Syndioselective Polymerization of a BN Aromatic Vinyl Monomer

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1. General Information

General Experimental Procedures: All experiments were performed under an atmosphere of dry nitrogen or argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a nitrogen glove box. All glassware was oven-dried overnight in a 175 °C oven.

Instrumentation: ^{1}H NMR, ^{13}C {^{1}H} NMR,^{11}B NMR and other 1D and 2D NMR experiments were recorded on a Bruker UltraShield Avance I 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in dimethyl sulfoxide-d_6 (DMSO-d_6) or 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) with the residual solvent peak as the internal standard (^{1}H NMR: DMSO δ = 2.50; TCE δ = 6.0). All ^{11}B polymer spectra were acquired using quartz NMR tubes from Norell or Wilmad. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz and integration is provided, along with assignments, as indicated. The UNIlab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. Polymer molecular weights were measured by gel permeation chromatography (GPC) (Tosoh Bioscience EcoSEC GPC workstation) using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min^{-1}, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 μm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4 μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was done using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF (1 mg mL^{-1}), filtered (Millex-FG Syringe Filter Unit, 0.20 µm, PTFE, EMD Millipore), and injected using an auto-sampler (10 µL). UV-Vis spectroscopy was performed on a Shimadzu UV-1800 UV-Vis spectrophotometer. The spectra were measured in THF and in DMSO in a quartz cuvette (10 mm) at room temperature. FT-IR (ATR) spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer equipped with iD5 ATR laminated diamond crystal attachment. Elemental analysis was performed by Robertson Microlit Laboratories. Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q20 V24.11 Build 124 and processing was performed using Universal V4.5A (TA Instruments). Polymer samples (2.0 – 5.0 mg) were sealed in Tzero aluminum pans, heated from 50 to 350°C (10 °C min^{-1}), and cooled from 350 to 55 °C, for three cycles under a purge gas of nitrogen (25 mL min^{-1}). Glass transition temperatures (T_g) and melting temperatures (T_m) were calculated from the second heating cycle (all second and third heating cycles traced, respectively) and the temperature of midpoint of glass transition and the temperature of midpoint of melting is reported as T_g and T_m respectively.

Materials: Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents used for workups were reagent grade and used as received. Reaction solvents toluene (Fisher, certified ACS) and pentane (Fisher, certified ACS) were dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina (except for toluene which is dried with neutral alumina and Q5 reactant, a copper(II) oxide oxygen scavenger), following the manufacturer's recommendations for solvent preparation and dispensation.

B-vinyl-2,1-borazanaphthalene (BN2VN) was synthesized as previously described.[1,2] Styrene was purchased from ACROS Organics and purified according to literature procedure.[3] 2-Vinylnaphthalene (2VN) was purchased from Aldrich and was sublimed and stored in the Glove box freezer. Cp*$TiCl_3$ was purchased from TCI America. Cp*$TiMe_3$ was synthesized as previously reported[4] and stored in a nitrogen filled glove box. $B(C_6F_5)_3$ was purchased from ACROS Organics. Methylaluminoxane (MMAO-12, 7wt% aluminum in toluene), PVA (98%

hydrolyzed, average MW 13000-23000), and sodium hydroxide (>97%) were purchased from Sigma Aldrich. Hydrogen peroxide (30% solution, stabilized) was purchased from EMD Millipore.

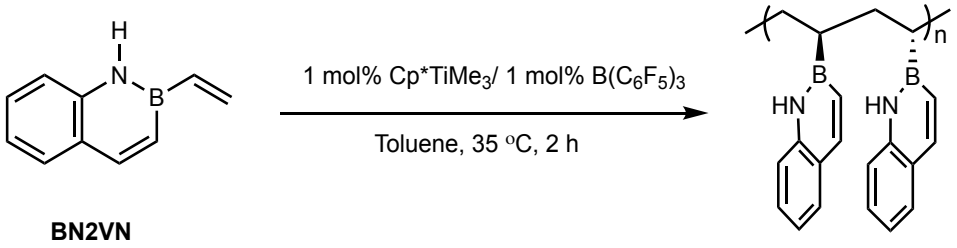
Dimethyl sulfoxide-d_6 (D, 99.9%) and 1,1,2,2-tetrachloroethane-d_2 (D, 99.6%) were purchased from Cambridge Isotope Laboratories, Inc.

UV-Vis studies and polymer oxidations were performed in non-stabilized THF from EMD Millipore. GPC studies were performed in butylated hydroxytoluene stabilized THF from EMD Millipore.

2. Experimental Procedures and Tabulated Characterization Data

2.1. Polymerization

2.1.1. Procedure for the Synthesis of Syndiotactic PBN2VN (sPBN2VN) using $Cp^*TiMe_3/B(C_6F_5)_3$ (adapted from Chung et al.).[5]



BN2VN **sPBN2VN**

In a glove box, a 2-5 mL microwave vial equipped with a stir bar was charged with BN2VN (6.45 mmol, 1 g) and toluene (1 mL). The mixture was stirred until BN2VN dissolved. A toluene solution (2.2 mL) of Cp^*TiMe_3 (6.45×10^{-2} mmol, 14.7 mg) and $B(C_6F_5)_3$ (6.45×10^{-2} mmol, 33 mg) was added via a glass pipette to the rapidly stirring monomer solution. The vial was crimped with an aluminum/PTFE/silicone septum seal, brought out of the glove box and placed on a preheated pie plate (35 °C) for 2 hours. Polymerization was quenched by opening the vial in air and dispensing into acidic methanol (1N HCl added to 100 mL of methanol until pH = 3). The quenched reaction mixture was stirred at room temperature for 15 minutes. Precipitated PBN2VN was isolated as an off-white solid by filtration. The recovered PBN2VN was washed with additional methanol and dried on the Schlenk line for 30 minutes then in a vacuum oven at 80 °C for 16 hours (yield 67%). PBN2VN was fractionated with acetone for 5 hours using a Soxhlet extractor to remove atactic PBN2VN. The insoluble fraction was recovered and dried on the Schlenk line for 30 min then in the vacuum oven at 80 °C for 16 hours (78 wt% recovered after fractionation).

Solutions of sPBN2VN for ^1H, ^{13}C, ^{11}B NMR spectroscopy and other 1D and 2D NMR experiments were prepared by dissolving 45 mg of sPBN2VN in 0.6 ml of DMSO-d_6 and spectra were recorded at 120 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (s, 1H), 7.48 – 7.37 (m, 1H), 7.32 (q, J = 10.0, 9.4 Hz, 1H), 7.19 (t, J = 7.0 Hz, 1H), 7.15 – 7.04 (m, 1H), 6.99 (d, J = 7.1 Hz, 1H), 6.38 (s, 1H), 1.42 (d, J = 13.8 Hz, 2H), 1.05 (d, J = 20.5 Hz, 1H).

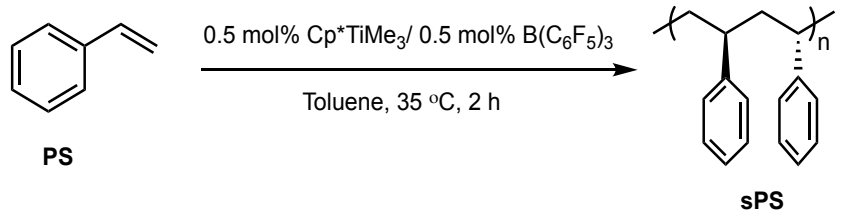
^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 142.26, 139.88, 128.72, 127.76, 126.35, 124.22, 118.83, 117.37, 38.31, 28.69.

^{11}B NMR (128 MHz, DMSO-d_6) δ 28.36

FTIR 3367, 3006, 2881, 2831, 1614, 1568, 1558, 1460, 1435, 1384, 1342, 1269, 1209, 1143, 1136, 937, 893, 804, 758, 741, 704 cm^{-1}

Anal. Calc. for C10H10BN: C, 77.5; H, 6.5; N, 9. Found: C, 77.2; H, 6.3; N, 8.9.

2.1.2. Procedure for the synthesis of syndiotactic polystyrene (sPS) using $Cp^*TiMe_3/B(C_6F_5)_3$ (adapted from Chung et al.).[5]



In a glove box, a 2-5 mL microwave vial equipped with a stir bar was charged with styrene (2.88 mmol, 300 mg) and toluene (1.5 mL). A toluene solution (1.5 mL) of Cp^*TiMe_3 (1.5×10^{-2} mmol, 3.42 mg) and $B(C_6F_5)_3$ (1.5×10^{-2} mmol, 7.7 mg) was added via glass pipette to the rapidly stirring monomer solution. The vial was crimped with an aluminum/PTFE/silicone septum seal, brought out of the glove box and placed on a preheated pie plate (35 °C) for 2 hours. Polymerization was quenched by opening the microwave vial in air and dispensing into acidic methanol (1N HCl added to 50 mL of methanol until pH = 3). The quenched reaction mixture was stirred at room temperature for 15 minutes. Precipitated PS was isolated as a white solid by filtration. The recovered PS was washed with additional methanol and dried on the Schlenk line for 30 minutes then in a vacuum oven at 80 °C for 16 hours (yield 86%). PS was fractionated with acetone for 5 hours using a Soxhlet extractor to remove atactic PS. The insoluble fraction was recovered and dried on the Schlenk line for 30 min then in the vacuum oven at 80 °C for 16 hours (97 wt% recovered after fractionation).

Solutions of sPS for ^1H and ^{13}C NMR spectroscopy were prepared by dissolving 45 mg of sPS in 0.6 ml of TCE-d_2 and spectra were recorded at 120 °C. ^1H and ^{13}C NMR data are consistent with literature reported data.[6]

^1H NMR (400 MHz, TCE-d_2) δ 7.12 (m, 3H), 6.64 (m, 2H), 1.95 (p, J = 6.5 Hz, 1H), 1.44 (t, J = 6.6 Hz, 2H).

^{13}C {^1H} NMR (101 MHz, TCE-d_2) δ 145.16, 127.61, 127.54, 125.28, 44.09, 40.86.

FTIR 3062, 3031, 3026, 2916, 2846, 1600, 1493, 1452, 1155, 1032, 1028, 904, 755, 748, 694 cm^{-1}

2.1.3. Procedure for the synthesis of syndiotactic P2VN using $Cp^*TiMe_3/B(C_6F_5)_3$ (adapted from Chung et al.).[5]

Procedure is similar to 2.1.2. For yields refer to table S1.

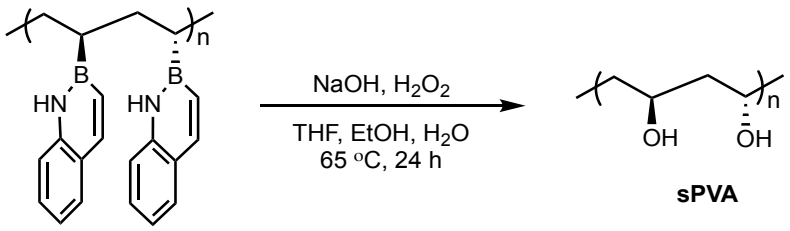
Solutions of syndiotactic poly(2-naphthalene) for ^1H spectroscopy were prepared by dissolving10 mg of the polymer in 0.6 ml of TCE-d_2 and spectra were recorded at 120 °C. ^1H NMR data are consistent with literature reported data.

