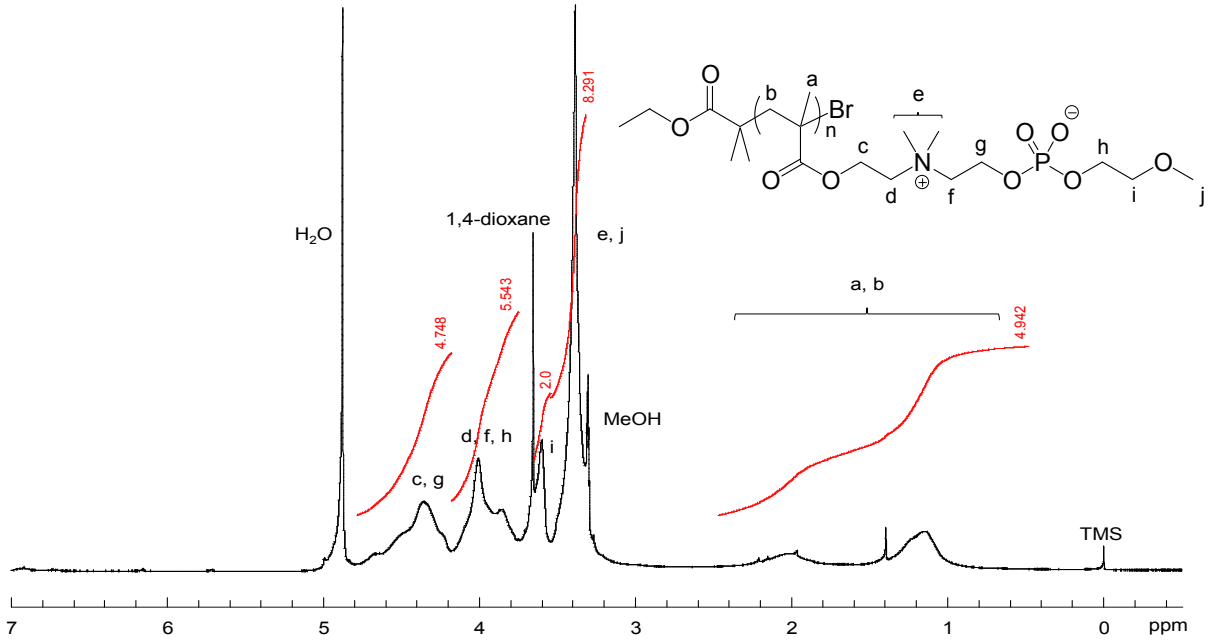

Figure S1-29. ^{1}H NMR spectrum of poly(MCP-MOE) in CD_3OD.

