Supporting Information

Synthesis of Zwitterionic Pluronic Analogs

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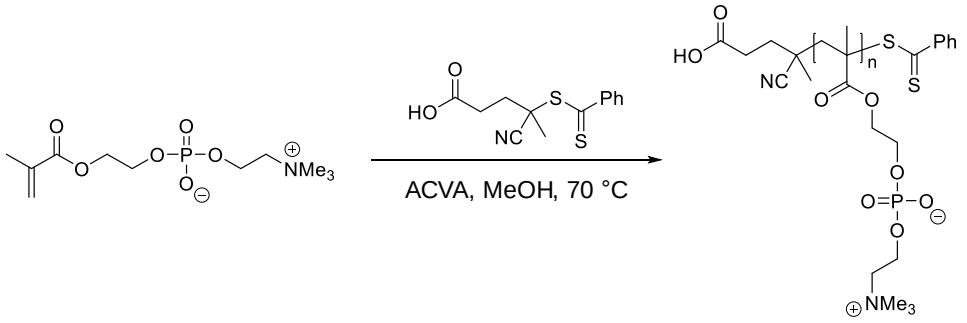
PolyMPC Homopolymer Synthesis



In a 20 mL glass vial charged with a stir bar, MPC (1.2034 g, 4.1 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (8.7 mg, 0.031 mmol), and ACVA (2.1 mg, 0.0075 mmol) were dissolved in MeOH (3 mL). The resulting solution was degassed with bubbling nitrogen for 15 minutes and was heated at 70 °C. At a monomer conversion of 87%, estimated using ^{1}H-NMR spectroscopy, the polymerization was quenched by exposure to air, and the solution was precipitated in THF (35 mL). The crude polymer product was isolated by centrifugation (4000 rpm, 5 min) and was purified by dialysis against water. Lyophilization

afforded polyMPC as a pink solid in a yield of 74%. ^{1}H-NMR (500 MHz, MeOD-d_4, δ, ppm): 0.66-1.34 (m, 3H), 1.65-2.20 (m, 2H), 3.26-3.36 (s, 9H), 3.64-3.78 (br, 2H), 3.96-4.12 (br, 2H), 4.12-4.26 (br, 2H), 4.26-4.38 (br, 2H). $M_{n,\,GPC}$ = 38,500 g/mol, PDI = 1.08.

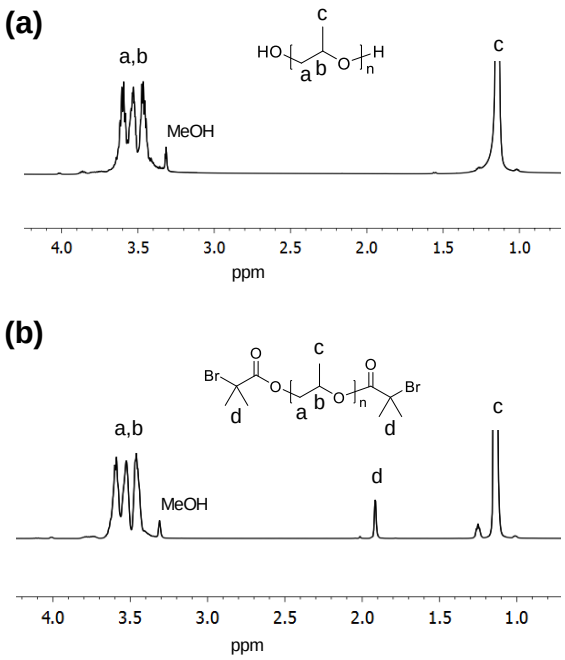


Figure S1. ^{1}H-NMR (500 MHz) spectra of the PPO starting material (a) and macroinitiator **1** (b) obtained in MeOD-d_4.

