

Using Reversibility of the Dynamic Covalent Bond to Create Porosity in Highly Ordered Polymer Thin Films under Mild Conditions and Nano-pore Functionalization in the Gas Phase

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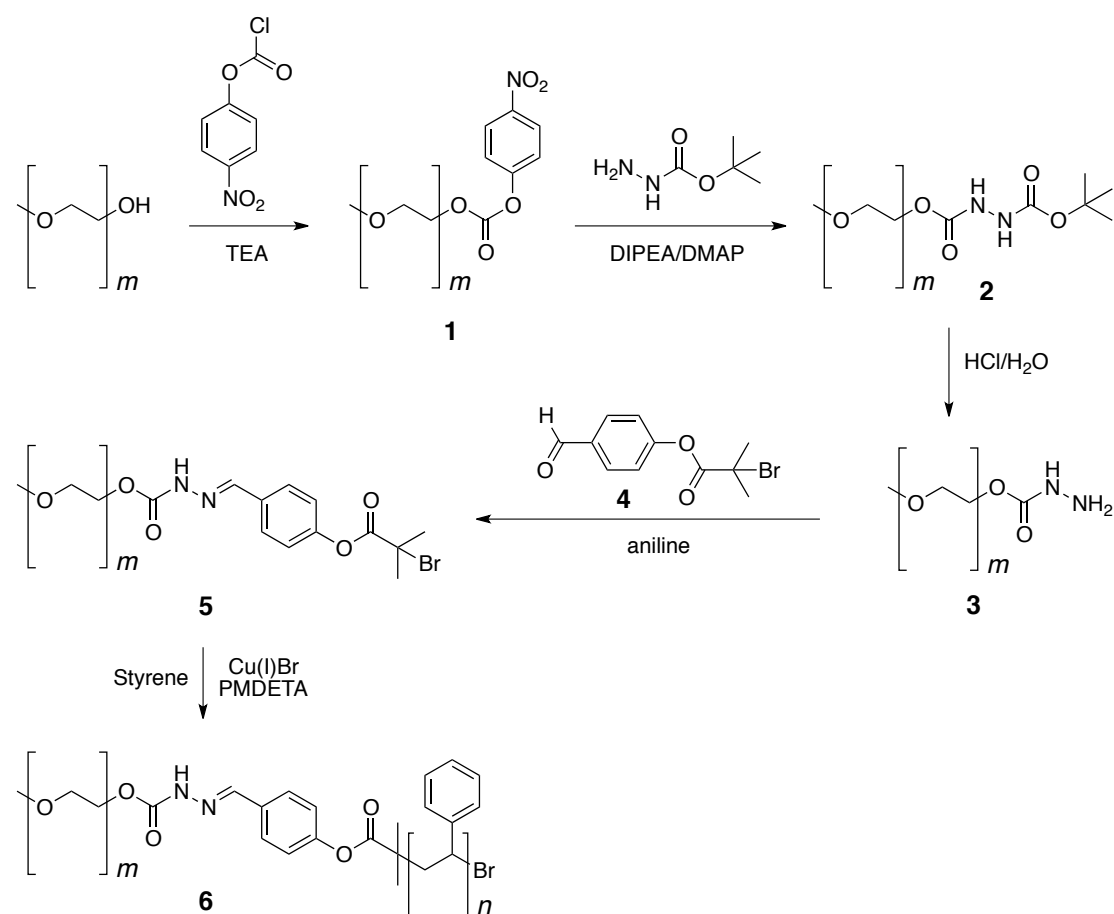
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General Methods and Materials