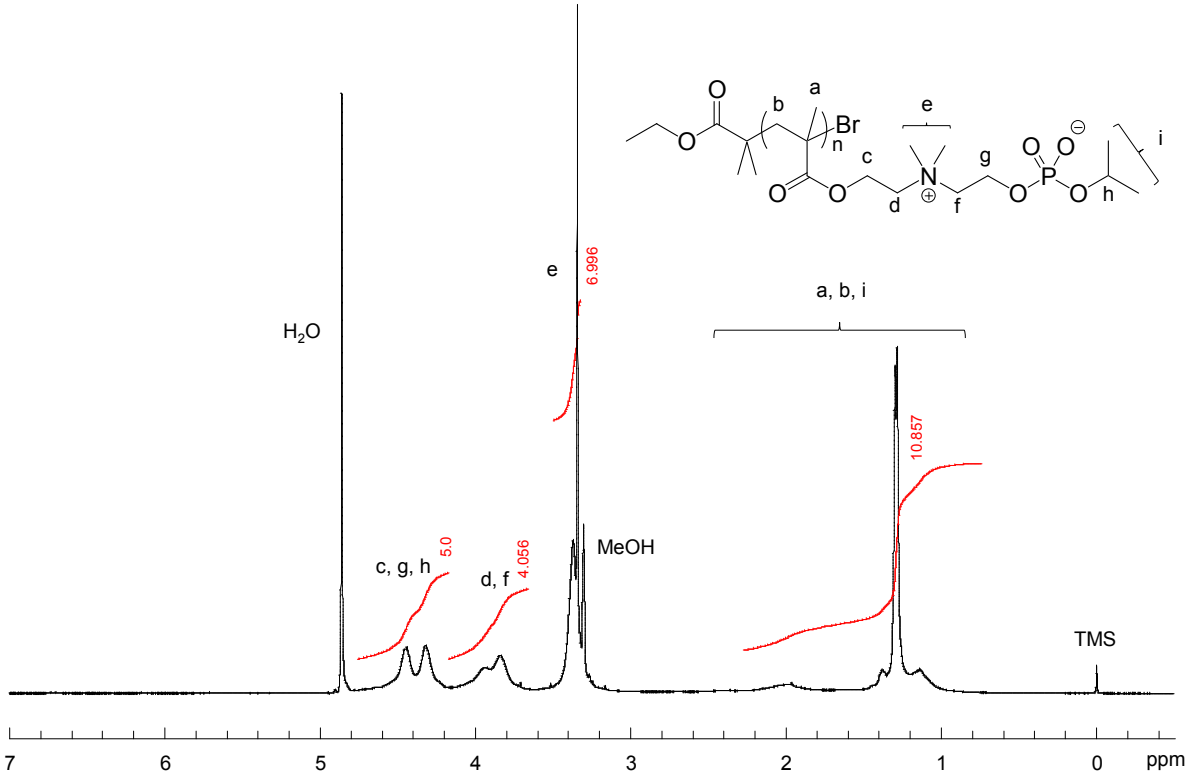

Figure S1-30. ^{1}H NMR spectrum of poly(MCP-iPr) in CD_3OD.

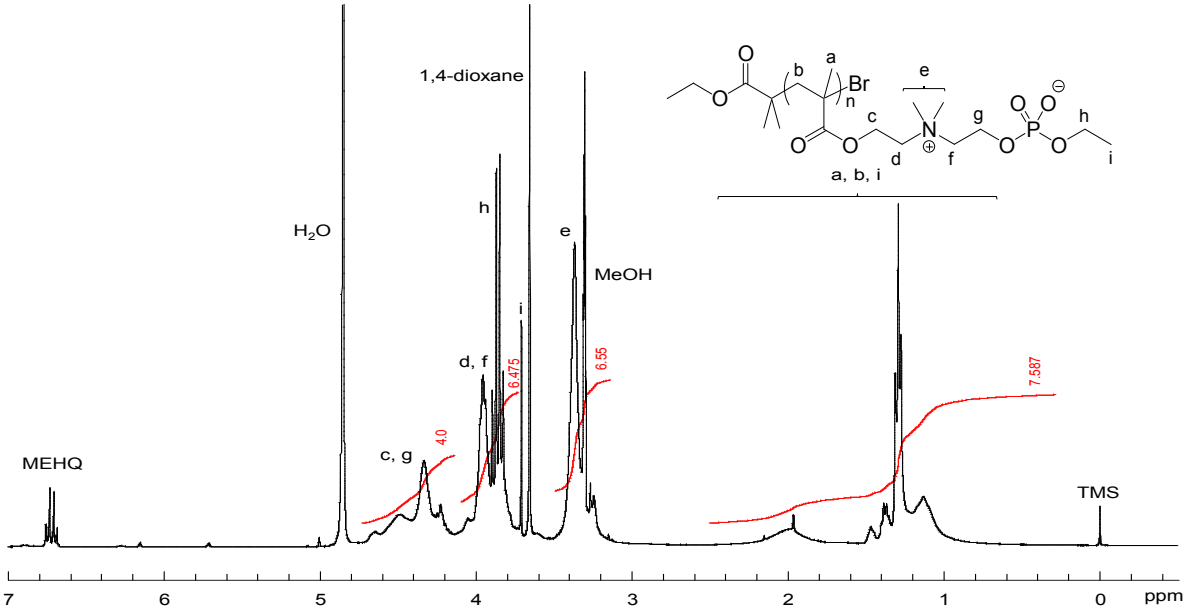

Figure S1-31. ^{1}H NMR spectrum of poly(MCP-Et) in CD_3OD.