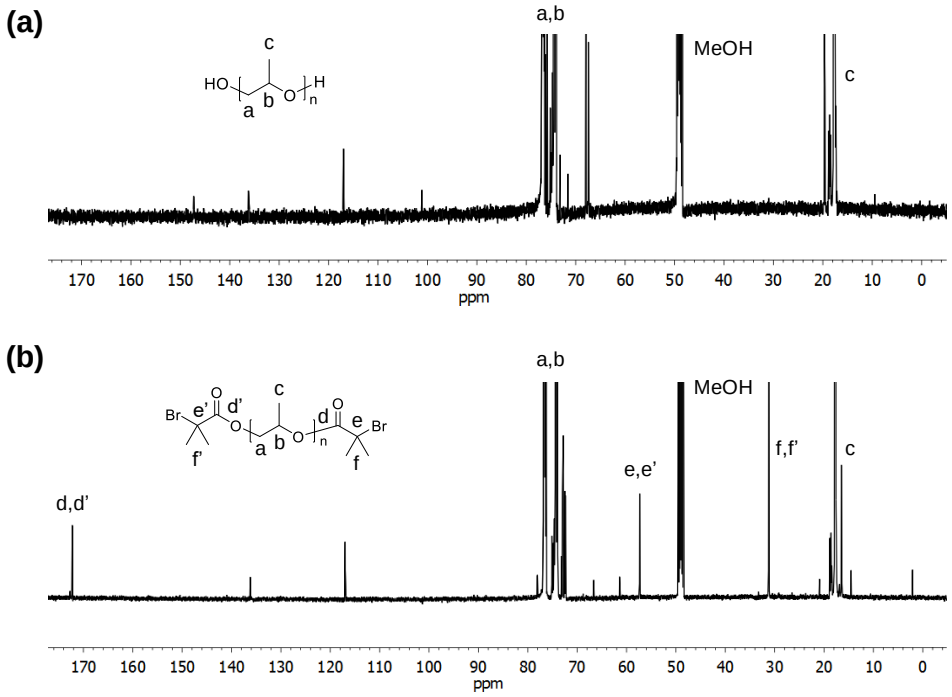


Figure S2. ^{13}C-NMR (125 MHz) spectra of the PPO starting material (a) and macroinitiator **1** (b) obtained in MeOD-d_4.

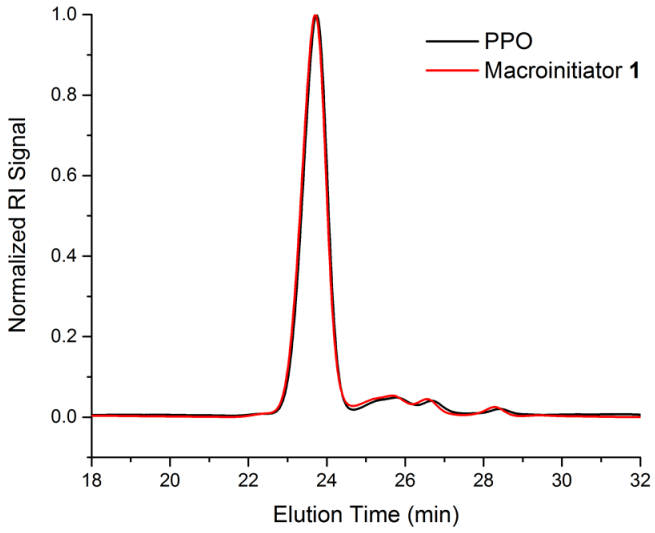


Figure S3. GPC chromatograms of the PPO starting material and macroinitiator **1** eluting in TFE.

