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Syndioselective Polymerization of a BN Aromatic Vinyl Monomer

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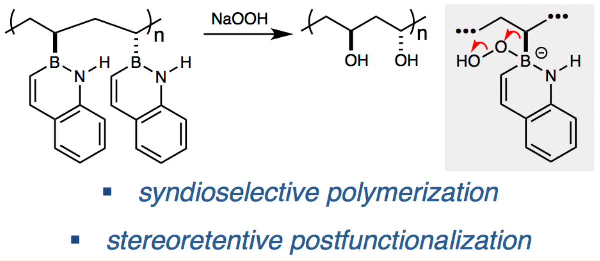
Supporting Information



ABSTRACT: A new synthetic platform accessing stereoregular polar polyolefins is introduced. We showcase the stability of aromatic azaborine derivatives by demonstrating the syndioselective polymerization of BN 2-vinylnaphthalene (BN2VN) by a monocyclopentadienyl titanium complex. Homogeneous early transition metal catalysts are well-established systems for the synthesis of highly stereoregular syndiotactic polystyrene (sPS), but the oxophilic nature of these complexes results in catalyst decomposition with polar monomers. BN2VN's compatibility with coordination polymerization, and its ability to intercept the mechanism of styrene polymerization, is attributed to its aromaticity. Stereoretentive postpolymerization oxidation of the organoborane side chain generates syndiotactic poly(vinyl alcohol) (sPVA), an example of PBN2VN's potential for diverse postfunctionalization.

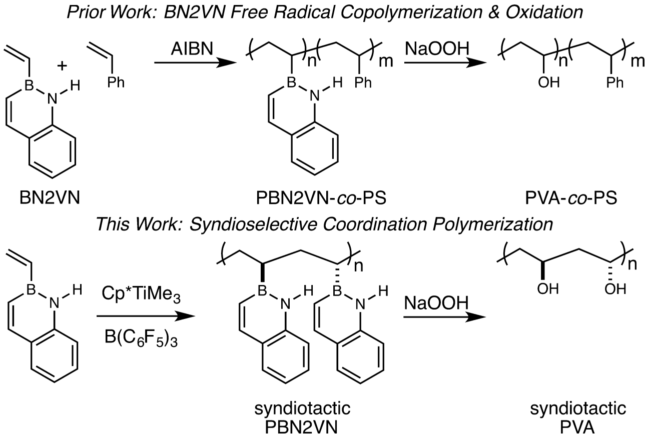
■ INTRODUCTION

Organoboranes are versatile reagents in organic synthesis,[1] and chiral alkylboronate esters are important precursors to enantioenriched alcohols and other functional groups.[2−4] The challenges associated with the synthesis of functionalized polyolefins by coordination−insertion polymerization[5−7] suggest that poly(vinyl boronate)s could represent an attractive solution via postpolymerization transformation of the side-chain C−B bond. However, there has been limited investigation of vinyl boronate polymerization, perhaps reflecting concerns about the Lewis acidity, propensity for cross-linking, and hydrolytic and oxidative sensitivity of organoboranes.[8,9]

We demonstrate that BN 2-vinylnaphthalene (BN2VN)'s[10−12] aromaticity[13−15] results in a functionalized vinyl monomer compatible with single-site olefin polymerization catalysts. Monocyclopentadienyl titanium catalysts that promote syndioselective styrene polymerization[16,17] yield syndiotactic BN2VN polymers (sPBN2VN, Scheme 1). We recently showed that free radical copolymerization of BN2VN and styrene provides a precursor to statistical styrene−vinyl alcohol copolymers (PVA-*co*-PS) via postpolymerization oxidation.[11,12] Herein, we show stereoretentive[18] oxidation of sPBN2VN to syndiotactic poly(vinyl alcohol) (sPVA).

