Urea-Bearing Copolymers for Guest-Dependent Tunable Self-Assembly

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Materials. All chemicals were purchased from Aldrich and used as received, unless specified otherwise. Methyl methacrylate was passed through neutral alumina immediately prior to use. ^{1}H and ^{13}C NMR Spectroscopy was performed on a Bruker Avance 400 MHz instrument, and referenced to residual solvent. ^{19}F NMR (376 MHz), the spectra were referenced to hexafluorobenzene (-163.0). Gel permeation chromatography was performed using a Waters chromatograph equipped with four 5 µm Waters columns (300 mm x 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å, using THF as the eluant, and calibrated with polystyrene standards (750-2 x 10^6 g/mol).

Synthesis of urea monomer 1a. Aniline (2.94 mL, 32.2 mmol) was added dropwise to a solution of isocyanatoethyl methacrylate (4.56 mL, 32.2 mmol) in 10 mL CH_2Cl_2 and the reaction mixture stirred for 16 h. The solvent was removed *in vacuo* and the remaining solid triturated with Et_2O. Recrystallization from THF/Hexanes afforded the white crystalline product (8.0 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.93 (s, 3H), 3.55 (t, 2H), 4.26 (t, 2H), 5.1-4.7 (bs, 1H), 5.58 (bs, 1H), 6.11 (bs, 1H), 6.9-7.1 (m, 3H), 7.5-7.8 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): 18.6, 39.6, 64.2, 121.0, 123.9, 126.5, 129.5, 136.3, 139.0, 156.8, 167.8; GC-MS $[M]^+$ = 248.1, expected $[M]^+$ = 248.1.

Synthesis of urea monomer 1b. This monomer was synthesized in a method analogous to the synthesis of **1a** using 4-fluoroaniline. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): 1.89 (s, 3H), 3.40 (t, 2H), 4.12 (t, 2H), 5.69 (m, 1H), 6.07 (t, 1H), 6.25 (bs, 1H), 7.07 (m, 2H), 7.39 (m, 2H), 8.59 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 18.7, 40.0, 64.2, 116.2, 116.4, 123.8, 123.9, 126.6, 134.6, 136.3, 156.3, 168.0; ^{19}F NMR (376 MHz, $CDCl_3$): 118.7; GC-MS $[M]^+$ = 266.1, expected $[M]^+$ = 266.1.

Tetrabutylammonium salts. The tetrabutylammonium salts **3a-c** and **4a-b** were synthesized by mixing a 1:1 mixture of Bu_4NOH with the corresponding acids (2:1 in the case of **3c**) for 1 h. The solvent was removed and the solid material dried under vacuum.

Representative procedure for RAFT polymerizations. Dithio(1-cyano-1-methylethyl)benzoate (45.7 mg, 0.206 mmol), monomer **1a** (513 mg, 2.06 mmol), MMA

(4.4 mL, 41.3 mmol), and AIBN (4.16 mg, 0.021 mmol) were dissolved in DMF. The reaction mixture was subjected to three freeze-pump-thaw cycles, and then heated to 75 °C for 17 h. The viscous mixture was diluted with CH_2Cl_2 and then precipitated in 9:1 (C_6H_{14}:Et_2O) to afford a pink solid. The polymer was then redissolved with CH_2Cl_2 and reprecipitated in 9:1 (C_6H_{14}:Et_2O) to afford the final polymer (4.2 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): 0.60-2.0 (m, CH, CH_2, CH_3), 3.41-3.63 (m, OCH_2, OCH_3), 3.83-4.0 (m, NCH_2), 6.20-6.33 (m, CH_2N-*H*), 6.9-8.0 (m, Ar-H), 8.48 (s, ArN-H).

