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BN Polystyrenes: Emerging Optical Materials and Versatile Intermediates

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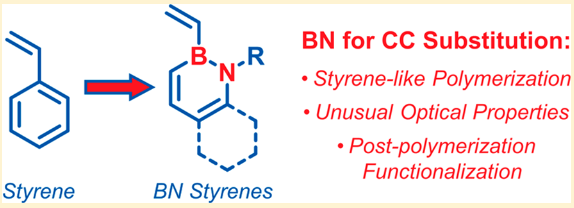
ABSTRACT: BN polystyrenes are an emerging class of polyolefins functionalized with aromatic side chains in which at least one CC bond is replaced with a BN bond. This class of structures exhibits unusual photophysical properties relative to organic polymers. BN polystyrenes serve as intermediates in the preparation of functional polymers, including stereoregular polar polyolefins. The consequences of BN for CC bond substitution on reactivity and properties are highlighted.



Styrene is a versatile monomer that is polymerized under free and controlled radical, thermal, anionic, cationic, and transition-metal-catalyzed conditions.[1] Polystyrene's properties are exquisitely controlled by synthesis (Figure 1a). Free-radical polymerization yields amorphous polystyrene (PS) for packaging applications.[2] Coordination−insertion polymerization provides crystalline high-melting stereoregular PS.[3] Controlled radical polymerization (CRP) yields well-defined block copolymers which self-assemble into nanoscale domains.[4]

PS derivatives with functionalized side chains are important materials in their own right. Cross-linking and Friedel−Crafts sulfonylation provide polystyrenesulfonate (PSS), the major component of the ion-exchange resin Dowex.[5] Polar functional groups improve adhesion to polar surfaces.[6] Borylated polymers are an active research area.[7,8] Tricoordinate boron-functionalized materials have found wide application in sensing,[9] nonlinear optics,[10] and *n*-type charge transport.[11] Isosteric and isoelectronic BN for CC bond substitution in aromatic compounds is an attractive approach to developing stable organoboranes.[12,13] BN for CC substitution in polymer backbones, either as poly(aminoborane)s[14−19] or as conjugated polymers (Figure 1b),[20−22] is well-precedented.

Vinyl monomers with BN aromatic side chains are less explored. Interest in these structures stems from several motivations. *i. Reactivity.* Styrene's synthetic versatility arises from the utility of the benzylic reactive intermediates implicated in styrene polymerization. How does a BN aromatic ring influence the reactivity of a benzylic radical, anion, or other reactive intermediate relevant to polymerization? *ii. Photophysics.* BN aromatics have unusual photophysical properties compared to benzene, including bathochromically shifted absorption and emission. *iii. Postfunctionalization.* Organoboranes are workhorse intermediates in chemical synthesis.[25,26] The C−B bond of *B*-vinyl polymers introduces opportunities for postpolymerization chemical modification, addressing challenges in the synthesis of functional polymers containing both polar and nonpolar functional groups.

This Synopsis focuses on "BN polystyrenes", defined as polymers arising from vinyl monomers with BN aromatic side chains (Chart 1). As a systematic nomenclature for BN aromatic rings and polymeric derivatives is still evolving,[12,13] materials in Chart 1 are named to emphasize similarity to polystyrene or other hydrocarbon. BN aromatic heterocycles incorporated as polyolefin side chains include borazine (Sneddon, 1991),[27] 1,2-azaborine and 4-(1,2-azaborine)benzene (Liu and Jäkle, 2016),[28] *N*-methyl-1,2-azaborine (Sönnichsen and Staubitz, 2017),[29] and BN naphthalene (Klausen, 2017).[30−33] BN aromatic rings, as determined by nucleus independent chemical shift (NICS) calculations, are less aromatic than benzene (Figure 1c).[23,24]

■ SYNTHESIS OF BN AROMATIC VINYL MONOMERS

Dewar reported the first syntheses of BN aromatic structures including BN phenanthrene[34] and BN naphthalene[35] beginning in the 1950s. Azaborine, the benzene analogue with the general formula C_4H_6BN, has three isomers, which remained elusive for decades after Dewar's initial work.[12,13] In recent years, modern methods enabled simplified synthetic access to monocyclic azaborines.[36] Despite advances, there remains a need for methods suitable for gram-scale and larger syntheses.[37]

Vinylborazine (VB). Sneddon reported the synthesis and polymerization of *B*-vinylborazine (VB) in 1991.[27] Rhodium-catalyzed coupling of borazine ($B_3N_3H_6$) and acetylene provided VB.[38] Alkylated variants (e.g., *B*-vinylpentamethylborazine) were synthesized by substitution reactions of *B*-haloborazines with Grignard reagents.[39]

BN Styrene (BNSt) and Substituted Styrenes. Ashe reported the first synthesis of BNSt in 2009 via ring expansion of 1,2-azaborolide **1**.[40] The six-step synthesis proceeded in 6% overall yield (Scheme 1a). The authors reported that the BNSt anion serves as a π-ligand in metal complexes but did not explore vinyl polymerization.