Poly(vinyl alcohol) (PVA) is a semicrystalline water-soluble polymer. PVA is typically synthesized by free radical polymerization of vinyl acetate, followed by saponification, yielding an atactic polymer.[19] PVA hydrogels have potential therapeutic applications, while high molecular weight PVA fibrils exhibit high tensile strength.[20−23] Tacticity has a profound effect on both these applications as relative stereochemistry influences the extent of intra- and intermolecular hydrogen bonding between hydroxyl groups.[23−25] sPVA has particularly strong intermolecular hydrogen bonds.

Scheme 1. Coordination Polymerization of BN2VN and Stereoretentive Oxidation



Synthetic routes to sPVA include cationic polymerization of vinyl ethers with bulky protecting groups[26−28] or radical polymerization of vinyl pivalate,[22,29] followed by protecting group cleavage. Syndiotacticties are typically modest, and cationic polymerizations yield low molecular weight materials. The limited substrate scope of cationic polymerization and the poor reactivity of vinyl ester-derived radicals also impose a limitation on the ability to tune PVA's properties through copolymerization with nonpolar monomers.

Coordination polymerization of BN2VN is a new synthetic approach to sPVA that proceeds by an orthogonal mechanism with the potential to address these limitations. Homogeneous

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Table 1. Group (IV) Transition Metal Catalysts for BN2VN Coordination Polymerization

				before fractionation			after fractionation		
entry	cat.	cocat.	[cat.]/[cocat.]	yield (%)	M_n[a] (kDa)	$Đ$	recovery (%)	M_n[a] (kDa)	$Đ$
1	Cp_2ZrCl_2[b]	MAO	0.025/20.0	0	n.d.	n.d.	n.d.	n.d.	n.d.
2	Cp_2TiCl_2[b]	MAO	0.025/22.5	36[e]	n.d.	n.d.	n.d.	n.d.	n.d.
3	Cp^*TiCl_3[b]	MAO	0.025/22.5	21[e]	n.d.	n.d.	n.d.	n.d.	n.d.
4	Cp^*TiMe_3[c]	$B(C_6F_5)_3$	0.50/0.50	33	12.2	2.33	74	12.1	2.33
5	Cp^*TiMe_3[d]	$B(C_6F_5)_3$	1.00/1.00	67	15.0	2.24	78	15.0	2.24
6	Cp^*TiMe_3[d]	$B(C_6F_5)_3$	1.00/1.50	85	16.0	2.41	74	16.0	2.41

[a] Determined by GPC at 254 nm relative to a polystyrene standard. [b] Conditions: 50 °C, 24 h, [BN2VN] = 2.0 M in toluene. [c] Conditions: 35 °C, 2 h, [BN2VN] = 0.95 M in toluene. [d] Conditions: 35 °C, 2 h, [BN2VN] = 2.0 M in toluene. [e] GPC analysis could not be performed due to the insolubility in THF at room temperature. Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; MAO = methylaluminoxane, cat. = catalyst, cocat. = cocatalyst.

early transition metal complexes are exceptional in their ability to provide highly stereoregular polymers.[30] The high activity of single site catalysts for olefin polymerization also expands the scope of compatible comonomers and resulting functional polyolefins. As first reported by Ishihara,[31] homogeneous monocyclopentadienyl complexes[32,33] such as Cp^*TiCl_3,[31] Cp^*TiMe_3,[17,34] $IndTiCl_3$,[35] and others[36] are effective catalysts for syndioselective styrene polymerization upon activation by methylaluminoxane (MAO) or tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). The powerful Lewis acid $B(C_6F_5)_3$ abstracts a methyl group from Cp^*TiMe_3, yielding the cationic active catalyst.[16,37−41] Stereoselectivity is typically very high (>98% syndiotactic).[33] Syndiotactic polystyrene (sPS) is a semicrystalline polymer with a high melting point (270 °C) and other attractive properties.[42,43] Coordination copolymerization of styrene and polar monomers like vinyl acetate is a significant challenge due to interactions between the polar functional group and Ti^+ or the Lewis acid cocatalyst.[7]