S2. SEC profiles of poly(MPC) and poly(MCP-R)

Into a plastic test tube, polymer-grafted silica particle (50 mg), water (4 mL), and magnetic stirring bar were added to give a dispersion mixture. A portion of HF (46.0-48.0%(mass/ mass) (1 mL) was added to the mixture to form a transparent colorless solution. After the stirring at room temperature for 2 h, the reaction mixture was poured into the THF to precipitate the polymers. The resulting polymers were dried under vacuum, and was used as sample for SEC measurement.

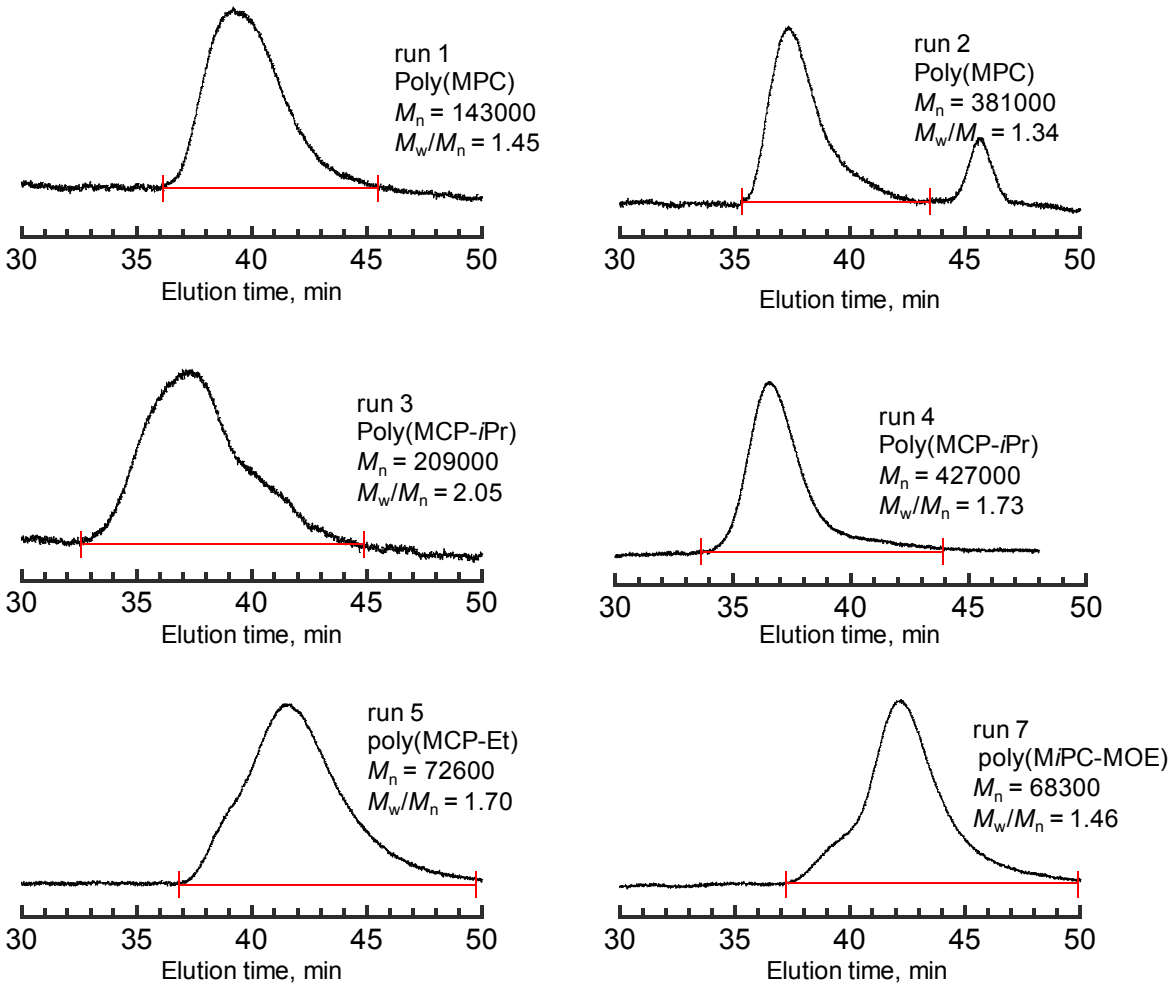

Figure S2-1. SEC profiles of poly(MPC), poly(MCP-iPr), poly(MCP-Et), and poly(MCP-MOE) using 0.2 M-NaCl aqueous solution as an eluent at a rate of 0.5 mL/min, and calibration of polyethyleneoxide standards. SEC curves of free polymers produced by EB are run 1, 3, and 5 (See Table 1), and that of grafted polymers cleaved from silica particle are run 2, 4, and 7, respectively.

S3. Solubilities of monomers and polymers

