Macromolecules

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Characterization of Styrene–Vinyl Alcohol Copolymers by CP-MAS NMR Spectroscopy

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Cite This: *Macromolecules* 2022, 55, 7032–7038 Read Online

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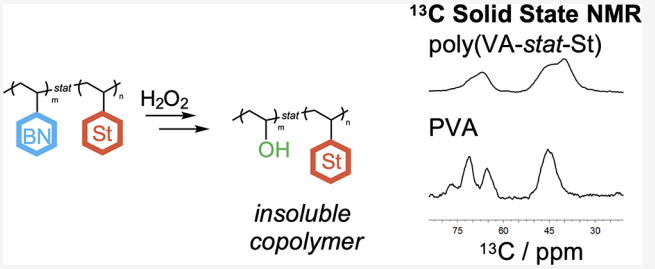
ABSTRACT: The first solid-state characterization of statistical copolymers of vinyl alcohol and styrene (poly(VA-*stat*-St)) by cross-polarization magic angle spinning (CP-MAS) spectroscopy is described. Poly(VA-*stat*-St) is not available from the traditional feedstocks styrene (St) and vinyl acetate (VAc) due to a mismatch in reactivity ratios. BN 2-vinylnaphthalene (BN2VN) is a synthetic solution to this challenge as it copolymerizes with activated monomers (e.g., styrene, methyl methacrylate), and the BN naphthalene side chain can be oxidatively converted to hydroxyl (−OH) side chains. While high levels of BN2VN incorporation are readily achieved (e.g., >75 mol % BN2VN), prior work has identified that poly(VA-*stat*-St) is poorly soluble in organic solvents when the molar fraction of VA exceeds 0.50, presumably due to the hydrophilic character of the hydroxyl group as well as possible interchain hydrogen bonding. Circumventing this solubility challenge, we describe quantitative solid-state ^{13}C CP-MAS spectra demonstrating high conversion (85–99%) of poly(BN2VN-*stat*-St) to poly(VA-*stat*-St). ^{11}B CP-MAS confirmed the removal of organoborane functional groups.



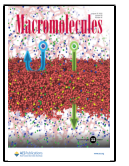
INTRODUCTION

Organoborane polymers appeal as intermediates to functional polyolefins[1] via the versatile chemistry of the C–B bond.[2] While boron can be introduced postpolymerization via hydroboration[3−5] or catalytic borylation,[6−8] in recent years, vinyl boranes[9,10] have sparked significant interest both to elucidate their reactivity as well as for their suitability as alternatives to the unactivated monomer vinyl acetate (VAc)[11] for the synthesis of poly(vinyl alcohols) (PVA).[12] We reported BN 2-vinylnaphthalene (BN2VN) as an aromatic[13,14] monomer that readily copolymerizes with activated monomers like 2-vinylnaphthalene,[15] styrene,[16−18] and methyl methacrylate.[19] BN2VN's aromaticity results in a close agreement in reactivity ratios with styrene (St) during radical polymerization (r_1(St) = 2.30; r_2(BN2VN) = 0.423)[16] and compatibility with coordination polymerization catalysts.[20,21] Organoborane oxidation under aqueous or organic conditions afforded vinyl alcohol (VA) (co)polymers.[17,19] Ouchi and Nishikawa have described isopropenyl pinacol boronate ester (IPBpin) as an electron-rich monomer[22] that copolymerizes with St (r_1(St) = 1.41; r_2(IPBpin) = 0.085) and can be oxidatively converted to methyl vinyl alcohol residues.[23,24] In 2021, Ouchi and Nishikawa reported vinyl pinacol boronate ester (VBpin)–styrene copolymerizations (r_1(St) = 3.77; r_2(VBpin) = 0.25) and postpolymerization organoborane oxidation.[25] Very recently, Chen et al. reported free-radical polymerization of gem-trifluoromethyl/boron-functionalized monomers.[26]

An advantage of organoborane monomers is a closer match in reactivity ratios with St that allows for higher incorporation of hydroxyl side chain precursors in copolymers. For example, we have reported styrenic copolymers with 50, 75%, and as high as 90% incorporation of BN2VN.[18] Oxidation typically proceeded to high conversion,[17] which should provide polyvinyl alcohols with styrene as a minimal comonomer.

