Supporting Information

Condensation of Arylboroxine Structures on Lewis Basic Copolymers as a Noncovalent Means of Polymer Functionalization

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Experimental

General. NMR spectra were acquired on either a 400 MHz Varian Mercury or a 500 MHz Varian INOVA system. ^{1}H NMR spectra are referenced to the deuterated solvent; ^{19}F chemical shifts are referenced to CCl_3F. Attenuated total reflection IR (ATR-IR) spectra were obtained using a Thermo Nicolet IR100 on solid samples. The PS/4-VP (90 mol % 4-VP) copolymer was purchased from Aldrich and used as received. The PS/4-VP (22 mol % 4-VP) copolymer was purchased from Polymer Source and used as received. The PS/4-VP (50 mol % 4-VP) copolymer was synthesized using conventional free radical polymerization techniques. The molecular weight of the 50 mol% 4-VP polymer was determined using GPC equipped with a Waters 410 differential refractometer in THF with a flow rate of 0.8 mL/min by comparison to polystyrene standards. 4-Fluorophenylboronic acid was purchased from Frontier Scientific and used as received. 4Å molecular sieves were purchased from Aldrich and activated prior to use.

Synthesis of arylboroxine functionalized PS/4-VP copolymers. The copolymer was dissolved in CH_2Cl_2 or CH_2Cl_2/DMF that had been pre-dried with $CaCl_2$ pellets. Activated 4 Å molecular sieves were added followed by enough 4-fluorophenylboronic acid to give a 2:1 4-VP:arylboroxine ratio. The samples were stirred for 2-3 hours at room temperature, decanted away from the molecular sieves, and the solvent removed under reduced pressure. The solid residue was dried in a 50˚C oven for approximately 18 hours at atmospheric pressure.

Thermal Analyses. Differential scanning calorimetry (DSC) measurements were performed on ca. 10 mg samples under continuous nitrogen purge (50 mL/min) on a TA

Instruments DSC 2010. Data represent the second heating cycles using a heating scan rate of 20 °C/min. The thermogravimetric analysis was performed on a TA Instruments model 2050 analyzer (TGA) using a heating scan rate of 20 °C/min.

Synthesis of PS/4-VP (50 mol% 4-VP). Styrene (26.0 g, 0.25 mol) and 4-vinylpyridine (26.3 g, 0.25 mol) were dissolved in ethyl acetate (28 mL) and sparged in a round bottom flask (Solution A). AIBN (0.5 g, 3 mmol) was dissolved in ethyl acetate (11 mL) and sparged (Solution B). To a three neck flask equipped with an overhead stirrer and reflux condenser was added 8 mL of Solution A and 3 mL of Solution B. The reaction was refluxed under nitrogen for 15 min at which time the remainder of Solution A and Solution B were added. The reaction mixture was refluxed for an additional 3 h. The polymer was precipitated, isolated, and washed with dilute HCl followed by dilute NaOH. The polymer was dried, taken up in CH_2Cl_2, and filtered. The methylene chloride was removed by rotary evaporation and the resulting polymer was dried again in an oven at 50˚C.

Figure S1. TG thermograms of parent polymer PS/4-VP (22 mol% 4-VP) and 4-fluorophenylboroxine functionalized copolymers having ratios of 4-VP/arylboroxine varying from 2.7:1 to 0.93:1.

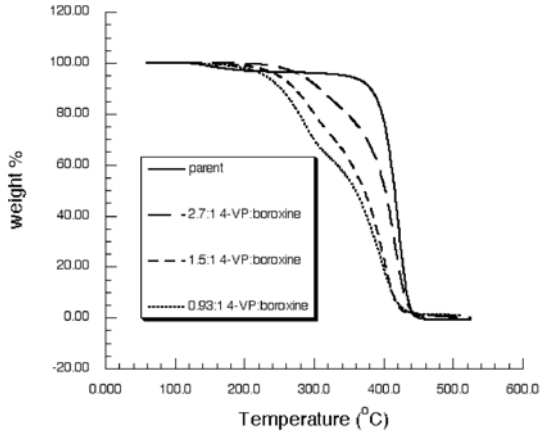

Figure S2. Room temperature ^{1}H NMR spectrum of functionalized 50 mol% 4-VP copolymer (sample concentration=8 mg/mL).