Building on Ashe's 2000 report of ring-closing metathesis (RCM) routes to 1,2-azaborines,[36] in 2013 Liu described a

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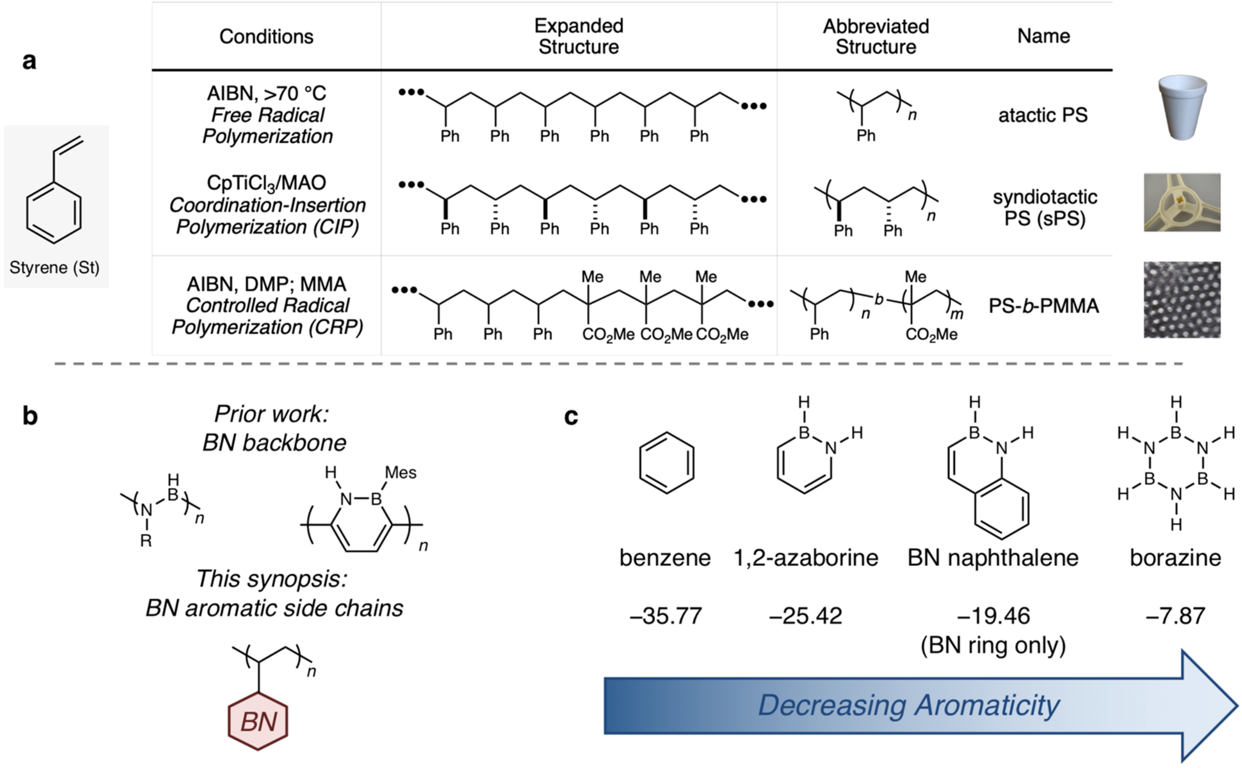
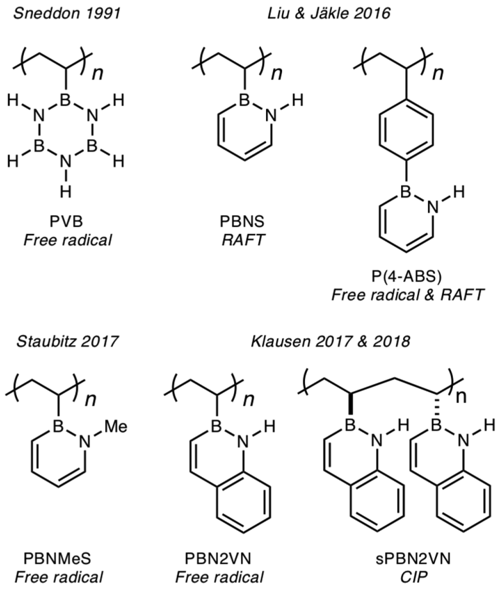


Figure 1. (a) Styrene polymerization and applications. (b) Prior work in BN for CC isosterism in polymeric materials. (c) BN aromaticity. NICS(0)$_{\pi zz}$ (ppm) values excerpted from Baranac–Stojanović et al.[23,24]

Chart 1. Polyolefins with BN Aromatic Side Chains[a]



[a]PVB = poly(vinyl borazine);[27] PBNS = BN polystyrene;[28] P(4-ABS) = poly(4-azaborinylstyrene);[28] PBNMeS = poly(1-methyl-2-vinyl-1,2-azaborine);[29] PBN2VN = poly(BN 2-vinylnaphthalene);[30−32] sPBN2VN = syndiotactic PBN2VN.[33] RAFT = reversible addition–fragmentation chain transfer; CIP = coordination–insertion polymerization.