Polyethylene glycol monomethyl ether ($M_n = 5000$), 4-nitrophenyl chloroformate (*p*-NPC), triethylamine, *N,N*-diisopropylethylamine (DIPEA), 4-dimethylaminopyridine (DMAP), *tert*-butyl carbazate, hydrochloric acid (HCl, 25% aqueous solution), 2-bromoisobutyryl bromide, 4-hydroxybenzaldehyde, aniline, styrene, Cu(I)Br, and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), and 40% methylamine solution in methanol were purchased from commercial sources. Compound **4** was prepared according to the literature procedure (R. Narain, S. P. Armes, *Biomacromolecules*, **2003**, *4*, 1746). NMR spectra were recorded on a Bruker AV300 MHz spectrometer, using CDCl₃ as the solvent. Analytical GPC measurements were performed using a Viscotek GPC system equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. IR spectra were recorded using a Bruker Tensor 27 ATR-FT-IR spectrometer (Bruker Optic GmbH, Vienna, Austria). Top-view microstructures of the thin films were characterized using scanning electron microscopy (FEG-SEM, Zeiss LEO Gemini 1530, Germany) with an in-lens detector. Prior to imaging, the thin films were coated with platinum in order to avoid charging and to allow imaging at higher resolutions. Further morphological and structural characterization was carried out by transmission electron microscope (TEM) (Philips, CM 12) operating at an accelerating voltage of 100 kV. The tapping mode AFM images were taken using a multimode microscope with a NanoScope IIIa Controller (Nanoscope IIIa, Veeco, USA). The polymer film thickness was determined by a variable-angle spectroscopic ellipsometer (VASE) (M-2000F, LOT Oriel GmbH, Darmstadt, Germany).

Synthesis



Synthetic Scheme

Carbonate-Functionalized PEG (1): Polyethylene glycol monomethyl ether (5.0 g, 1 mmol) and triethylamine (0.3 g, 3 mmol) were dissolved in 50 mL anhydrous DCM at 0 °C, followed by the addition of *p*-NPCl (0.4 g, 2 mmol). After the addition was completed within ~30 min, the reaction mixture was allowed to warm to the room temperature and stirred for 24 h. After partially removing the solvent, the reaction mixture was precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 4.6 g (92%). ¹H NMR (δ , ppm, 300 MHz, CDCl₃): 3.37 (m, CH₃), 3.40-3.80 (br, CH₂CH₂O), 3.87 (t, CH₂), 4.44 (t, CH₂), 7.38 (d, 2H, Ar), 8.26 (d, 2H, Ar). ¹³C-NMR (δ , ppm, 125 MHz, CDCl₃): 59.1, 69.1-72.0, 122.3, 125.9, 145.2, 153.3, 157.7.

Boc-Protected PEG (2): To a solution of compound **1** (3 g, 0.6 mmol), *tert*-butyl carbazate (0.63 g, 4.8 mmol), DIPEA (0.39 g, 3 mmol), DMAP (0.04 g, 0.3 mmol), anhydrous DCM (30 mL) was added and the resulting reaction mixture was stirred at room temperature for 24h. After removing the solvent, the crude product was

dissolved in chloroform and thoroughly washed with aq. Brine solution. The organic layer was then dried over MgSO_4 , concentrated, and dissolved in a minimum amount of DCM and precipitated into an excess of anhydrous diethyl ether for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 2.6 g (88%). $^1\text{H-NMR}$ (δ , ppm, 300 MHz, CDCl_3): 1.45 (s, CH_3), 3.33 (m, CH_3), 3.40-3.73 (br, $\text{CH}_2\text{CH}_2\text{O}$), 3.86 (t, CH_2), 4.27 (t, CH_2), 6.61 (br, NH), 6.92 (br, NH). $^{13}\text{C-NMR}$ (δ , ppm, 125 MHz, CDCl_3): 18.8, 59.0, 64.6, 66.5, 69.4-71.9, 161.3.

Hydrazide End-functionalized PEG (3): Compound **2** (2.0 g, 1 mmol) was dissolved in 10 mL of H_2O at 0 °C, followed by the addition of HCl (2 mL). The reaction mixture was then stirred for 1 h. After removing the solvent, the crude product was dissolved in a mixture of DCM (10 mL) and triethylamine (3 mL) and stirred for another 1 h. The mixture was thoroughly washed with brine. Organic layer was then dried over MgSO_4 , concentrated, and dissolved in a minimum amount of DCM and precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 1.7 g (85%). $^1\text{H NMR}$ (δ , ppm, 300 MHz, CDCl_3): 3.37 (m, CH_3), 3.40-4.02 (br, $\text{CH}_2\text{CH}_2\text{O}$), 4.33 (br, CH_2), 8.84 (br, NH), 10.05 (br, NH). $^{13}\text{C-NMR}$ (δ , ppm, 125 MHz, CDCl_3): 59.1, 64.5, 69.3-71.9, 161.3.

