Supporting Information

A Facile Synthesis of Clickable and Acid-Cleavable PEO for Acid-Degradable Block Copolymers

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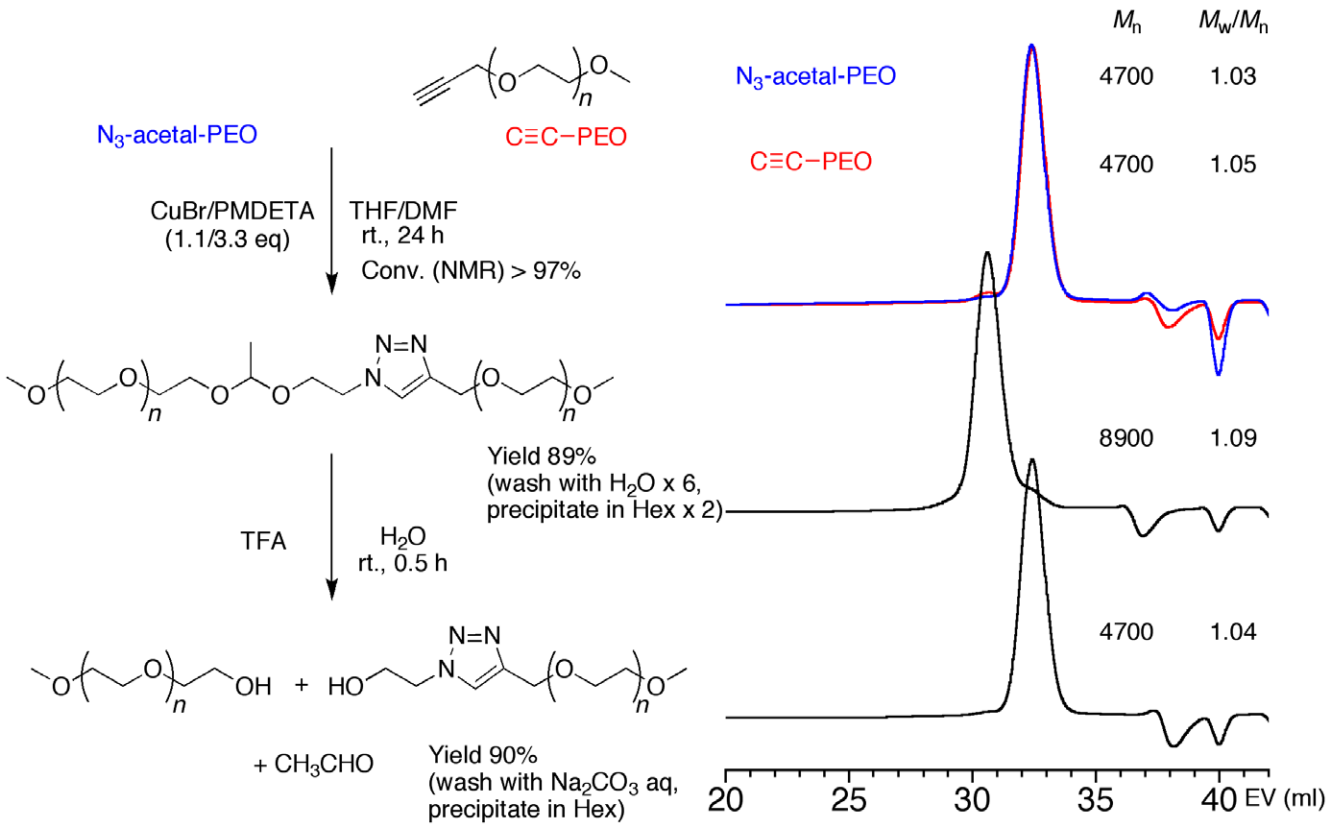

Figure S1. GPC curves during CuAAc click reaction between PEO-acetal-N_3 and and PEO-alkyne: $[\text{PEO-acetal-N}_3]_0 = [\text{PEO-alkyne}]_0 = 0.21$ mmol (1.1 g), $[\text{CuBr}]_0 = 0.23$ mmol, $[\text{PMDETA}]_0 = 0.69$ mmol in 30 mL of THF/DMF (1/1 v/v) at r.t. for 24 h, and followed by intentional cleavage of acetal junction: $[\text{PEO-acetal-PEO}]_0 = 0.02$ mmol (0.2 g) and TFA (1.0 mL) in H_2O at r.t. for 0.5 h.