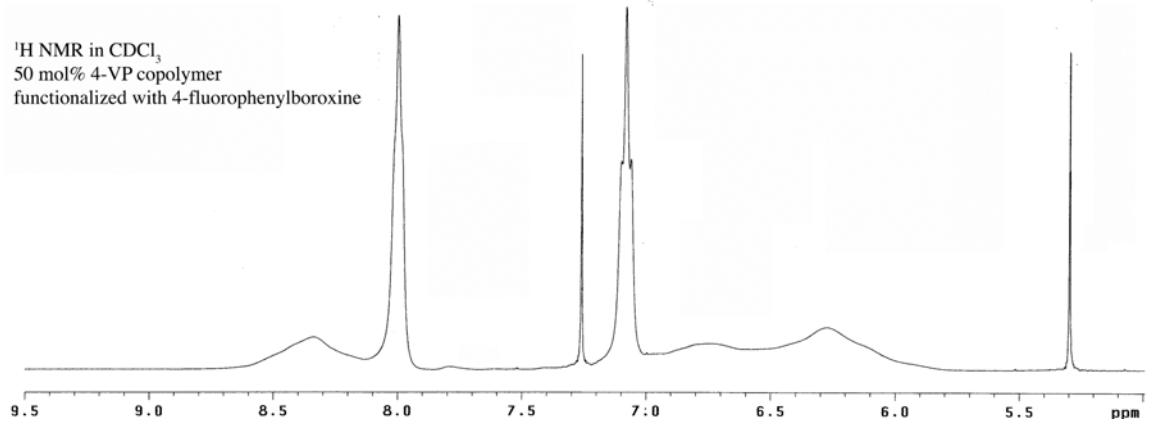

Figure S3. Room temperature ^{19}F NMR spectrum of functionalized 50 mol% 4-VP copolymer (sample concentration=8 mg/mL).

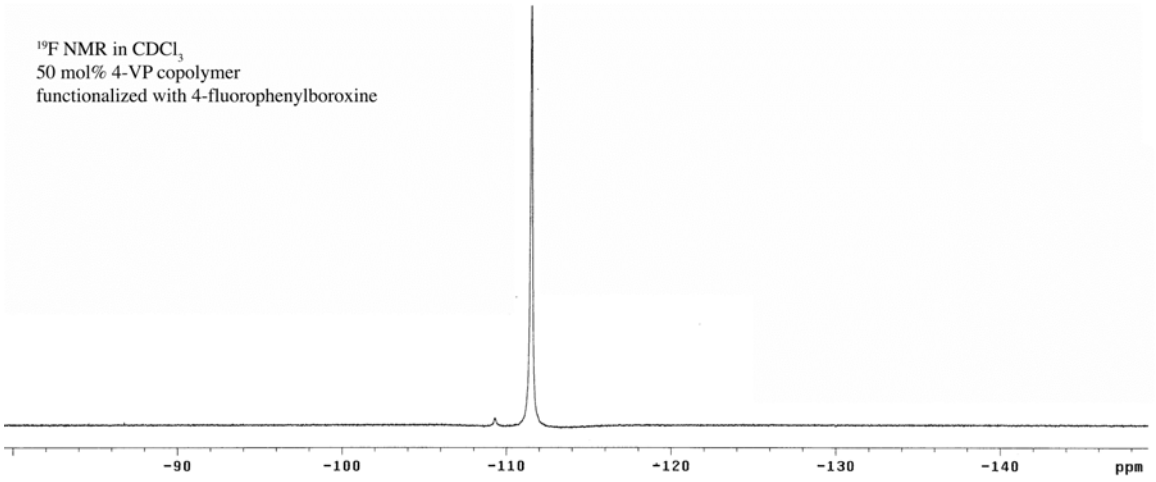

Figure S4. Room temperature ^{1}H NMR spectrum of functionalized 90 mol% 4-VP copolymer (sample concentration=8 mg/mL).

