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Authors: Heidi Lee van de Wouw, Jae Young Lee, Elorm C. Awuyah, and Rebekka S. Klausen

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A BN Aromatic Ring Strategy for Tunable Hydroxyl Content in Polystyrene

Heidi L. van de Wouw,[a] Jae Young Lee,[a] Elorm C. Awuyah,[a] Rebekka S. Klausen*[a]

Dedication ((optional))

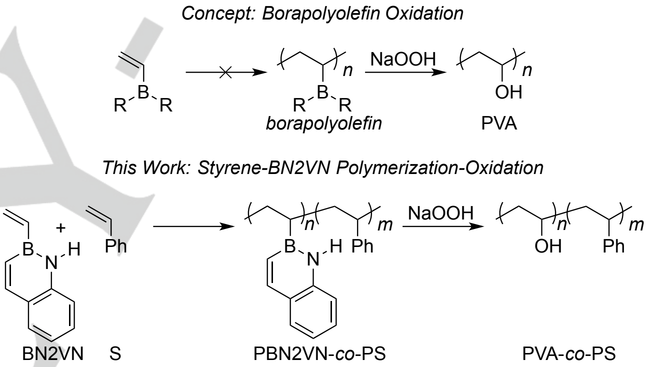
Abstract: BN 2-vinylnaphthalene, a BN aromatic vinyl monomer, is copolymerized with styrene under free radical conditions. Oxidation yields styrene-vinyl alcohol (SVA) statistical copolymers with tunable hydroxyl content. Comprehensive spectroscopic investigation provides proof of structure. Physical properties that vary systematically with hydroxyl content include solubility and glass transition temperature. BN aromatic polymers represent a platform for the preparation of diverse functional polymeric architectures via the remarkable reaction chemistry of C-B bonds.

The incorporation of polar functional groups into nonpolar polymers is an essential strategy for modifying the strength, toughness, and solvent resistance of a polymeric material.[1–4] Industrial examples include acrylonitrile-butadiene-styrene (ABS) and ethylene-vinyl acetate (EVA).[5,6] Challenges in the copolymerization of nonpolar and polar monomers include phase separation,[7] significant differences in reactivity (reactivity ratios),[8,9] and the limited compatibility of polar functional groups with polymerization catalysts.[4,10–12]

Here we describe a synthetic strategy that converts a nonpolar BN aromatic group into a polar hydroxyl substituent. This strategy ensures comonomer miscibility and compatible reactivity, while caging the potent reactivity of organoboranes within in a stable aromatic core, and accesses structures that are a challenge for existing technology. Our solution is based on the unique properties of 1,2-azaborines, aromatic rings in which one CC bond is replaced with the BN bond.[13–15] Recognizing the versatility of organoboranes in synthesis,[16,17] we hypothesized that sodium hydroperoxide (NaOOH) oxidation[18] of a vinylborane polymer would yield derivatives of water-soluble poly(vinyl alcohol) (PVA) (Scheme 1). However, concerns about the hydrolytic and oxidative stability of boron reagents, as well as the propensity of vinyl boronic acids to undergo protodeboronation,[19] have contributed to limited investigation of vinyl boronate polymerization.[20]

Polymerization of azaborine vinyl monomers is promising given their increased stability relative to other boranes.[21,22] Building on Sneddon's description of the polymerization of vinyl borazine,[23] several groups have recently reported free radical polymerization of azaborine vinyl monomers.[24–26] This complements progress on inorganic main chain BN polymers and azaborine-derived conjugated polymers.[15,27–31] We described the synthesis and gram-scale free radical polymerization of BN 2-vinylnaphthalene (BN2VN), as well as the preparation of copolymers with 2-vinylnaphthalene (2VN).[26]

BN2VN polymers are attractive candidates for investigating borapolyolefin oxidation due to the scalable monomer synthesis.[26,32,33] We prepare BN2VN in high overall yield and in two steps from commercially available starting materials. The multistep syntheses of monocyclic azaborine vinyl monomers limit polymerizations to milligram scale.[24,25] The successful copolymerization of BN2VN and 2VN suggests the feasibility of copolymerization of styrene and BN2VN (PBN2VN-*co*-PS).