^1H NMR (400 MHz,) δ 7.99 – 7.03 (m, 6H), 6.69 (d, J = 80.5 Hz, 1H), 2.03 (s, 1H), 1.50 (s, 2H).

FTIR 3049, 3043, 2913, 2894, 1599, 1506, 1448, 1342, 1269, 1126, 944, 860, 821, 814, 741 cm^{-1}

2.2 Polymer Oxidation

2.2.1 Synthesis of sPVA via oxidation of sPBN2VN



sPBN2VN **sPVA**

In a 500 mL round bottom flask, sPBN2VN (265 mg) was stirred in THF (75 mL) at room temperature until the polymer dissolved. Ethanol (8 mL) and aqueous sodium hydroxide (6N, 8 mL) were added by pipet, followed by the dropwise addition of aqueous hydrogen peroxide (30%, 16 mL) by pipet. The reaction was stirred at room temperature for 30 min, then capped with an open reflux condenser and refluxed at 65 °C for 24 hours. After cooling to room temperature, the reaction mixture was concentrated by removing organic solvents via rotary evaporation. Upon addition of distilled water (50 mL), the polymer precipitated. The precipitated polymer was isolated as a clumpy white solid via filtration while washing with excess water (100 mL). The isolated polymer was transferred to a 500 mL round bottom flask, which was charged with methanol (150 mL) and concentrated under vacuum at 60 °C to remove residual boric acid as $B(OMe)_3$ (b.p 68 – 69 °C). sPVA was isolated via filtration as a white powder and dried on a Schlenk line for 30 min then in the vacuum oven at 90 °C for 16 hours (23 mg, 31% yield).

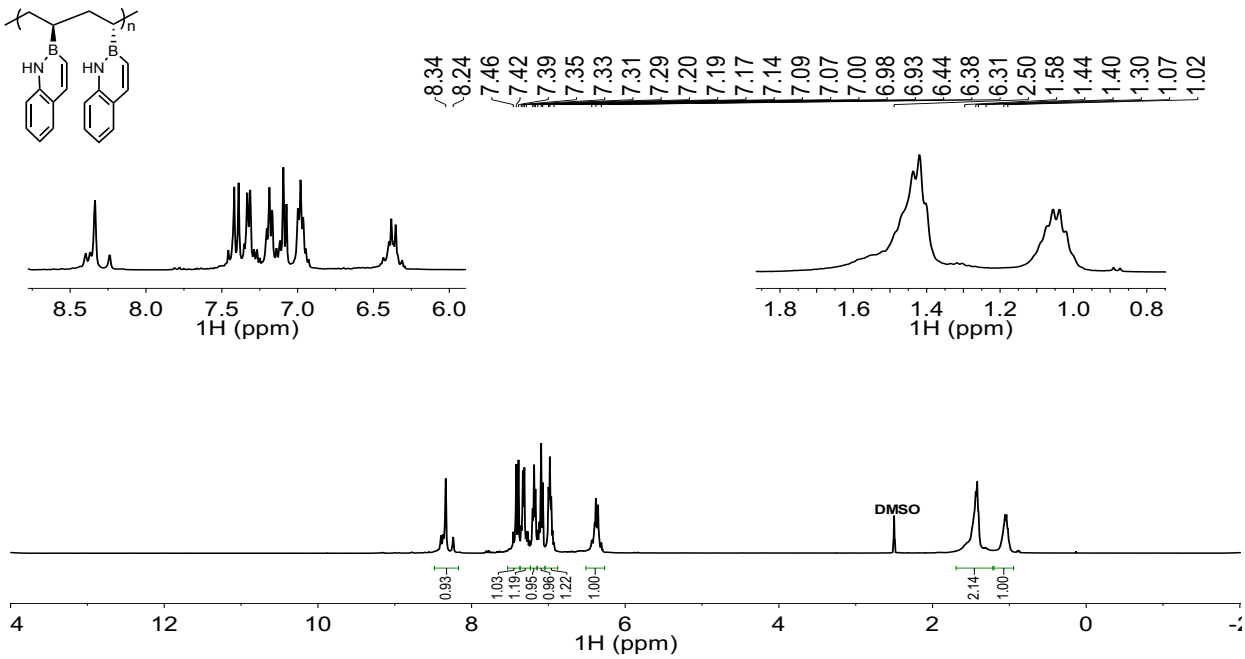
^{1}H NMR ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.67 – 4.07 (m, 1H), 3.92 (s, 1H), 1.36 (s, 2H).

FTIR 3267, 2937, 2897, 1404, 1342, 1228, 1145, 1081, 914, 849 cm^{-1}

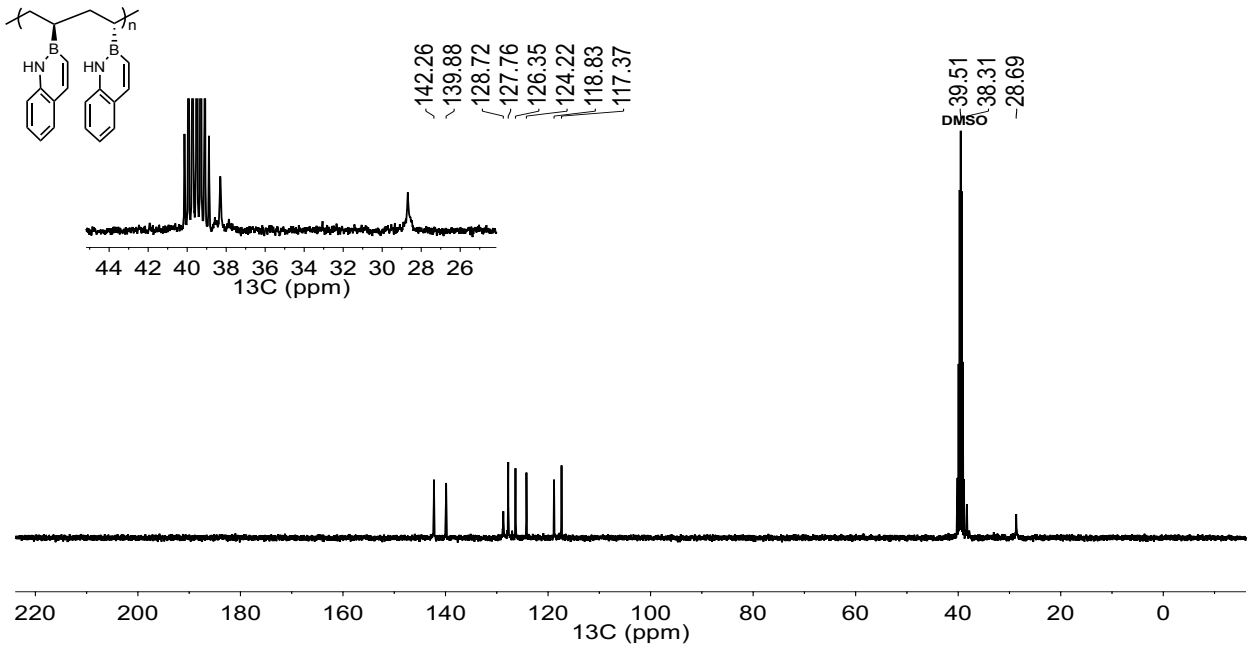
3. NMR Spectra

3.1 sPBN2VN

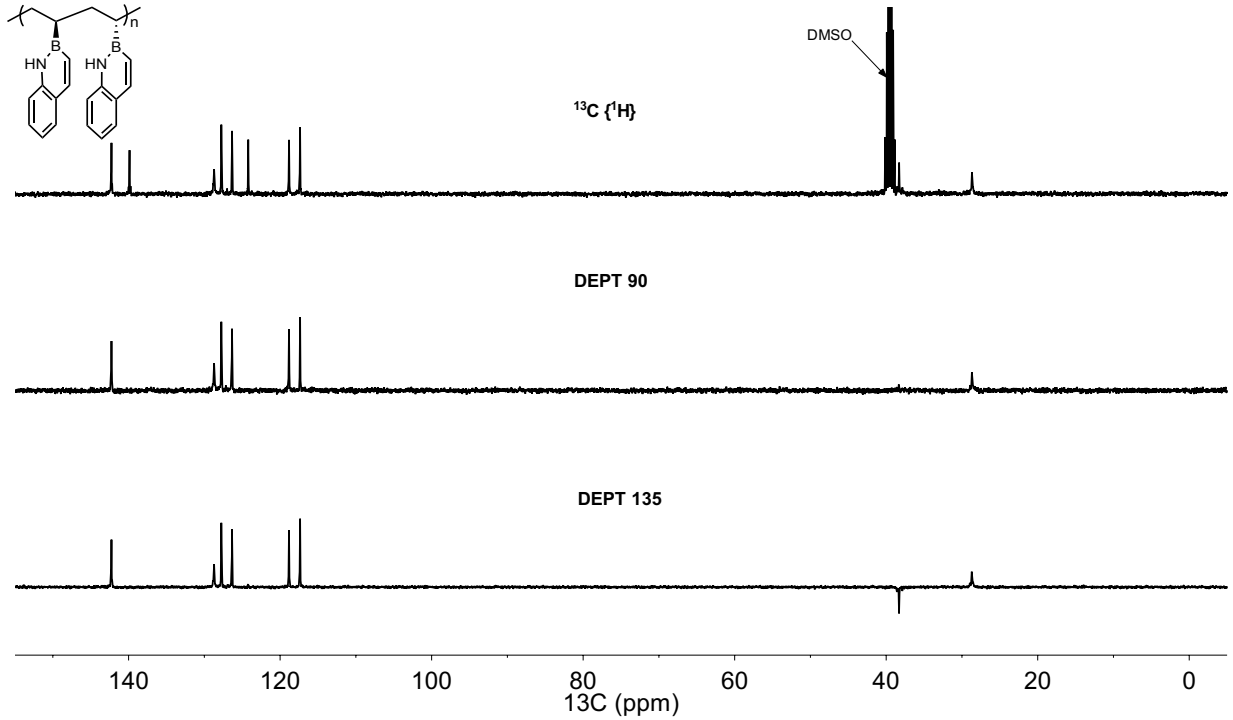
3.1.1 ^{1}H NMR Spectrum (400 MHz, DMSO-d_6)