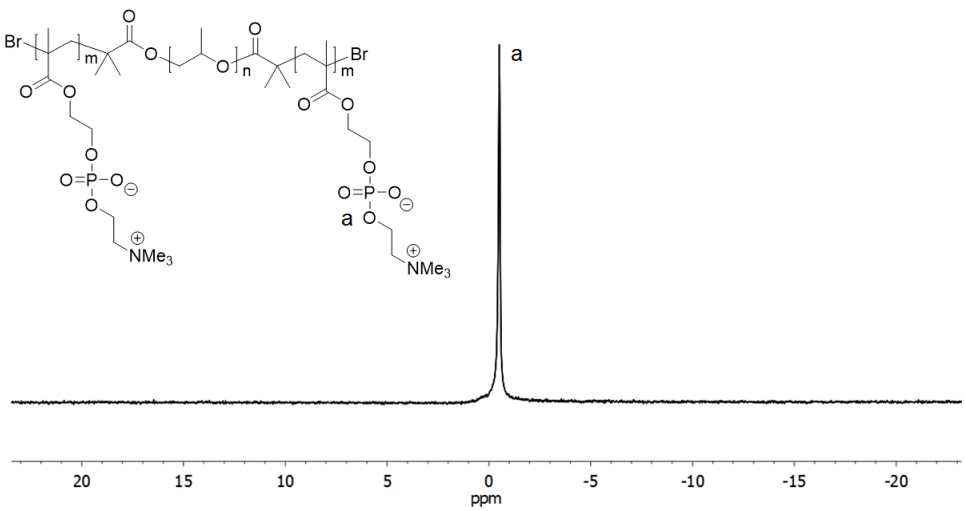


Figure S4. ^{31}P-NMR (202 MHz) spectrum of **PCZ5** obtained in MeOD-d_4.

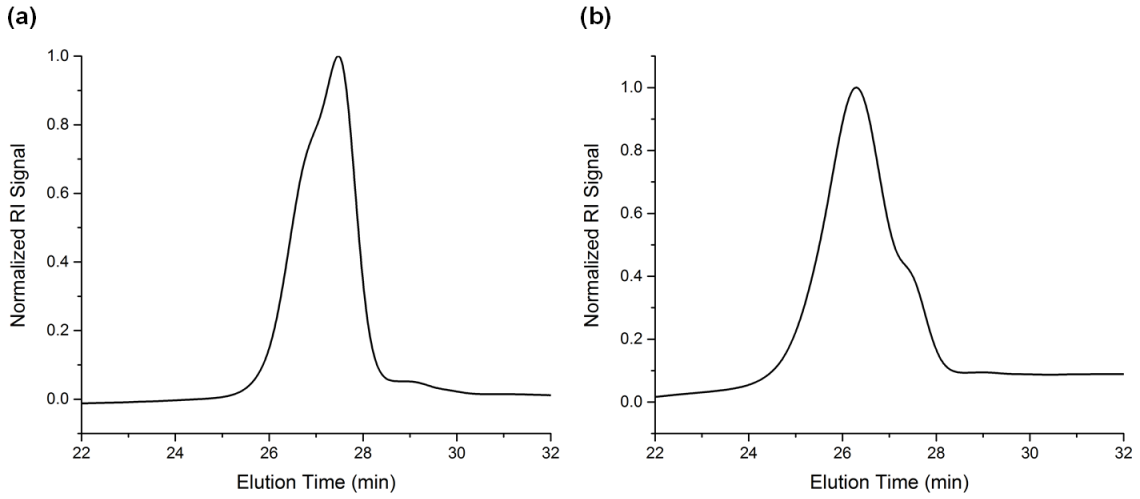


Figure S5. GPC chromatograms of PC-Zwitteronics eluting in TFE prepared using MeOH as the polymerization solvent with polyMPC X_n values of 5 (a) and 18 (b).