RCM/aromatization sequence (Scheme 1b) to 1,2-azaborines[41] of the general type **4** which serve as common intermediates in the preparation of functionalized monocyclic BN aromatics. In 2016, Liu and Jäkle described derivatization of **4** with vinyl and *p*-styryl organometallic reagents to provide BNSt and 4-(1,2-azaborinyl)styrene (4-ABSt), respectively.[28] Sönnichsen and Staubitz reported a modification of the RCM/aromatization strategy to prepare BNMeSt, the *N*-methyl analogue of BNSt (four steps, 15% overall yield).[29]

BN 2-Vinylnaphthalene (BN2VN). The key step in Dewar's 1959 synthesis of BN naphthalene was the condensation of 2-vinylaniline with trichloroborane, followed by reduction.[35] More recently, Molander reported the synthesis of dozens of substituted BN naphthalenes via the one-pot condensation of vinylanilines with dichloroorganoboranes generated in situ from potassium organotrifluoroborate salts.[42]

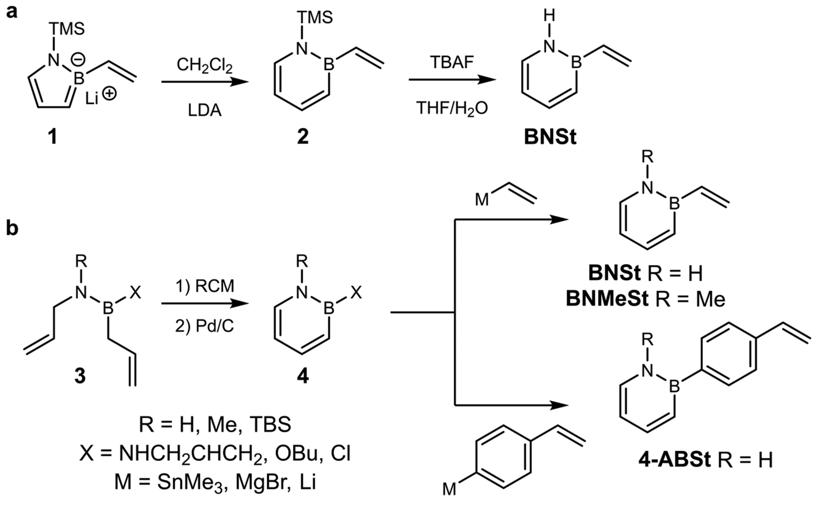
Based on this precedent, we targeted BN 2-vinylnaphthalene (BN2VN) as a more synthetically accessible monomer compared to monocyclic structures. We developed a two step, multigram scale synthesis of BN2VN (55% overall yield, Scheme 2).[30,31] 2-Aminophenethyl alcohol **5** was converted to 2-vinylaniline **6** in 63% yield by vacuum distillation in the presence of potassium hydroxide.[43] Condensation with potassium vinyltrifluoroborate provided BN2VN in 88% yield.

■ RADICAL POLYMERIZATION

Free-radical polymerization of all of the monomers discussed above has been reported. Table 1 summarizes representative results. In addition, there is one report each of controlled radical and coordination–insertion polymerization, from Liu and Jäkle and us, respectively. The potential for future investigation is significant, including both further development of existing methods, as well as unexplored avenues like anionic polymerization.

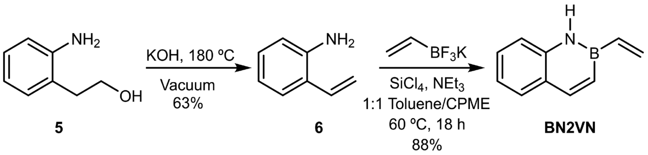
Free-Radical Homopolymerization. Sneddon reported VB polymerization initiated by azoisobutyronitrile (AIBN), which provided two fractions: a major fraction consisting of soluble, moderate molecular weight (M_n = 10.7 kDa) material

Scheme 1. (a) Ashe: Ring Expansion and Deprotection of 1,2-Azaborolide 1 Provides BNSt.[40] (b) Liu: Ring-Closing Metathesis (RCM) and Aromatization Provides 4, a Versatile Intermediate in the Synthesis of BN Aromatic Vinyl Monomers[29,41],[a]



[a]LDA = lithium diisopropylamide; TMS = trimethylsilyl; TBAF = tetrabutylammonium fluoride; TBS = *tert*-butyldimethylsilyl.

Scheme 2. Synthesis of BN2VN (55% Overall Yield)[30],[a]



[a]CPME = cyclopentyl methyl ether.

assigned to a polyolefin with borazine side chains and a smaller fraction (<15−20%) of high molecular weight material arising from cross-linking of the borazine side chains.[27,44] Alkylated vinylborazines did not polymerize under free-radical conditions.[39,45]

Free-radical polymerization of vinyl monomers with 1,2-azaborine-derived substituents proceeds under similar conditions as reported for VB (AIBN, 70−90 °C). No side-chain cross-linking was observed. BN2VN, BNMeSt, and 4-ABSt polymerization provided high molecular weight polymers (Table 1), but PBNS was only isolated in low molecular weight (M_n = 1.6 kDa). The origin of this divergent reactivity is not yet clear. Free-radical polymerization of vinyl boronic esters is known,[46,47] suggesting that α-boryl radicals are generally suitable for polymerization, an observation further supported by the high reactivity of BN2VN and BNMeSt. A potential explanation is chain transfer to monomer, the phenomenon in which the polymer radical abstracts a weakly bonded atom from the monomer. The formation of a molecular radical at the expense of a polymeric radical results in short chain lengths. However, calculations suggest that azaborine's C−H and N−H bonds are strong, with bond dissociation enthalpies ranging between 105−112 kcal mol^{-1} (CAM-B3LY/6-311G(d,p)).[32]

To date, only BN2VN polymerization has been carried out on multigram. BNSt polymerization was reported on a 10 mg scale and BNMeSt polymerization on a ca. 150 mg scale.