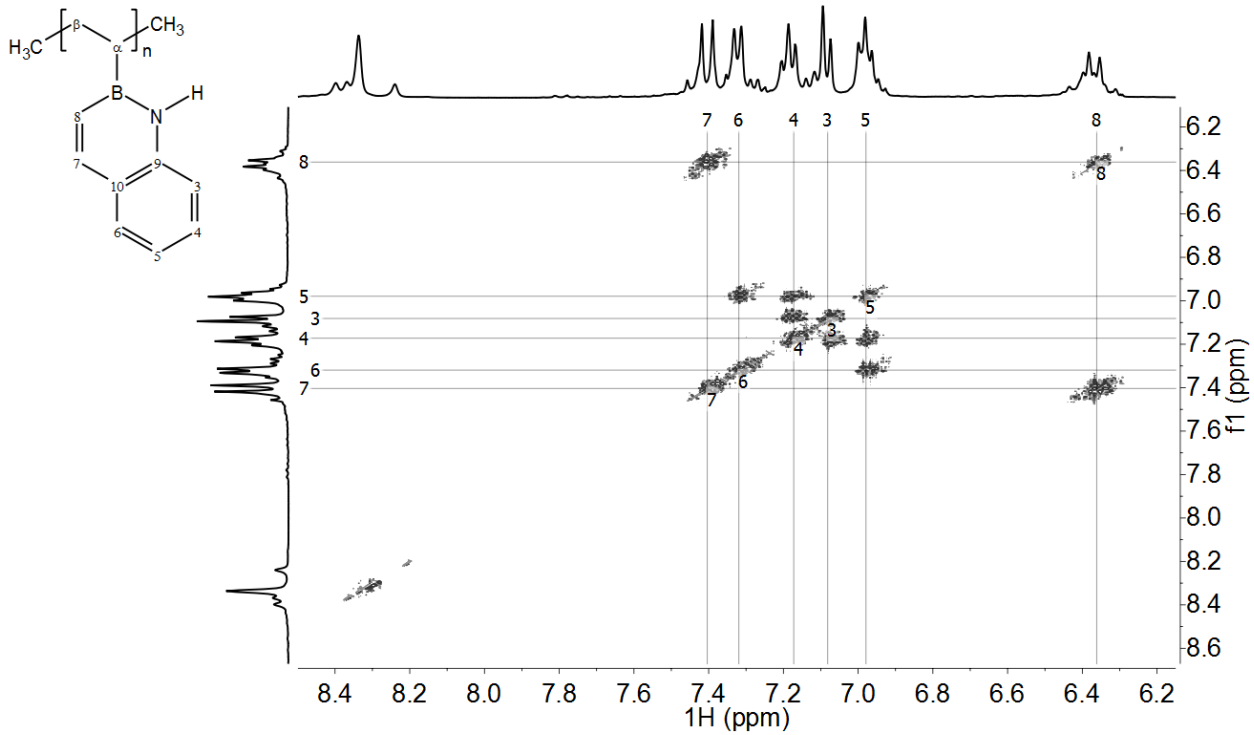
3.1.2 ^{13}C {^{1}H} NMR Spectrum (101 MHz, DMSO-d_6)



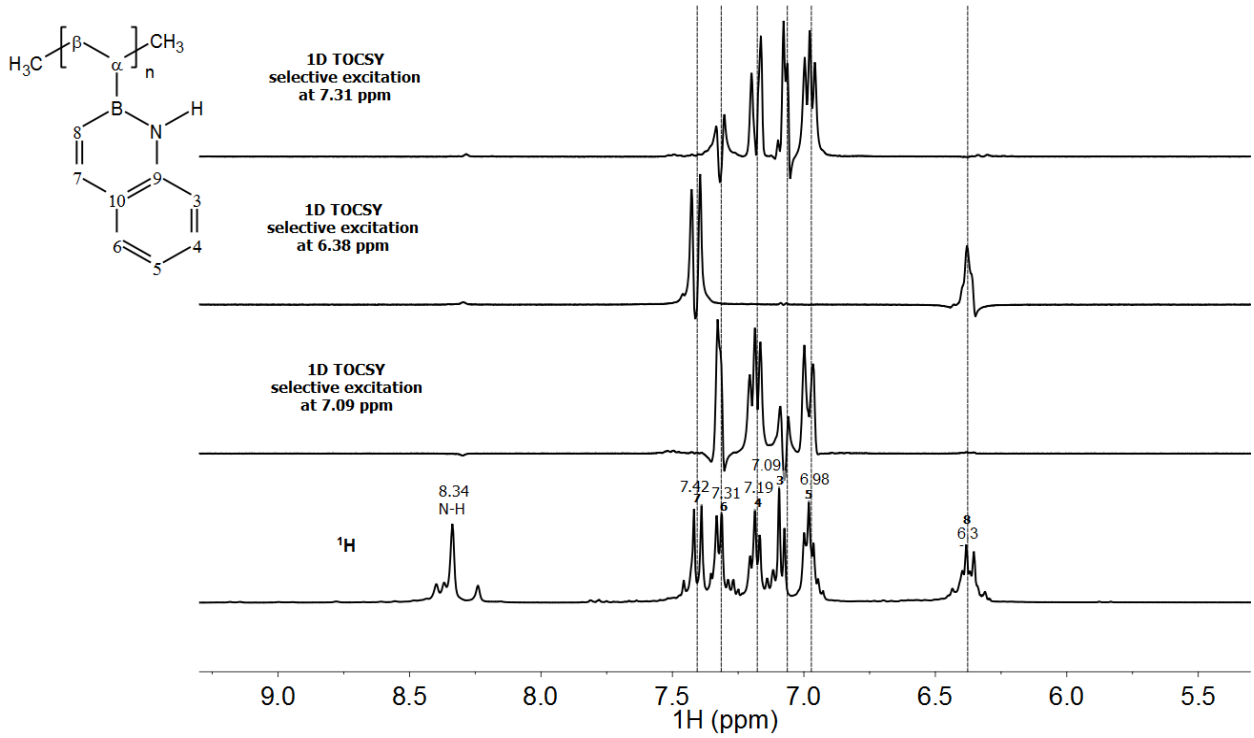
3.1.3 ^{13}C DEPT NMR Spectrum (101 MHz, DMSO-d_6)



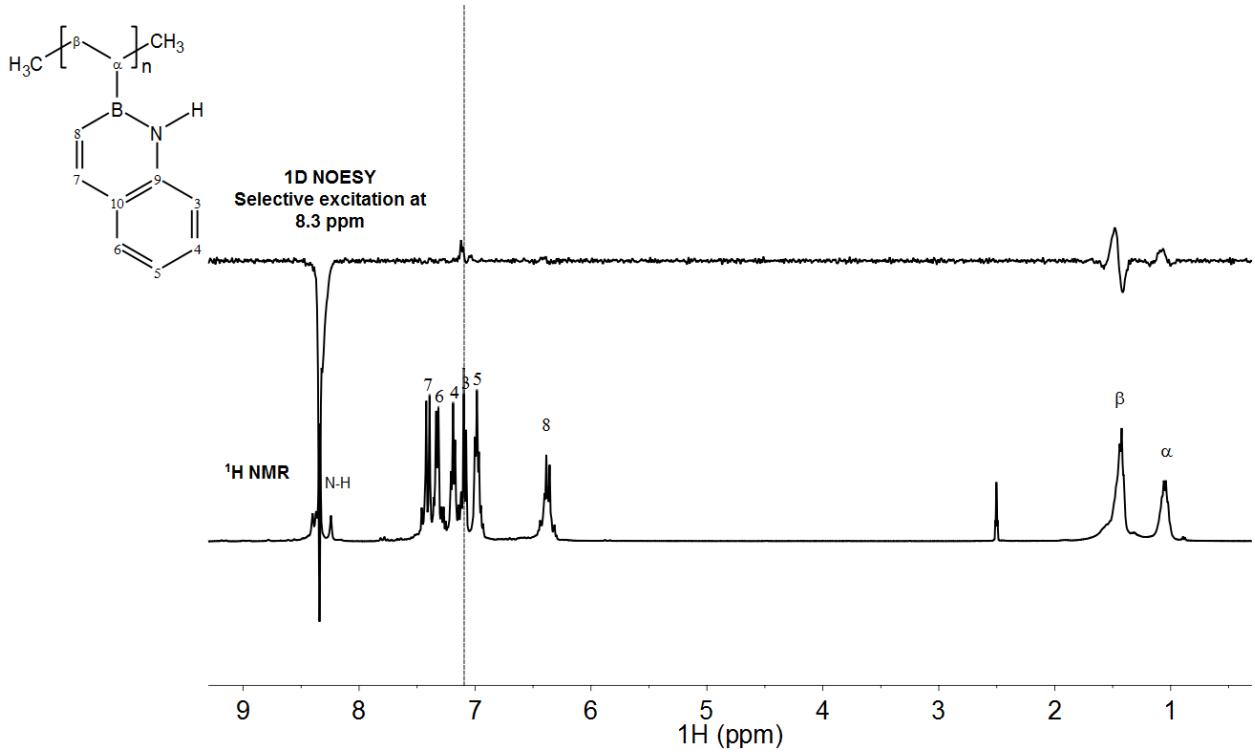
3.1.4 ^{1}H-^{1}H COSY NMR Spectrum (400 MHz, DMSO-d_6)



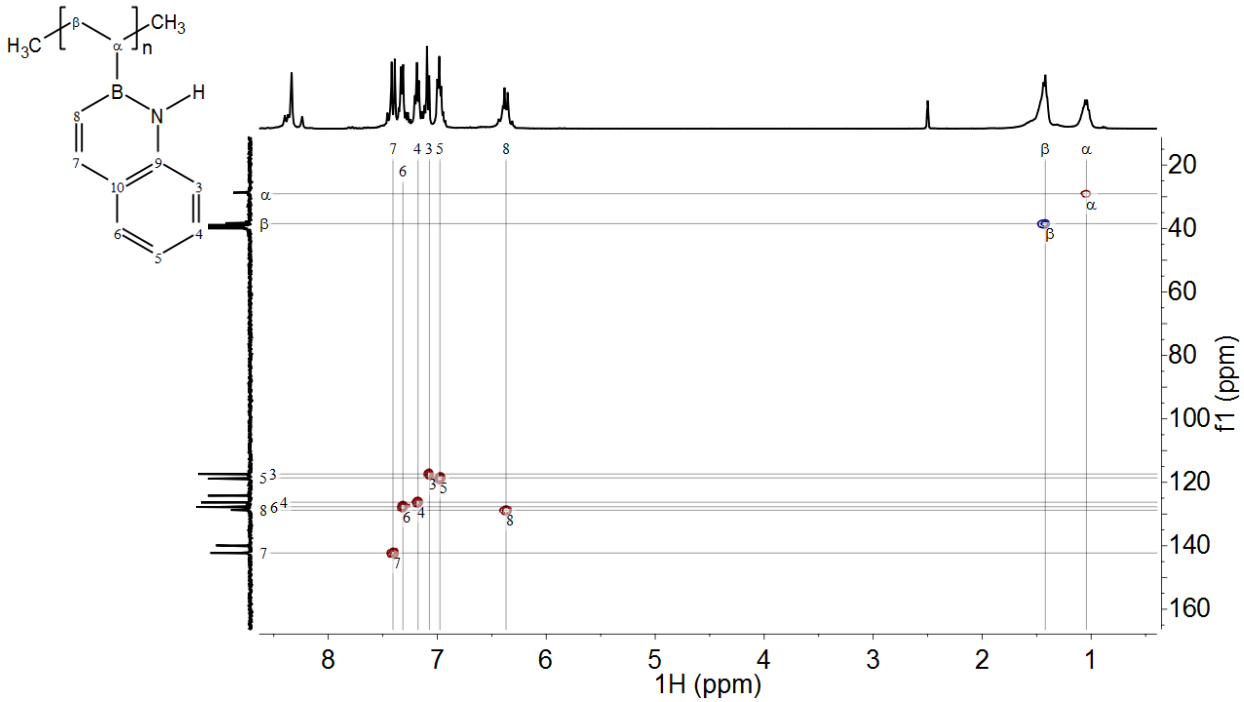
3.1.5 1D Selective Gradient TOCSY (400 MHz, DMSO-d_6)