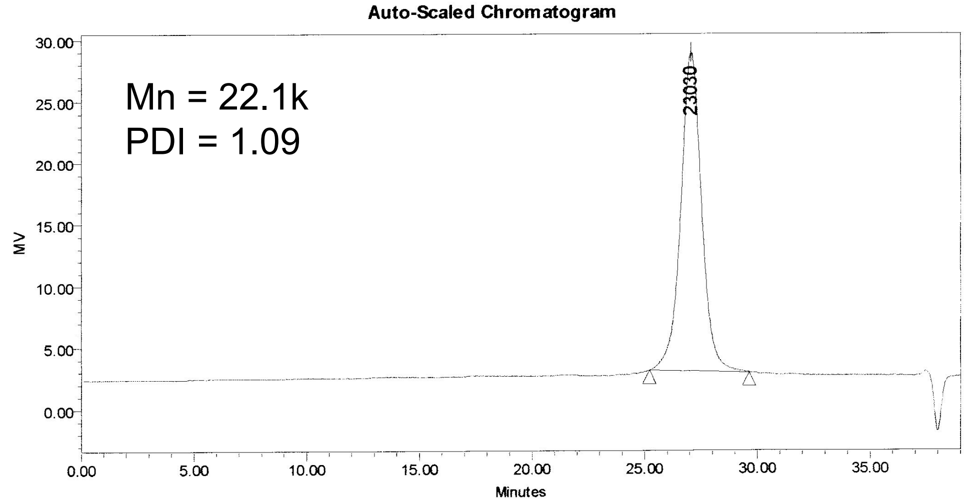

Fig. S1 GPC of polymer **2a**.

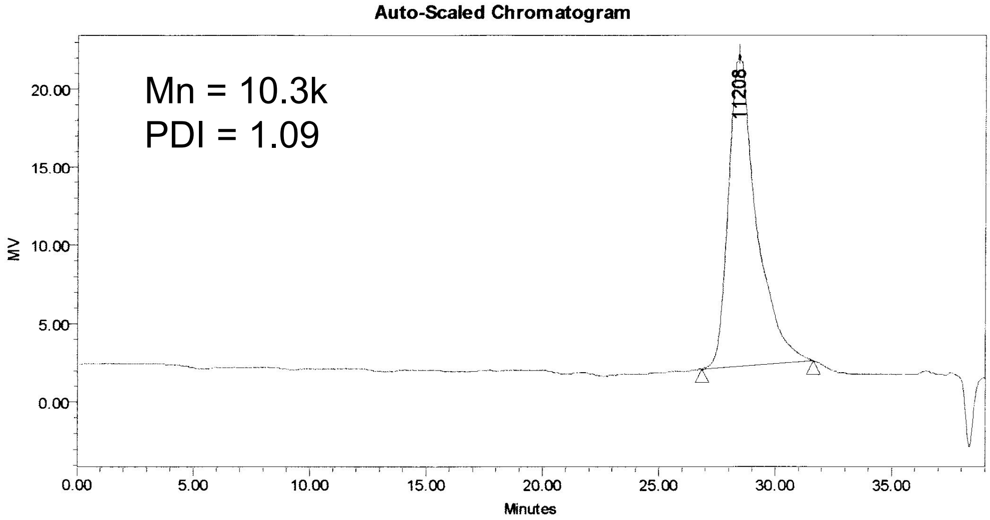

Fig. S2 GPC of polymer **2b**.