All BN polystyrenes showed optical properties distinct from hydrocarbon analogues (Table 2); for example, PBN2VN is pale yellow, whereas P2VN is white. In general, the longest wavelength absorption (λ_{max}) bathochromically shifted and intensified upon BN substitution. The magnitude of the bathochromic shift varied from 16 nm (PS vs PBNS) to 43 nm (P2VN vs PBN2VN). The emission spectra of BN polystyrenes also differed from hydrocarbon polymers, with larger Stokes shifts seen in BN polystyrenes than in hydrocarbon polymers. Similar trends are observed in molecular systems, including the monomers themselves.[48]

Controlled Radical Polymerization. Controlled radical polymerization (CRP) introduces a dynamic equilibrium between propagating and dormant polymer chains (Scheme 3a).[51] The low concentration of propagating polymer chain ends suppresses chain recombination and other termination events that contribute to a broad distribution of chain lengths (dispersity, $Đ$) in free-radical polymerization. CRP is desirable for applications requiring control of molecular weight, dispersity, and end group structure. Notable examples include atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition−fragmentation chain transfer (RAFT) polymerization. RAFT polymerization is convenient, as typically a chain-transfer agent (CTA) is simply added to free-radical polymerizations.[52]

Table 1. Free-Radical Polymerization of BN Aromatic Vinyl Monomers[a]

entry	monomer (solvent)	radical initiator	temp (°C)	time (h)	yield (%)	M_n (kDa)	$Đ$	ref
1	VB (C_6H_6)	AIBN (1 mol %)	80	20	25	10.7	1.68	27
2	BNSt (C_6D_6)	ACHN (1 mol %)	90	72	50[b]	1.6	1.33	28
3	BNMeSt (neat)	AIBN (1 mol %)	85	72	51	16.5	1.51	29
4	BN2VN (neat)	AIBN (1 mol %)	70	24	75	20.5	3.87	31
5	4-ABSt (THF)	AIBN (2.5 mol %)	70	20	>99[b]	38.5	3.91	28

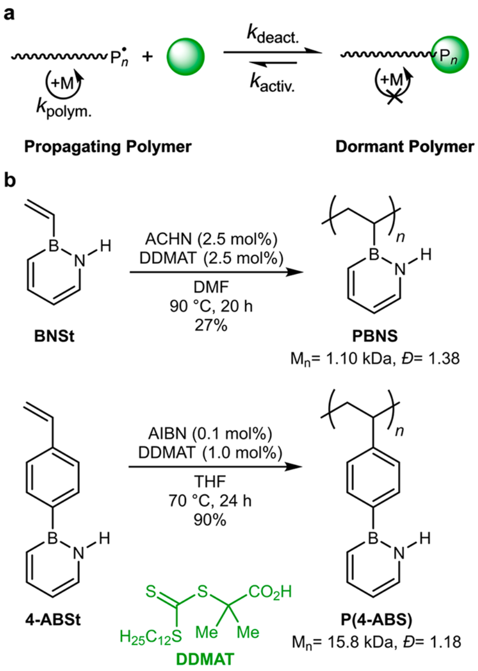
[a]AIBN = 2,2′-azobis(2-methylpropionitrile); ACHN = 1,1′-azobis(cyanocyclohexane). [b]Percent conversion.

Table 2. Selected BN Polystyrene Photophysical Data Compared to Hydrocarbon Polymers

	BN aromatic side chains				hydrocarbon aromatic side chains			
entry	polymer	λ_{max} (nm)[a]	λ_{em} (nm)[b]	ref	polymer	λ_{max} (nm)[a]	λ_{em} (nm)[b]	ref
1	PBNS	277	344	28	PS	261	278	49
2	P(4-ABS)	299	369	28	PVBP	nd	313	50
3	PBNMeS	279	nd	29	P2MeS	265	nd	29
4	PBN2VN	320	398	30	P2VN	277	335, 401	30

[a] Longest wavelength absorption. [b] Wavelength emitted after excitation at λ_{max}. PVBP = poly(vinyl biphenyl); P2MeS = poly(2-methylstyrene); P2VN = poly(2-vinylnaphthalene).

Scheme 3. (a) Controlled Radical Polymerization by Reversible Deactivation.[a] (b) Liu and Jäkle: RAFT Polymerization of BNSt and 4-ABSt[28],[b]



[a] Green sphere represents a generic deactivating agent. [b] DDMAT = 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid; DMF = dimethylformamide; ACHN = 1,1′-azobis(cyanocyclohexane).

Different CTA structures are optimal for styrenes, acrylates, and other monomers.