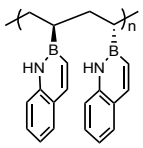
3.1.6 1D Selective Gradient NOESY (400 MHz, DMSO-d_6)

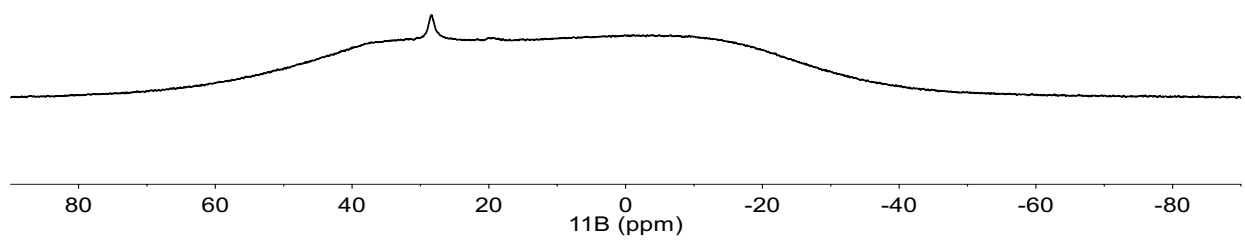


3.1.7 ^{1}H-^{13}C HSQC (400 MHz, DMSO-d_6)

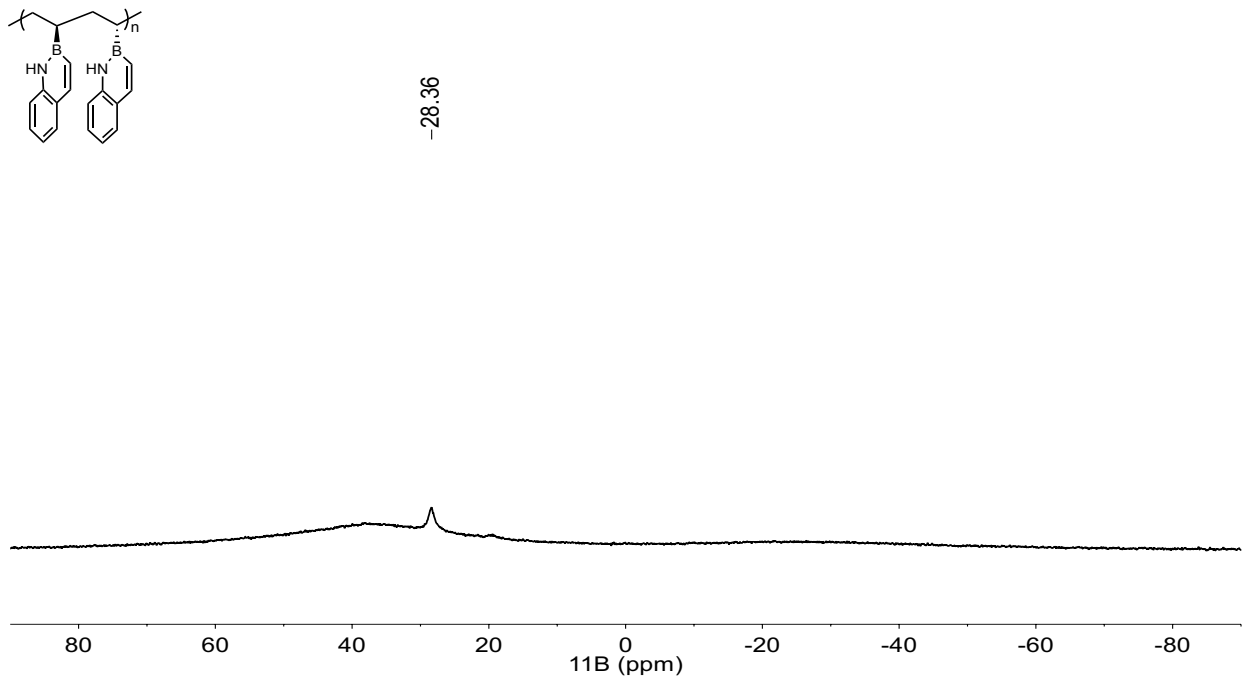


3.1.8 ^{11}B NMR Spectrum (128 MHz, DMSO-d_6)



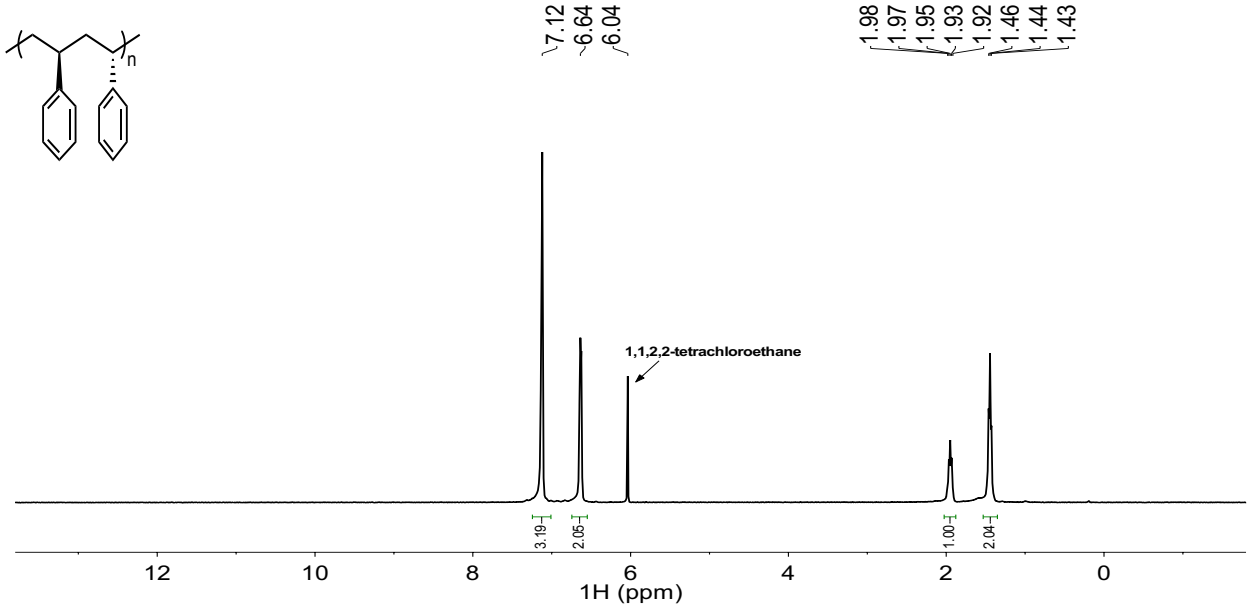


3.1.9 ^{11}B NMR Spectrum (128 MHz, DMSO-d_6), background subtracted

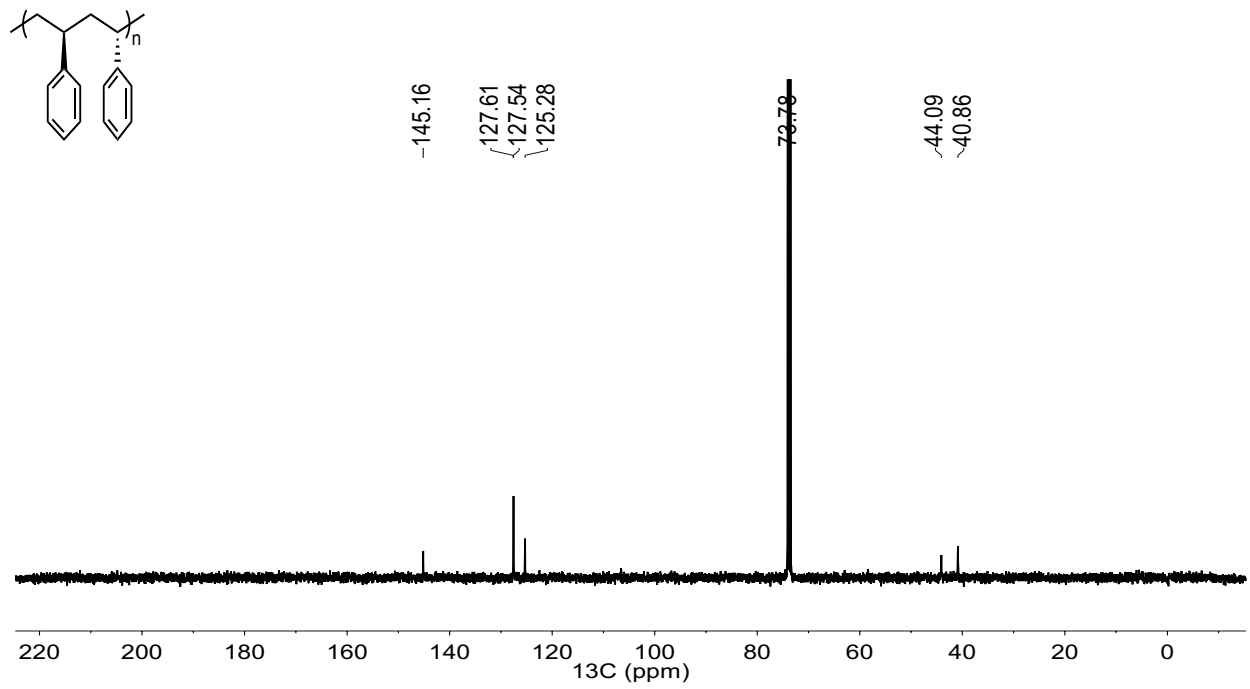


3.2 NMR Spectra of sPS

3.2.1 ^{1}H NMR Spectrum (400 MHz, 1,1,2,2-tetrachloroethane-d_2)

