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

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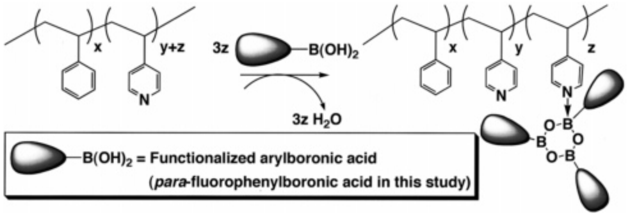
Noncovalent functionalization of polymers is an attractive synthetic strategy because self-assembly processes minimize the complications associated with postpolymerization modification while simultaneously providing access to materials with physical properties distinct from the parent polymer. Expanding the functional and structural complexity of self-assembled polymeric materials requires a repertoire of different recognition motifs. To this end, hydrogen-bonding and metal−ligand interactions have been used extensively.[1−8] However, functionalization via Lewis acid−base interactions appears less frequently in the literature.[9−14]

In previously published work our group has outlined the use of ligand-facilitated trimerization of arylboronic acids in the synthesis of tripodal arylboroxine-containing molecular architectures.[15−17] In this one-pot dehydration−ligation reaction, a monomeric arylboronic acid is combined with a Lewis base, such as pyridine. The condensation reaction is both rapid and efficient and therefore an attractive method for creating functionalized polymers through reversible, noncovalent interactions. With the popularity of metal-based coupling methodologies employing arylboronic acids, a wide assortment of substituted arylboronic acids are commercially available and synthetically accessible, meaning that a potentially large, structurally diverse, and functional pool of monomers can be readily incorporated into a polymer environment. In terms of the rational design of mechanical and functional polymer characteristics, the arylboroxine rings add an additional level of design freedom above and beyond the polymer backbone and covalent side chains.[4] In this way, a single, easily accessible polymer scaffold can be used to systematically probe structure−property relationships using noncovalent modification. We describe here several proof-of-principle experiments that demonstrate how arylboroxine rings can be used to functionalize Lewis basic side chains rapidly and efficiently. The impact of noncovalent modification on polymer physical properties will also be discussed.

Three different polystyrene-*co*-4-vinylpyridine (PS/4-VP) polymers, containing 22−90 mol % 4-VP, were used in this study (Scheme 1). The arylboroxine-functionalized copolymers were synthesized by stirring the parent polymer and 4-fluorophenylboronic acid in CH_2Cl_2 or a CH_2Cl_2/DMF solution (5% DMF v/v) in the presence of 4 Å molecular sieves for 2−3 h at room temperature.[18] The final ratio of 4-vinylpyridine:arylboroxine in each copolymer ranged from approximately 1:1 to 1.5:1. To facilitate characterization, 4-fluorophenylboronic acid was used in the functionalization reaction as it provides both ^{19}F NMR and ^{1}H NMR spectroscopic handles.

Scheme 1. Ligand-Facilitated Trimerization of Arylboronic Acids as a Means of Noncovalently Functionalizing a Lewis Basic Copolymer



The results of the arylboroxine condensation onto PS/4-VP copolymers, as assessed by solution NMR, are summarized in Table 1, and representative ^{1}H and ^{19}F NMR data for the copolymer containing 22% 4-VP are shown in Figure 1. The chemical shifts of the protons *ortho* to the boron on the 4-fluorophenyl rings are highly sensitive to environment (i.e., arylboronic acid vs arylboroxine vs arylboroxine•ligand) (vide infra). When interpreting the chemical shifts of arylboroxine•pyridine adducts, it is important to note that the pyridine ligand is in fast exchange on the NMR time scale. Therefore, the observed resonances for the arylboroxine species correspond to a weighted average of ligated and unligated arylboroxine with the terminal points being separated by ∼0.2 ppm. The ^{19}F NMR spectrum is especially valuable in the context of assessing the efficiency of the polymer functionalization reaction as the resonances are generally sharp and spread over a large chemical shift range.

Parts a and b of Figure 1 are the ^{1}H and ^{19}F NMR spectra of the 4-fluorophenylboroxine-functionalized copolymer containing 22 mol % 4-VP; parts c and d of Figure 1 are the ^{1}H and ^{19}F NMR spectra for the analogous nonpolymeric 4-fluorophenylboroxine•pyridine adduct. On the basis of the ^{1}H and ^{19}F data (4-fluorophenylboronic acid has δ 7.8 ppm for the protons *ortho* to the boron and δ −109 ppm for the ^{19}F in $CDCl_3$), one can establish a lower threshold for the ratio of 4-fluorophenylboroxine:4-fluorophenylboronic acid of >20:1. In the functionalized polymer, the chemical shift of the aromatic protons *ortho* to the boron at δ 8.0 ppm in the ^{1}H NMR spectrum is consistent with the arylboroxine moieties being ligated (the chemical shift of the unligated arylboroxine is approximately δ 8.2 ppm). The data suggest that in halogenated solvent the arylboronic acid monomers have been efficiently converted to arylboroxine rings and that the arylboroxine rings are, at any given time, close to fully associated with pyridine rings.