Liu and Jäkle reported RAFT polymerization of both BNSt and 4-ABSt using the chain-transfer agent 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (Scheme 3b), a CTA optimized for styrene polymerization. Only P(4-ABS) demonstrated one of the signatures of CRP, chain extension upon introduction of additional monomer. Chain extension indicates end-group fidelity, that the chain cap can still be reversibly cleaved to allow further polymerization.

The outlook for BN aromatic vinyl monomer CRP is very promising. Future efforts will undoubtedly continue to explore methods in addition to RAFT, as well as the preparation of block copolymers containing BN aromatic side chains.

■ COPOLYMERIZATION

Copolymerization of two or more monomers is an essential strategy for tuning the physical properties of a polymer. The binary copolymerization behavior of two monomers M_1 and M_2 is described by their reactivity ratios r_1 and r_2, where r_1 is the ratio of the rate constants for M_1−M_1 homopolymerization divided by M_1−M_2 crosspolymerization and r_2 describes the ratio of the rate constants for M_2−M_2 homopolymerization divided by M_2−M_1 cross-polymerization. Alternating copolymers arise when $r_1 = r_2 \ll 0$, indicating a preference for cross-polymerization. This behavior is seen for structurally dissimilar monomers, such as the radical copolymerization of electron-rich styrene with electron-poor maleic anhydride. Statistical copolymerizations arise when r_1 and r_2 are both close to 1 and is typically only observed with structurally similar monomers.

Copolymerization of BN aromatic vinyl monomers with hydrocarbons is therefore an opportunity to assess the styrene-like reactivity of the organoborane. Copolymerizations with 2-methylstyrene (2MeSt), 2-vinylnaphthalene (2VN), and styrene have been reported. These studies uniformly suggest that BN aromatic vinyl monomers have comparable, but somewhat lower, reactivity compared to the analogous hydrocarbons.

BN-Methylstyrene (BNMeSt) and 2-Methylstyrene. Sönnichsen and Staubitz contrasted the homopolymerizations of BNMeSt and 2MeSt and also reported the free-radical copolymerization of 2MeSt and BNMeSt.[29] 2MeSt polymerization proceeded to higher conversion and provided higher molecular weight polymer than observed for free-radical polymerization of BNMeSt under similar reaction conditions (P2MeS, M_n = 46.7 kDa; PBNMeS, M_n = 16.5 kDa). A binary free-radical copolymerization (1:1 molar ratio of monomers) provided the atactic statistical copolymer P(2MeS-*co*-BNMeS) (M_n = 21.8 kDa) which was determined to be enriched in 2MeSt by NMR spectroscopy. The authors concluded that the relative rates of 2MeSt and BNMeSt homo- and crosspolymerization are of comparable magnitude, but 2MeSt is more reactive. Reactivity ratios were not reported.

The physical properties of the copolymer are intermediate between the parent homopolymers. P2MeS is an indefinitely stable white solid, while PBNMeS decomposes in air from a white to a brown solid within 72 h. P(2MeS-*co*-BNMeS) discolors more slowly than PBNMeS. A single copolymer glass transition temperature (T_g), the temperature at which the material transforms from a glassy to rubbery state, was observed at 114 °C. This single T_g, intermediate between the homopolymers (P2MeS, T_g = 132 °C; PBNMeS, T_g = 85 °C), supported microstructural assignment to a statistical copolymer.

BN2VN and 2-Vinylnaphthalene. In 2017, we described the free-radical copolymerization of BN2VN and 2VN.[30] Gel permeation chromatography (GPC) revealed a unimodal distribution of copolymer molecular weights. A bimodal molecular weight distribution would suggest formation of two homopolymers instead of a single copolymer. A suite of NMR spectroscopies (^{1}H, ^{11}B, ^{13}C) aided copolymer characterization. A UV−vis spectroscopic assay based on the different absorption intensities at 320 nm of the BN naphthalene and naphthalene side chains quantified BN2VN incorporation. Based on this assay, a close agreement between monomer feed ratio and copolymer composition was determined. P(BN2VN-*co*-2VN) was prepared with between 9.2 and 74 wt % BN2VN. Copolymer molecular weights (M_n) ranged between 6.0 and 8.4 kDa, with the highest molecular weight copolymers obtained from copolymers enriched in 2VN. Our results again suggested that the vinyl borane has comparable, but lower, reactivity than the hydrocarbon analog.

BN2VN and Styrene. In early 2018, we reported free-radical copolymerization of styrene and BN2VN. An optical assay based on the selective absorption at 320 nm of the BN naphthalene side chain confirmed BN2VN incorporation into the copolymer at levels commensurate with the feed ratio.[31] Reactivity ratios for BN2VN and styrene were determined from low conversion free-radical copolymerizations using both traditional linearization methods and modern nonlinear least-squares statistical analysis (Table 3 and Figure 2).[32] The reactivity ratios (r_1(BN2VN) = 0.423 and r_2(St) = 2.30) indicated a statistical copolymerization. Styrene is more reactive than BN2VN and at low conversion styrene-enriched copolymers were obtained. These insights enabled control over copolymer properties, such as the T_g.