PEG Macroinitiator 5: Hydrazide end-functionalized PEG **3** (1.0 g, 0.2 mmol) and aldehyde **4** (0.27 g, 1 mmol) were dissolved in 25 mL of chloroform, followed by the addition of aniline (9.3 mg, 0.1 mmol). The reaction mixture was stirred at room temperature for 24 h. After partially removing the solvent, the reaction mixture was precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solids were dried in a vacuum oven overnight at room temperature with a yield of 0.96 g (82%). $^1\text{H NMR}$ (δ , ppm, 300 MHz, CDCl_3): 2.06 (s, CH_3), 3.37 (m, CH_3), 3.40-4.05 (br, $\text{CH}_2\text{CH}_2\text{O}$), 4.38 (t, CH_2), 7.16 (d, 2H, Ar), 7.76 (d, 2H, Ar), 7.93 (s, CH), 8.88 (br, NH). $^{13}\text{C-NMR}$ (δ , ppm, 125 MHz, CDCl_3): 30.6, 55.2, 59.0, 61.7, 69.3-71.9, 121.3, 128.4, 132.1, 154.3, 169.9; GPC (CHCl_3): $M_n = 5800$, $M_w = 6200$, PDI (M_w/M_n) = 1.07.

PEG-*b*-PS Dynamic Covalent Block Copolymer 6: Macroinitiator **5** (0.5 g, 0.1 mmol), styrene (5.2 g, 50 mmol), PMDETA (35 mg, 0.2 mmol), and Cu(I)Br (14.3 mg, 0.1 mmol) were taken in a schlenk tube and degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred under N_2 at 110 °C for 5 h. After the

reaction was complete, it was cooled to room temperature and then precipitated into hexane for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 1.04 g (18%). ^1H NMR (δ , ppm, 300 MHz, CDCl_3): 0.82-2.37 (br, CH_2CH backbone; and α -CH from the end group, PS), 3.37 (m, CH_3 , PEG), 3.40-4.05 (br, $\text{CH}_2\text{CH}_2\text{O}$, PEG), 4.40 (t, CH_2 , PEG), 6.27-7.46 (br, Ar-H backbone, PS), 7.58 (t, 2H, Ar), 7.87 (s, CH), 8.74 (br, NH). GPC (CHCl_3): $M_n = 20000$, $M_w = 22000$, PDI (M_w/M_n) = 1.10.