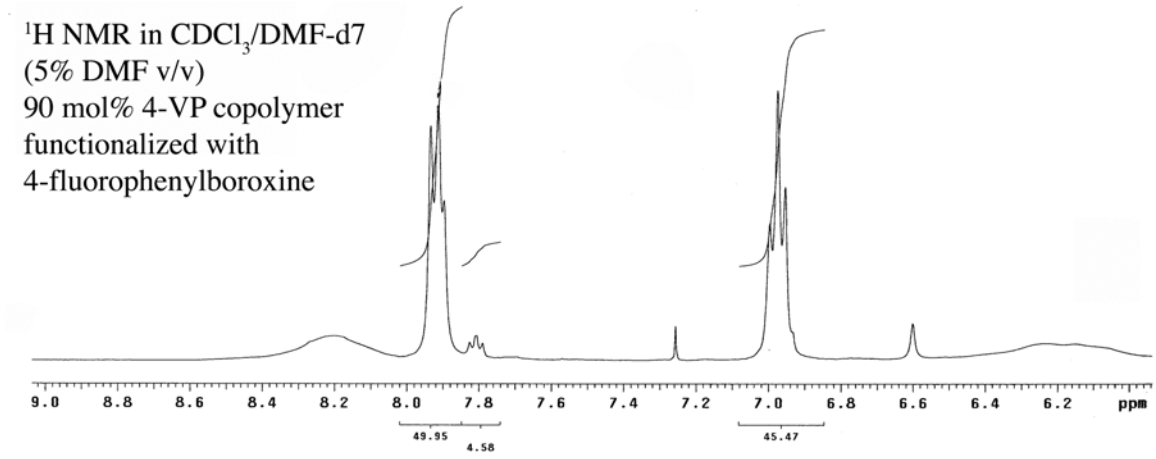

Figure S5. Room temperature ^{19}F NMR spectrum of functionalized 90 mol% 4-VP copolymer (sample concentration=8 mg/mL).

