# SUPPORTING INFORMATION

RAFT Polymerization of an Aromatic Organoborane for Block Copolymer Synthesis

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### 1. Supplemental Figures



Figure S1. Molecular weight data for RB synthesis time studies at two different experiment ratios Monomer:CTA:Initiator (Left 100:1:0.1 Right 100:1:0.9).



Figure S2. Theoretical and experimental molecular weight data for RB studies.



Figure S3. Solution phase <sup>1</sup>H NMR spectra stack of RS (top), RS-b-RB (middle), and PS-b-PVA (bottom) where the BN2VN precursor block is small.



Figure S4. MALDI data of RS (top), RS-*b*-RB (middle), and PS-*b*-PVA (bottom). CPDTterminated chains most likely fragment to create vinyl-terminated (for RS and RS-*b*-RB) and Hterminated (for PS-b-PVA) molecular weights. Structure deduction informed by Hufnagel, M., Fischer, M., Thurn-Albrecht, T., and Thelakkat, M. *Polym. Chem*, 2015, *6*, 813-826.



Figure S5. DOSY of the unsuccessful RB chain extension with two major diffusion coefficients, suggesting a mix of homopolymer PS and macro-RAFT block RB. RB block comes from Ouchi-like ratios: [BN2VN]:[CPDT]:[AIBN] = 100:1:0.9.



Figure S6. DOSY of the unsuccessful RB chain extension with two major diffusion coefficients, suggesting a mix of homopolymer PS and macro-RAFT block RB. RB block comes from typical RAFT ratios: [BN2VN]:[CPDT]:[AIBN] = 100:1:0.1.





Figure S7. Molecular weight data over time for the chain extension of RS with BN2VN.  $\blacksquare$  = Mn;  $\circ$  = M<sub>w</sub>/M<sub>n</sub>.

Figure S8. Molecular weight data for varying BN2VN feed ratio in the chain extension of RS.

Polymer	Technique	Retention	Mn	Mw	M <sub>w</sub> /M <sub>n</sub>
		Time (min)	(g/mol)	(g/mol)	
RS	GPC RI	4.70	7510	8950	1.19
	MALS		7530	9930	1.32
RS- <i>b</i> -RB 4:1	GPC RI	4.89	8100	10800	1.34
	MALS		10100	13800	1.37
RS- <i>b</i> -RB 2:1	GPC RI	4.85	4100	5900	1.44
	MALS		11400	16500	1.44
RS- <i>b</i> -RB 1:1	GPC RI	4.78	5050	9130	1.81
	MALS		13500	26500	1.96

Table S1. Tabulated molecular weight data for varying BN2VN feed ratio in the chain extension of RS.







Figure S10. Attempts to dissolve PS-*b*-PVA BCPs with longer PVA block lengths proved difficult.



Figure S11. UV-Vis of starting macro-RAFT block, block copolymer, and oxidized block copolymer.



Figure S12. Oxidation of RS results in loss of trithiocarbonate and appearance of sharp C-OH peak in solid state <sup>13</sup>C NMR.

## 2. General Information

**General Experimental Procedure:** All reactions were conducted under a positive pressure of inert atmosphere (nitrogen) in a glovebox or Schlenk line unless otherwise indicated. All glassware was oven-dried overnight in a 175 °C oven and cooled to room temperature under vacuum.

**Instrumentation:** <sup>1</sup>H NMR, <sup>11</sup>B NMR, and <sup>13</sup>C NMR solution phase 1D and 2D spectra were recorded on either a Bruker Avance III 400 MHz Spectrometer or Bruker Avance 300 MHz Spectrometer. Chemical shifts are reported in parts per million (ppm). Spectra were recorded in chloroform-*d* with the residual solvent peak as the internal standard (<sup>1</sup>H NMR: CHCl<sub>3</sub>,  $\delta$  = 7.26 ppm. <sup>13</sup>C NMR: CHCl<sub>3</sub>,  $\delta$  = 77.16 ppm). Solid phase <sup>13</sup>C NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer. Carbons bound to boron are not observed due to the quadrupolar relaxation of boron. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz (Hz) and integration is noted.

The UNIIab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere.

Polymer molecular weights were measured by gel permeation chromatography (GPC) and multiangle light scattering (MALS) on a Tosoh Bioscience EcoSEC GPC workstation using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min<sup>-1</sup>, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4  $\mu$ m, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4  $\mu$ m, Tosoh Bioscience) and Tosoh LenS3 MALS Detector (0.35 mL min<sup>-1</sup>, 20Hz Acquisition Rate). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience) and SECview software (Version 1.0.1224, Tosoh Bioscience). Polymers were dissolved in THF (1 mg mL<sup>-1</sup>), filtered (Millex-FG Syringe Filter Unit, 0.20  $\mu$ m, PTFE, EMD Millipore), and injected using an auto-sampler (10  $\mu$ L).

Attenuated total reflectance (ATR) spectra were collected on Thermo Scientific Nicolet iS50 ATR. UV-Vis spectroscopy was performed on a Shimadzu UV-1800 UV-Vis spectrophotometer measured in non-stabilized THF in a quartz cuvette (10 mm) at room temperature.