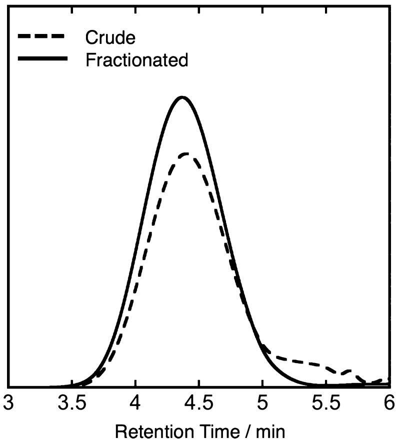

Figure 1. SEC data before (dashed) and after (solid) fractionation in acetone. Response by absorbance at 310 nm. Relative to a polystyrene standard.

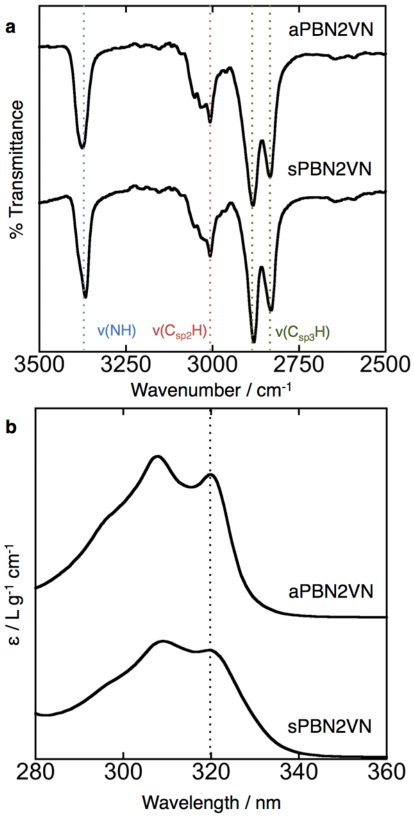

Figure 2. (a) Cropped FTIR spectra of aPBN2VN (from AIBN) and sPBN2VN. (b) Cropped UV−vis spectra of aPBN2VN and sPBN2VN. The absorption band at 320 nm is labeled. THF, [polymer] = 0.02 mg mL^{-1}, 25 °C.

■ RESULTS AND DISCUSSION

We hypothesized that an aromatic cage around boron and nitrogen would reduce Lewis acidity and basicity, resulting in compatibility with coordination polymerization catalysts. Additionally, BN2VN's aromaticity suggests its ability to intercept the mechanism of styrene syndioselective polymerization. While several aromatic vinyl boronates are known,[44−46] BN2VN's scalable two-step synthesis is attractive for postfunctionalization studies.[10,47] A series of group IV catalysts known to promote styrene polymerization were examined in BN2VN polymerization (Table 1). No conversion was observed with Cp_2ZrCl_2/MAO (entry 1). More promising levels of conversion were observed with Cp_2TiCl_2/MAO and Cp^*TiCl_3/MAO (entries 2 and 3). $Cp^*TiMe_3/B(C_6F_5)_3$ provided good yields of moderate molecular weight polymers with a significant reduction in cocatalyst loading compared to Ti/MAO systems (entries 4−6). In general, polymerization of BN2VN and the nonpolar hydrocarbon 2-vinylnaphthalene (2VN) results in lower yields and molecular weights than observed with styrene coordination polymerization (Table S1).