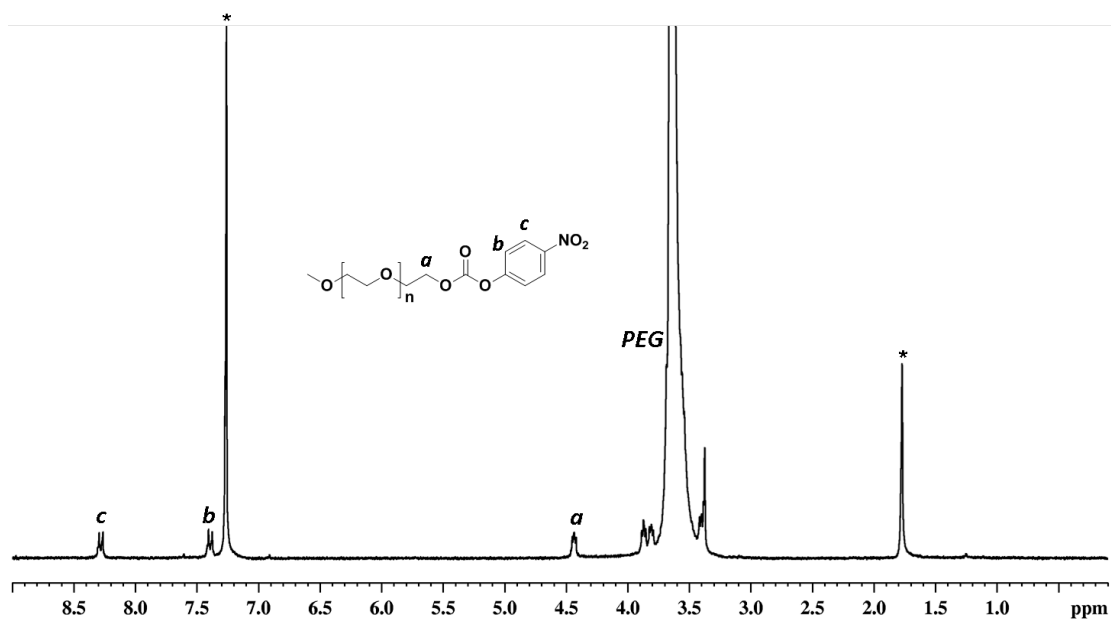


Figure S1. ^1H -NMR spectra of 1.

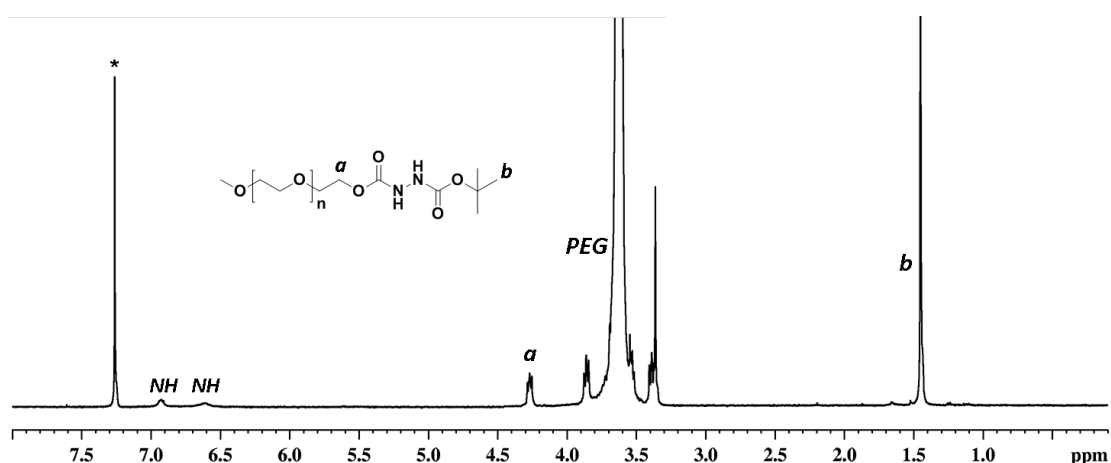


Figure S2. ^1H -NMR spectra of 2.

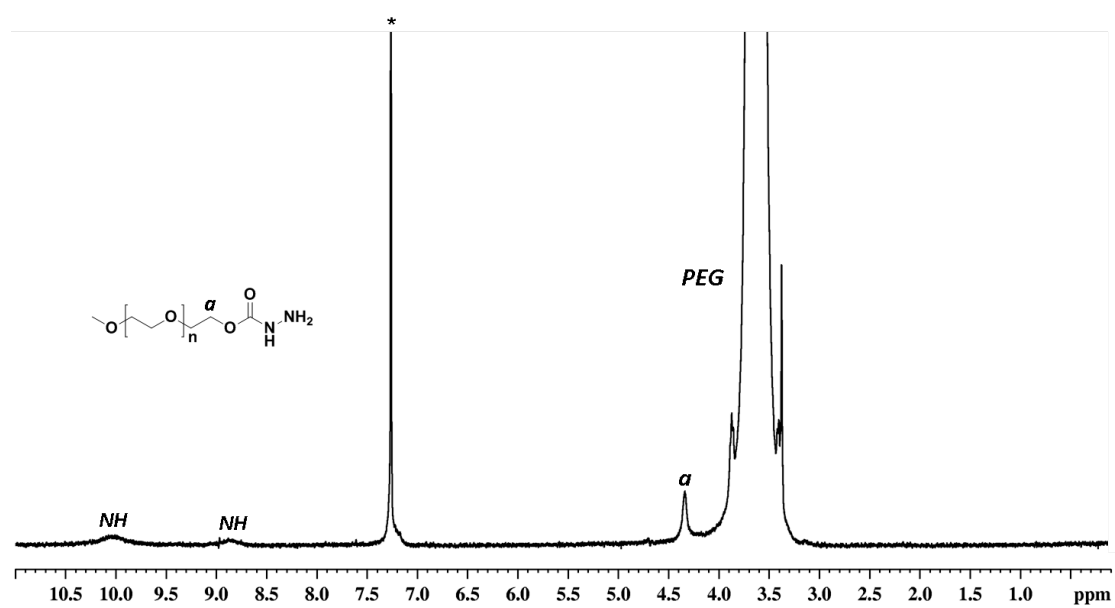


Figure S3. $^1\text{H-NMR}$ spectra of **3**.