The functionalization reaction was less efficient for the 90 mol % 4-VP copolymer. In this case, DMF was added to CH_2Cl_2 (5% v/v) to fully solvate the 4-VP copolymer in both the functionalization reaction and the NMR measurements. Consistent with our previously published data on the solution thermodynamics of nonpolymeric arylboroxines,[17] the addition of polar solvent decreased the ratio of arylboroxine:arylboronic acid relative to the cases where only halogenated solvent was employed.

Since the arylboroxine•pyridine linkage is reversible, ligation in solution does not prove that the arylboroxine rings remain bound to pyridine in the solid state. However, on the basis of the high affinity of Lewis acidic arylboroxine rings for nitrogeneous ligands, especially in halogenated solvents, and the

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Table 1. Polymer Characterization Data for PS/4-VP Copolymers Containing 22−90 % 4-VP Functionalized with 4-Fluorophenylboroxine

entry	mol % 4-VP	molar ratio 4-VP:arylboroxine[a]	solvent(s) used in preparation	ratio arylboroxine:boronic acid[b]	M_n (kg/mol)[c]	M_w (kg/mol)[c]	M_w/M_n [c]
1	22	1.5:1	CH_2Cl_2	>20:1	25[d]	40	1.6
2	50	1.2:1	CH_2Cl_2	>20:1	15[e]	47	3.13
3	90	1.4:1	CH_2Cl_2/DMF 19:1 (v/v)	4:1	1200−1500[f]	ND[g]	ND[g]

[a] Determined by integration of the protons in 4-fluorophenylboroxine (δ 8.0 ppm) and 4-vinylpyridine (δ 8.4 ppm, br) in ^{1}H NMR spectrum in $CDCl_3$ (22 and 50 mol % 4-VP) and $CDCl_3$/DMF-d_7 (5% DMF v/v) (90 mol % 4-VP). [b] Determined by integration of the ^{1}H and ^{19}F NMR spectra. See note *a* for NMR solvents. [c] All molecular weight data corresponds to the unfunctionalized parent polymers. [d] Reported value from Polymer Source by SEC. [e] Determined in THF vs polystyrene standards. [f] Reported value is M_v (from Aldrich Chemical Co.). [g] ND = not determined

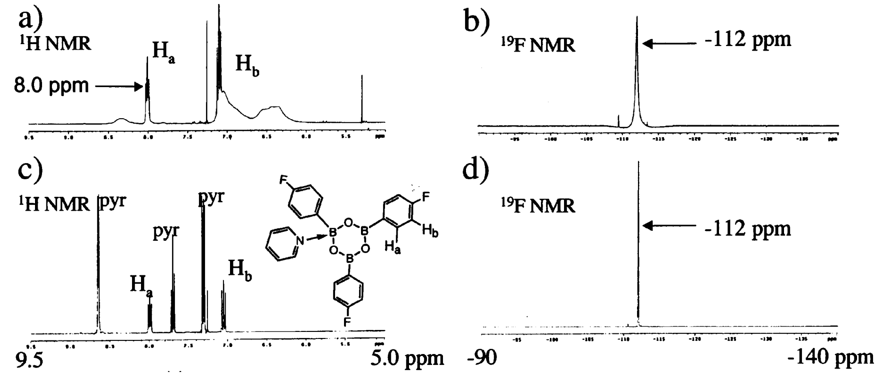

Figure 1. NMR spectra in $CDCl_3$ at 25 °C illustrating the functionalization of the 22 mol % 4-VP copolymer (Table 1, entry 1) with 4-fluorophenylboroxine: (a) ^{1}H (8 mg/mL) and (b) ^{19}F NMR (8 mg/mL) spectra of the polymer containing 1.5:1 4-VP:arylboroxine; (c) ^{1}H (26 mM) and (d) ^{19}F NMR spectra (26 mM) of the corresponding nonpolymeric 4-fluorophenylboroxine•pyridine complex.

tendency of solutions of arylboronic acids to spontaneously dehydrate when concentrated,[19] it is not expected that the arylboroxine•pyridine interaction would be disrupted by the removal of solvent. Attenuated total reflection IR (ATR-IR) spectra of arylboroxine-functionalized PS/4-VP copolymers (Supporting Information, Figures S8−S10) confirm the presence of arylboroxine in the solid state[20−23] and are similar to the spectrum of the small-molecule pyridine:4-fluorophenylboroxine model compound (Figure S6); amine adducts of triarylboroxines have previously been characterized in the solid state by IR, but this method does not clearly distinguish between ligated and unligated boroxine.[20] Further studies using solid-state ^{11}B NMR are planned.