Scheme 1. Preparation of PVA derivatives via organoborane oxidation. S = styrene; BN2VN = BN 2-vinylnaphthalene; PVA = poly(vinyl alcohol).

Oxidative cleavage of the C-B bonds in PBN2VN-*co*-PS yields PVA-*co*-PS, a copolymer of nonpolar styrene and polar vinyl alcohol, in which the hydroxyl content is tuned by the BN2VN content in the starting copolymer. The styrene-vinyl alcohol (SVA) statistical copolymer is not directly accessible from free radical copolymerization of styrene and vinyl acetate; styrene-enriched polymer is obtained due to the reactivity of the styrene radical relative to the vinyl acetate radical.[34]

The oxidation was probed with model compound **1** (Figure 1). Upon treatment with NaOOH, complete conversion of **1** to two products of was observed within 10 minutes at 0 °C. ^{1}H NMR spectroscopic analysis of the unpurified reaction mixture and comparison to authentic samples supports the assignment of these products as indole **2** and phenethyl alcohol **3** (Figure 1). Indole arises from oxidation of both C-B bonds of **1** to an intermediate enol that tautomerizes and cyclizes. Liu *et al.* recently described oxidative functionalization of the exocyclic C-B bond of azaborines in which the alkyl fragment dimerizes.[35]

Having established the viability of the organoborane oxidation, we investigated the free radical copolymerization of

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[a] Ms. H. L. van de Wouw, Mr. J. Y. Lee, Mr. E. Awuyah, Prof. R. S. Klausen*
Department of Chemistry
Johns Hopkins University
3400 N. Charles St, Baltimore, MD 21218
E-mail: klausen@jhu.edu

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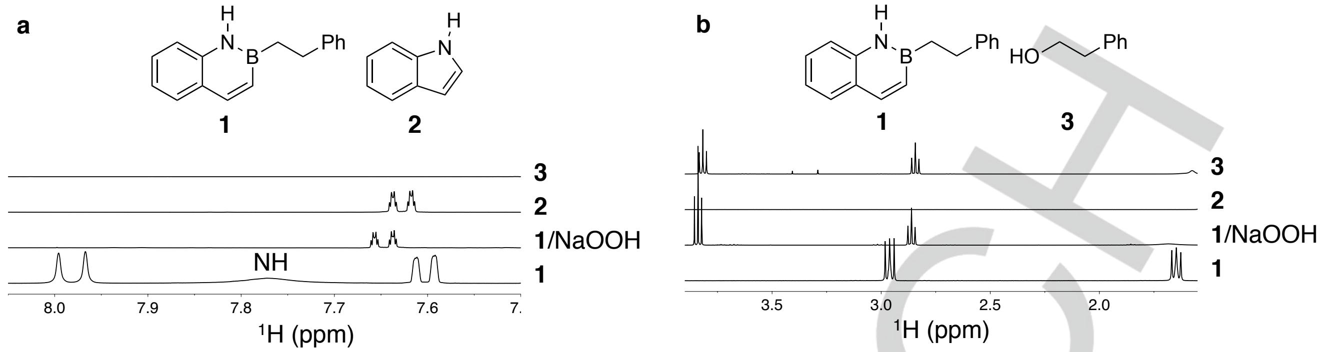

Figure 1. ^{1}H NMR analysis of NaOOH-mediated oxidation of compound **1** (CD_2Cl_2). Top to bottom: Phenethyl alcohol (**3**), indole (**2**), unpurified reaction mixture, **1**. a) Aromatic region. b) Aliphatic region.