However, we have not previously reported the synthesis of poly(St-*stat*-VA) with molar fraction VA over 50% because the insolubility in both organic solvents and in water precluded solution-phase characterization by NMR or ultraviolet–visible (UV–vis) spectroscopy, which provides quantitative estimates of functional group conversion.[15,16] The low solubility was attributed to the combination of both hydrophilic and hydrophobic segments in the macromolecule, as well as the possibility of intra- and interchain hydrogen bonding.[27] Therefore, our structural characterization was limited to infrared (IR) spectroscopy of thin films, which provided only qualitative evidence of functional group interconversion. As the properties of PVA obtained from side chain hydrolysis of PVAc[28] strongly depend on conversion, a quantitative method for determination of side chain functional group interconver-

Received: May 13, 2022
Revised: July 15, 2022
Published: August 1, 2022



https://doi.org/10.1021/acs.macromol.2c01009
Macromolecules 2022, 55, 7032–7038

sion is critical for understanding structure−property relationships.

Herein, we report solid-state cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy to structurally characterize poly(VA-*stat*-St) arising from oxidation of poly(BN2VN-*stat*-St). Spectroscopic signatures consistent with side chain C−OH and C−Ph groups were identified. By optimizing acquisition parameters (e.g., contact time), we obtained quantitative spectra which estimated 85-99% conversion of BN naphthalene side chains to −OH groups. We also report ^{11}B CP-MAS spectra confirming consumption of the BN naphthalene side chain. We expect the solid-state NMR analytical methods described herein to facilitate the further study and use of amphiphilic copolymers.

EXPERIMENTAL SECTION

General Procedure: (Co)polymerization. An oven-dried 15 mL heavy walled cylindrical pressure vessel equipped with a stir bar was brought into a nitrogen-filled glovebox and charged with the appropriate monomer(s) (10 mmol total) and AIBN (1 mol %, 0.1 mmol, 16.4 mg). The pressure vessel was sealed with a Teflon cap and brought out of the glovebox, covered by aluminum foil, and heated (in a preheated oil bath) at 60 °C for 24 h with vigorous stirring. The flask was cooled to room temperature and quenched by opening the reaction flask in air. The polymer was isolated by dissolving in toluene (5 mL) and immediately pipetting the solution into a beaker of methanol (200 mL). Over the course of 20 min, the polymer precipitated from solution and was isolated by filtering off the methanol solution through a fritted funnel. The collected polymer was washed with additional methanol (2 × 50 mL), then transferred with a spatula to an empty round bottle flask. The precipitation−filtration process was repeated twice. The precipitate was transferred to a tared scintillation vial for storage, dried on the Schenk line for about 30 min, and then finally dried in a vacuum oven for 36 h at 85 °C.

PS (762.8 mg, 74%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.36−6.11 (m, 5H), 2.32−0.95 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 145.79, 145.40, 127.97, 127.65, 125.64, 44.10, 40.38. ATR ν_{max}: 3026 (m), 2924 (m), 2850 (w), 1601 (w), 1493 (m), 1452 (m), 756 (m), 699 (s) cm^{-1}.

P28−B (856.4 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.36−6.11 (m, 5H), 2.32−0.95 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 145.79, 145.40, 127.97, 127.65, 125.64, 44.10, 40.38. ATR ν_{max}: 3026 (m), 2924 (m), 2850 (w), 1601 (w), 1493 (m), 1452 (m), 756 (m), 699 (s) cm^{-1}.

P47−B (941.6 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.81−5.83 (m, 6H), 2.48−0.17 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 145.95, 143.98, 139.84, 129.05, 127.87, 125.55, 125.32, 120.40, 117.73, 42.89, 40.63, 27.66, 25.64. ATR ν_{max}: 3372 (w), 3006 (m), 2880 (m), 2832 (w), 1612 (m), 1557 (s), 1433 (s), 802 (m), 755 (s), 696 (s), 592 (w), 455 (s) cm^{-1}.

P63−B (911.1 mg, 84.0%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.36−6.11 (m, 5H), 2.32−0.95 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 145.79, 145.40, 127.97, 127.65, 125.64, 44.10, 40.38. ATR ν_{max}: 3026 (m), 2924 (m), 2850 (w), 1601 (w), 1493 (m), 1452 (m), 756 (m), 699 (s) cm^{-1}.