Both sPS and sPBN2VN are much less soluble in organic solvents than their atactic counterparts.[48] Soxhlet extraction in acetone yielded a soluble atactic fraction and an insoluble

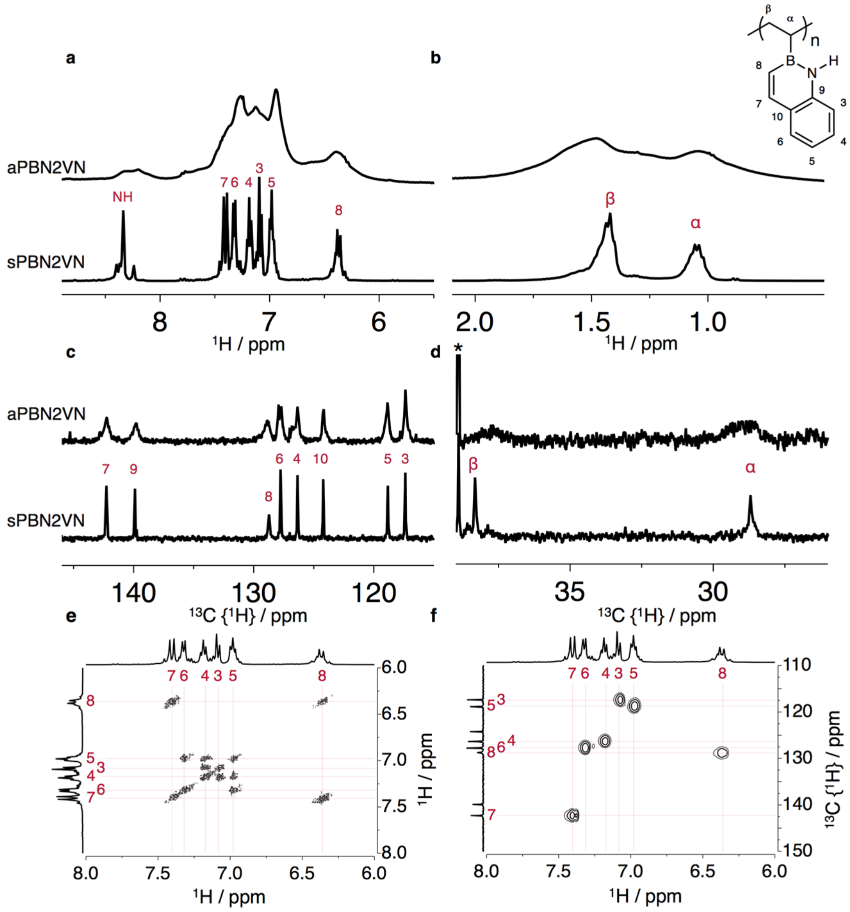

Figure 3. NMR spectra of PBN2VN. (a, b) Cropped ^{1}H NMR spectra (400 MHz, 120 °C, DMSO-d_6). Top: aPBN2VN (from AIBN); bottom: sPBN2VN (from Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$). (c, d) Cropped ^{13}C {^{1}H} NMR spectra (101 MHz, 120 °C, DMSO-d_6). Top: aPBN2VN (from AIBN); bottom: sPBN2VN (from Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$). (e) Cropped ^{1}H−^{1}H COSY spectrum of sPBN2VN. (f) Cropped ^{1}H−^{13}C HSQC spectrum of sPBN2VN (400 MHz, 120 °C, DMSO-d_6). Peak assignments are indicated. Asterisk indicates solvent signal. See the Supporting Information for full spectra.

stereoregular fraction (74−78 wt % % recovery, Table 1). The sPBN2VN fraction is an off-white powdery solid that is sparingly soluble in THF at room temperature. At elevated temperatures (100−120 °C), good solubility in DMSO and limited solubility in 1,1,2,2-tetrachloroethane (TCE) are observed. Results of size exclusion chromatography (SEC) before and after fractionation are shown in Figure 1.