Table S3-1. Solubility of phosphobetaine monomer and polymers [a]

solvent	MPC	poly(MPC)	MCP-*i*Pr	poly(MCP-*i*Pr)	poly(MCP-Et)	poly(MCP-MOE)
n-hexane	I	I	I	I	I	I
carbon tetrachloride	I	I	I	I	I	I
benzene	I	I	I	I	I	I
toluene	I	I	I	I	I	I
diethyl ether	I	I	I	I	I	I
1,4-dioxane	I	I	I	I	I	I
chloroform	S	I	S	I	I	I
ethyl acetate	I	I	I	I	I	I
THF	I	I	I	I	I	I
acetone	I	I	I	I	I	I
methylene chloride	I	I	S	I	I	I
triethylamine	I	I	I	I	I	I
2-propanol	S	I	S	I	I	I
1-propanol	S	S	S	S	S	S
ethanol	S	S	S	S	S	S
TFE	S	S	S	S	S	S
methanol	S	S	S	S	S	S
NMP	I	I	I	I	I	I
DMF	I	I	I	I	I	I
acetonitrile	S	I	S	I	I	I
DMAc	I	I	I	I	I	I
ethylene glycol	S	S	S	S	S	S
DMSO	S	I	I	I	I	I
pure water	S	S	S	S	S	S

[a] S : Soluble I : Insoluble

THF: tetrahydrofuran, TFE: 2,2,2- trifluoroethanol, NMP: *N*-methylpyrrolidone, DMAc: *N,N,*-dimethylacetamide, DMF: *N,N,*-dimethylformamide, DMSO : dimethylsulfoxide.

S4. XPS spectra of polymer brushes

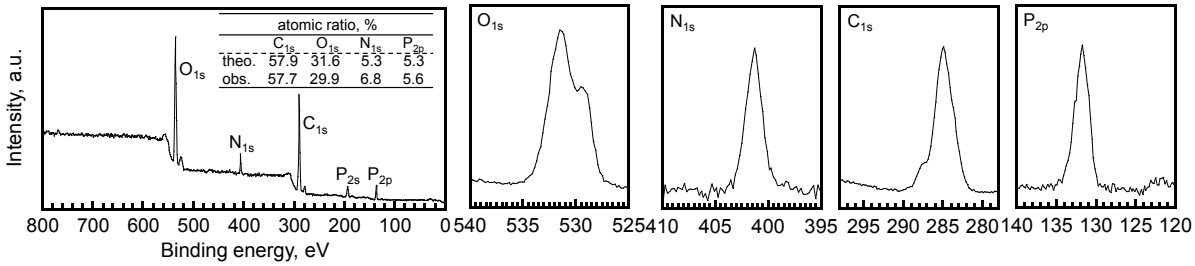

Fig. S4-1. XPS spectra and atomic ratio of poly(MPC) brush.