PBN2VN (560.1 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 8.07−5.64 (m, 7H), 2.48−0.18 (m, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 143.78, 139.87, 127.68, 129.03, 125.19, 120.30, 117.61, 38.90, 29.72. ATR ν_{max}: 3381 (m), 3008 (w), 2885 (m), 2836 (m), 1613 (m), 1562 (m), 1437 (s), 807 (m), 761 (s) cm^{-1}.

General Procedure: Oxidation. An oven-dried round bottle flask (250 mL) equipped with a stir bar was charged with copolymer (300 mg). Tetrahydrofuran (30 mL), ethanol (10 mL), aqueous sodium hydroxide (6 N, 15 mL), and H_2O_2 (30% v/v, 10 mL) were added into the flask at room temperature. The reaction was stirred at room temperature for 30 min, and an open reflux condenser was added afterward. The reaction was then heated to 65 °C for 18 h. The reaction vessel was cooled to room temperature, and deionized water (100 mL) was added to precipitate the polymer. The precipitate was collected by filtration through a frittered filter and washed with an additional 100 mL of H_2O. The polymer was transferred to a tared scintillation vial and dried in a vacuum oven at 85 °C for 16 h.

P28−OH (128.6 mg, 64%). ^{13}C CP-MAS NMR (125 MHz, 20k Hz): δ 141.9−133.4, 120.2−112.1, 65.6−73.2, 47.4−27.6. ATR ν_{max}: 3583 (w), 3439 (w), 3026 (m), 2924 (m), 2850 (w), 1601 (w), 1493 (m), 1452 (m), 1028 (w), 758 (m), 699 (s) cm^{-1}.

P47−OH (170.2 mg, 57%). ^{13}C CP-MAS NMR (125 MHz, 20k Hz): δ 140.8−136.1, 121.7−109.3, 65.4−73.1, 46.6-26.83. ATR ν_{max}: 3579 (w), 3433 (w), 3025 (m), 2926 (m), 2850 (w), 1601 (w), 1492 (m), 1451 (m), 1025 (w), 759 (m), 693 (s) cm^{-1}.

P63−OH (125 mg, 41%). ^{13}C CP-MAS NMR (125 MHz, 20k Hz): δ 141.1−135.5, 120.8−111.1, 65.4−73.6, 47.5−27.2. ATR ν_{max}: 3581 (w), 3438 (w), 3025 (m), 2926 (m), 2852 (w), 1604 (w), 1492 (m), 1453 (m), 1028 (w), 758 (m), 699 (s) cm^{-1}.

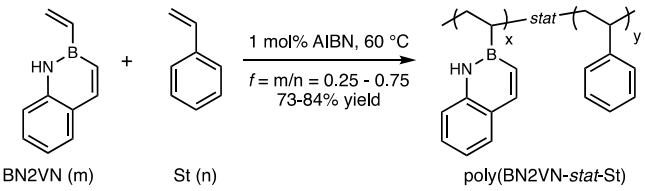
^{1}H NMR, ^{13}C {^{1}H} NMR, ^{11}B NMR, and other one-dimensional (1D) and two-dimensional (2D NMR) experiment spectra were recorded on a Bruker UltraShield Avance III 400 MHz spectrometer, and chemical shifts were reported in parts per million (ppm). Spectra were recorded in dichloromethane-d_2 with the residual solvent peak as the internal standard (^{1}H NMR: CH_2Cl_2, δ = 5.32 ppm; ^{13}C NMR: CH_2Cl_2, δ = 53.84 ppm). Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). All polymer spectra were acquired using quartz NMR tubes from Wilmad.

^{11}B and ^{13}C cross polarization magic angle spinning (CP-MAS) experiment spectra were recorded on a Bruker Ascend spectrometer (500 MHz), and chemical shifts were reported in parts per million (ppm). Around 20 mg of polymer samples were packed into a sample rotor compatible with a 3.2 mm Phoenix HX probe. Spectral data was acquired at a spinning speed of 20 kHz.