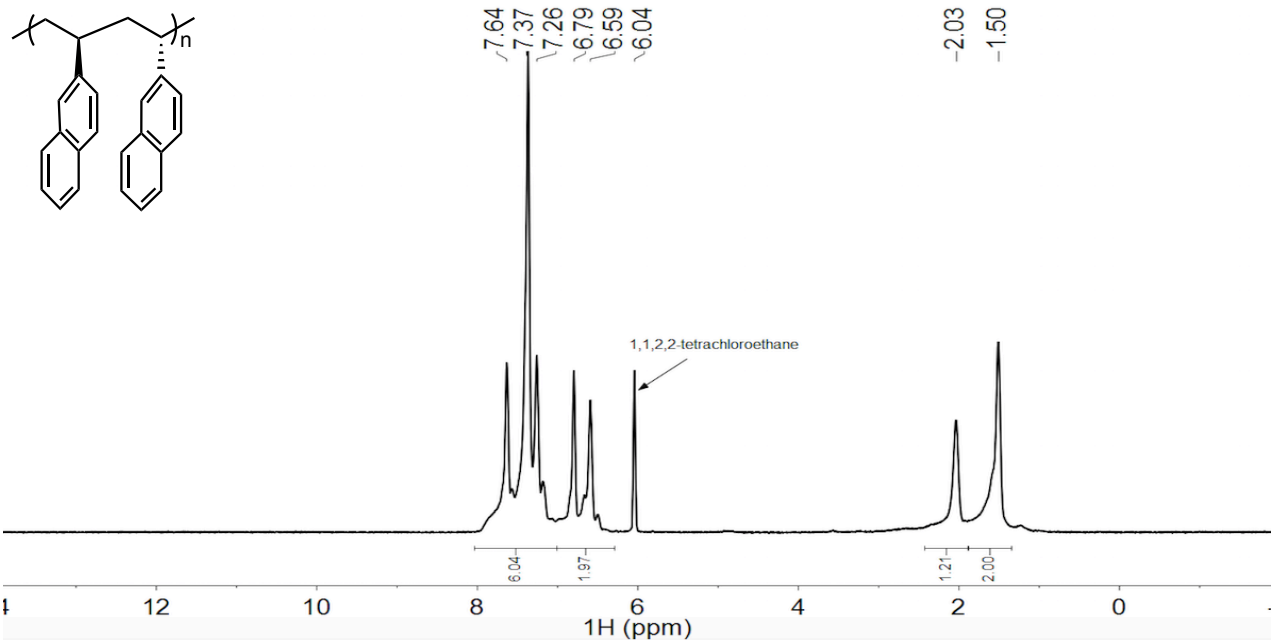


3.2.2 ^{13}C {^{1}H} NMR Spectrum (101 MHz, 1,1,2,2-tetrachloroethane-d_2)

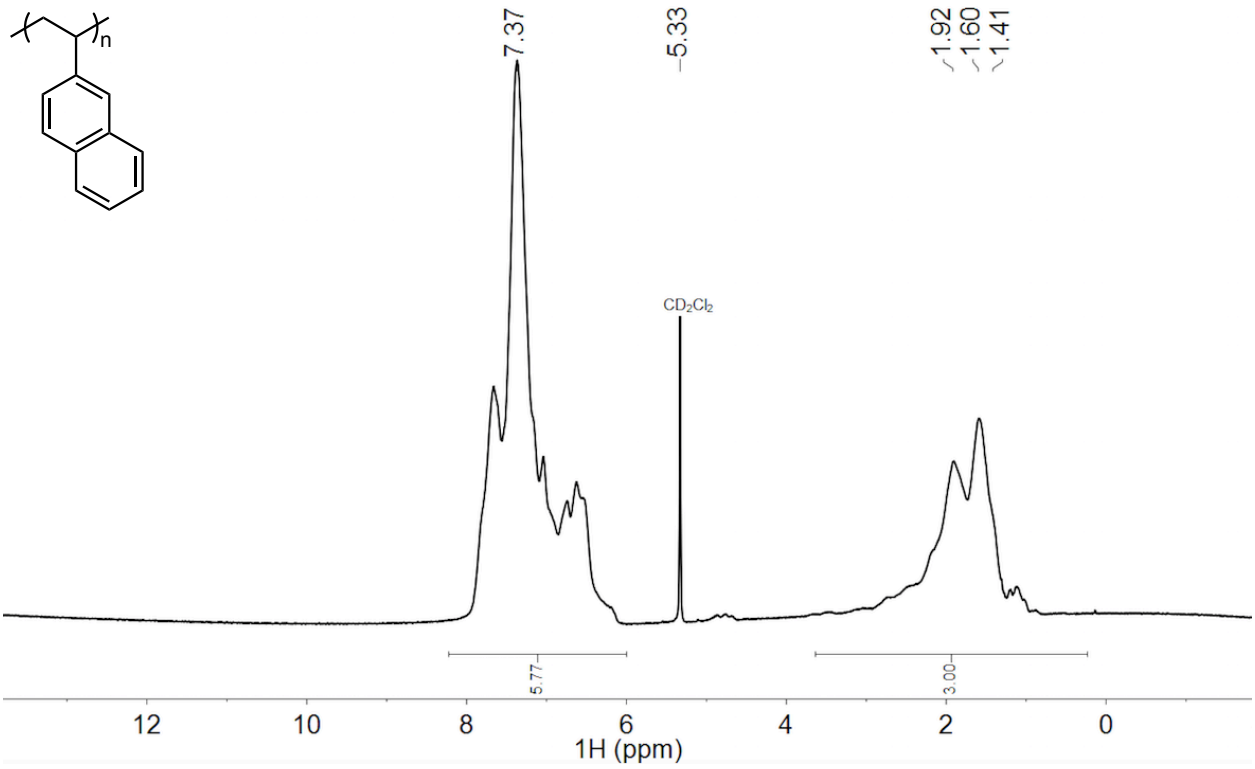


3.3 NMR Spectra of poly(2-naphthalene)

3.3.1 ^{1}H NMR Spectrum (400 MHz, 1,1,2,2-tetrachloroethane-d_2)-Table S1; entry 2-6

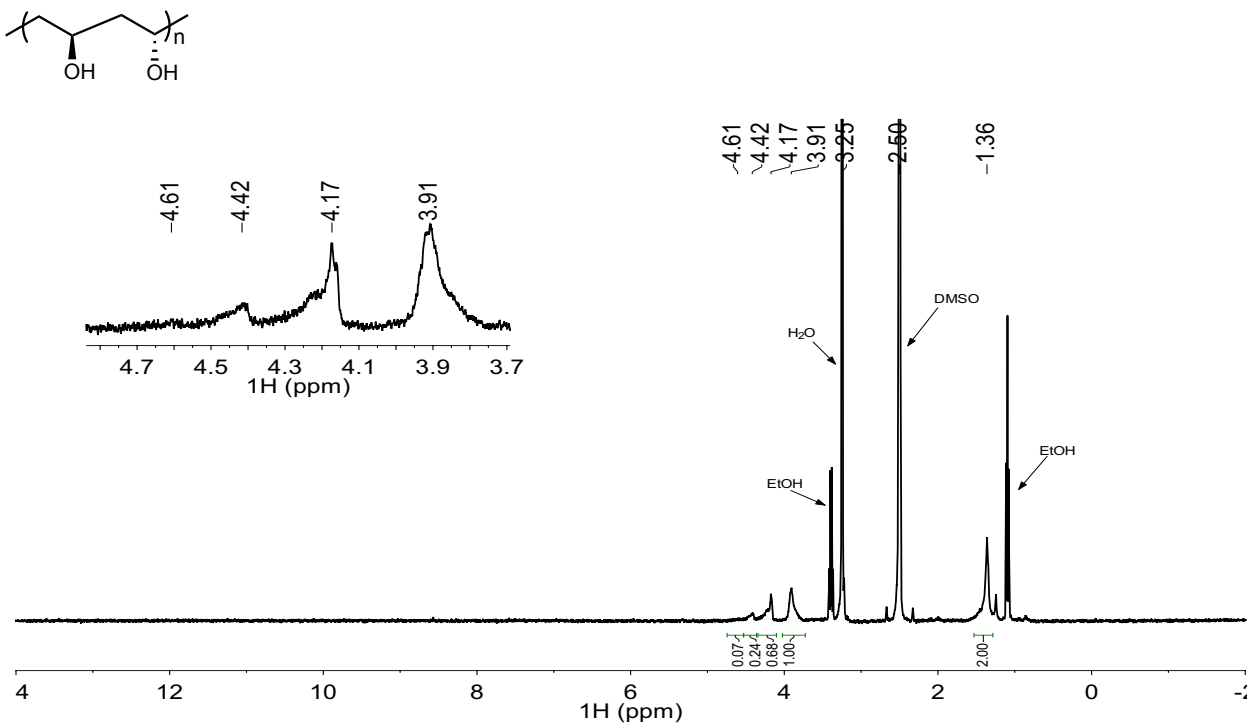


3.3.2 ^{1}H NMR Spectrum (400 MHz, 1,1,2,2-tetrachloroethane-d_2)-Table S1; entry 1