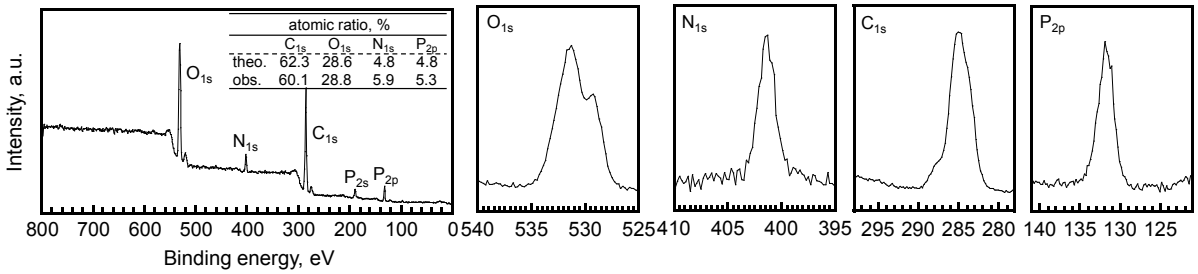

Fig. S4-1. XPS spectra and atomic ratio of poly(MCP-*i*Pr) brush.

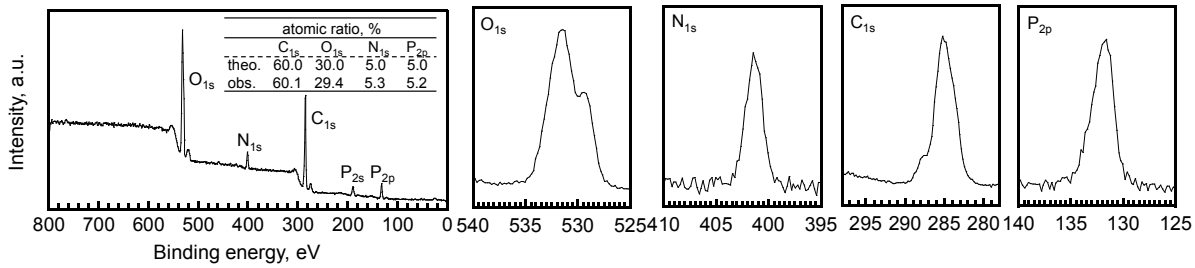

Fig. S4-2. XPS spectra and atomic ratio of poly(MCP-Et) brush.

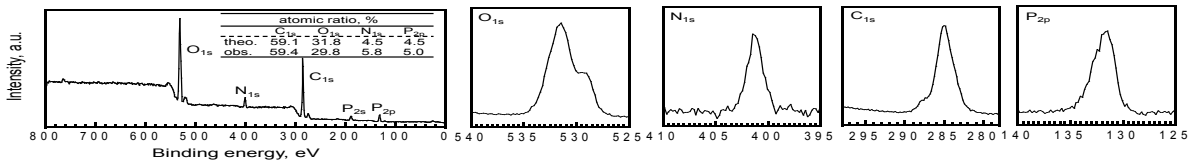

Fig. S4-3. XPS spectra and atomic ratio of poly(MCP-MOE) brush.