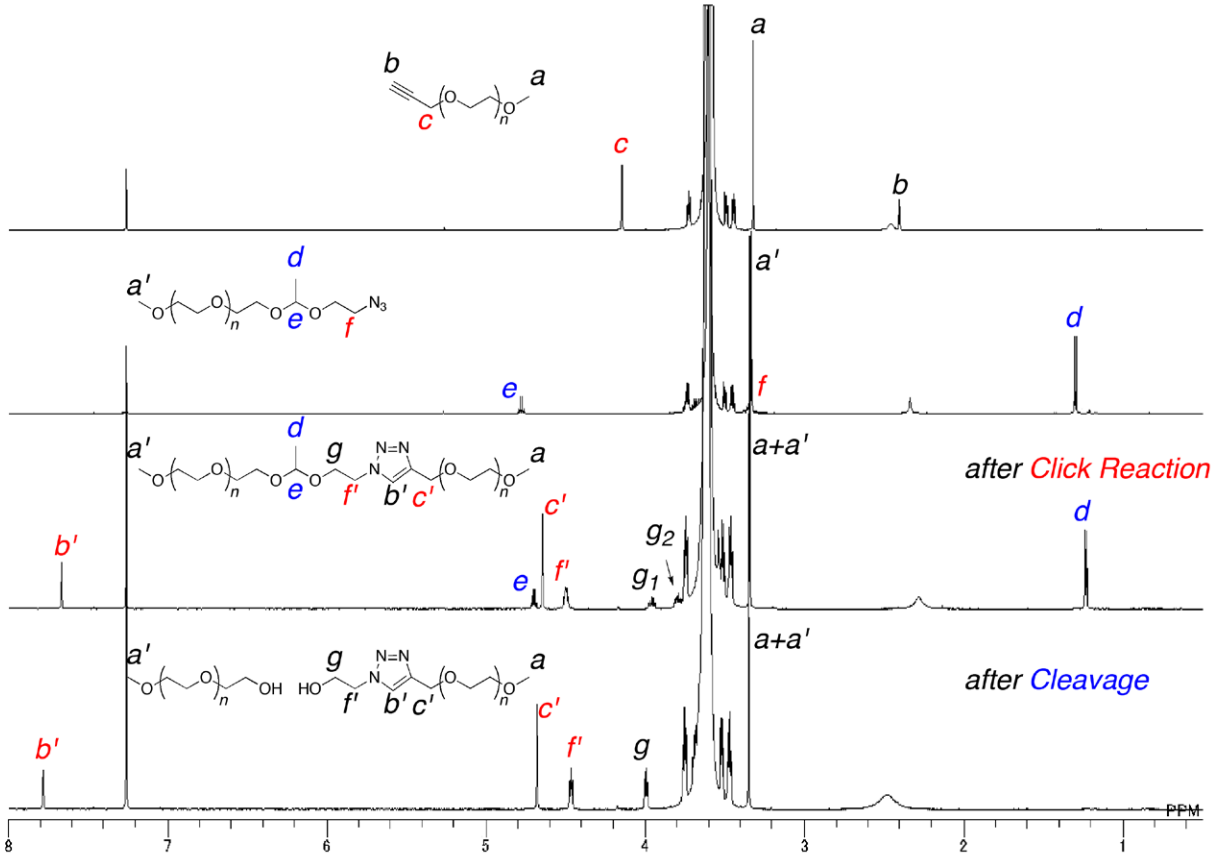

Figure S2. ^{1}H NMR spectra ($CDCl_3$, r.t.) of PEOs obtained in the same experiments as for Figure S1.

