Supporting Information

Facile Strategy to Well-Defined Water-Soluble Boronic Acid (Co)polymers

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Materials. 2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl-propionic acid (DMP) was prepared as previously reported.[1] *N*,*N*-Dimethylacrylamide (DMA, Fluka, 98%) was passed through a small column of basic alumina for catalyst removal prior to polymerization. 2,2'-Azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized from ethanol. *N*,*N*-Dimethylformamide (DMF, EMD 99.9%), anisole (Alfa Aesar, 99%), hexanes (Fisher, 98.5%), tetrahydrofuran (THF, EMD, 99.5%), $CDCl_3$ (Cambridge Isotope, 99% D), CH_2Cl_2 (EMD, HPLC), molecular sieves (Aldrich), and polystyrene-supported boronic acid resin (Lancaster, ~3.0 mmol/g) were used as received.

Synthesis of 4-pinacolatoborylstyrene. The title compound was prepared by modification of a previously reported method.[2] Preheated (185 ^{o}C) molecular sieves (1 g) were charged to a 250 mL round bottom flask and cooled to room temperature under nitrogen flow. CH_2Cl_2 (100 mL) was added and the mixture was rapidly stirred while 4-vinylphenylboronic acid (5.0 g, 33.8 mmol) pinacol (4.2 g, 35.5 mmol) were added. The mixture was stirred for 18 h, and the molecular sieves were removed by celite filtration and washed with CH_2Cl_2 (100 mL). The filtrate was concentrated under vacuum to give a residual oil in 97% yield. ^{1}H-NMR (400 MHz, $cdcl_3$): 7.82-7.80 (d, 2H, J = 7.8 Hz, Ph-***H***C2 and Ph-***H***C6), 7.45-7.43 (d, 2H, J = 7.8 Hz, Ph-***H***C3 and Ph-***H***C5), 6.76-6.72 (dd, 1H, J = 10.9 and 6.7 Hz, Ph-C***H***=CH_2), 5.87-5.82 (d, 1H, J = 17.6 Hz, Ph-CH=C$\boldsymbol{H}_2$-E), 5.33-5.31 (d, 1H, J = 10.9 Hz, Ph-CH=C$\boldsymbol{H}_2$-Z), 1.38 (s, 12H, ([C$\boldsymbol{H_3}$]$_2$C-C[C$\boldsymbol{H_3}$]$_2$). ^{13}C-NMR (100.6 MHz, $cdcl_3$): 140.1 (Ph***C***4-CH=CH_2), 136.8 (Ph-***C***H=CH_2), 134.9 (Ph-H***C***2 and Ph-H***C***6), 125.4 (Ph-H***C***3 and Ph-H***C***5), 114.8 ((Ph-CH=$\boldsymbol{C}H_2$), 83.7 ([CH_3]$_2$***C***-***C***[CH_3]$_2$), 24.8([$\boldsymbol{C}H_3$]$_2$C-C[$\boldsymbol{C}H_3$]$_2$), IR ((neat): 2980 and 2932 (C-C*s*), 1610,1514, 1360 (C=C), 1144, 1089(C=C*b*), 858 and 739 (C-C*b*) cm^{-1}.

RAFT polymerizations of 4-pinacolatoborylstyrene (pBSt). An example RAFT polymerization procedure was as follows. pBSt (1.527 g, 6.642 mmol), DMP (0.0236 g, 0.0647 mmol), AIBN (1.65 g, 0.0101 mmol), and anisole (1.5 mL) were sealed in a 20 mL vial and purged with nitrogen for 30 min. The reaction vial was placed in a preheated reaction block at 70 °C. Samples were removed periodically by syringe to determine molecular weight, polydispersity index, and monomer conversion by gel permeation chromatography (GPC). The polymerization was quenched after 9 h by removing the polymerization from heat and exposing the reaction solution to air. The resulting poly(4-pinacolatoborylstyrene) (PpBSt) (74% conversion; M_n = 16,900 g/mol; M_w/M_n = 1.16) was isolated by precipitation into hexanes, filtration, and drying under vacuum.

RAFT block copolymerizations of *N,N*-dimethylacrylamide (DMA) with pBSt. An example RAFT polymerization procedure was as follows. DMA (0.362 g, 3.65 mmol), PpBSt macro CTA (M_n = 19,100 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.10) (0.45 g, 0.024 mmol), AIBN (1.58 mg, 0.0096 mmol), and anisole (1.0 mL) were sealed in a 20 mL vial and purged with nitrogen for 30 min. The reaction vial was placed in a preheated reaction block at 70 °C. Samples were removed periodically by syringe to determine molecular weight, polydispersity index, and monomer conversion by GPC. The polymerization was quenched after 6 h by removing the polymerization from heat and exposing the reaction solution to air. The resulting poly(4-pinacolatoborylstyrene)-*b*-poly(*N*,*N*-dimethylacrylamide) (PpBSt-*b*-PDMA) (99% conversion; M_n = 36,600 g/mol; $M_\mathrm{w}/M_\mathrm{n}$ = 1.08) was isolated by precipitation into hexanes, filtration, and drying under vacuum.