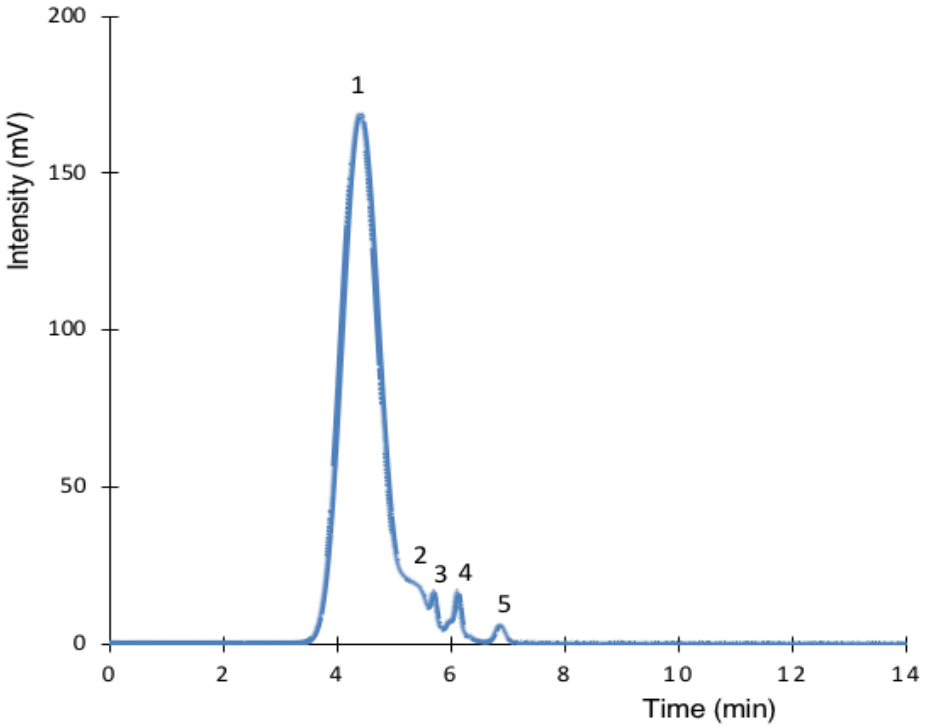
3.4 NMR Spectra of sPVA

3.4.1 ^{1}H NMR Spectrum (400 MHz, DMSO-d_6) at 50 °C



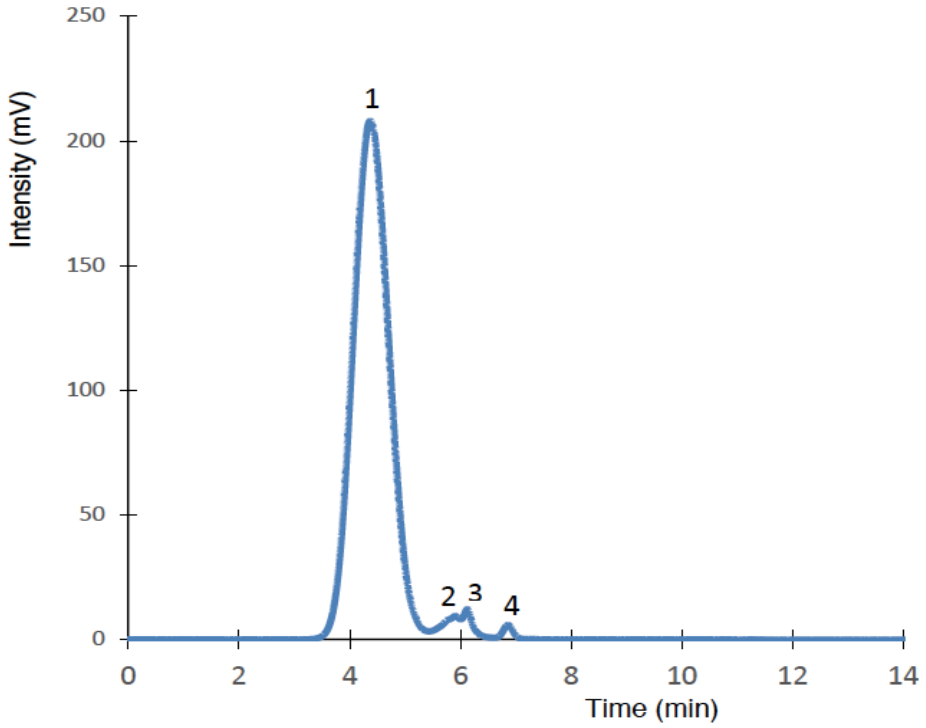
4. GPC Spectra

4.1 GPC Spectrum of syndiotactic PBN2VN (before fractionation) at 254 nm



Peak	R_f (min)	M_n (Da)	M_w (Da)	M_w/M_n
1	4.39	13.9×10^3	31.6	2.26
2	5.21	1.14×10^3	1.27×10^3	1.11
3	5.68	474	488	1.03
4	6.11	133	160	1.20
5	6.86	15.0	16.0	1.08

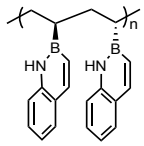
4.2 GPC Spectrum of syndiotactic PBN2VN (after fractionation with acetone) at 254 nm

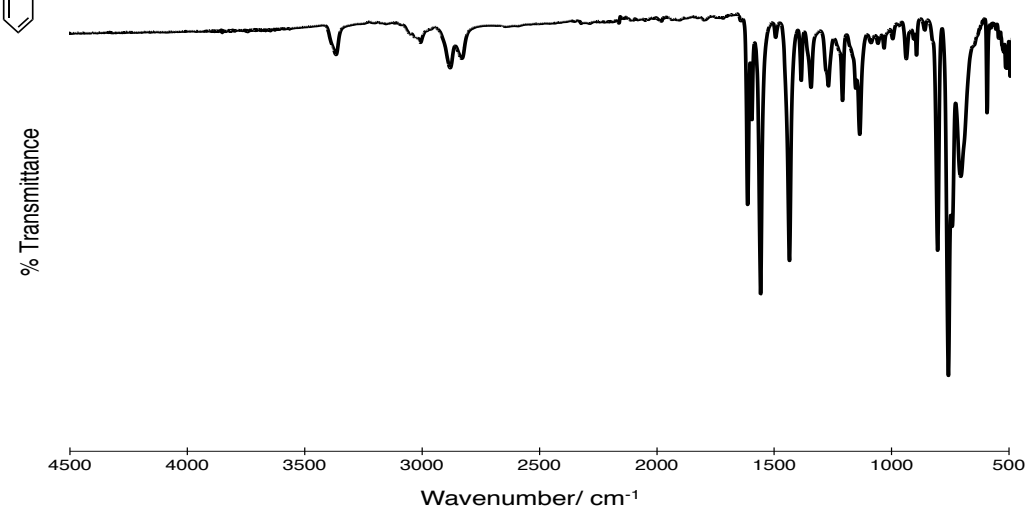


Peak	R_f (min)	M_n (Da)	M_w (Da)	M_w/M_n
1	4.37	15.0×10^3	33.8×10^3	2.25
2	5.91	346	429	1.24
3	6.13	107	123	1.15
4	6.86	15	16	1.09