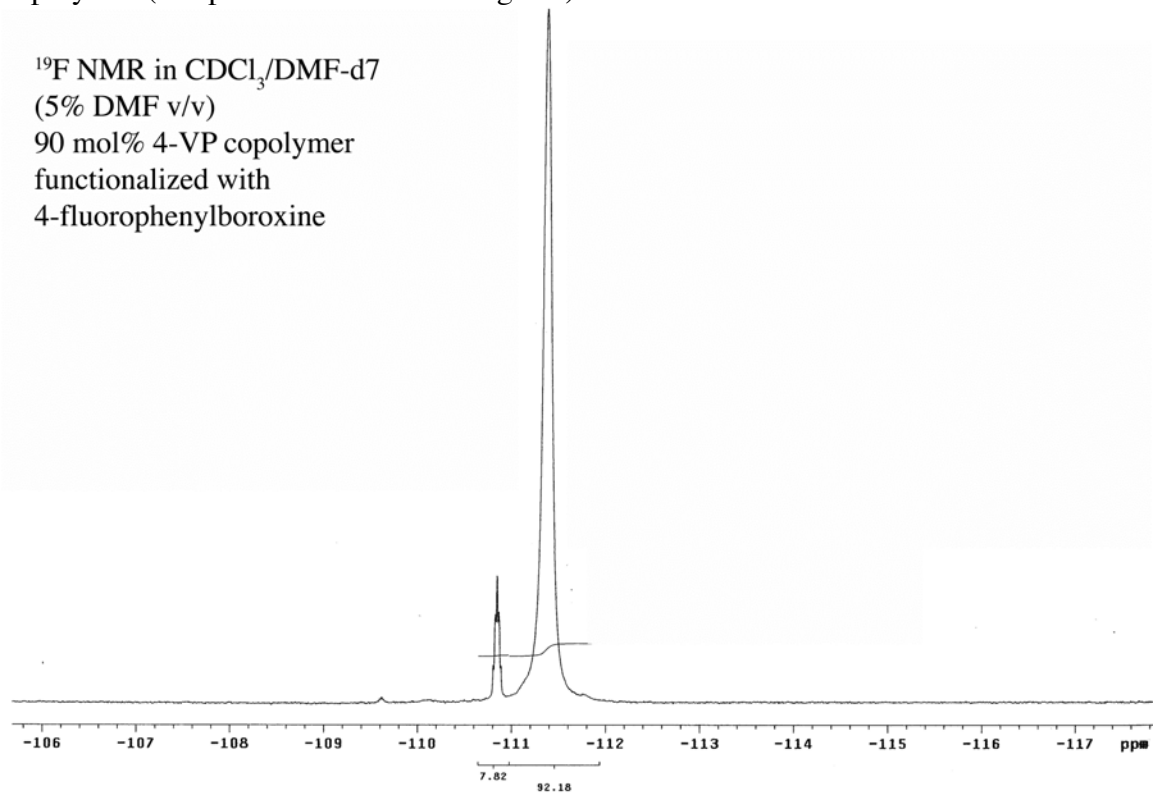

Figure S6. FT-IR spectrum of 4-fluorophenylboroxine•pyridine adduct.

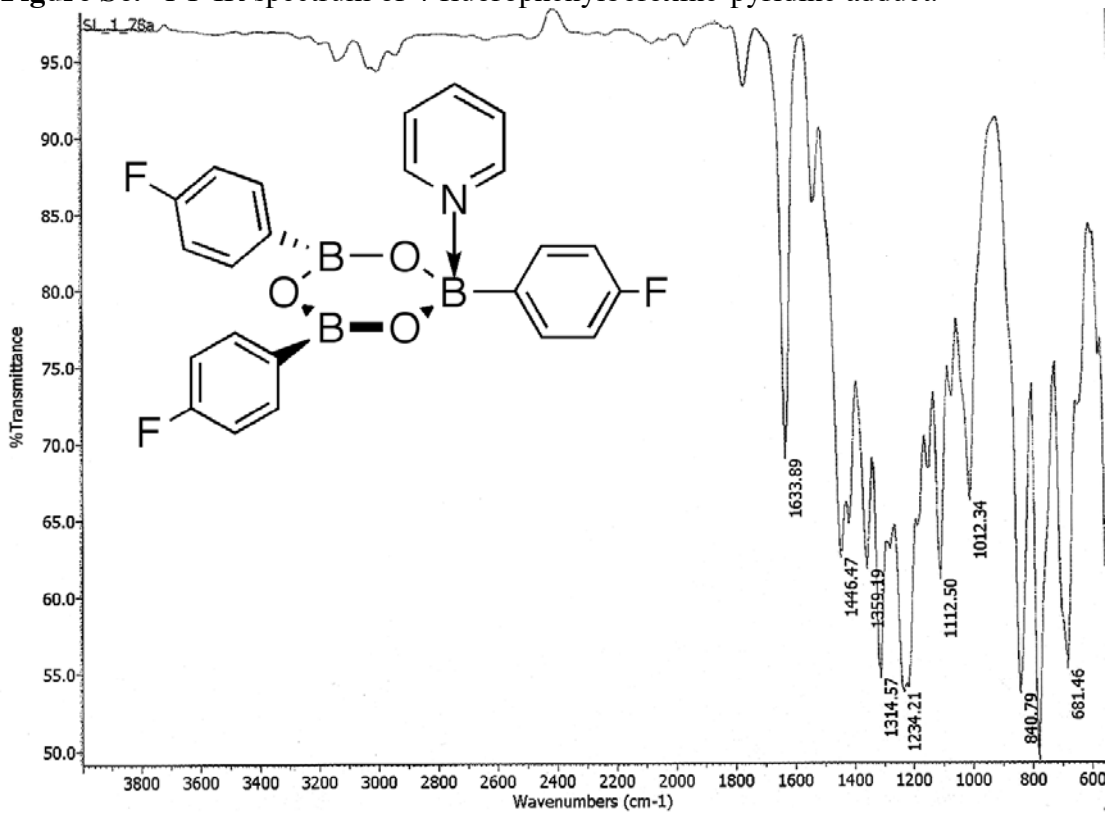

Figure S7. FT-IR spectrum of PS/4-VP (22 mol% 4-VP) parent random copolymer.