Deprotection of polymeric pinacol ester to yield boronic acid polymers. An example procedure is as follows. PpBSt (0.100 g, 0.437mmol, M_n = 19,000 g/mol, M_w/M_n = 1.12) was mixed with an excess amount (×9) of polystyrene-supported boronic acid (1.31 g, 3.9 mmol, ~3.0 mmol/g) in a 50 mL round bottom flask containing of acetonitrile/2 vol.-% trifluoroacetic acid (15 mL), and the reaction mixture was refluxed for 24 h. After this time, the solvent was evaporated, and DMF/5 vol.-% deionized water was added to the reaction mixture. The solution was filtered to remove the polystyrene-supported boronic acid resin, and the solvent was evaporated. The remaining solid was dissolved in 5% (w/v) aqueous NaOH solution and dialyzed against the 5% (w/v) aqueous NaOH (24 h) followed by deionized water (24 h). The polymer precipitated during dialysis with deionized water, and was then filtered and dried. ^{1}H NMR spectroscopy of this sample was conducted in D_2O. The addition of NaOD was required for solubility.

Micellar solution preparation. PpBSt-*b*-PDMA (25 mg M_n = 60,800, M_w/M_n = 1.09) was dissolved in THF (0.5 mL). The resulting solution was placed in 3,500 MWCO dialysis tubing and dialyzed overnight against deionized water (1000 mL) with constant stirring. The resulting solution was sonicated for 1 h and then filtered with a 0.45 μm nylon syringe filter. DLS measurements on this solution were recorded at 25 °C.

Analyses. GPC was conducted in DMF at 55 °C with a flow rate of 1.0 mL/min (Viscotek GPC Pump; Columns: ViscoGel I-Series G3000 and G4000 mixed bed columns: molecular weight range $0 – 60 \times 10^3$ and $0 – 400 \times 10^3$ g/mol, respectively). Detection consisted of a Viscotek refractive index detector operating at λ = 660 nm, a Viscotek UV-Vis detector operating at λ = 254 nm, and a Viscotek Model 270 Series Platform, consisting of a laser light scattering detector (operating at 3 mW, λ = 670 nm with detection angles of 7° and 90°) and a four capillary viscometer. Molecular weights were determined by the triple detection method. For the PpBSt homopolymers, a d*n*/dc = 0.109 mL/g was employed. Block copolymer molecular weights were determined by in situ calculation of d*n*/dc, assuming 100% mass recovery. ^{1}H NMR spectroscopy was conducted in $CDCl_3$ or DMSO-d_6 with a Bruker Avance 400 spectrometer operating at 400 MHz. Dynamic light scattering was conducted with a Malvern Zetasizer Nano-S equipped with a 4 mW, 633 nm He-Ne laser, and an Avalanche photodiode detector at an angle of 173°.

Example GPC traces from the homopolymerization of pBSt.

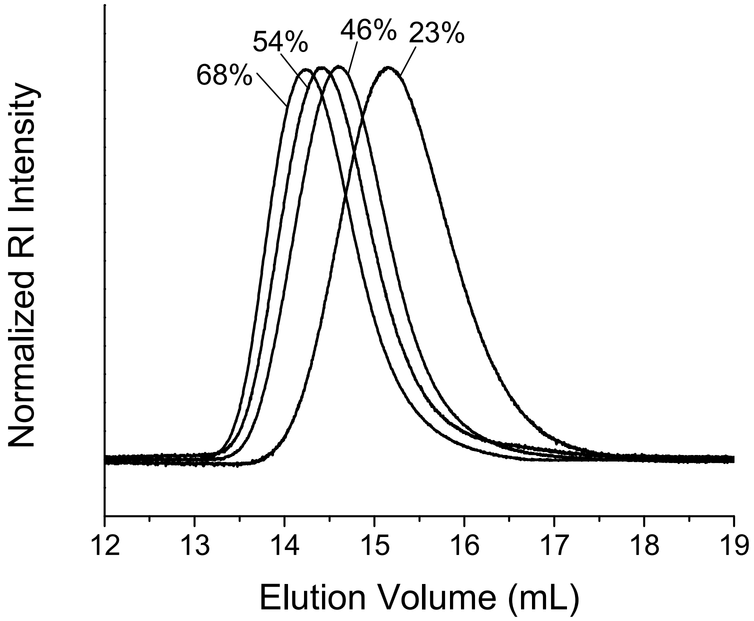

Figure S1. GPC traces as a function of monomer conversion for the RAFT polymerization of pBSt ([pBSt]: [CTA]: [Init] = [200]: [1]: [0.3], 50 vol.-% anisole, T = 70 °C.

References

(1) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002,** *35,* 6754.
(2) Vogels, C. M.; Wellwood, H. L.; Biradha, K.; Zaworotko, M. J.; Westcott, S. A. *Can. J. Chem.* **1999,** *77,* 1196.