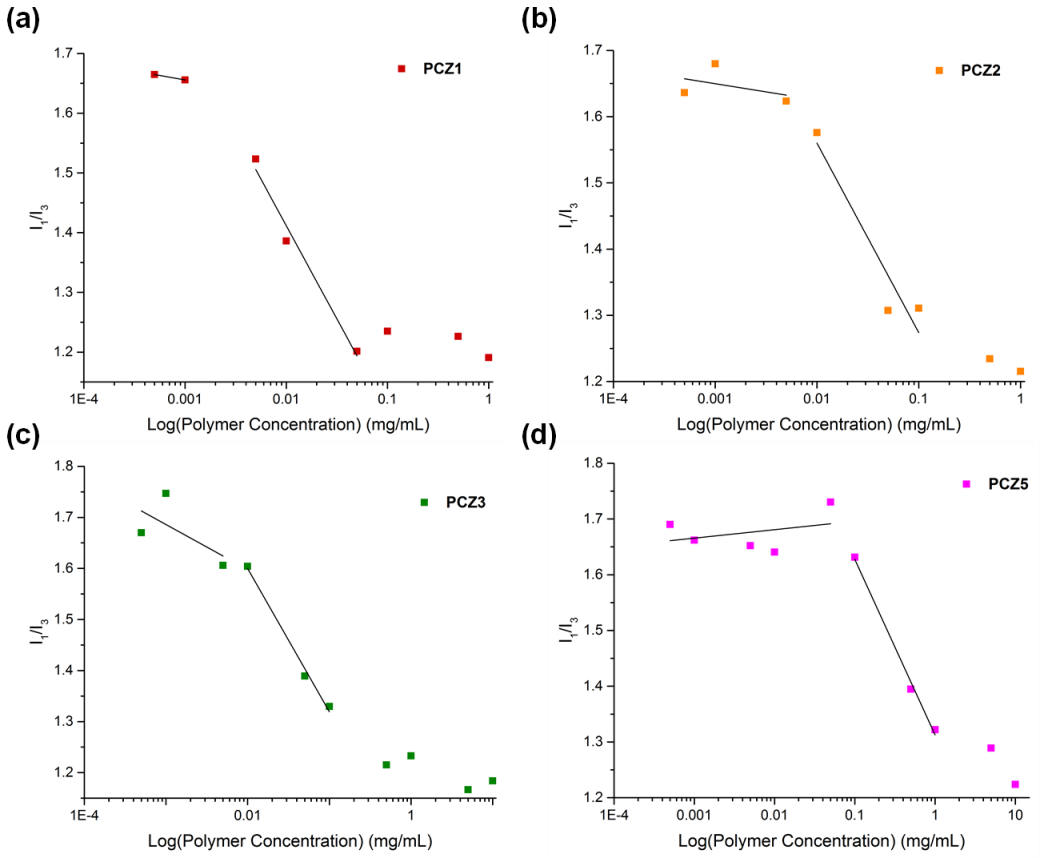


Figure S6. Relative fluorescence intensities of the first (I_1) and third (I_3) vibronic bands for pyrene in aqueous solutions at varying **PCZ1** (a), **PCZ2** (b), **PCZ3** (c), and **PCZ5** (d) concentrations

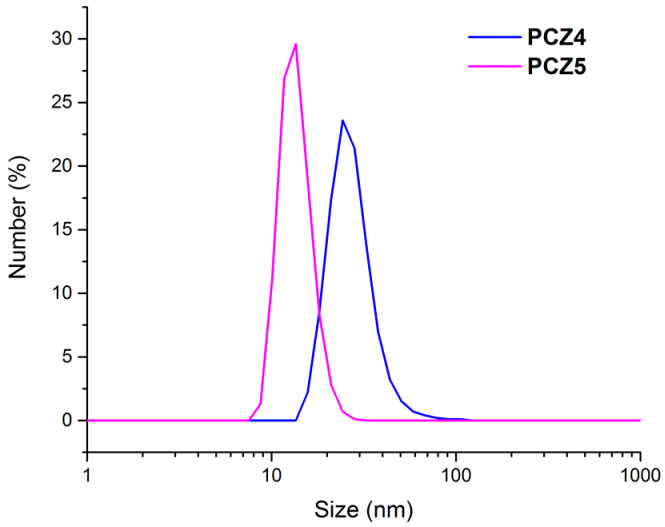


Figure S7. DLS plots by number percent for 1 mg/mL aqueous suspensions of **PCZ4** and **PCZ5** showing the smaller aggregates observed in the intensity plots to be the predominant species.