Table 3. Reactivity Ratios for the Copolymerization of BN Aromatic Vinyl Monomers and Styrene

M_1	r_1	M_2	r_2	ref
VB	0.078	styrene	4.02	27
BN2VN	0.423	styrene	2.30	31

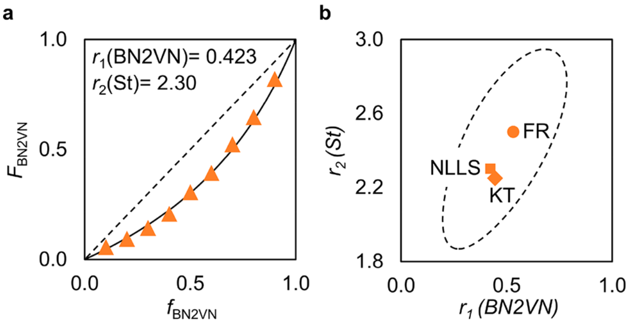


Figure 2. Klausen: styrene–BN2VN reactivity ratios. (a) Mayo–Lewis plot for the statistical copolymerization of BN2VN and styrene with AIBN.[32] Dashed line represents a random copolymerization ($r_1 = r_2 = 1$); solid curve is a fit to the experimental data and indicates a statistical copolymerization where $r_1 = 0.423$ and $r_2 = 2.30$. F_{BN2VN} = fractional composition of BN2VN in the copolymer; f_{BN2VN} = fractional composition of BN2VN in the monomer feed. (b) Reactivity ratios of statistical copolymerization of BN2VN and styrene with AIBN by Fineman–Ross (FR), Kelen–Tüdös (KT), and nonlinear least-squares (NLLS) analysis. Dashed ellipsoid represents the 95% confidence interval of NLLS analysis.[32]

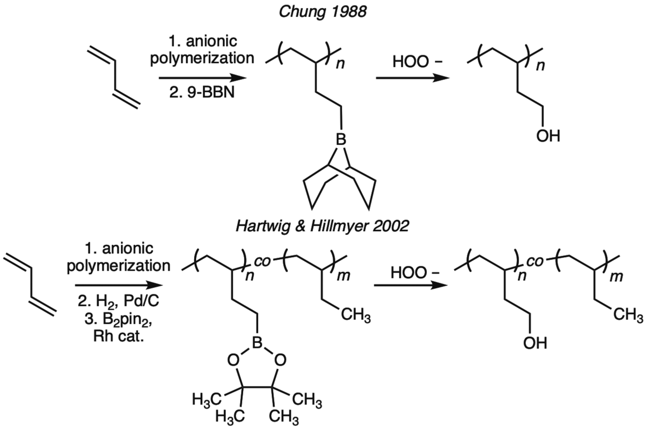
Sneddon reported the radical copolymerization of VB and styrene in 1991.[27] The reactivity ratios (r_1(VB) = 0.078 and r_2(St) = 4.02) indicated a greater reactivity mismatch between styrene and VB than between styrene and BN2VN. We attribute this reactivity difference to the increased aromaticity of BN naphthalene compared to borazine.[23,24,32]

BN2VN polymers show exciting potential as a solution to the challenge of preparing hydroxyl-functionalized polyolefins via postpolymerization modification. In the following section, we summarize oxidative postfunctionalization of PBN2VN-*stat*-PS yielding statistical styrene-vinyl alcohol copolymers.

■ POSTPOLYMERIZATION MODIFICATION

Organoboranes are versatile intermediates in synthetic chemistry, serving as precursors to alcohols, amines, and other functional groups.[25,26] This versatility highlights the potential for boron-functionalized polymers to serve as a platform to functional materials, but the challenge of introducing boron into the polymer limits the scope of relevant polymer architectures. Chung et al. functionalized alkenyl side chains in high-vinyl polybutadiene via hydroboration–oxidation,[53] while Hartwig and Hillmyer demonstrated catalytic C–H activation of poly(ethylethylene) (PEE)[54] to yield partially hydroxylated polymers (Scheme 4). Hillmyer et al. also reported C–H functionalization of the commodity polymers linear low-density polyethylene (LLDPE) and polypropylene.[55,56]

Scheme 4. Borane Strategy for Polyalcohol Synthesis



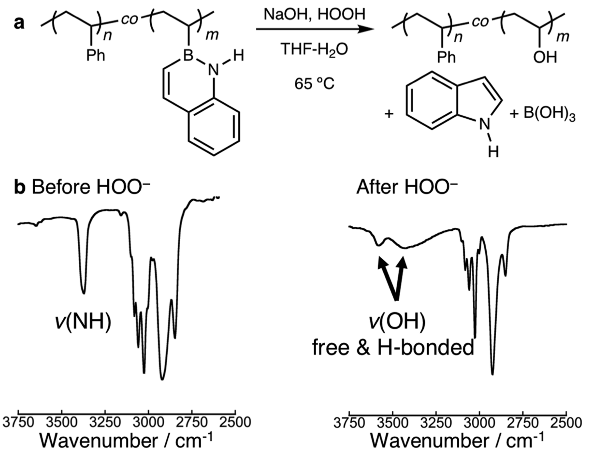
Challenges in the vinyl polymerization of trialkylboranes include deactivation of the double bond and the oxidative and hydrolytic instability of trialkylboranes. Chung reported Ziegler–Natta polymerization of the mono-hydroboration products derived from long-chain dienes, which were converted to polyalcohols by hydroperoxide oxidation.[57] A four-carbon or longer spacer was needed between the double bond and boron to avoid suppressing reactivity. Vinylboronic ester polymerization has been reported, but polymer sensitivity in air to hydrolysis and cross-linking limited characterization.[46,47]