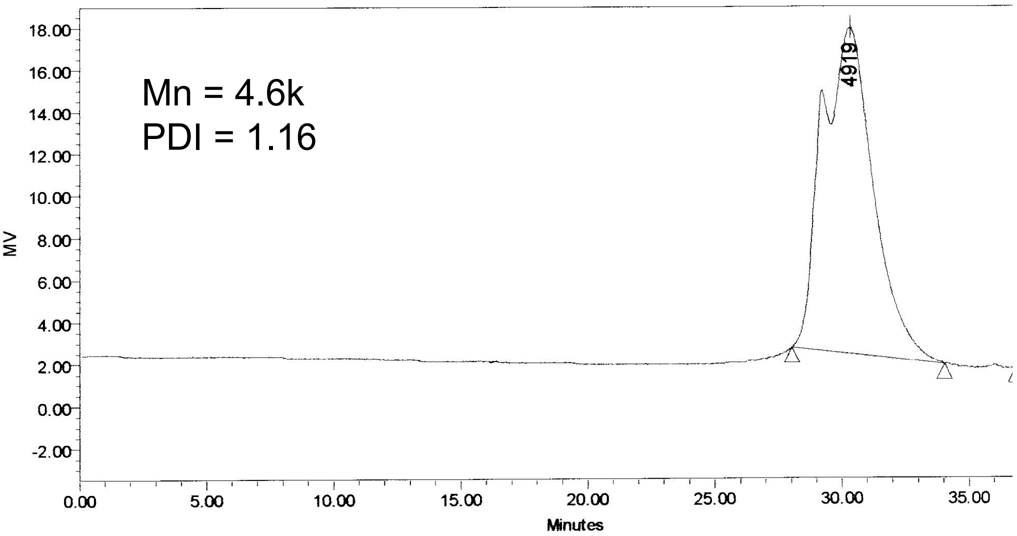

Fig. S3 GPC of polymer **2c**.

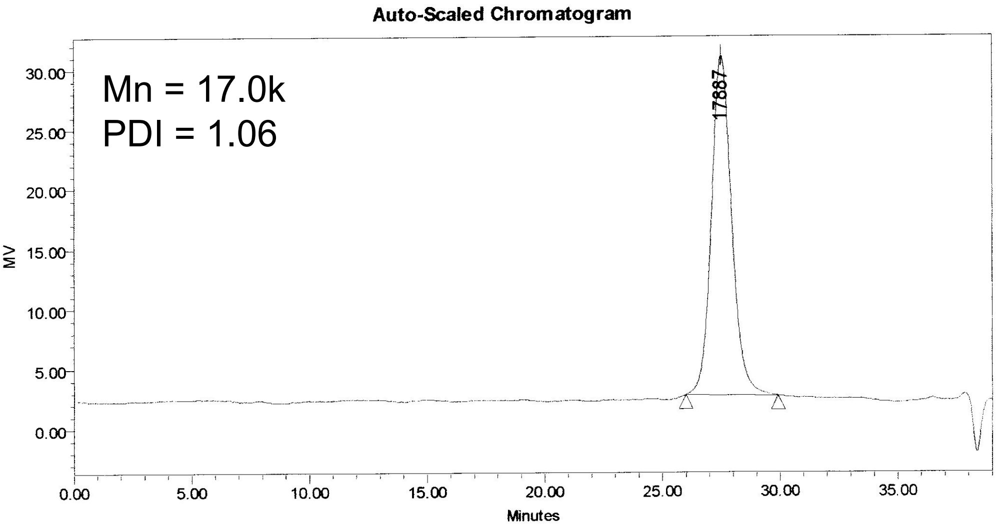

Fig. S4 GPC of polymer **2d**.

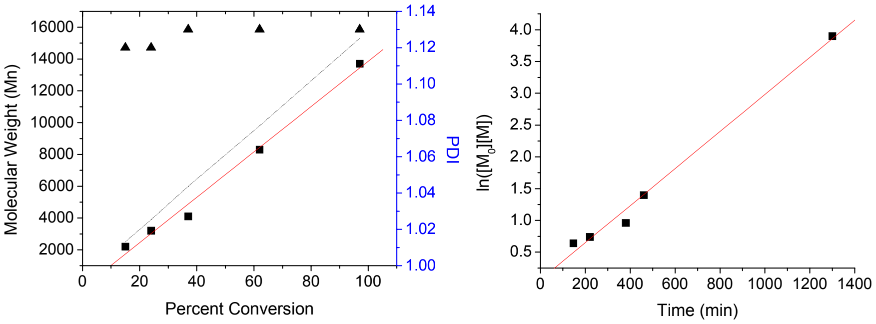

Fig. S5 RAFT copolymerization of **1b** and MMA in DMF (65 °C). (a) M_n and PDI (determined by GPC) versus percent conversion. The dotted line represents the theoretical molecular weight. (b) Semi-logarithmic plot versus reaction time.