RESULTS AND DISCUSSION

BN2VN−St Copolymerization and Characterization. Free-radical copolymerization of styrene (St) and BN2VN was initiated by AIBN (1 mol %) in the absence of solvent at 60 °C (Scheme 1). These polymerization conditions were chosen

Scheme 1. Free-Radical Bulk Copolymerization of BN2VN and St[a]



[a]AIBN = azoisobutyronitrile; f = molar fraction of BN2VN in monomer feed.

based on extensive prior investigation of reaction parameters to maximize molecular weight.[18] The yield of copolymers ranged from 73 to 84% after precipitation in methanol. The molar fraction (f) of BN2VN in the monomer feed varied between 0.25, 0.50, and 0.75. The amount of BN2VN incorporated into the final copolymer was determined by a previously reported UV−vis spectroscopic assay (Table 1).[16] Copolymers were named as P28−B, P47−B, or P63−B to reflect the molar fraction of BN2VN in the copolymer (F). Post oxidation (vide infra), copolymers were named as P28−OH, P47−OH, or P63−OH. Weight-average molecular weight (M_w) of the copolymers were in the range 10^5−10^6 g mol^{-1}. Broad molecular weight distributions (M_w/M_n) with bimodal size exclusion chromatograms were observed (Figure S1). This has

https://doi.org/10.1021/acs.macromol.2c01009
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Table 1. Molecular Weight Information of BN2VN−St Copolymers with Different Feed Ratios

name	f^a	F^b	M_n (kg mol^{-1})^c	M_w (kg mol^{-1})^c	M_w/M_n
PS	0	0	59.5	289	4.85
P28−B	0.25	0.28	21.9	243	11.1
P47−B	0.50	0.47	45.3	270	5.96
P63−B	0.75	0.63	28.2	203	7.19
PBN2VN	1.00	1.00	29.5	293	10.1

[a]Molar fraction of BN2VN in monomer feed. [b]Molar fraction of BN2VN in the copolymer. [c]Determined by gel permeation chromatography (GPC) analysis with RI detection to polystyrene standard (THF, 20 μL, 35 mL min^{-1}, 40 °C).

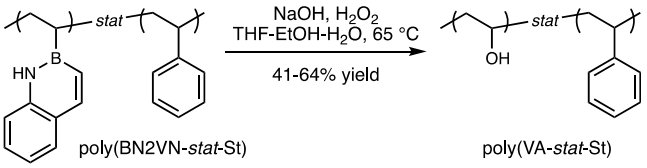
previously been attributed to chain transfer to polymer in the bulk polymerization.

The soluble statistical copolymers poly(BN2VN-*stat*-St) were characterized by attenuated total reflectance (ATR) spectroscopy and ^{1}H, ^{11}B, and ^{13}C nuclear magnetic resonance (NMR) spectroscopy in solution (Figure 1). Complete details of structural characterization have been reported previously[17,18] but are briefly summarized here for comparison to poly(VA-*stat*-St) samples. Diagnostic resonances by ATR include the NH stretching frequency at ca. 3375 cm^{-1} (Figure 1a), which was seen in both PBN2VN and copolymers. ^{1}H and ^{13}C NMR spectroscopy also indicated resonances consistent with both side chains. P63−B had a broad aromatic region (δ 6.24−8.21, Figure 1b) corresponding to overlapping BN2VN and St side chains. The methine and methylene groups also overlapped (δ 0.53−2.26). Similar conclusions were drawn with regard to the ^{13}C NMR spectra (Figure 1c). The quadrupolar ^{11}B nucleus had a weakening effect on adjacent ^{13}C resonances.[29]

Oxidation. Aqueous oxidation (H_2O_2/NaOH) effected the conversion of BN naphthalene side chains to vinyl alcohol residues (Scheme 2). The three copolymers exhibited very different solubility properties. Only P28−OH was soluble in $CDCl_3$, while P47−OH and P63−OH were insoluble. On the other hand, P63−OH was completely soluble in methanol-*d*, but P28−OH and P47−OH were not (Figure 2). These solubility trends precluded direct comparison of all three copolymers to each other under similar conditions. In addition, comparison of P63−OH to prior published spectra of poly(VA-*stat*-PS) samples prepared in $CDCl_3$ to confirm structural identity was not possible. Solution-phase NMR spectroscopic characterization of P28−OH in $CDCl_3$ confirmed the presence of signatures consistent with OH groups (Figure S2),[17] and UV−vis spectroscopy estimated 91% conversion of BN2VN to VA (Figure S3).