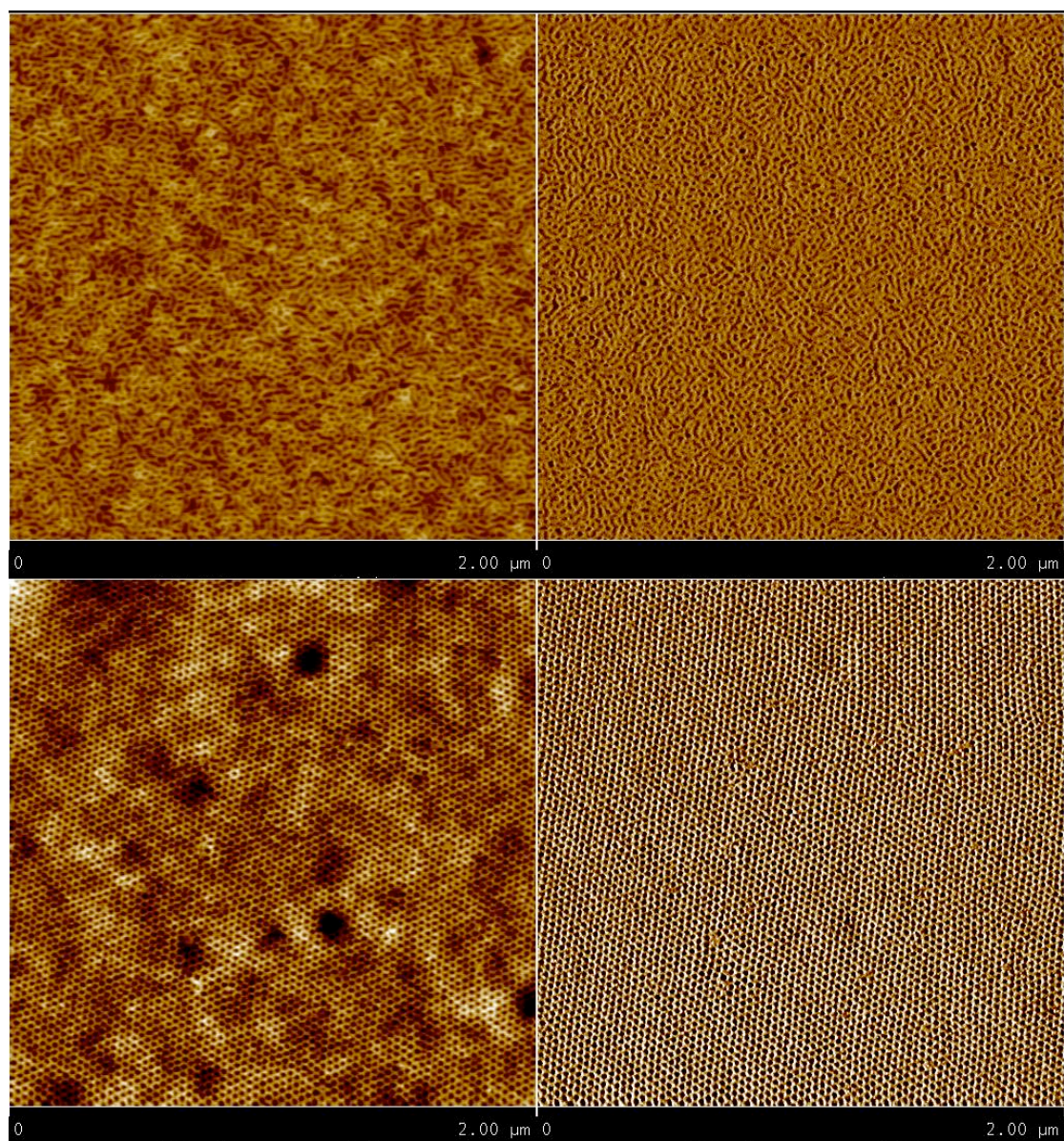


Figure S4. AFM images of PEG-*b*-PS thin film under different solvent annealing conditions: as-spun film (top), thin film annealed for 12 h (bottom).