BN2VN and styrene with a focus on quantifying the incorporation of BN2VN. Polymerizations were conducted with azoisobutyrylnitrile (AIBN, 1 mol%) in toluene or in neat styrene (Table 1). Copolymerizations were conducted with feed ratios of 60 wt. %, 33 wt. %, or 14 wt. % BN2VN.

Table 1. PBN2VN-*co*-PS and PS molecular weight characteristics.

Sample Name[a]	Before H_2O_2/NaOH[b]		After H_2O_2/NaOH[b],[c]	
	M_n (kDa)	$Đ$	M_n (kDa)	$Đ$
Polymerization conditions: AIBN (1 mol%), toluene ([monomers] = 10 M).				
P(BN2VN$_{48}$-*co*-S$_{51}$)	12.8	1.72	7.84	2.23
P(BN2VN$_{32}$-*co*-S$_{92}$)	14.5	1.75	9.65	2.01
P(BN2VN$_{14}$-*co*-S$_{119}$)	14.6	1.78	12.1	1.87
PS$_{129}$	13.5	1.88	14.8	1.76
Polymerization conditions: AIBN (1 mol%), neat.				
P(BN2VN$_{127}$-*co*-S$_{141}$)	34.4	4.23	24.1	2.01
P(BN2VN$_{87}$-*co*-S$_{236}$)	38.1	4.91	21.6	2.55
P(BN2VN$_{32}$-*co*-S$_{332}$)	39.6	5.40	34.3	2.72
PS$_{313}$	32.6	5.03	33.8	4.79

[a] Subscript = average degree of polymerization of comonomer. [b] Determined by GPC analysis at 254 nm relative to a polystyrene standard. [c] Oxidation conditions: 6 N NaOH, 30% H_2O_2, THF-EtOH, 65 °C, 15 hours.

All polymerizations proceeded to >75% conversion. The use of toluene resulted in polymers of moderate molecular weight and dispersity (12.8-14.6 kDa, $Đ$ = 1.72-1.88 Table 1). Similar results are obtained in a control reaction with styrene alone (PS$_{129}$). Gel permeation chromatography (GPC) curves of the polymers are unimodal, consistent with formation of a single copolymer instead of two homopolymers (Figure 2a).

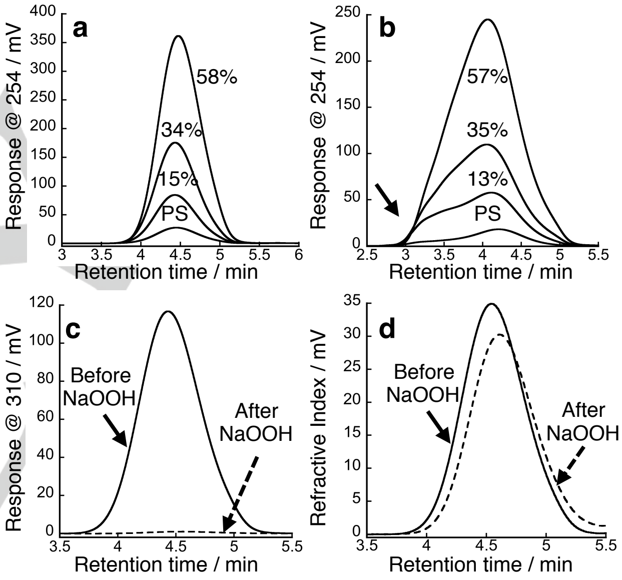

Figure 2. GPC curves of copolymers. a) Polymerization in toluene. Labels refer to the wt. % of BN2VN. b) Polymerization in neat styrene. Arrow indicates a high molecular weight shoulder. c) Response by absorbance at 310 nm. GPC curves of PBN2VN$_{32}$-*co*-PS$_{92}$ before (solid) and after (dashed) NaOOH treatment. d) Response by refractive index. GPC curves of PBN2VN$_{32}$-*co*-PS$_{92}$ before (solid) and after (dashed) NaOOH treatment.