The impact of noncovalent polymer modification on the physical properties of the PS/4-VP copolymer containing 22 mol % 4-VP was assessed using DSC and TGA. Three 4-fluorophenylboroxine-functionalized copolymers were synthesized with the mole ratio of 4-VP to arylboroxine varying from 2.7:1 to 1.5:1 to 0.93:1. The DSC scans of the unfunctionalized parent polymer and the three functionalized copolymers are shown in Figure 2.

The DSC results indicate that T_g increases from 101 to 134 °C as the amount of arylboroxine increases. Once the arylboroxine rings are ligated to the 4-VP, they can be considered rigid, sterically bulky side chains. In the case of covalent side-chain modification with anthracene moieties,[24] increasing incorporation of anthracene increased T_g by decreasing polymer chain mobility. The noncovalently bound arylboroxine seems to be producing a similar effect in this case. Other weak interactions may also contribute; both arylboroxine−arylboroxine π-stacking interactions and interchain cross-linking, in copolymers where there is an excess of pyridyl sites relative to arylboroxine, are possible.[25,26] However, cross-linking is less likely to occur since arylboroxines exhibit a strong thermodynamic preference to form 1:1 arylboroxine•ligand adducts in the solid state;[27−32] the 1:2 and 1:3 arylboroxine•ligand adducts are energetically unfavorable.[16,32]

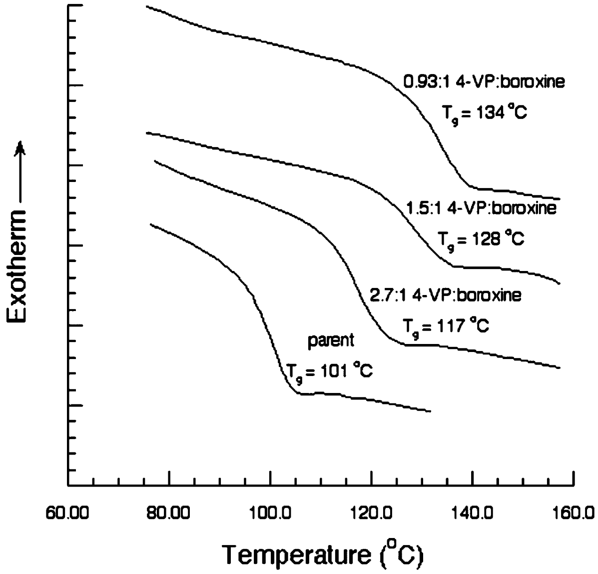

Figure 2. DSC curves for a series of 4-fluorophenylboroxine functionalized PS/4-VP random copolymers. The parent copolymer corresponds to a 22 mol % 4-VP copolymer ($M_n \times 10^3 = 25$, $M_w/M_n = 1.6$).

TGA thermograms were measured for the parent PS/4-VP (22 mol % 4-VP) copolymer as well as the three 4-fluorophenylboroxine functionalized copolymers (see Supporting Information, Figure S1). The parent polymer shows no significant weight loss until 400 °C, consistent with other reports of the thermal degradation of polystyrene and poly(4-vinylpyridine) homopolymers.[33−35] Degradation is observed at increasingly lower temperatures as the amount of incorporated 4-fluorophenylboroxine increases. Although the exact mechanism responsible for the thermal decomposition in these functionalized copolymers remains unclear, preliminary TGA−mass spectrometry analysis indicates that the initial fragmentation of the arylboroxine at 220 °C[36] may be generating radicals capable of catalyzing the degradation of the polystyrene/4-VP at temperatures below 400 °C.[37]

In conclusion, we have demonstrated that the incorporation of arylboroxines into PS/4-VP random copolymers is synthetically straightforward, increases polymer T_g, and lowers the onset temperature of thermal degradation. Current and future work will be directed toward expanding the structural and functional complexity of the arylboronic acids used in the functionalization reaction and further understanding the role of arylboroxines in modifying the properties of PS/4-VP random and block copolymers.

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Supporting Information Available: Full experimental section detailing the DSC and TGA experiments as well as the synthetic procedure for the preparation of the 50 mol % 4-VP random copolymer; TGA thermograms; ^{1}H and ^{19}F NMR spectra corresponding to the functionalized 90 and 50 mol % 4-VP copolymer with 4-fluorophenylboroxine; and ATR-IR spectra for the nonpolymeric 4-fluorophenylboroxine•pyridine adduct, the parent 22 mol % 4-VP copolymer, and the 22 mol % 4-VP copolymer functionalized with three different loadings of 4-fluorophenylboroxine. This material is available free of charge via the Internet at http://pubs.acs.org.

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