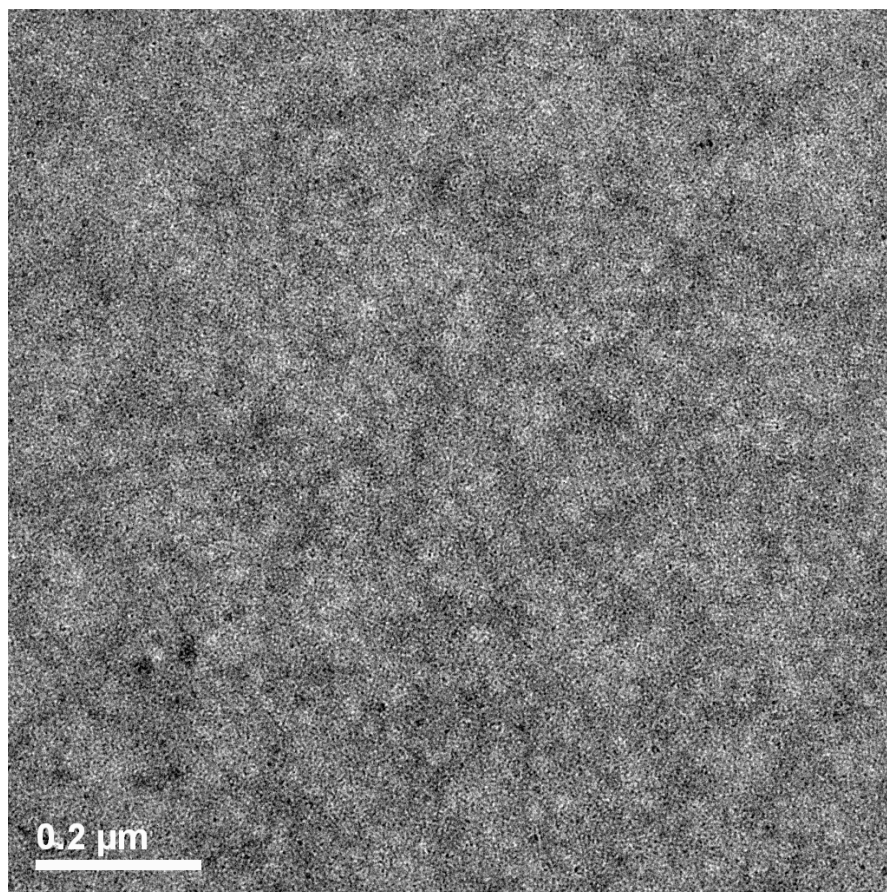


Figure S5. TEM image of the PEG-*b*-PS thin film before immersing into the water/methanol (2:1) bath.