Neat reaction conditions provided high molecular weight polymers with high molecular weight distributions (32.6-39.6 kDa, $Đ$ = 4.23-5.40, Table 1). GPC curves show a shoulder at high molecular weight that contributes to the high dispersity (Figure 2b, shoulder indicated with a black arrow). Homopolymerization of each monomer is unlikely as the shoulder is also observed in the PS control reaction. Additionally, the molecular weight distribution is unchanged when the absorbance wavelength is changed from 254 nm to 310 nm (Figure S1). Since PS is transparent at 310 nm, if two homopolymers were present, only one peak should be observed at 310 nm. Instead, we suggest that the shoulder is a consequence of the gel effect in which at

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high molecular weight, the slow diffusion of the viscous polymer results in accelerated chain growth.[9]

In our prior work on BN2VN-2VN copolymerization, we described a UV-vis absorbance spectroscopy assay for BN2VN incorporation based on the differential absorption of naphthalene and BN-naphthalene at 320 nm.[26] A similar calibration curve was constructed for BN2VN and styrene (Figure S2). A plot of extinction coefficient at 320 nm (ε_{320}) versus the wt. % PBN2VN in binary mixtures of the homopolymers yields a straight line. A linear regression analysis of the data yields eq. 1 in which X = the weight percent of BN2VN incorporation. Using the experimentally determined copolymer ε_{320} and eq. 1, the PBN2VN-*co*-PS samples were analysed for wt. % BN2VN incorporation. The experimentally determined incorporation closely matched the feed ratio (Table 2). Elemental analysis is consistent as well.

$$\varepsilon_{320} = 28.2X + 0.208\ (eq\ 1)$$

Table 2. Copolymer optical properties and BN2VN incorporation.

Sample Name	Feed Ratio wt. % BN2VN	ε_{320} [a]	Experimental wt. % BN2VN[b]
P(BN2VN$_{48}$-*co*-S$_{51}$)	60	16.8	58
P(BN2VN$_{32}$-*co*-S$_{92}$)	33	9.74	34
P(BN2VN$_{14}$-*co*-S$_{119}$)	14	4.50	15
P(BN2VN$_{127}$-*co*-S$_{141}$)	60	16.4	57
P(BN2VN$_{87}$-*co*-S$_{236}$)	33	10.2	35
P(BN2VN$_{32}$-*co*-S$_{332}$)	14	3.79	13

[a] In L g^{-1} cm^{-1}. [b] Determined by ε_{320} according to eq. 1.

NaOOH oxidation of PBN2VN-*co*-PS copolymers was conducted. Data for P(BN2VN$_{32}$-*co*-S$_{92}$) are described here as a representative example (see Figure S3 for other copolymers). Reaction progress is monitored by GPC analysis at 310 nm. The loss of absorption at 310 nm before and after oxidation (Figure 2c) is consistent with cleavage of the BN2VN chromophore from the polymer. Extended reaction times and heating (15 h/65 °C) are required to observe >90% loss of signal at 310 nm. The need for forcing conditions is attributed to *in situ* cross-linking of the polymer with boric acid formed from oxidation of the azaborine (indole is also observed in crude reaction mixtures). During isolation, a methanol azeotrope removes boric acid as trimethyl borate.

Comparing GPC traces of oxidized P(BN2VN$_{32}$-*co*-S$_{92}$) measured by optical response at 310 nm versus refractive index (RI) provides compelling evidence that the polymer chains are intact. While no absorbance at 310 nm is observed after oxidation (Figure 2c), the RI data show a unimodal distribution and a modest decrease in molecular weight consistent with loss of the large BN naphthalene group (Figure 2d). Control reactions with PS$_{129}$ and PS$_{313}$ do not show a decrease in molecular weight. If unselective oxidation leading to backbone fragmentation were occurring, the GPC traces of the borapolyolefins and PS samples would no longer be unimodal. The intact macromolecular backbone is consistent with prior work by Chung and others on functionalization of polyethylene and polypropylene by hydroboration-oxidation of vinyl end groups[3,36] or internal unsaturation arising from copolymerization with dienes.[37–39] Table 1 summarizes the molecular weight characteristics of all polymers in this study before and after oxidation. Polymer fractionation during reisolation may be occurring, as the polymers exhibiting a high molecular weight shoulder (Figure 2c) show a narrower and more unimodal dispersity after reisolation.