S5. Force curve measurement

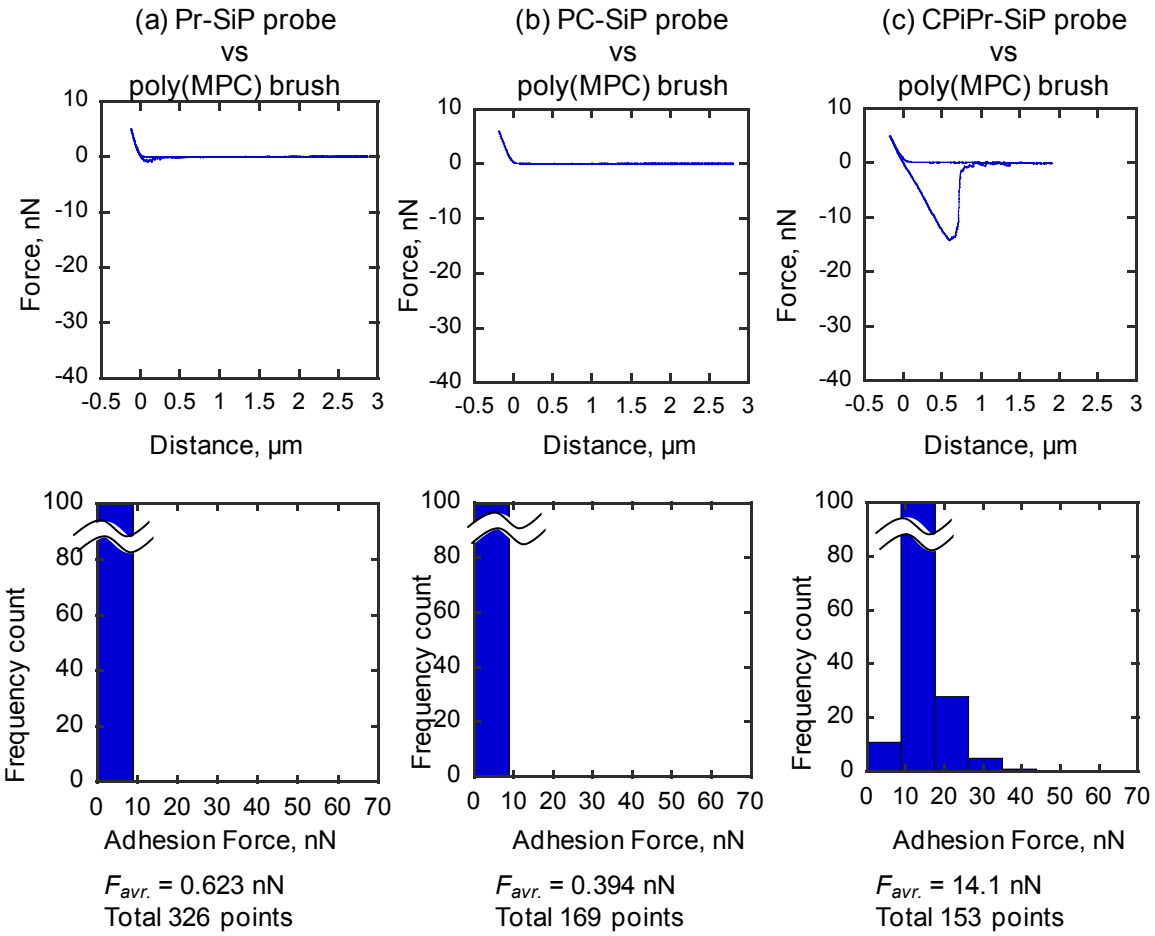

Figure S5-1. Typical force curves and histograms on the surface of poly(MPC) brush in water at 298 K obtained by force curve measurement using (a) propyl-modified, (b) PC-modified, and (c) CPiP-modifies SiP probes.