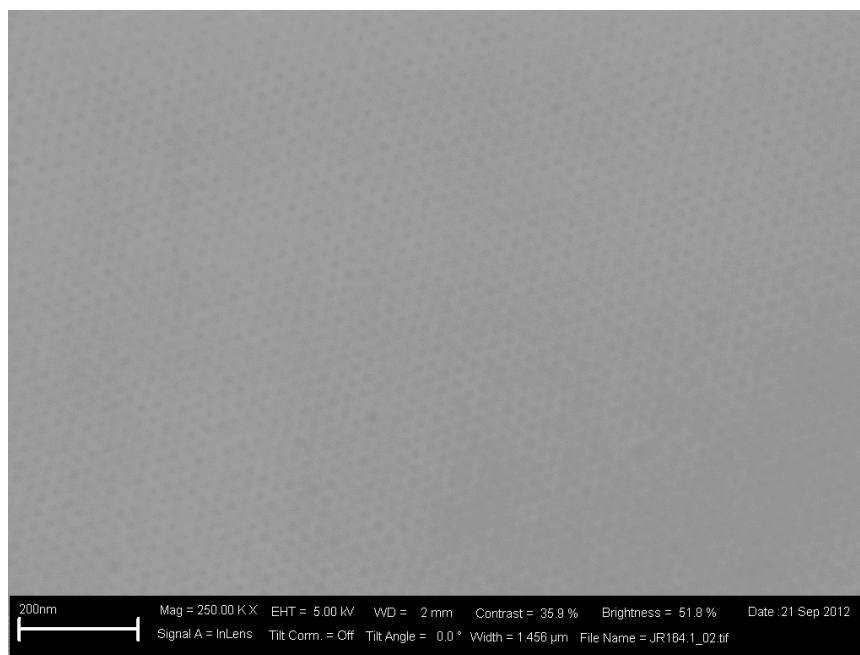


Figure S6. SEM image of the PEG-*b*-PS thin film before immersing into water/methanol (2:1) bath.

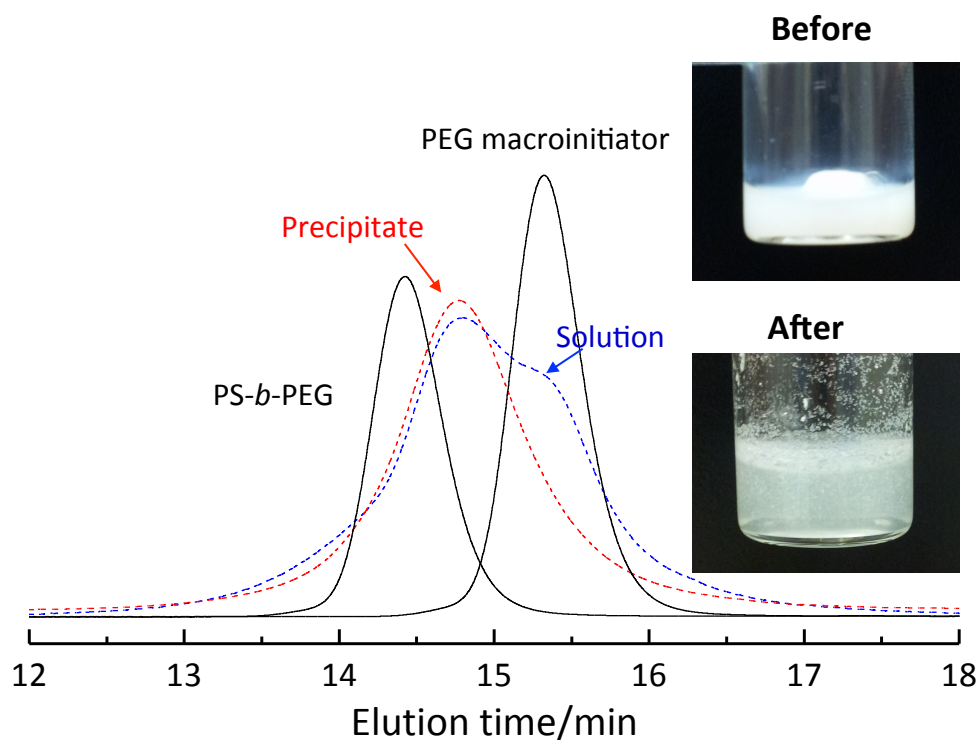


Figure S7. The diblock copolymer **4** in water before addition of HCl and after addition of HCl. The precipitate after addition of acid is most likely from polystyrene (PS) homopolymer. The blue GPC curve is obtained by evaporating water and redissolution of the material into chloroform.



Figure S8. Experimental set-up of the film functionalization.