Spectroscopic characterization confirms that the BN naphthalene side chain survives polymerization. The Fourier transform infrared (FTIR) spectra of sPBN2VN and aPBN2VN from free radical polymerization agree (Figure 2a). The characteristic NH stretching frequency (ca. 3370 cm^{-1}) is observed as well as CH stretching frequencies. Like aromatic hydrocarbons, extended azaborines rings show intense absorption bands in the ultraviolet to visible region.[49,50] The UV−vis spectrum of sPBN2VN exhibits the characteristic 320 nm absorption band of the BN naphthalene side chain (Figure 2b).[10,11]

NMR spectroscopy supports a stereoregular structure. Much sharper peaks are observed in the ^{1}H NMR spectra of sPBN2VN samples compared to aPBN2VN. The seven peaks in the aromatic region of the ^{1}H NMR spectrum are assigned to the BN naphthalene side chain (Figure 3a). Peaks at δ 1.44 and δ 1.05 are assigned to the methylene (β) and methine (α) protons of the polymer backbone (Figure 3b). NMR spectra were collected in DMSO-d_6, a coordinating solvent. UV−vis spectra of PBN2VN in DMSO and THF are identical and show the characteristic 320 nm transition consistent with aromaticity, suggesting that DMSO does not coordinate BN2VN (Figure S1). DMSO-d_6 may hydrogen bond to the polymer, as the NH resonance is observed at δ 8.34, a downfield shift of over 1 ppm compared to dichloromethane-d_2.[10]

While the resonances of carbon atoms attached to boron (δ 128.7 (C8) and δ 28.7 (α)) are broad due to the quadrupolar relaxation of boron-11 ($s = 3/2$),[51] peak shapes are singlets and generally narrower than observed in the spectrum of aPBN2VN arising from free radical polymerization (Figure 3c,d), suggesting a very high degree of stereoregularity. Peak assignments were made on the basis of COSY, NOESY, TOCSY, and ^{1}H−^{13}C HSQC NMR experiments (Figure 3e,f and Supporting Information).

The challenging analysis of organoboranes by ^{13}C NMR spectroscopy limits the utility of quantitative NMR experiments in the assignment of stereoregular PBN2VN microstructure to syndiotactic or isotactic. Nor are small molecule analogues of BN2VN *meso* and *racemo* diads known. For these reasons, characterization of tacticity is based on conversion to PVA, as diagnostic spectroscopic signatures are known for both isotactic and syndiotactic PVA.[52] Organoborane oxidation with alkaline hydrogen peroxide proceeds by a stereoretentive mechanism in which hydroperoxide ion (HOO−) coordinates

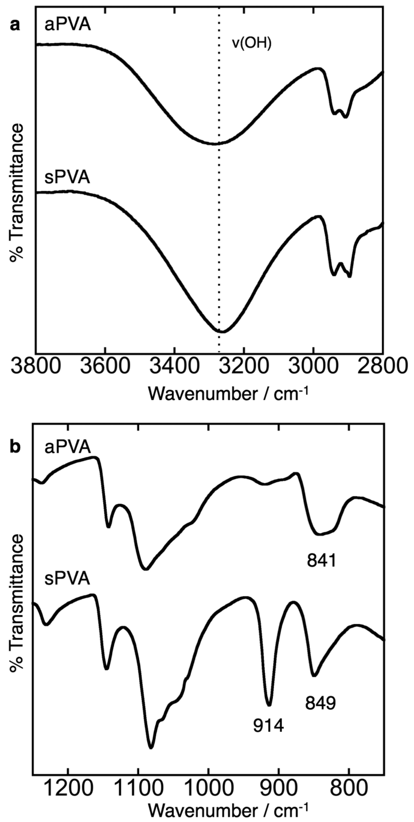

Figure 4. Cropped FTIR spectra of an authentic sample of aPVA and sPBN2VN-derived sPVA highlighting (a) ν(OH) and (b) bands characteristic of syndiotacticity.

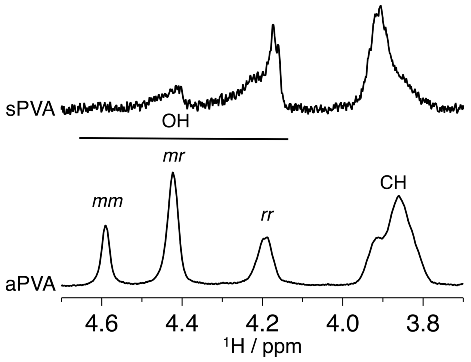

Figure 5. Cropped ^{1}H NMR (400 MHz, DMSO-d_6) spectra of sPVA (top) and aPVA (bottom). Peak assignments are indicated. See the Supporting Information for full spectra.