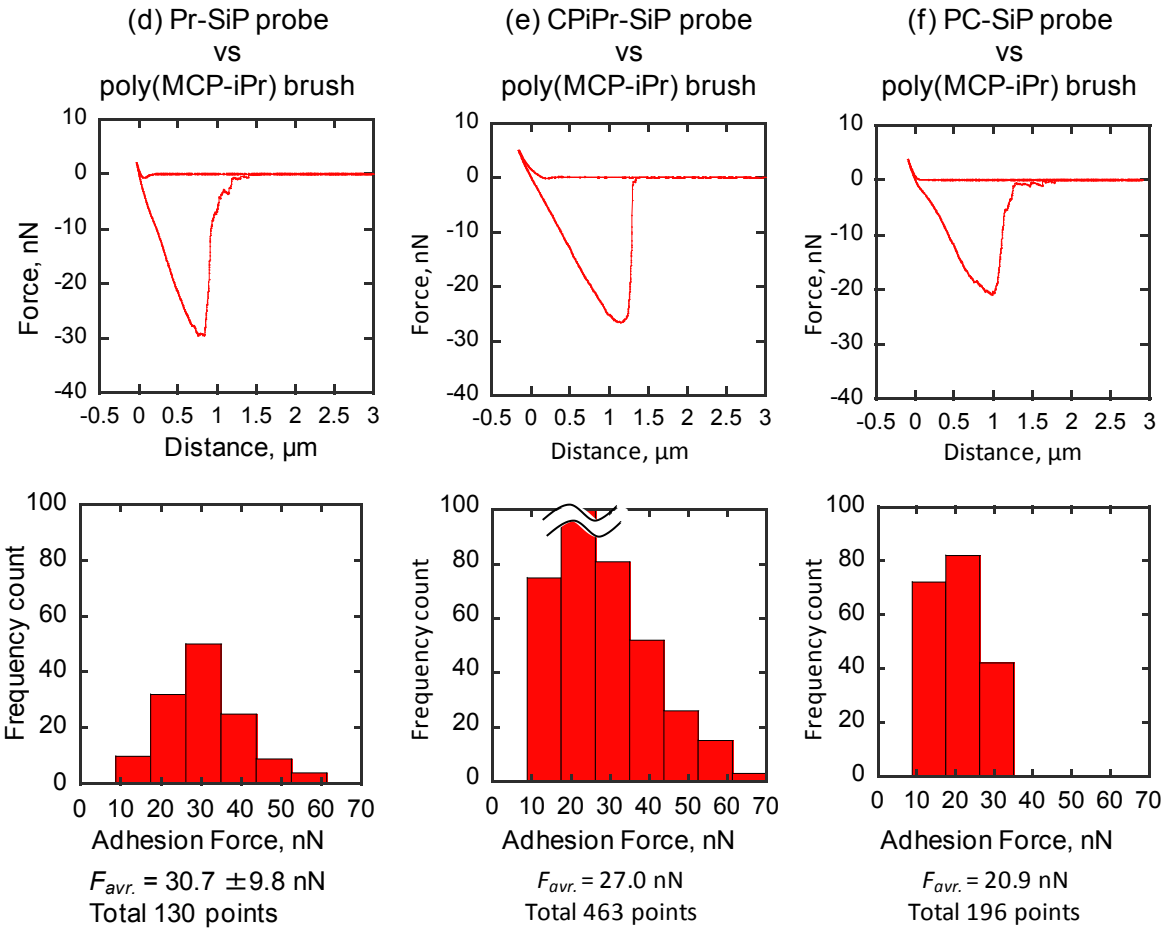

Figure S5-2. Typical force curves and histograms on the surface of poly(MCP-iPr) brush in water at 298 K obtained by using (d) Pr-modified, (d) CPiPr and (d) PC-modified SiO_2 probes.