For chloroform-insoluble P47−OH and P63−OH, initial characterization by ATR spectroscopy (thin film) confirmed

Scheme 2. Synthesis of Poly(VA-*stat*-St)



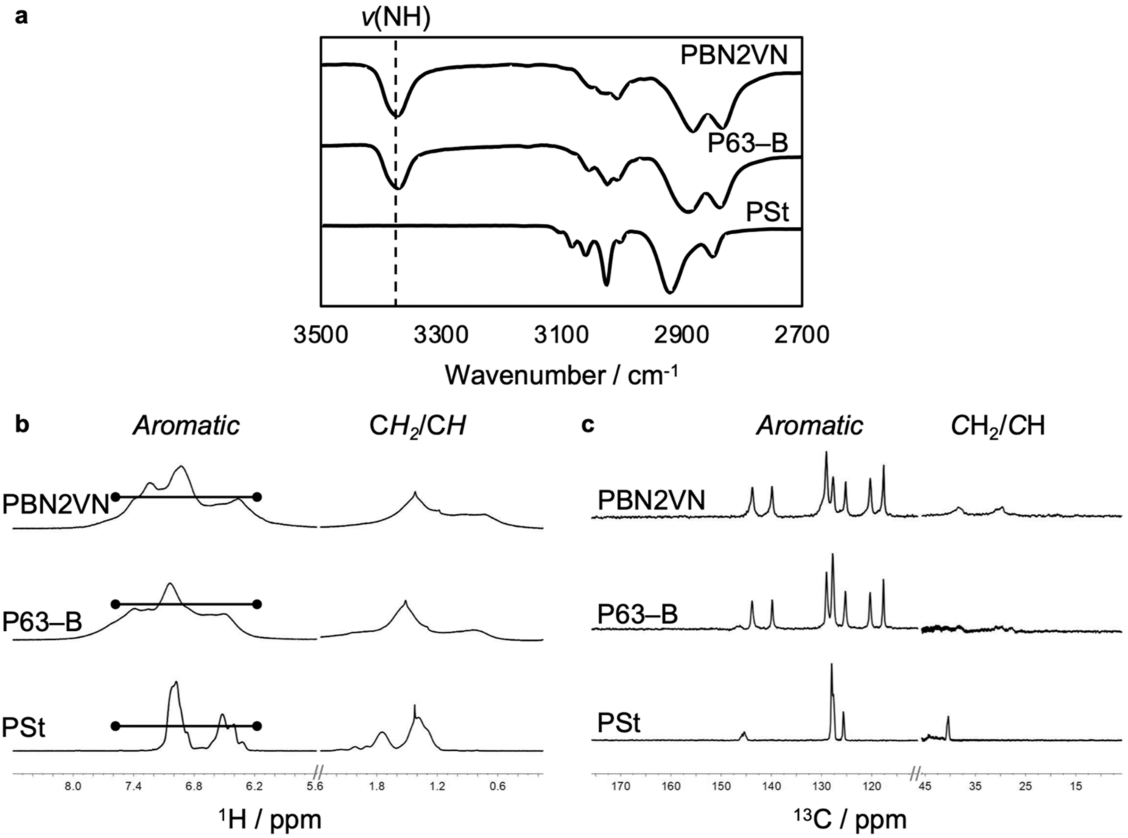


Figure 1. (a) Cropped IR spectra of (top to bottom) PBN2VN, P63−B, and PS. (b) ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of (top to bottom) PBN2VN, P63−B, and PS. (c) ^{13}C NMR spectra of (400 MHz, CD_2Cl_2) of (top to bottom) PBN2VN, P63−B, and PS.