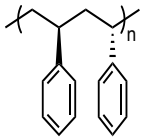
5. FT-IR Spectra

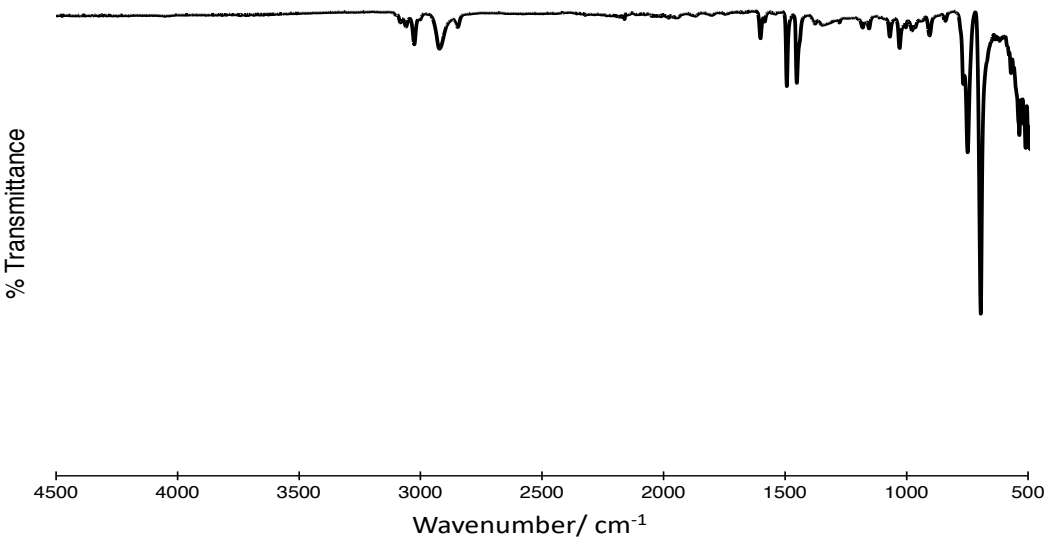
5.1 FT-IR (ATR) spectrum of sPBN2VN



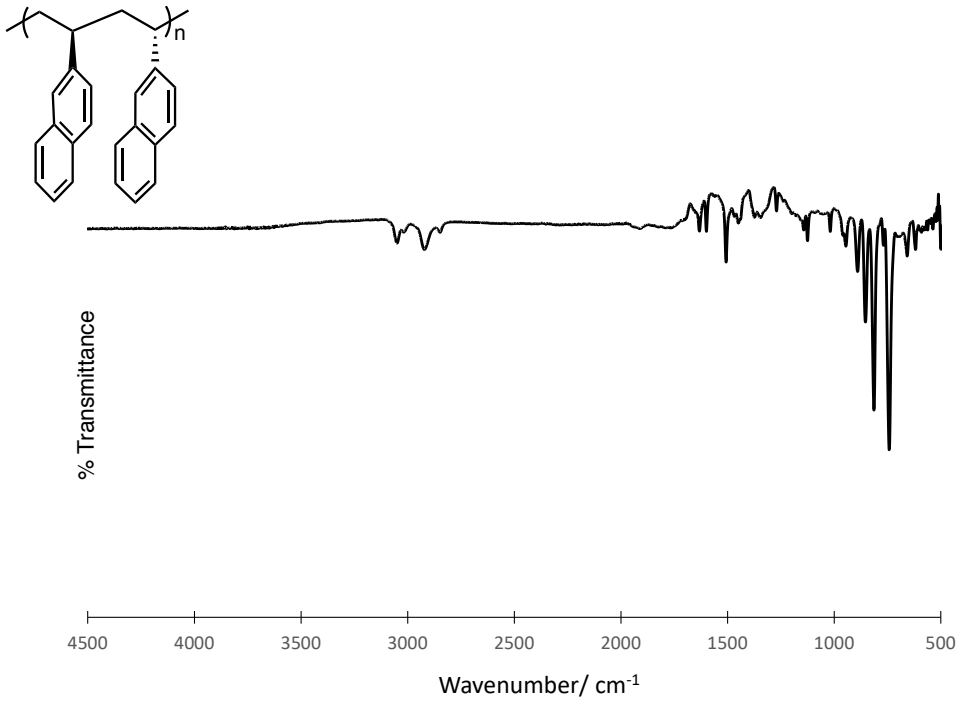


5.2 FT-IR (ATR) spectrum of sPS

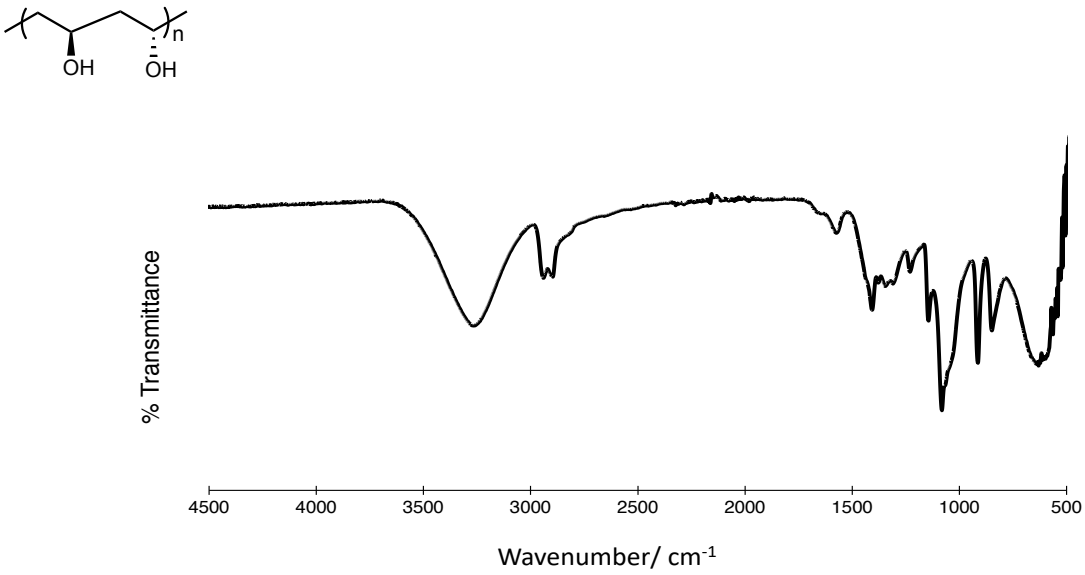




5.3 FT-IR (ATR) spectrum of syndiotactic poly(2-vinyl naphthalene)

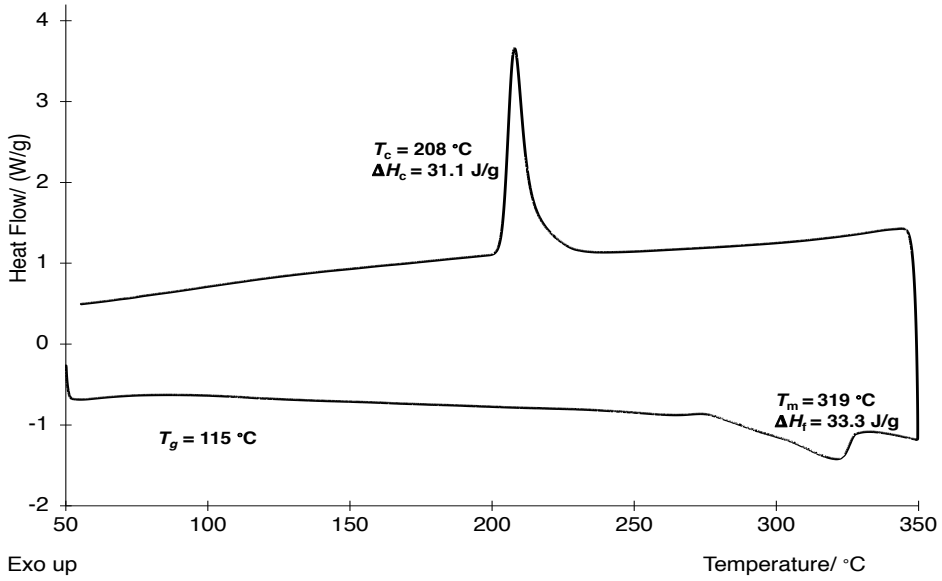


5.3 FT-IR (ATR) spectrum of sPVA

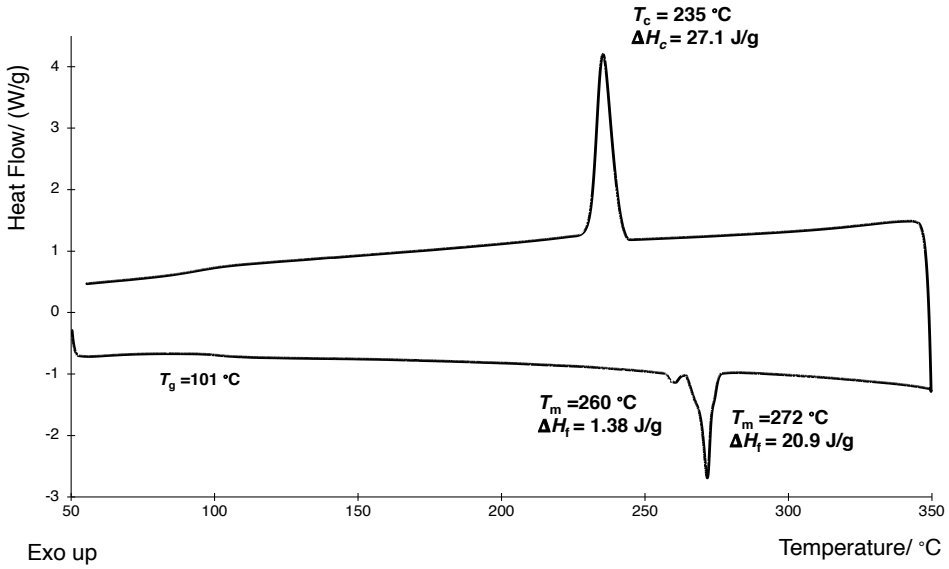


6. DSC Thermograms

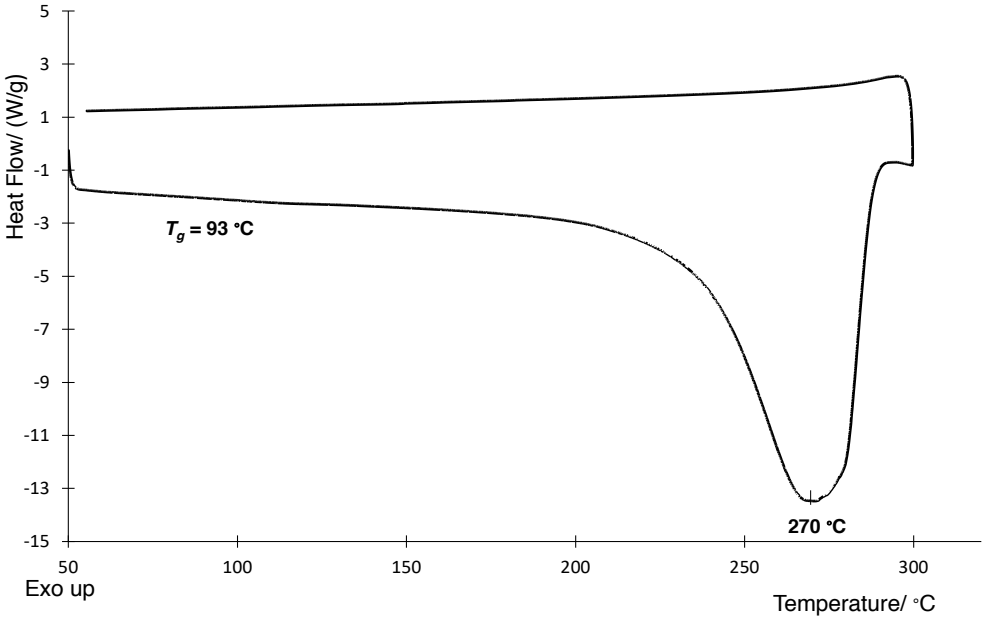
6.1 DSC Thermogram of sPBN2VN



6.2 DSC Thermogram of sPS



6.3 DSC Thermogram of sPVA.



7. Supplemental Data

Table S1. Comparison of BN2VN, styrene, and 2-vinylnapthalene (2VN) coordination polymerization.

Note: sPS is insoluble in THF, precluding GPC characterization of molecular weight characteristics by available instrumentation. All sPS molecular weight data in Table S1 are literature values and references are provided. Literature GPC conditions: 1,2-dichlorobenzene at 135° C.[7] Both sP2VN and sPBN2VN are sufficiently soluble in THF for GPC characterization and these data were collected as described in the General Information.

		Yield, %			M_n, kDa (M_w/M_n)		
Entry	Cat./Cocat.	Styrene	2VN	BN2VN	Styrene	2VN	BN2VN
1	Cp_2ZrCl_2/MAO[a]	0	15[g]	0	n.a.	29.1 (1.77)	n.a.
2	Cp_2TiCl_2/MAO[a]	36	40	18	n.d.[d]	25.3 (1.84)	2.08 (1.63)
3	$CpTiCl_3$/MAO[b]	61	81	12	34.3 (2.8)[e]	52.9 (3.01)	4.58 (1.32)
4	(Indenyl)$TiCl_3$/MAO[a]	60	86	0	n.d.[f]	17.0 (2.09)	n.a.
5	Cp*$TiCl_3$/MAO[b]	>99	50	21	46.9 (3.6)[e]	17.6 (1.69)	4.50 (1.24)
6	Cp*$TiMe_3$/$B(C_6F_5)_3$[c]	86	82	33	66.4 (2.56)[e]	17.4 (1.68)	12.2 (2.33)

[a] 2.5×10^{-2} mol% catalyst, [cat.]/[cocat.] = 0.025/20.0, 50 °C, 24 h, toluene, 2.0 M. [b] 2.5×10^{-2} mol% catalyst, [cat.]/[cocat.] 0.025/22.5, 50 °C, 2 h, toluene, 2.0 M. [c] 35 °C, toluene, 0.95 M, 0.5 mol% Cp*$TiMe_3$, 0.5 mol% $B(C_6F_5)_3$. [d] Molecular weight characteristics not reported (see reference 8). [e] Excerpted from reference 9. [f] Molecular weight characteristics not reported (see reference 10). [g] Atactic polymer obtained. n.a. = not applicable; n.d. = not determined.

Figure S1. Comparison of aPBN2VN UV-vis spectra in THF and DMSO. Agreement between spectra suggests DMSO is not coordinating BN naphthalene. [aPBN2VN] = 0.021 g L^{-1}, RT.

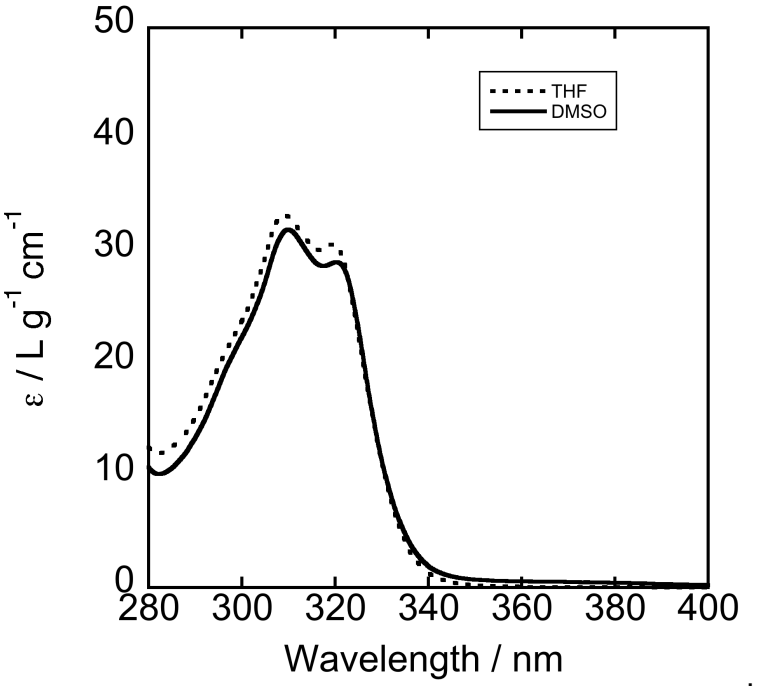


Figure S2. UV-vis spectra of sPBN2VN and sPVA showing loss of BN naphthalene chromophore after oxidation. DMSO, [polymer] = 0.021 g L^{-1}, RT.