Thermogravimetric analysis (TGA) curves were collected with samples (~ 20 mg) in a pan heated from room temperature to 600 °C under N<sub>2</sub> atmosphere at a heating rate of 3 °C/min and N<sub>2</sub> flow rate of 100 mL/min. Differential scanning calorimetry (DSC) curves were collected on and processed with TA Instruments Q20 V24.11 Build 124 using aluminum pans; samples (~ 2 mg) were heated from room temperature to 250 °C at a rate of 10 °C/min under N<sub>2</sub> (25 mL/min) and cooled at a rate of 3 °C/min back to room temperature before repeating for at least three cycles.

Matrix-Assisted Laser Desorption Ionization Time of Flight mass spectrometry (MALDI-TOF) spectra were collected on [name of instrument], equipped with a [laser specs]. All spectra were collected in linear, positive-ion mode as the sum of 5000 shots. The instrument was operated using flexControl (Bruker Daltronics Inc., Billerca, MA) and data were analyzed with flexAnalysis (Bruker Daltronics Inc., Billerca, MA). Solutions in acetone of analyte polymer (1.2 mM), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (10 mg/mL), and silver trifluoroacetate (10 mg/mL) were mixed to a mass ratio of 1:35:0.5, respectively, and 1  $\mu$ L was spotted on a polished steel Bruker MTP 384-target TF plate and air dried.

**Materials**: Unless otherwise specified, all chemicals were used as purchased without further purification.

Reaction solvents THF, toluene, dichloromethane (DCM) (Sigma Aldrich, HPLC grade) were dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina and Q5 reactant, a copper (II) oxide oxygen scavenger, following the manufacturer's recommendations for solvent preparation and dispensation. Chloroform-*d* (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc.

### BN2VN Monomer Synthesis

Triethylamine (Sigma Aldrich, >99%) was dried over potassium hydroxide and distilled under argon just prior to use an purchased from Fisher Scientific. Boron trifluoride diethyl etherate (BF<sub>3</sub>•OEt<sub>2</sub>) was purchased from Sigma Aldrich. Potassium vinyltrifluoroborate (95%) was purchased from Sigma Aldrich. Silicon tetrachloride (SiCl<sub>4</sub>) (SureSeal, 99%) was purchased from Sigma Aldrich. Cyclopentyl methyl ether (CPME) (anhydrous, 99.9%) was purchased from Sigma Aldrich.

### **RAFT** Polymerizations

2,2'-Azobis(2-methylpropionitrile) (98%) (AIBN) was purchased from Sigma Aldrich. 2-Cyano-2-propyl dodecyl trithiocarbonate (97%, HPLC) (CPDT) was purchased from Sigma Aldrich. Styrene was filtered through an aluminum oxide column to remove inhibitor, and degassed via freeze-pump-thaw before bringing into the glovebox.

### Oxidations

Methanol (MeOH) was purchased from Sigma Aldrich. 6M NaOH was made from NaOH pellets purchased from Sigma Aldrich and DI water. Hydrogen peroxide (30%) was purchased from Sigma Aldrich.

### 3. Experimental Procedures

Azaborine (BN2VN) Monomer Synthesis. See Section 3.1 in Supporting Information of *Chem. Commun.*, 2017,53, 7262-7265 DOI: <u>https://doi.org/10.1039/C7CC02300F</u>



RAFT polymerization of BN2VN. In a glovebox to a thick-walled vessel (10 mL) was added a rare earth stir bar and 3.22 mmol of BN2VN. Via microsyringe, 23 uL of CPDT stock solution in THF (1.4 M) was added to the vessel (0.033 mmol). Via microsyringe, 75 uL of an AIBN stock solution in THF (0.39 M) was added to the vessel (0.029 mmol). The vessel was sealed, removed from the glovebox, and submerged in a 60 °C preheated oil bath. After completion, the reaction was stopped by submerging the vessel in a dewar with liquid nitrogen then uncapped

and opened to air. Product was dissolved in minimal DCM (5 mL) and precipitated in MeOH (50 mL), isolated via filtration. The precipitation and filtration process was repeated three times. The final product was dried in a vacuum oven overnight at 60 °C before characterization.

RB

 $\delta$   $_{\rm H}$  (400 MHz, CDCl<sub>3</sub>): 8.61 – 6.10 (m, 2.05H), 2.79 (m, 0.01H), 2.60 – 0.53 (m, 1H)  $\delta$   $_{\rm C}$  (400 MHz, CDCl<sub>3</sub>): 147.68, 144.20, 139.95, 129.39, 128.54, 127.91, 125.32, 120.46, 117.81, 38.20, 29.52, 22.34, 22.84

ATR-IR Spectroscopy (cm<sup>-1</sup>): 456, 482, 516, 502, 545, 593, 700, 757, 803, 858, 894, 967, 995, 1032, 1084, 1135, 1154, 1209, 1269, 1278, 1344, 1385, 1435, 1494, 1508, 1513, 1558, 1595, 1614, 2836, 2884, 2981, 3025, 3052, 3372, 3656