Table 2. Physical Properties of Polymers

entry	polymer	T_g[a] (°C)	T_m[b] (°C)
1	aPS	100	n.a.
2	sPS	101	272
3	aPBN2VN	135	n.a.
4	sPBN2VN	131	319
5	aPVA	85	n.a.
6	sPVA	93	n.d.[c]

[a]Temperature of midpoint of glass transition. [b]Temperature of midpoint of melting. [c]sPVA decomposed during analysis.

boron, followed by concerted 1,2-alkyl migration and O–O bond cleavage.[18]

Oxidation confirms a syndiotactic microstructure. A THF–ethanol solution of sPBN2VN was treated with alkaline hydrogen peroxide for 24 h at 65 °C. sPVA was isolated as a white powder in 31% yield by precipitation into water. Synthetic sPVA is UV-inactive, indicating cleavage of the BN naphthalene chromophore (Figure S2). FTIR spectroscopy shows the characteristic broad ca. 3250 cm^{-1} hydroxyl stretching frequency (Figure 4a). Murahashi et al. reported IR spectra of both isotactic and syndiotactic PVA and identified features at 916 and 849 cm^{-1} as diagnostic of sPVA.[52] Both resonances are readily identified in our synthetic sample of sPVA and are not apparent in a commercially available sample of aPVA (Figure 4b).

The poor solubility of sPBN2VN-derived sPVA complicates NMR spectroscopic analysis of stereoregularity. PVA tacticity is typically quantified by ^{1}H NMR spectroscopy at room temperature or 50 °C in DMSO-d_6, as hydroxyl protons associated with isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triads resolve.[53,54] However, sPVA solubility is known to decrease with increasing syndiotacticity,[55] and our sPVA is poorly soluble in DMSO. It is insoluble in DMSO-d_6 at room temperature and 50 °C. ^{1}H NMR spectra recorded at these temperatures do not show PVA resonances. After heating to 120 °C, ^{1}H NMR signatures of sPVA are observed (Figure S3); however, the known coalescence of hydroxyl and methine resonances at elevated temperatures[54] precludes direct determination of % syndiotacticity from the 120 °C spectrum. Upon cooling back to 50 °C, hydroxyl resonances in the ^{1}H NMR spectrum resolve and show that sPBN2VN-derived sPVA is enriched in *rr* (syndiotactic) triads compared to aPVA (Figure 5). Solid-state carbon-13 NMR spectroscopy of PVA is not suitable for quantitative determination of tacticity as intra- and intermolecular hydrogen bonding influence methine carbon chemical shift.[56]

Like sPS, sPBN2VN is a semicrystalline solid. It has not only a glass transition temperature (T_g) comparable to aPBN2VN but also a high melting point above 300 °C (Table 2). Synthetic sPVA derived from sPBN2VN is a solid at room temperature, but decomposition of neat samples was observed during thermal analysis by differential scanning calorimetry (see the Supporting Information).[57]

■ CONCLUSION

We report the synthesis of a stereoregular poly(vinyl boronate) via single site catalysis of BN2VN polymerization. Achieving the synthesis of sPBN2VN facilitates the preparation of stereoregular functional polyolefins via the versatile chemistry of organoboranes, as demonstrated in a synthesis of syndiotactic PVA. Aromaticity is key to the stability of the polar monomer and interception of the proposed mechanism of syndioselective styrene polymerization. The mechanistically unique route to sPVA reported herein supports the future development of stereoregular functional polyolefins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01707.

Synthetic procedures, tabulated characterization data, copies of spectra, supplemental figures and data (PDF)

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Notes

The authors declare no competing financial interest.

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