https://doi.org/10.1021/acs.macromol.2c01009
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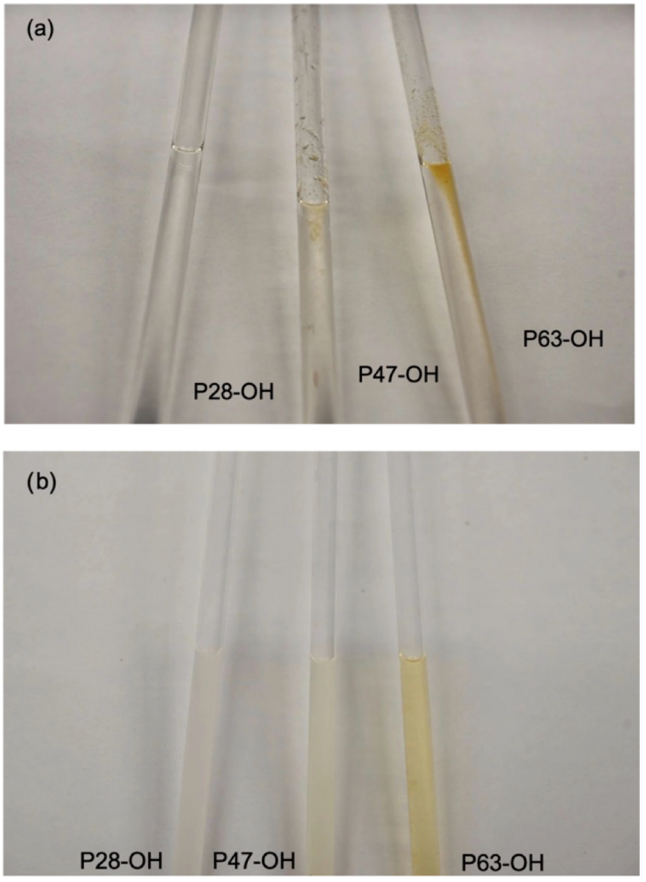

Figure 2. (a) Solubility characteristics of (left to right) P28−OH, P47−OH, and P63−OH (5 mg polymer in 0.7 mL $CDCl_3$). (b) Solubility characteristics of (left to right) P28−OH, P47−OH, and P63−OH (5 mg polymer in 0.7 mL CD_3OD). The yellow color is attributed to residual indole, a byproduct of BN naphthalene oxidation.

the disappearance of the ν(NH) band and growth of a broad peak from ca. 3600 to 3200 cm^{-1} assigned to the ν(OH) resonance (Figure 3).[30,31] We also noted a reduction in the intensity of C(sp^2)−H stretching frequencies at ca. 3100 cm^{-1} consistent with loss of BN naphthalene and retention of minimal styrene residues. However, these methods did not allow for the quantitative determination of conversion. The heterogeneous oxidation procedure occurs at the interface between the insoluble polymer chain and the aqueous solution of sodium hydroperoxide and could be expected to have variable conversion efficiencies, due to the variable solubility and assembly of the starting and intermediate copolymers.

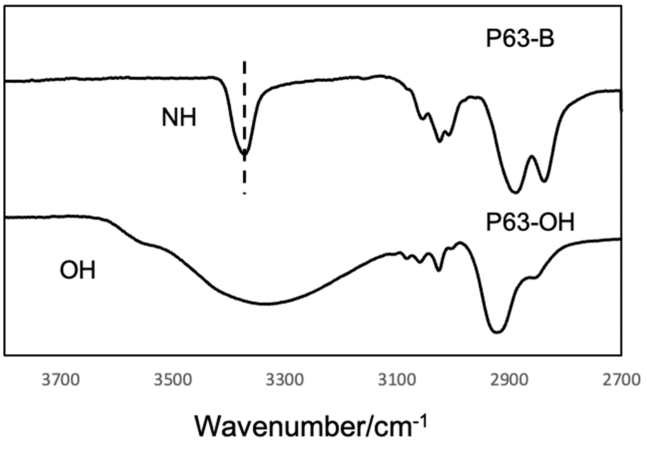

Figure 3. Cropped IR spectra of P63−B (top) and P63−OH (bottom). See Figure S4 for spectra of other copolymers.

CP-MAS Spectroscopy. To complete the characterization of P47−OH and P63−OH, we turned to CP-MAS ^{13}C NMR of the polymer in the solid state, which provided unambiguous and quantitative confirmation of the conversion of BN2VN side chains to OH groups.

The ^{13}C CP-MAS spectra of PVA and PS homo- and copolymers are shown in Figure 4. The characteristic *C*(OH)H resonance of PVA at δ 65−74 (labeled b) was split into three lines, which has been attributed to different hydrogen-bonding environments (e.g., two, one, or no hydrogen bonds).[32,33] The CH_2 resonance was labeled as a. For PS, overlapping CH and CH_2 bands (c, d) were found as well as two aromatic resonances (e−h). The ^{13}C CP-MAS spectrum of P63−B was similar to PS, albeit with broader peaks reflecting more aromatic C atoms in the BN naphthalene side chain (k−r) and tacticity. After oxidation, the aromatic region of P63−OH resembled PS (e″−h″), reflecting the loss of the BN naphthalene side chain. Most importantly, a broad band (δ 60−80, b′) was observed that we assigned to the *C*(OH)H resonance. The CH and CH_2 backbone resonances were also found (a′, c″, d″). Similar spectra were obtained for P28−OH and P47−OH (Figure S5).