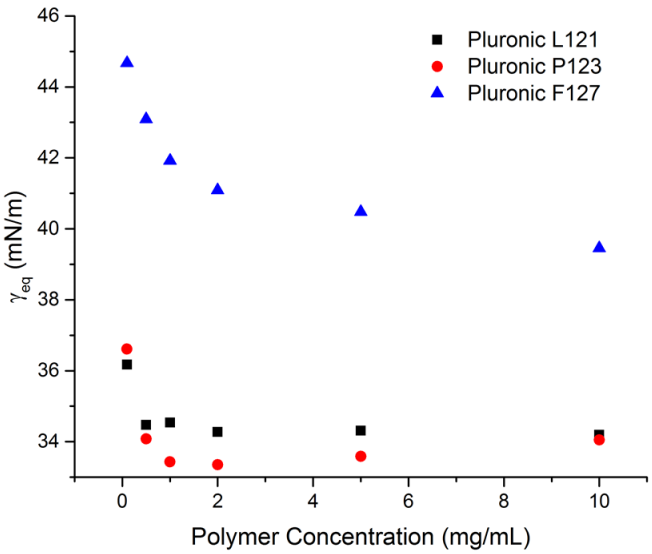


Figure S8. Room temperature equilibrium surface tension (γ_{eq}) values measured for Pluronics L121, P123, and F127 at varying polymer concentrations in pure water.

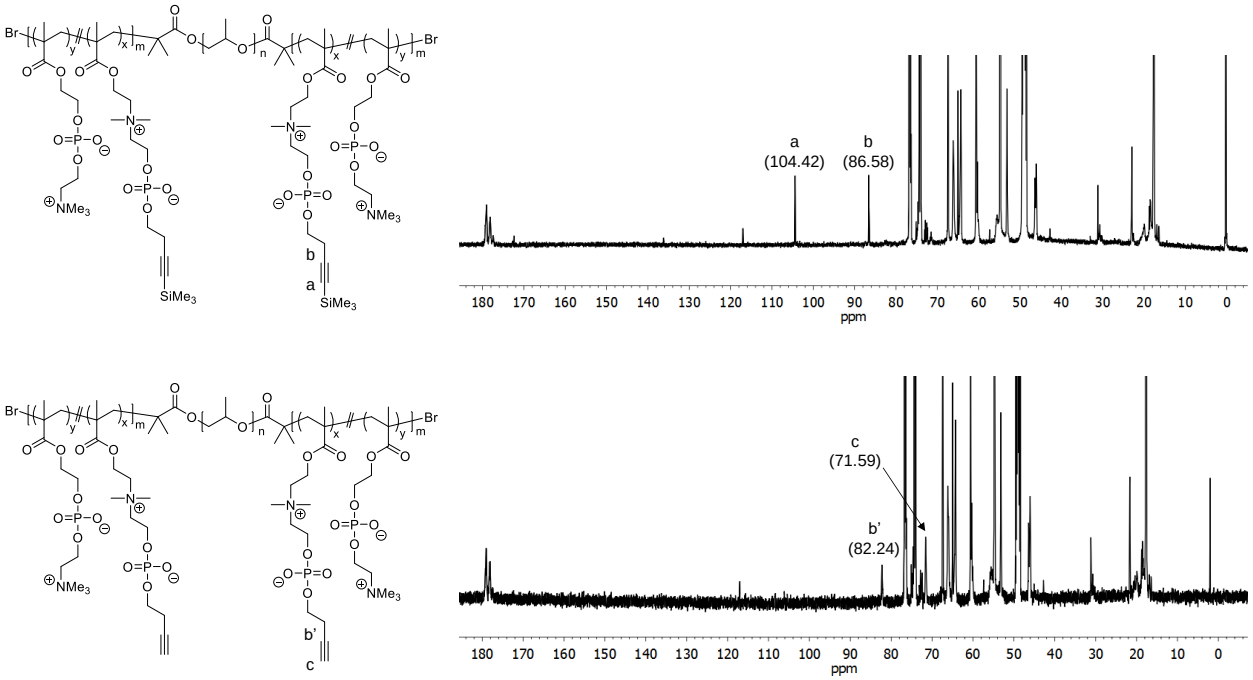


Figure S9. Representative ^{13}C-NMR (125 MHz) spectra of **FZ2** before (top) and after (bottom) removal of the TMS protecting groups. Protected and deprotected alkynes exhibited carbon resonances at 104.42/86.68 ppm and 82.24/71.59 ppm, respectively.