Nonetheless, the significant commercial interest in the incorporation of a controlled amount of a polar functional group into a nonpolar polymer continues to motivate research into strategies for polymer functionalization. Polar functional groups play an essential role in modifying a plastic's strength, toughness, melting point, and solvent compatibility.[58,59] Examples of commercial polar–nonpolar copolymers include acrylonitrile-butadiene-styrene (ABS) and ethylene-vinyl acetate (EVA).[2,60] Challenges in the direct copolymerization of polar and nonpolar monomers are many but include the incompatibility of a Lewis basic functional group with the polymerization catalyst and significant mismatch in reactivity ratios.[61−63]

Styrene (St) and vinyl acetate (VAc) are a comonomer pair with fundamentally incompatible reactivity: St is far more reactive than VAc, and no VAc is incorporated in a binary copolymerization (r_1(St) = 55 and r_2(VAc) = 0.01).[64,65] The reactivity mismatch between VAc and conjugated monomers limits VAc's utility as a precursor to hydroxy-functionalized copolymers, even though poly(vinyl acetate) is a commodity polymer and precursor to poly(vinyl alcohol) (PVA) via side-chain saponification.[66]

The efficient statistical copolymerization of styrene and BN2VN suggested a solution to this challenge via oxidative conversion of the C−B bond into a C−O bond. We showed that alkaline hydrogen peroxide converted PBN2VN-*co*-PS to PVA-*co*-PS (Scheme 5a). Copolymers with variable BN2VN content (13−58 wt %) and molecular weights (M_n = 12.8−39.6 kDa) were investigated. In all cases, complete consumption of the organoborane side chain was observed. Overoxidation of the BN naphthalene side chain resulted in formation of indole and boric acid as byproducts. A methanol azeotrope removed residual boric acid as trimethyl borate. Infrared spectroscopy provided evidence of the characteristic hydroxy group stretching frequency (Scheme 5b).

Scheme 5. Klausen: Postfunctionalization of BN2VN Copolymers. (a) Typical Reaction Conditions for Oxidation of PBN2VN-*co*-PS to PVA-*co*-PS. (b) Cropped IR Spectra Highlighting the Disappearance of BN2VN ν(NH) Feature and Appearance of PVA ν(OH) Features after Oxidation[a]



[a] IR spectra reprinted with permission from ref 31. Copyright 2018 Wiley.

BN2VN enabled the first synthesis of statistical styrene-vinyl alcohol (SVA) copolymers. SVA copolymers showed tunable variation in physical properties with hydroxy content. Solubility in polar, protic solvents like methanol increased with increasing hydroxy concentration. Differential scanning calorimetry (DSC) also showed systematic variation in the T_g. While PBN2VN-*co*-PS had a T_g intermediate between PS and PBN2VN, after oxidation, the T_g was intermediate between PS and PVA.

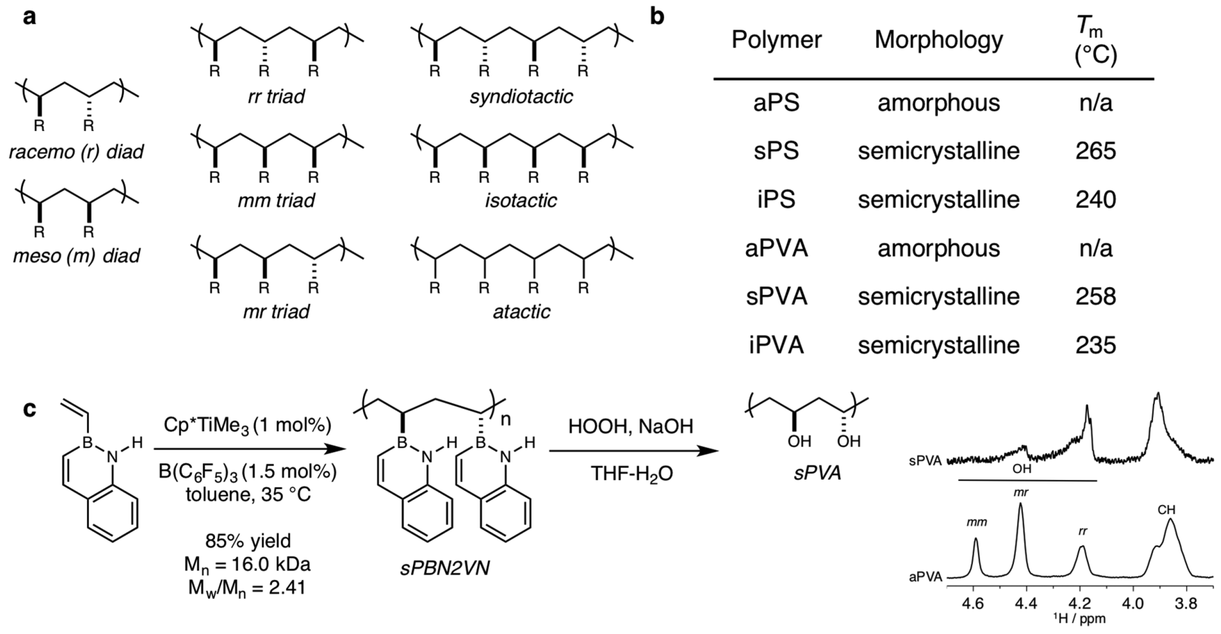
In the following section, we highlight a different application of postfunctionalization of BN aromatic side chains.