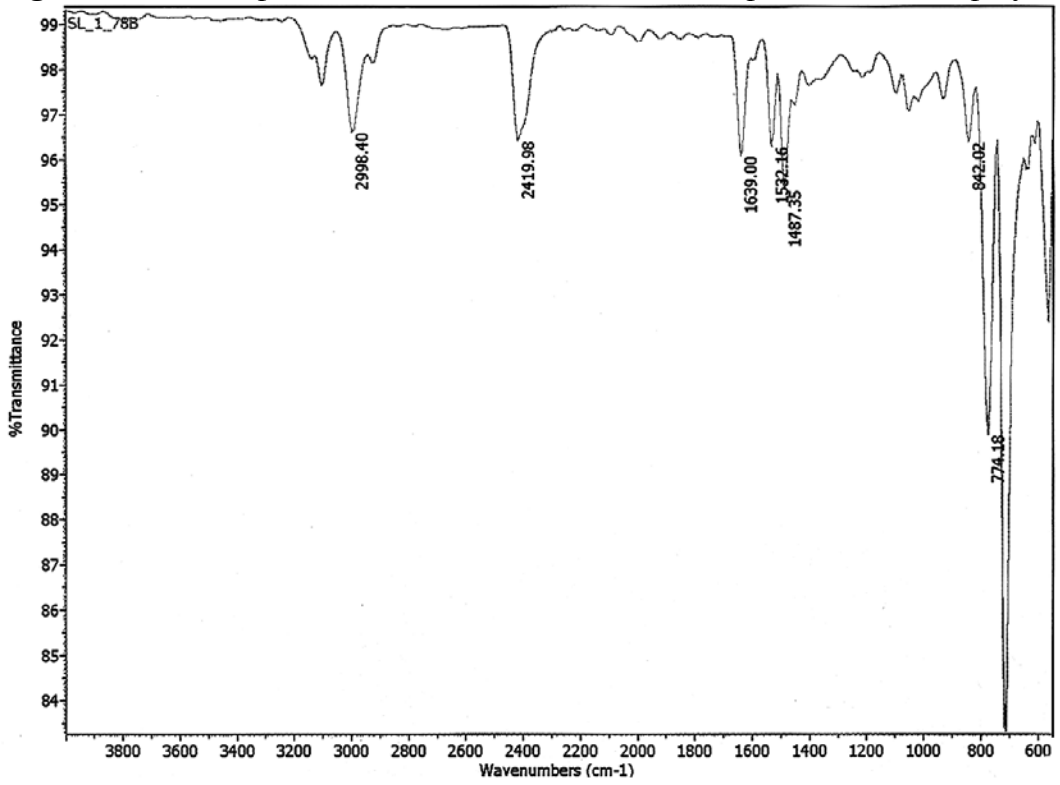

Figure S8. FT-IR spectrum of PS/4-VP (22 mol% 4-VP) random copolymer with a 4-VP:4-fluorophenylboroxine molar ratio of 2.7:1.