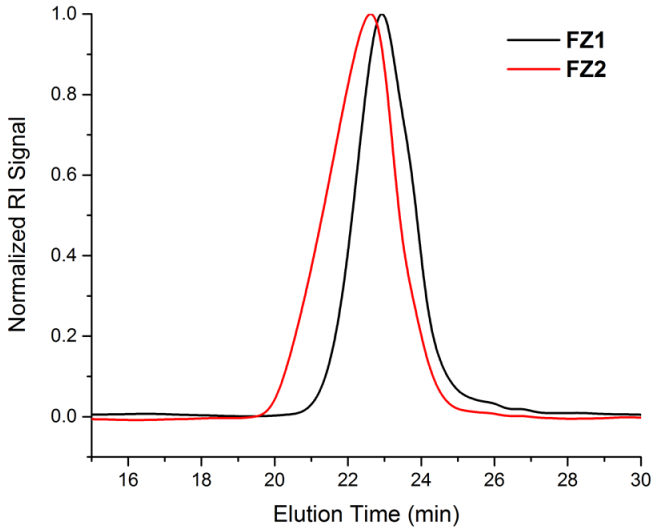


Figure S10. GPC chromatograms of functional Zwitteronics **FZ1** and **FZ2** eluting in TFE.

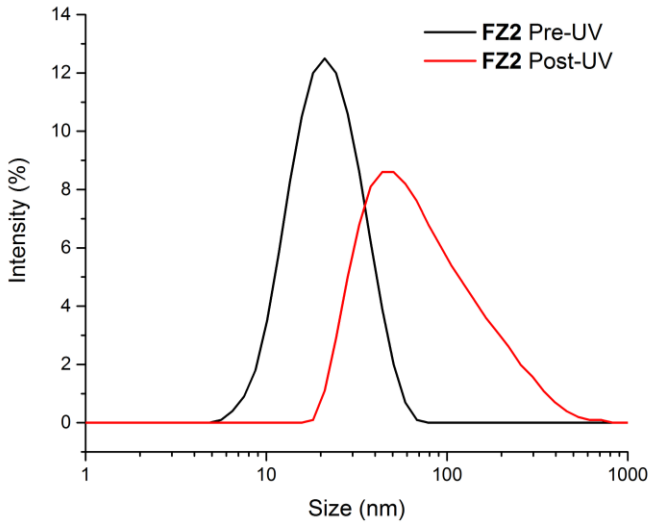


Figure S11. DLS plots of 1 mg/mL solutions of **FZ2** in MeOH before and after UV-initiated (λ = 365 nm) thiol-yne crosslinking.

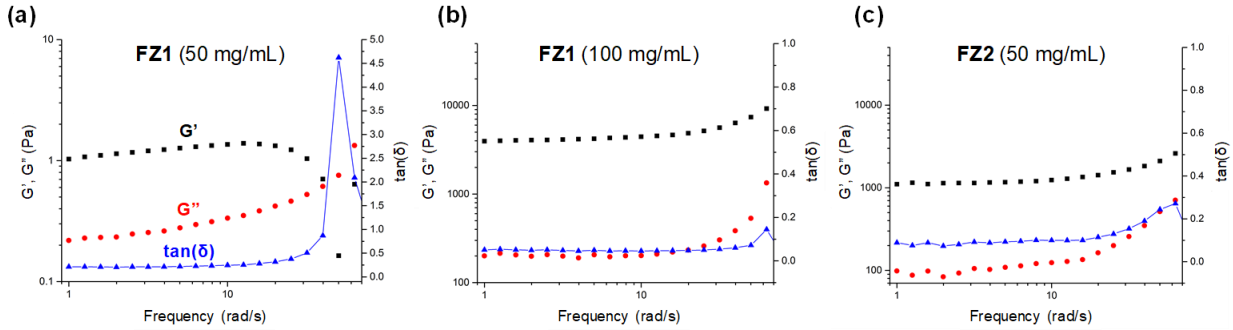


Figure S12. Plots of storage modulus (G'), loss modulus (G"), and tan(δ) measured for the 50 mg/mL **FZ1** (a), 100 mg/mL **FZ1** (b), and 50 mg/mL **FZ2** (c) hydrogels.