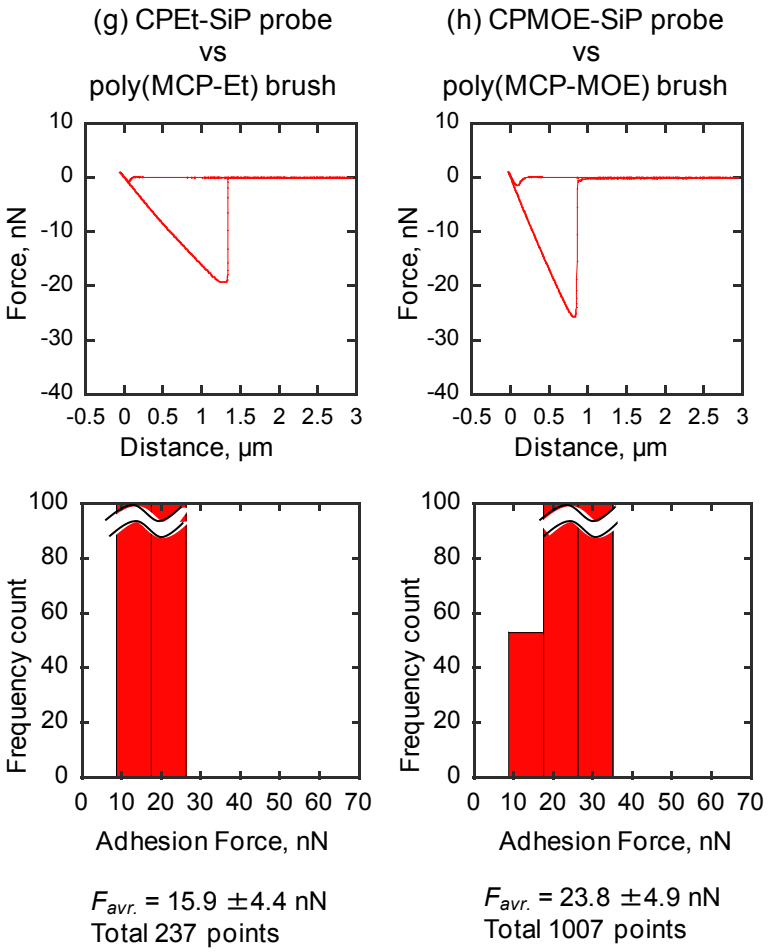

Figure S5-3. Typical force curves and histograms on the surface of (g) poly(MCP-Et) brush and (h) poly(MCP-MOE) brush in water at 298 K obtained by force curve measurement using (g) CPEt-modified and (h) CPMOE-modified SiO_2 probes.

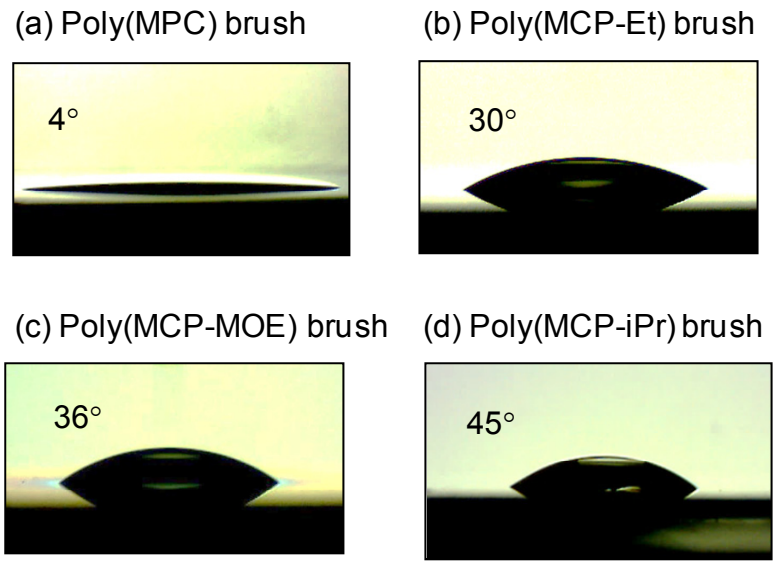

Figure S6. Photographs of water and contact angle on the surface of (a) poly(MPC), (b) poly(MCP-Et), (c) poly(MCP-MOE), and (d) poly(MCP-iPr) brushes