COORDINATION−INSERTION POLYMERIZATION

Transition-metal complexes catalyze coordination−insertion polymerization of ethylene, propylene, and other vinyl monomers, yielding high molecular weight commercial polymers. Rational ligand design in homogeneous catalysts has yielded highly stereoregular polymers.[67]

Polymer physical properties depend on the stereochemical relationships between adjacent repeat units in a polymer chain (Scheme 6a,b). There are three types of tactic, or stereoregular, polymers: atactic, syndiotactic, and isotactic. If the stereochemical configuration of two adjacent repeating units is the same, it is a *meso* (*m*) diad, while in a *racemo* (*r*) diad the configurations are different in the two repeating units. Two adjacent *racemo* diads make a *rr* triad, two adjacent *meso* diads make a *mm* diad, and adjacent *meso* and racemo diads make a *mr* triad. A perfectly syndiotactic macromolecular chain consists of exclusively *rr* triads, a perfectly isotactic chain consists

Scheme 6. (a) Stereoregular Polymer Nomenclature. (b) Variation in Physical Properties with Tacticity. (c) Klausen: Synthesis of Syndiotactic PBN2VN by Coordination−insertion Polymerization[a]



Polymer	Morphology	T_m (°C)
aPS	amorphous	n/a
sPS	semicrystalline	265
iPS	semicrystalline	240
aPVA	amorphous	n/a
sPVA	semicrystalline	258
iPVA	semicrystalline	235

[a] Oxidation yields syndiotactic poly(vinyl alcohol) (sPVA). Inset shows cropped ^{1}H NMR spectra (400 MHz, DMSO-d_6) of sPVA and aPVA highlighting the hydroxy triads. Spectrum reprinted with permission from ref 33.

exclusively of *mm* triads, and an atactic chain consists of a statistical distribution of *rr*, *mm*, and *mr* triads.

The synthesis of highly stereoregular polar polyolefins is limited by the challenge of identifying catalysts compatible with polar functional groups.[59,61] Open coordination sites on the metal interact with carbonyl, amine, and other functional groups, resulting in catalyst and/or polymer decomposition. Nonetheless, stereoregular polar polyolefins have interesting properties and applications. PVA hydrogels have potential therapeutic applications, and high molecular weight PVA fibrils exhibit high tensile strength.[68−70] Tacticity has a profound effect on both applications as relative stereochemistry influences the extent of intra- and intermolecular hydrogen bonding between hydroxy groups.[71,72] Synthetic routes to sPVA include cationic polymerization of vinyl ethers with bulky protecting groups[73−75] or radical polymerization of vinyl pivalate,[76,77] 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.

We demonstrated that syndioselective BN2VN coordination−insertion polymerization followed by stereoretentive oxidation provided sPVA by an orthogonal mechanism with the potential to address these limitations.[33] Homogeneous monocyclopentadienyl complexes[78,79] activated by Lewis acids are known to catalyze syndioselective styrene polymerization and are also effective BN2VN polymerization catalysts. BN2VN's aromaticity, and the dative interaction between neighboring elements, reduced the Lewis acidity and basicity of boron and nitrogen, resulting in compatibility with the oxophilic Ti catalyst. Additionally, BN2VN's aromaticity suggested its ability to intercept the mechanism of styrene syndioselective polymerization.[80] Indeed, we found that Cp*TiMe$_3$ and B(C$_6$F$_5$)$_3$ provided syndiotactic PBN2VN (sPBN2VN) in high yield (Scheme 6c). ^{1}H and ^{13}C NMR studies, as well as thermal properties, suggested a highly stereoregular structure. Sodium hydroperoxide oxidation of sPBN2VN yielded sPVA, as confirmed by ^{1}H NMR and IR spectroscopy.

■ OUTLOOK

The studies highlighted herein showcase the potential for BN polystyrenes to impact fundamental and applied polymer science. BN aromatic vinyl monomers exhibit styrene-like reactivity and versatility in several contexts, including facile radical copolymerization with aromatic hydrocarbons and the ability to intercept reaction mechanisms dependent on aromaticity. The unusual photophysical properties of BN polystyrenes not only point to sensing applications but also facilitate quantitative copolymer characterization. New directions for BN polystyrenes as intermediates in the preparation of functional copolymers and stereoregular polymers were emphasized. Future work will continue to expand the potential of these materials, including the preparation of other BN aromatic isomers (e.g., 1,3- or 1,4-azaborines) and the further development of modern polymerization chemistries.

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Notes

The authors declare the following competing financial interest(s): A patent application has been submitted by Johns Hopkins University based on an aspect of this research with H.L.V.D.W. and R.S.K. as co-inventors.

Biographies

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