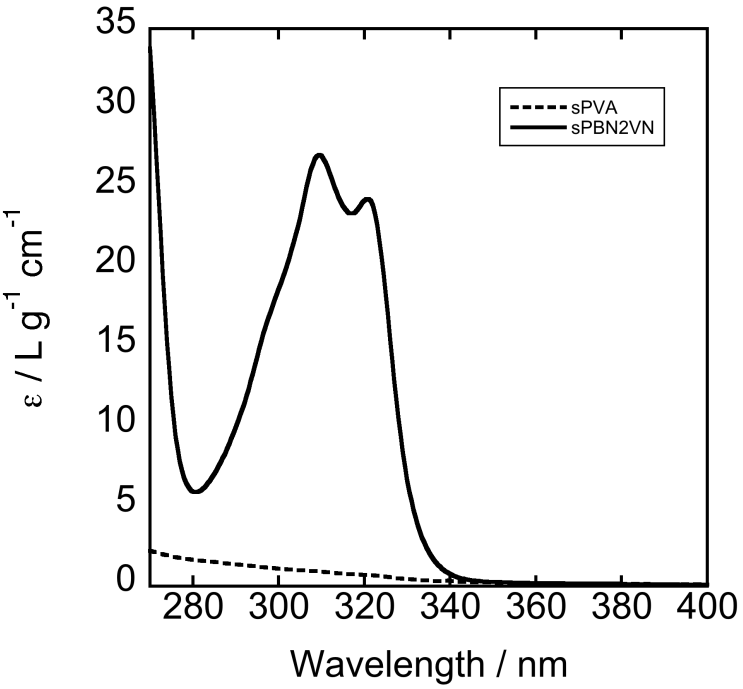


Figure S3. Temperature dependent ^{1}H NMR spectra of sPVA (400 MHz, DMSO-d_6). PVA resonances are not observed until 120 °C. As reported by Moritani, the hydroxyl resonances coalesce with the methine resonance at elevated temperature.[11] The chemical shift of water in DMSO is temperature dependent.[12]

Ethanol (EtOH) is observed upon heating from room temperature to 50 °C. Two sources of ethanol are possible. (1) Ethanol is a cosolvent in the oxidation reaction. Crystalline sPVA may form clathrates that release ethanol upon heating. (2) Ethanol is a known byproduct of PVA thermal decomposition.[13] While thermal decomposition is typically investigated above 200 °C, the fact that ethanol is also observed upon heating commercial PVA to 50 °C (see Figure S4) suggests that ethanol is not a byproduct of the synthesis condition.

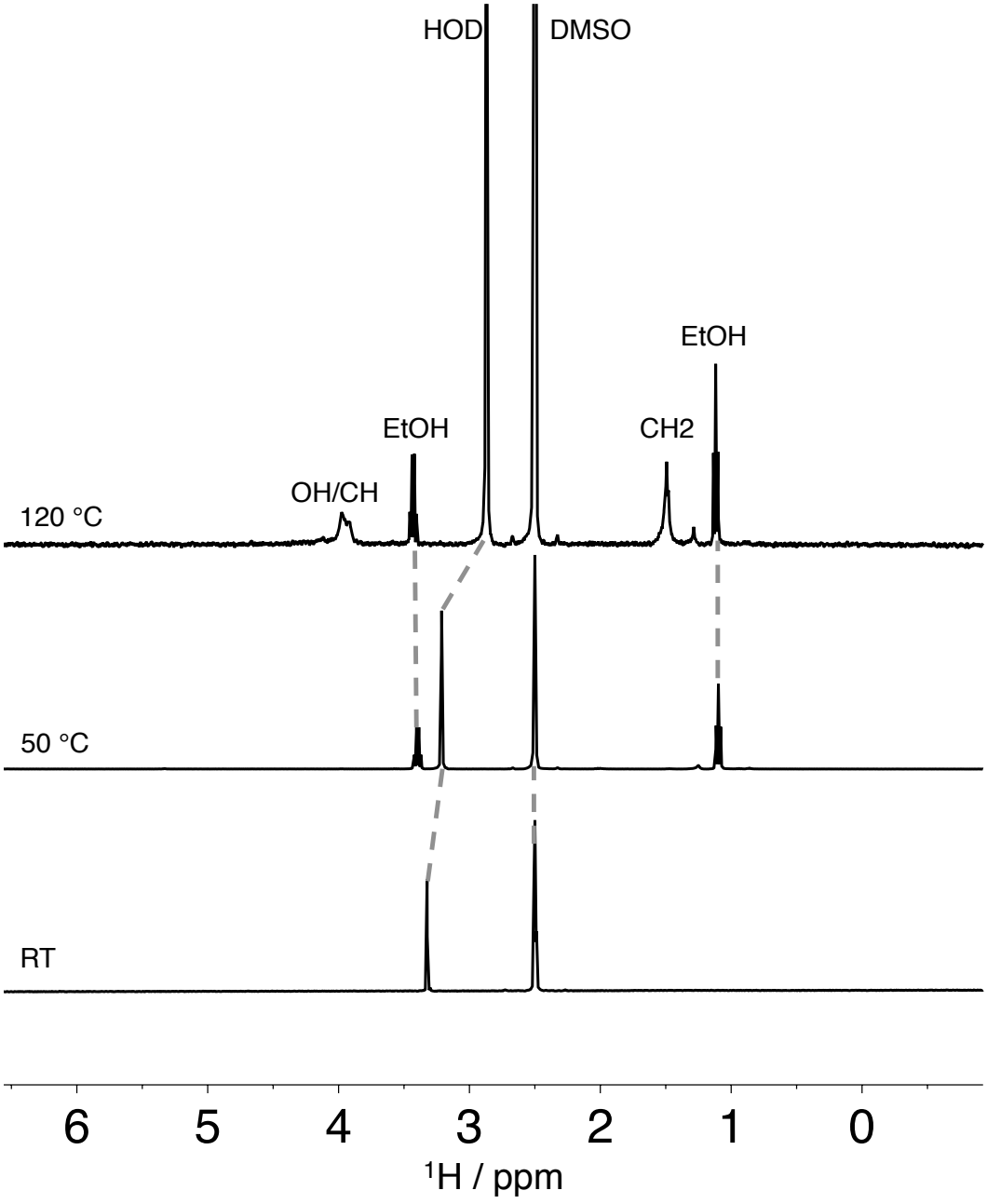
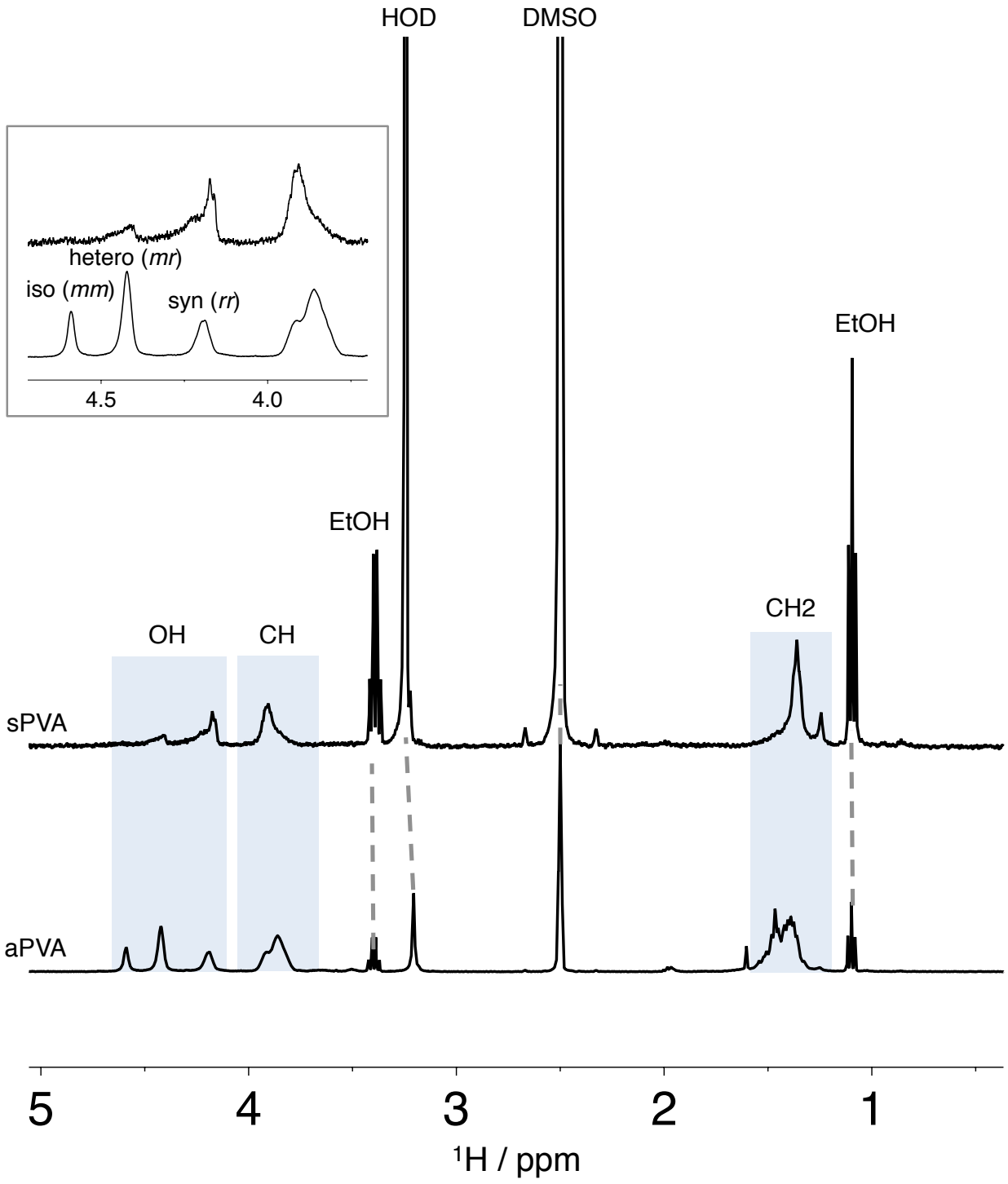


Figure S4. Comparison of synthetic sPVA and commercially available aPVA at 50 °C (400 MHz, DMSO-d_6). Samples were heated to 120 °C, then cooled to 50 °C for data collection. Inset shows hydroxyl resonances. Synthetic sPVA is enriched in syndiotactic (rr) triads hydroxyl resonances. Spin-spin splitting of hydroxyl resonances is not observed in either sample.[11,14] Ethanol is observed in both synthetic and authentic PVA.



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