NMR Titration Experiments. Association constants were determined by ^{1}H NMR or ^{19}F NMR spectroscopy titrating an 80 mM solution of guest in DMSO-d_6 into a 10 mM solution (relative to urea functionalities) of polymer host in DMSO-d_6. The change in chemical shift of the urea proton (N—H) at 8.56 ppm with respect to the concentration of guest added (Figure 1S and 2S) was then fitted using the NMR-Tit curve fitting program.

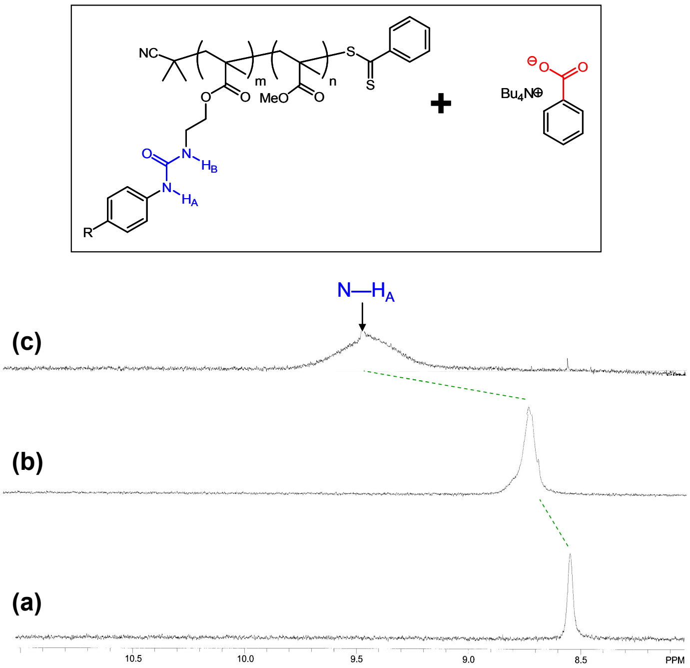

Fig. S6 Representative ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K) showing the downfield shift of the N-H$_A$ resonance (10mM solution of polymer with respect to the urea functionalities) (a) in the absence of carboxylate guest, (b) with 0.07 equivalents of guest, and (c) with 0.53 equivalents of guest in solution.

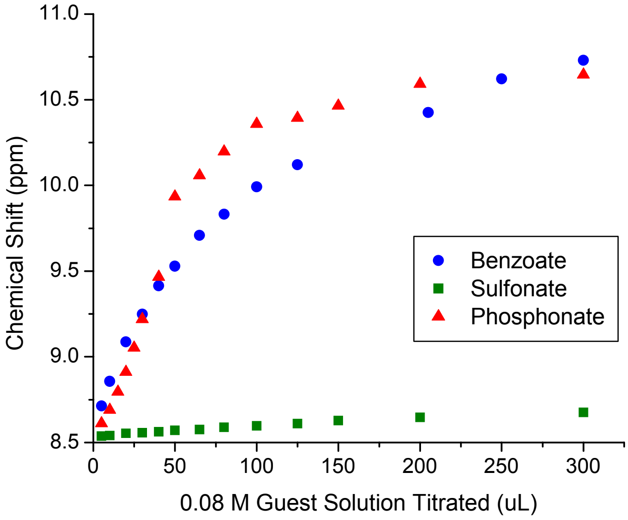

Fig. S7 A plot representing the changes in chemical shift of the urea N—H resonance of polymer **2a** (10 mM) with the addition of guest **3a**, **3b**, or **3c** (80 mM) in DMSO-d_6 (^{1}H NMR Spectroscopy, 400 MHz, 298 K).