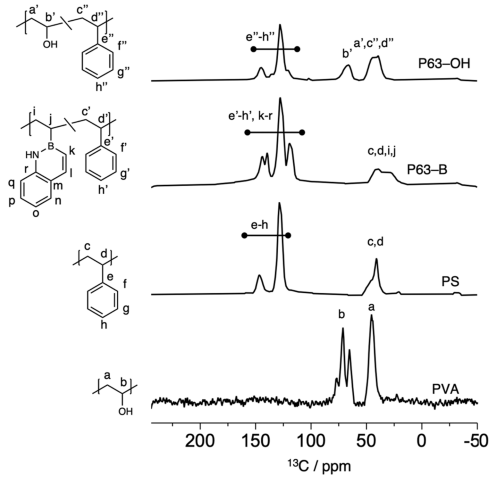

Figure 4. ^{13}C CP-MAS solid-state spectra of (top to bottom) P63−OH, P63−B, PS, and PVA.

^{11}B CP-MAS also supported the structural assignment (Figure 5). In PBN2VN and P63−B, a broad resonance (δ 24.2−1.50) consistent with trisubstituted boron was observed. After oxidation, this peak disappeared. A weak feature at δ −12.32 could indicate residual boric acid ($B(OH)_4^-$).[34]

We sought to quantify the fraction of hydroxyl groups in the copolymer to confirm the % conversion of BN naphthalene side chains to hydroxyl groups. Smith et al. demonstrated that utilization of ramped-amplitude cross-polarization (RAMP-CP) MAS NMR leads to a fast magnetization buildup of different spins and therefore improves the signal intensity and quantitation.[35,36] Herein, we present a similar strategy of optimizing the contact time (tcp) and recycle delay (d1) to achieve a reproducible integration ratio between methine

https://doi.org/10.1021/acs.macromol.2c01009
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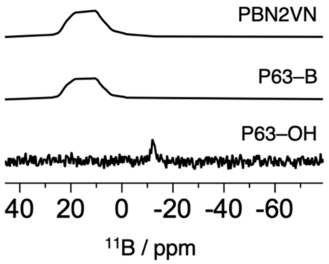

Figure 5. Cropped ^{11}B CP-MAS spectra of (top to bottom) PBN2VN, P63−B, and P63−OH.

CH(OH) resonance and methylene CH_2 and methine CH resonances. We first plotted the signal intensity buildup of three P63−OH spins assigned to vinyl alcohol (b′), backbone (a′, c″, d″), and aromatic (e″−h″) carbons over a wide tcp range (10 μs to 10 ms, Figure 6a). We found stable signal

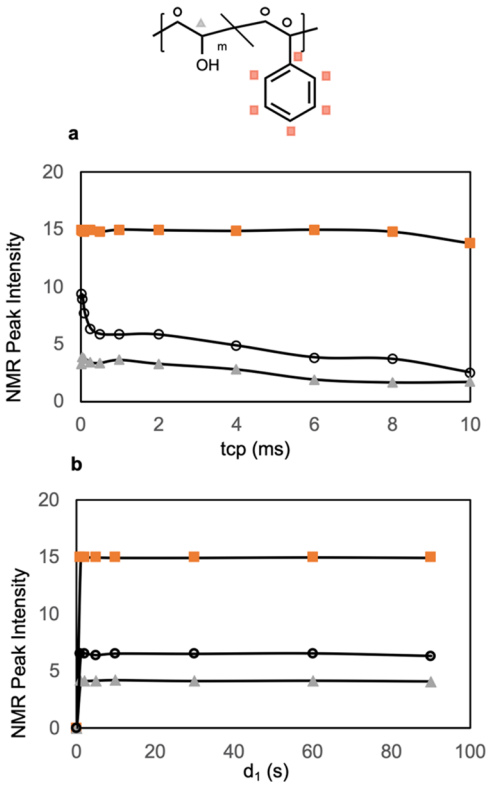

Figure 6. CP magnetization buildup curves for different types of ^{13}C spins in P63−OH. (a) Buildup curves of NMR peak intensity vs tcp. (b) NMR signal intensity vs d1 when tcp is 2 ms.