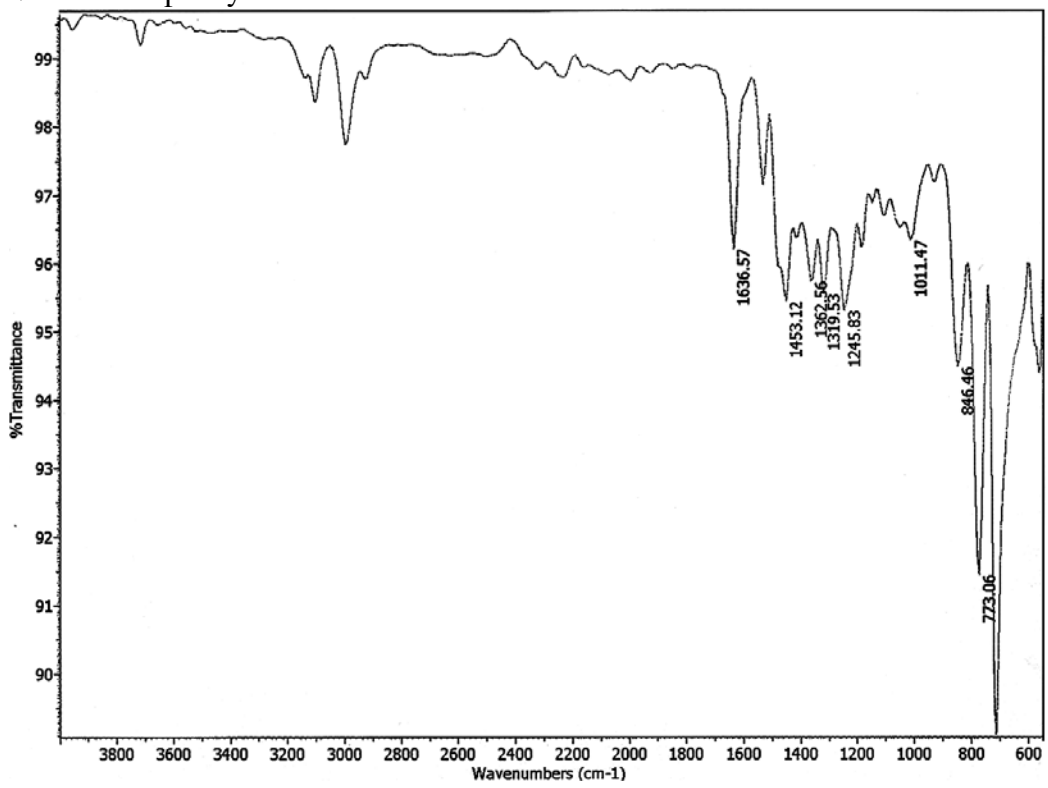

Figure S9. FT-IR spectrum of PS/4-VP (22 mol% 4-VP) random copolymer with a 4-VP:4-fluorophenylboroxine molar ratio of 1.5:1.

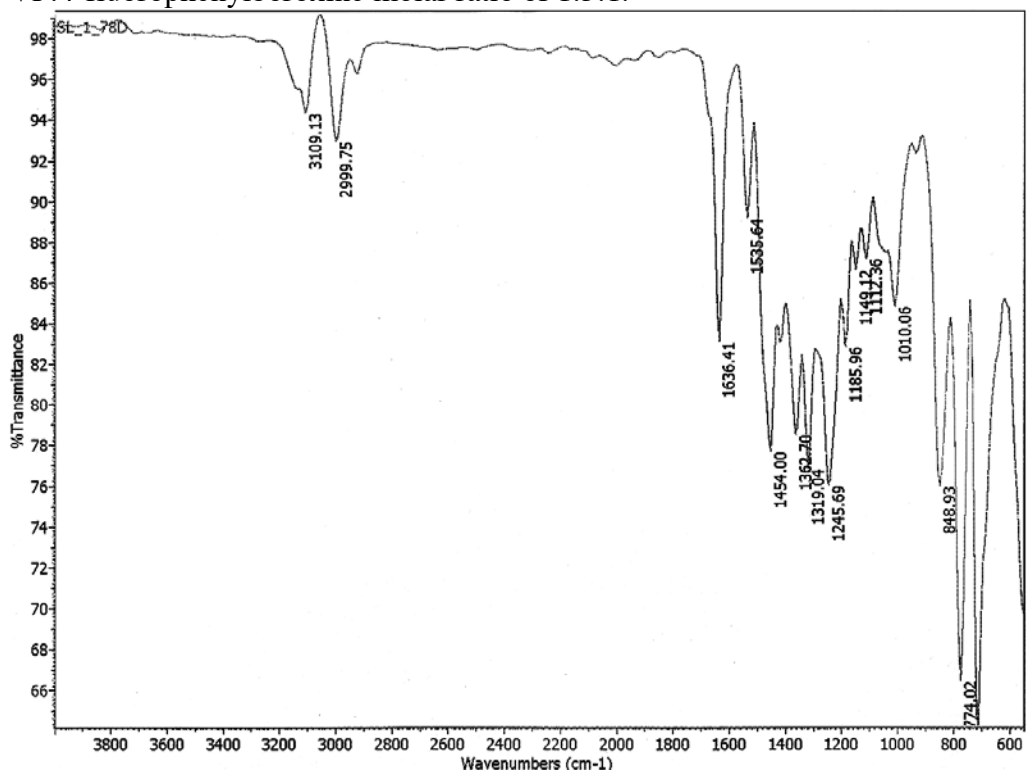

Figure S10. FT-IR spectrum of PS/4-VP (22 mol% 4-VP) random copolymer with a 4-VP:4-fluorophenylboroxine molar ratio of 0.9:1.