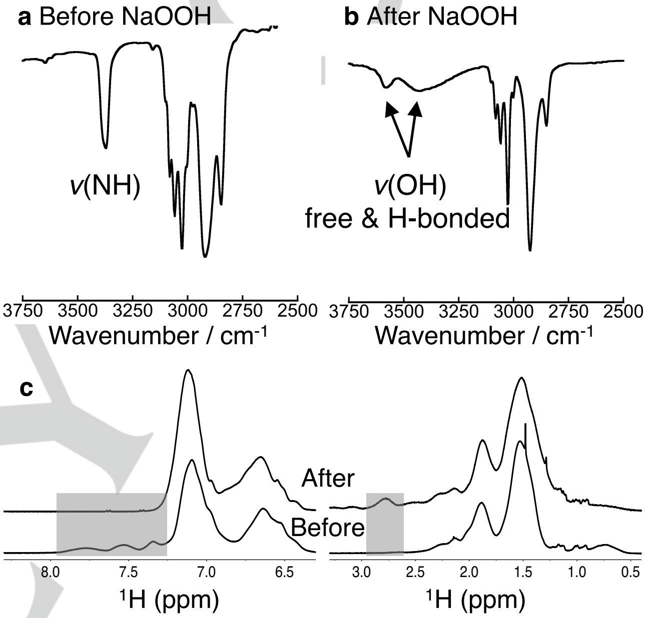

Figure 3. a) FTIR spectrum of P(BN2VN$_{32}$-*co*-S$_{92}$). b) FTIR spectrum of oxidized P(BN2VN$_{32}$-*co*-S$_{92}$). c) ^{1}H NMR spectra of P(BN2VN$_{32}$-*co*-S$_{92}$) before (bottom) and after (top) NaOOH treatment. The gray box (left) highlights changes in the aromatic region. The gray box (right) highlights the appearance of new signals at higher field after oxidation.

Infrared (IR) spectroscopy of the oxidized copolymers is consistent with a PVA-*co*-PS structure. PVA has several characteristic features in its IR spectrum, including a strong, broad OH stretching frequency at 3340 cm^{-1}.[40] Hydrogen-bonding is well known to broaden and shift the OH resonance to lower frequencies[41] and the unusually low frequency hydroxyl resonance in PVA is attributed to strong hydrogen-bonding networks.[40] FTIR spectroscopic analysis of P(BN2VN$_{32}$-*co*-S$_{92}$) before and after NaOOH treatment shows significant changes (Figure 3a-b), including the loss of the NH stretching frequency, but retention of aromatic CH stretching frequencies consistent with polystyrene.[42] After oxidation, two features consistent with an OH stretch are observed, a comparatively sharp resonance at 3570 cm^{-1} and a broader resonance at 3430 cm^{-1} (Figure 3b). These resonances are assigned to free OH and hydrogen-bonded OH groups, respectively. As the BN2VN content of the original copolymers increases, the resonance assigned to the hydrogen-bonded OH group broadens, intensifies, and shifts to even lower frequency, consistent with increased hydrogen-bonding (Figure S4). There is no evidence of hydroxyl groups in NaOOH-treated PS control samples.