intensities for each spin were achieved in the tcp range from 100 μs to 4 ms, with an excellent signal-to-noise ratio (>40.27). We assumed the cross-polarization for all three spins was efficient in this tcp range, and the quantitation of the signals was reliable. The influence of d1 on signal intensity was investigated over a wide d1 range from 1 to 90 s with tcp set at 2 ms (Figure 6b). As d1 was increased, the ratio between the relative integration of the alcohol carbon (integral 1, b′, labeled with p) and the backbone carbons (integral 2, a′, c″, d″, labeled with o) remained constant within ±5% (Table 2).[35] With increasing d1, the signal-to-noise ratio also increased (Table S1). Herein, we compare the integration values of

Table 2. Integration of P63−OH ^{13}C CP-MAS Resonances

d1 (s)	integral 1[a]	integral 2[b]	mol % OH[c]
1	1.00	2.31	60.4
2	1.00	2.35	59.8
5	1.00	2.20	62.5
10	1.00	2.18	62.9
30	1.00	2.18	62.9
60	1.00	2.18	63.0
90	1.00	2.15	63.4

[a]Integral 1 refers to integral value of area 1 (defined as δ 88.4−56.3). [b]Integral 2 refers to integral value of area 2 (defined as δ 56.3−16.2). [c]Calculated according to eq 1.

−CO− and backbone carbons (Table 2), and the molar fraction of −OH groups could be calculated from eq 1.

$$\text{OH mol \%} = \frac{2 \times \text{integral 1}}{\text{integral 1} + \text{integral 2}} \quad (1)$$

Using eq 1, we obtained quantitative estimates of the molar fraction of alcohol carbons in P63−OH at each value of d1. A derivation of the equation is included in the Supporting Information (SI). Based on the constant relative integration with d1 > 10 s, we estimated the molar fraction of OH side chains as 63%. This compares very well with the molar fraction of BN naphthalene side chains in the precursor polymer P63−B. We suggest these results indicate >99% conversion of BN naphthalene side chains under aqueous conditions (NaOH/H_2O_2). A similar analysis was conducted for P47−OH (Figures S8, S9, and Tables S2, S3) and resulted in an estimated VA molar fraction of 40%, suggesting 85.1% conversion, lower than the quantitative conversion observed for P63−OH.

CONCLUSIONS

Herein, we reported the quantitative characterization by ^{13}C CP-MAS spectroscopy of amphiphilic statistical copolymers of styrene and vinyl alcohol (poly(VA-*stat*-St)) obtained from aqueous oxidation of the organoborane copolymer poly(BN2VN-*stat*-St). Through optimization of two acquisition parameters (contact time, tcp, and recycle delay time, d1), quantitative ^{13}C CP-MAS spectra could be obtained. Very high conversion >99% of P63−B to P63−OH was estimated based on ^{13}C integrations showing molar fractions of VA residues equivalent to the molar fraction of BN2VN in precursor polymers. Somewhat lower (85.1%) conversion was estimated for P47−B to P47−OH using the same technique. ^{11}B CP-MAS spectra were consistent with the removal of BN naphthalene side chains.

CP-MAS spectra were useful to characterize under a standard set of conditions the chemical structure of copolymers of variable composition and solubility properties. Confirming the extent of removal of BN naphthalene side chains was important for understanding structure−property relationships as residual BN naphthalene side chains could influence physical properties, and it is well-known that residual acetate side chains in PVA obtained from saponification of PVAc also influence physical properties and applications. The results herein should not only be helpful in the characterization of other amphiphilic copolymers but also provides confidence in the structural assignment of an elusive copolymer, facilitating future work in understanding properties and potential applications.

https://doi.org/10.1021/acs.macromol.2c01009
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01009.

Tabulated spectral data; gel permeation chromatograms; copies of spectra (UV−vis, IR, ^{1}H NMR, ^{13}C NMR, ^{13}C CP-MAS solid-state NMR, ^{11}B CP-MAS solid-state NMR); and supplemental figures, tables, and formula (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under grant CHE-1752791. CP-MAS spectroscopy was made possible through the National Science Foundation Major Research Instrumentation grant CHE-2018176.

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https://doi.org/10.1021/acs.macromol.2c01009
Macromolecules 2022, 55, 7032−7038