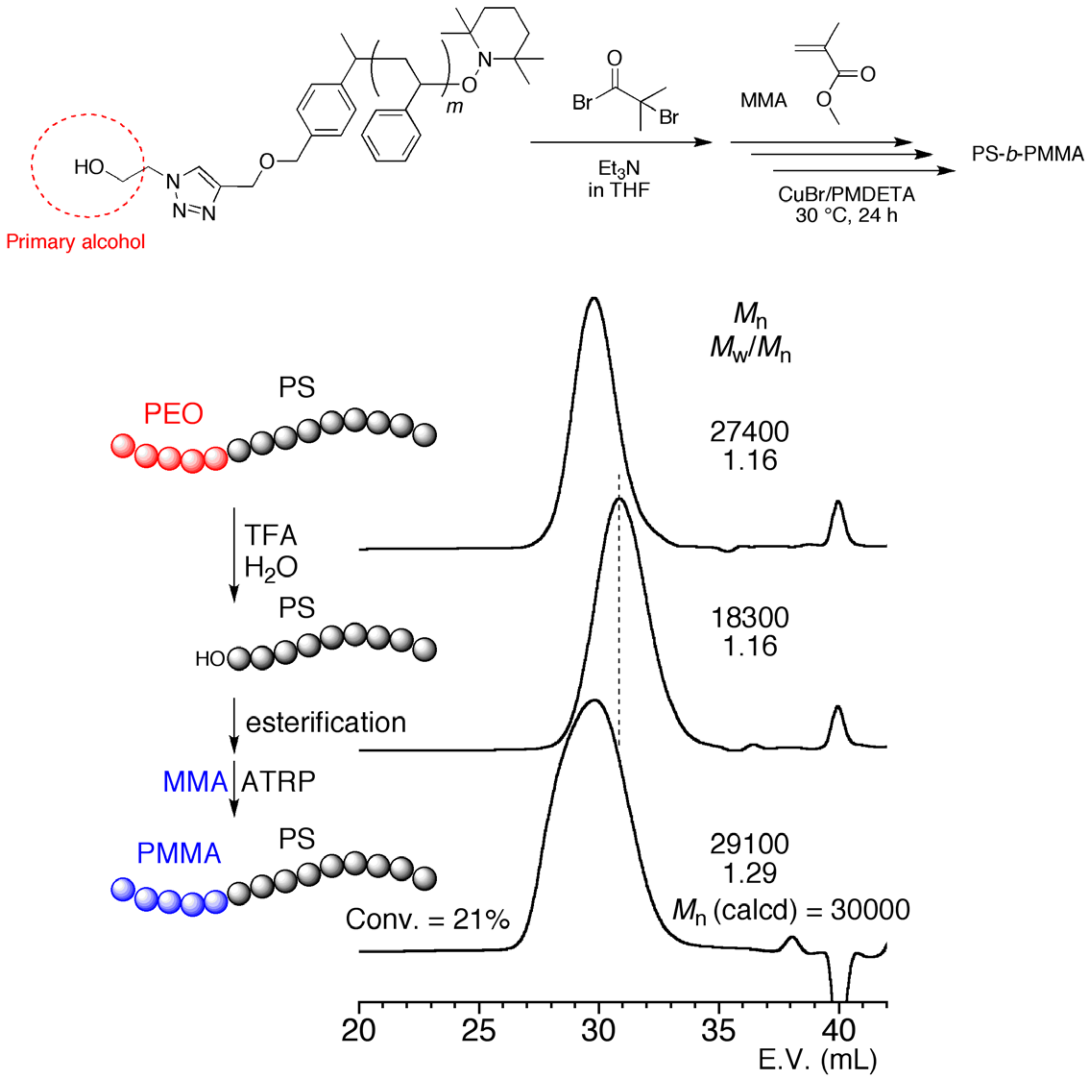

Figure S3. GPC curves for removal PEO segment from PEO-acetal-PS diblock copolymer, followed by Cu-catalyzed ATRP of MMA. For esterification: $[PS\text{-}OH]_0$ = 9.0 μmol (177 mg), [2-bromoisobutyryl bromide]$_0$ = 0.81 mmol, $[Et_3N]_0$ = 7.2 mmol in THF (5mL) at 0 °C for 15 h. For ATRP: $[PS\text{-}Br]_0$ = 4.0 μmol (79 mg), $[MMA]_0$ = 2.0 mmol, $[CuBr]_0$ = 0.04 mmol, $[PMDETA]_0$ = 0.08 mmol in toluene (1.8 mL) at 30 °C for 24 h (MMA conversion = 21%).