^{1}H NMR spectra of P(BN2VN$_{32}$-*co*-S$_{92}$) before and after NaOOH treatment show disappearance of the BN2VN peaks in the aromatic region, but not the loss of styrenic signals in the aromatic region (left box, Figure 3c). In the aliphatic region, after NaOOH treatments new peaks are observed at 2.5-3.0 ppm that are not observed in the borapolyolefin (right box, Figure 3c). These peaks are assigned to protons adjacent to hydroxyl functionality. This assignment is consistent with the greater than 2.0 ppm change in chemical shift of the protons adjacent to the boron atom upon oxidation to phenethyl alcohol observed in model system **1** (Figure 1).

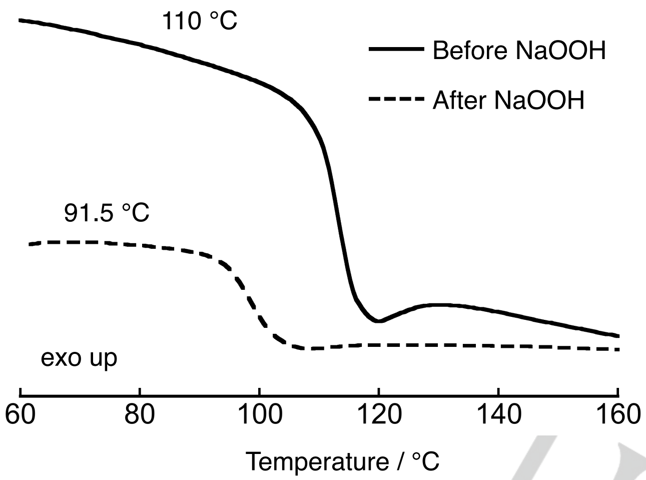

Figure 4. DSC curves of P(BN2VN$_{87}$-*co*-S$_{236}$) before (solid) and after (dashed) NaOOH treatment. The onset T_g is indicated.

The white powdery SVA copolymers exhibit physical properties that vary with hydroxyl content, including miscibility with polar, protic solvents and glass transition temperature (T_g). While low hydroxyl content polymers like P(BN2VN$_{14}$-*co*-S$_{119}$) are purified by precipitation into methanol, polymers with higher hydroxyl content are soluble in methanol and must be isolated by precipitation into water. Glass transition temperatures (T_g's) were determined by differential scanning calorimetry (DSC). Borapolyolefin P(BN2VN$_{87}$-*co*-S$_{236}$) has a single glass transition with an onset at 110 °C, intermediate between PS (104 °C) and PBN2VN (129 °C) and consistent with a statistical copolymer. After NaOOH treatment, a single T_g is observed intermediate between PS (104 ºC) and PVA (85 ºC) and significantly lower than PBN2VN (Figure 4).

Here we demonstrate that BN2VN, a BN aromatic vinyl monomer, exhibits styrene-like reactivity and forms statistical S-BN2VN copolymers under free radical conditions. Chemoselective organoborane oxidation providing novel SVA statistical copolymers is demonstrated. The hydroxyl content is tuned by the starting BN2VN content. This synthetic strategy opens up a pathway for modulating the properties of two industrially relevant polymers, PS and PVA. The concept of oxidizing a protected borane is not limited to the statistical copolymers described herein and BN2VN copolymers represent a platform for the preparation of diverse polymeric architectures via the remarkable chemistry of C-B bonds.

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Keywords: copolymerization • boranes • heterocycles • amphiphiles • oxidation

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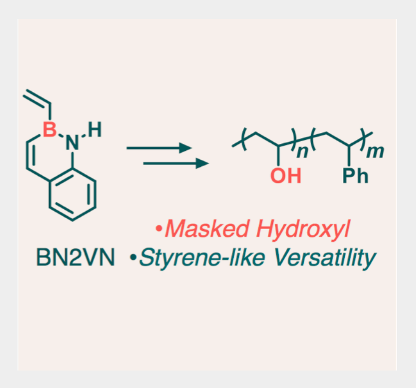
A versatile strategy for functional polymer synthesis is described. An aromatic cage around a vinyl boron compound lends it styrene-like reactivity, while postpolymerization oxidation reveals a hydroxyl functional group.



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