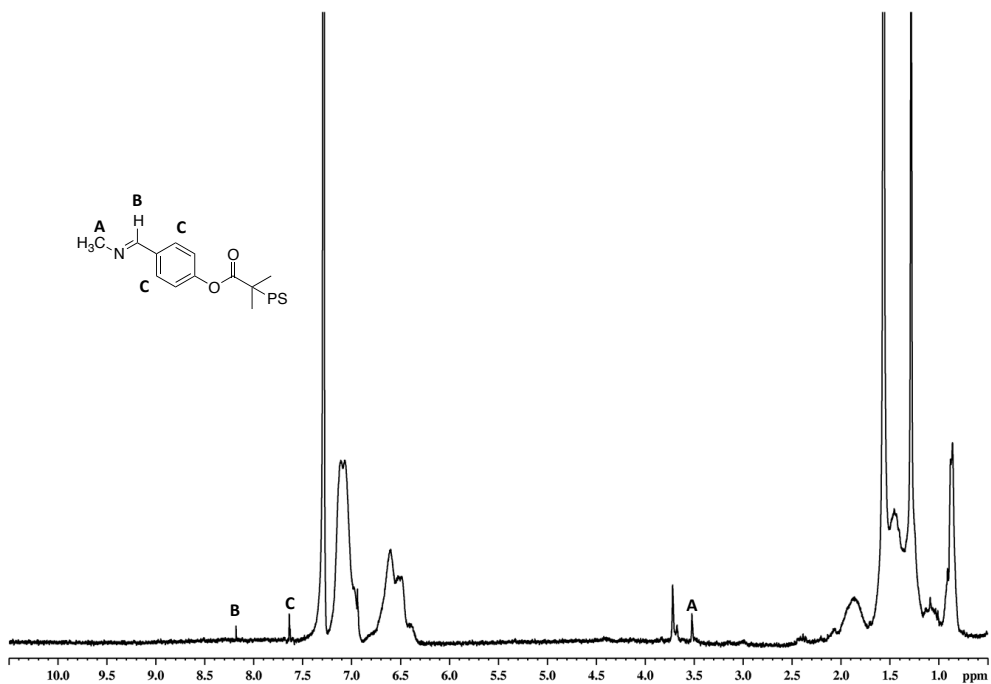


Figure S9. ¹H-NMR of the thin film after functionalization in deuterated chloroform. Prior to NMR analysis, the film was dried under high vacuum conditions for 3 days to remove traces of physically absorbed methanol and methylamine molecules.

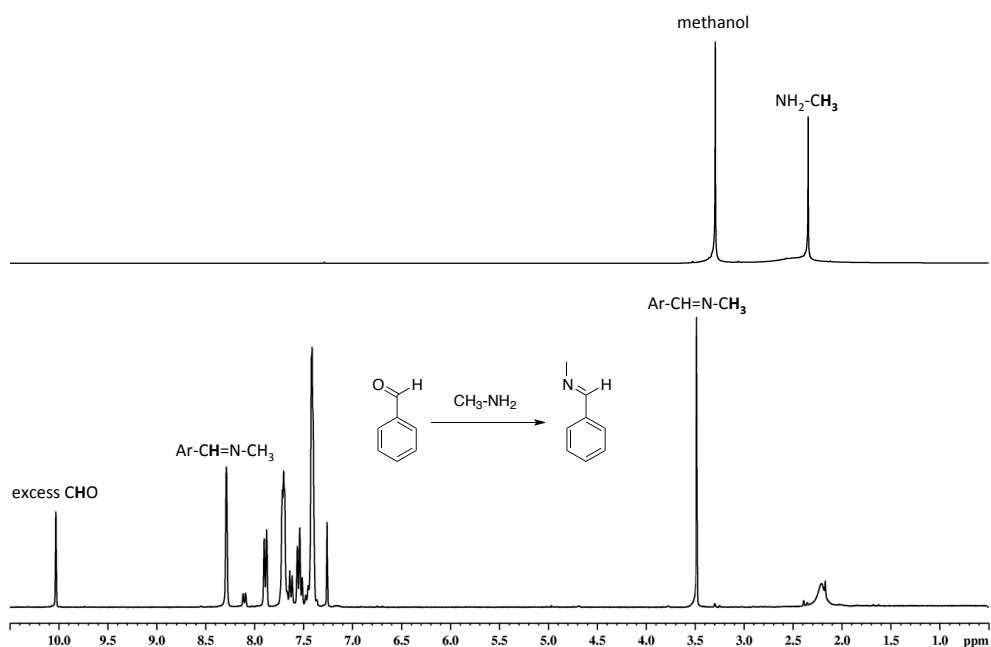


Figure S10. ¹H-NMR of methylamine in methanol (top) and the model reaction (bottom).