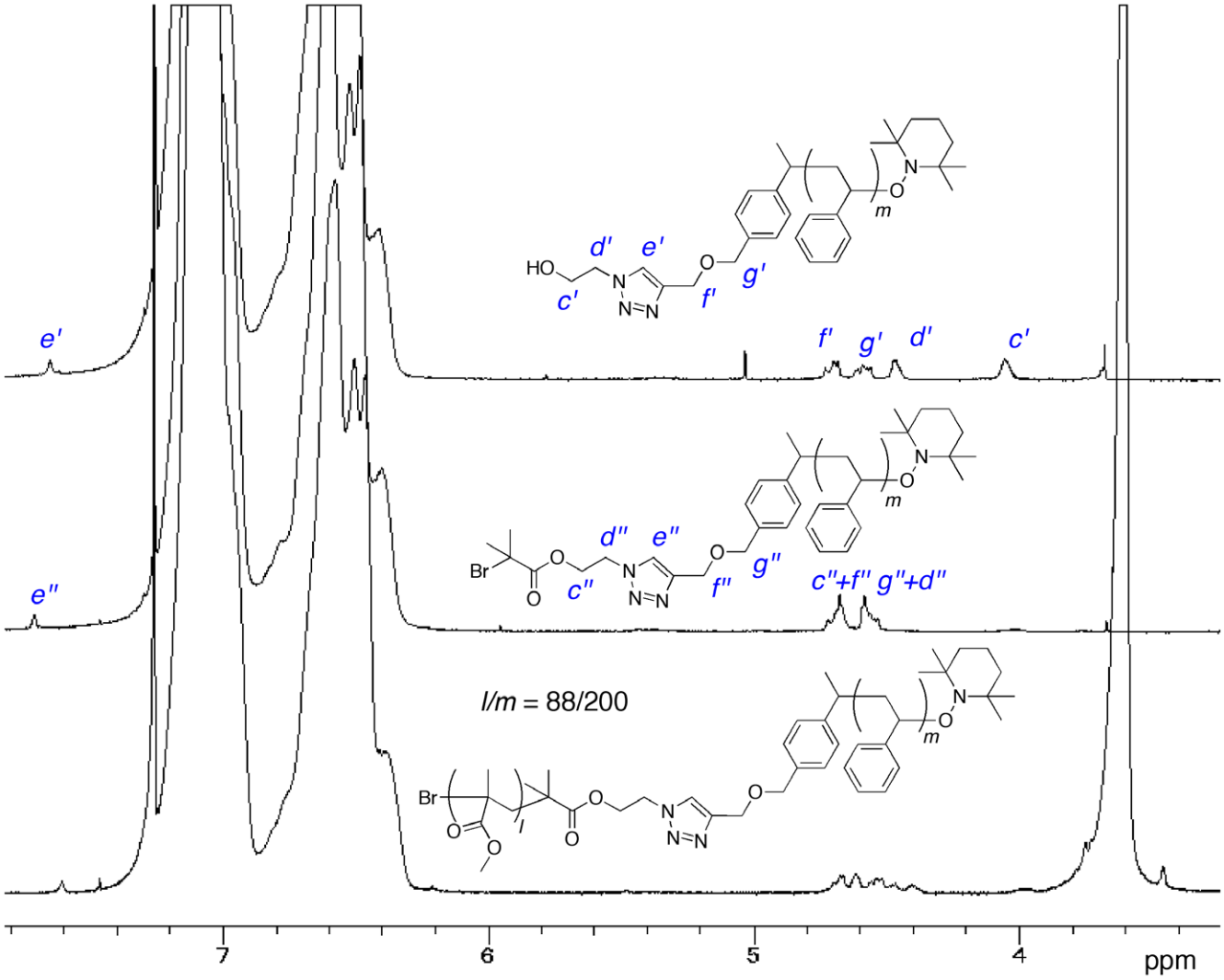

Figure S4. ^{1}H NMR spectra ($CDCl_3$, r.t.) of PS-OH, PS-Br, and PS-*b*-MMA block copolymer obtained in the same experiments as for Figure S3.

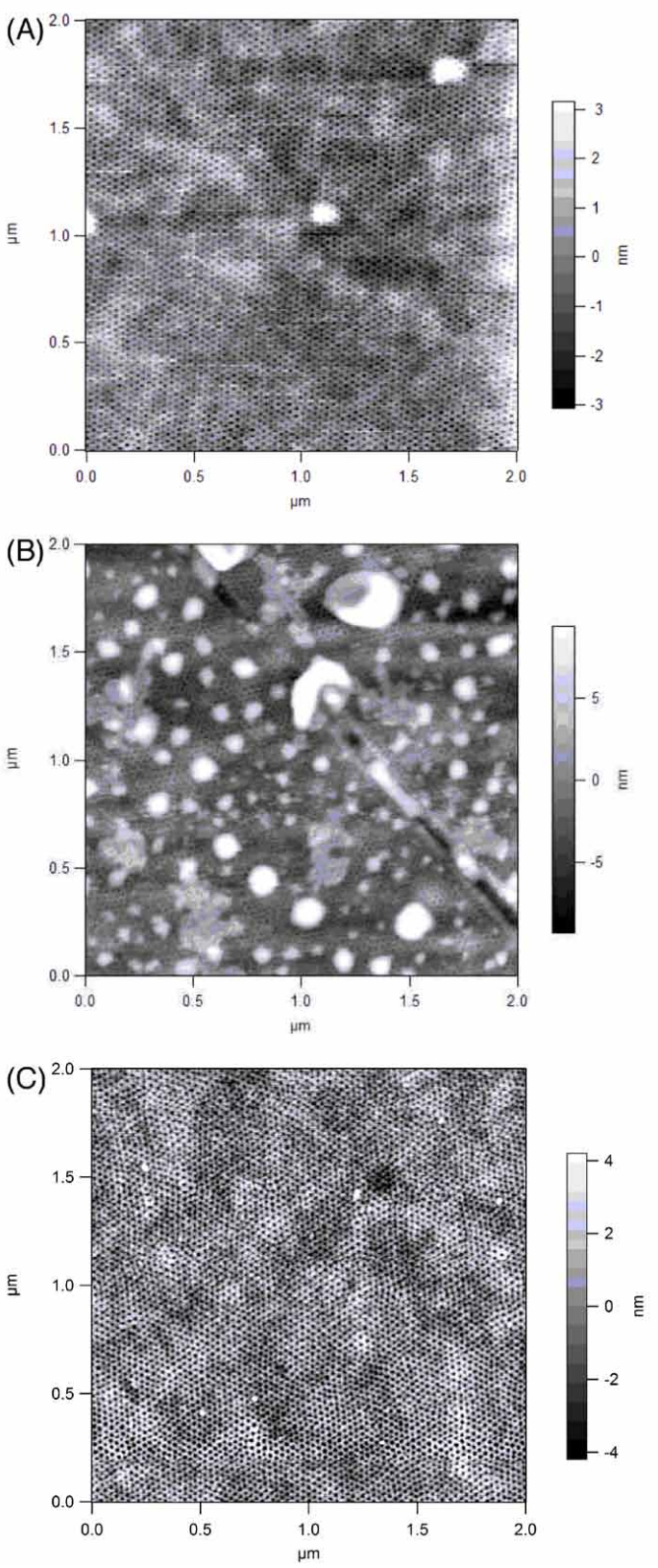

Figure S5. AFM images for morphologies of solvent-annealed films of the PEO-acetal-PS diblock copolymer (A), after exposure to TFA vapor for 4 h (B), and nanoporous film after immersion in methanol for 4h (C).