RAFT polymerization of styrene. The large-scale bulk polymerization was performed in a glovebox. To a 100 mL Schlenk flask was added a large rare earth stir bar and 20.83 g (0.2 mol) filtered inhibitor-free styrene. 0.691 g of CPDT was weighed out and added to the vessel (0.002 mol). 32.8 mg of AIBN was added to the vessel (0.0002 mol). The flask was sealed with an adapter and septum, removed from the glovebox, attached to a Schlenk line and opened to argon then submerged stirring in a 70 °C preheated oil bath. After completion, the reaction was stopped by submerging the vessel in a dewar with liquid nitrogen then uncapped and opened to air. Product was dissolved in rounds of DCM (5 mL) until viscous but pipette-able and precipitated in MeOH (50 mL) until and isolated via filtration. The precipitation and filtration process was repeated three times. The final product was dried in a vacuum oven overnight at 60 °C before characterization.

CPDT-PS

δ н (400 MHz, CDCl<sub>3</sub>): 7.30 – 6.28 (m, 1.45H), 3.34 – 3.21 (m, 0.01H), 2.31 – 0.84 (m, 1H)

δ<sub>C</sub> (400 MHz, CDCl<sub>3</sub>): 145.43, 128.11, 127.80, 125.79, 125.65, 40.51

 $\delta$  c (500 MHz, solid state): 151.85-139.21, 133.71-121.71, 69.51-62.51, 55.15-34.16, 33.45-25.09

ATR-IR Spectroscopy (cm<sup>-1</sup>): 538, 621, 695, 753, 812, 841, 906, 943, 964, 980, 1004, 1028, 1068, 1110, 1155, 1181, 1226, 1229, 1248, 1260, 1313, 1329, 1369, 1406, 1452, 1492, 1583, 1601, 1803, 1871, 1940, 1946, 2849, 2921, 3002, 3025, 3060, 3082, 3102

Macro-RAFT Chain Extensions



Macro-RAFT extension of RB with styrene. In a glovebox, 100 mg of CPDT-PBN2VN was added to a thick-walled 10 mL vessel. 69.8 mg of filtered inhibitor-free styrene (0.67 mmol) was added to the vessel. 0.1 mL (0.67uM) of an AIBN stock solution in THF (1.1 mM) was added to the vessel via syringe. The vessel was then sealed, removed from the glovebox, and submerged in a 70 °C preheated oil bath. After completion, the reaction was stopped by submerging the vessel in a dewar with liquid nitrogen then uncapped and opened to air. Product was dissolved in minimal DCM (3 mL) and precipitated in MeOH (30 mL), isolated via filtration. The precipitation and filtration process was repeated three times. The final product was dried in a vacuum oven overnight at 60 °C before characterization. Chain extension yielded unreacted starting materials.



Macro-RAFT extension of RS with BN2VN. For 1:1 mass feed ratio, in a glovebox 0.5 g of CPDT-PS and 0.5 g of BN2VN (3.22 mmol) were crushed and combined with mortar and pestel into a homogenous powder, then added to a thick-walled 10 mL vessel with a rare-earth stir bar. 75 uL of an AIBN stock solution in THF (0.39 M) was added to the vessel (0.029 mmol). The vessel was sealed, removed from the glovebox and submerged in a preheated 60 °C oil bath. After completion, the reaction was stopped by submerging the vessel in a dewar with liquid nitrogen then uncapped and opened to air. Product was dissolved in minimal DCM (5 mL) and precipitated in MeOH (50 mL), and isolated via filtration. The precipitation and filtration process was repeated three times. The final product was dried in a vacuum oven overnight at 60 °C before characterization.

CPDT-PS-b-PBN2VN

 $\delta$  H (400 MHz, CDCl<sub>3</sub>): 8.09 – 5.89 (m, 1H), 3.90 (m, 0.01H), 2.48 – 0.44 (m, 0.43H) δ c (400 MHz, CDCl<sub>3</sub>): 145.44, 144.01, 139.94, 129.39, 127.79, 125.35, 120.51, 117.81, 40.53, 29.79

δ c (500 MHz, solid state): 148.33 – 133.15, 132.68 – 109.64, 49.02 – 18.67

ATR-IR Spectroscopy (cm<sup>-1</sup>): 458, 539, 593, 696, 758, 805, 840, 895, 907, 938, 965, 1029, 1069, 1139, 1154, 1181, 1209, 1280, 1345, 1437, 1451, 1474, 1493, 1560, 1597, 1615, 2849, 2921, 3025, 3059, 3082, 3374

Oxidation of Block Copolymers



Oxidation of RS-*b*-RB to PS-*b*-PVA. In a 200 mL round bottom equipped with a stir bar was added 200 mg block copolymer PBN2VN-b-PS, 5 mL of 6M NaOH, 25 mL THF, and 5 mL ethanol. Once stirring, 10 mL of 30% H<sub>2</sub>O<sub>2</sub> was added dropwise with a glass pipette. A condenser was added and the reaction was left to stir open to air for 30 minutes before heating to 65 °C and running overnight with a yellow tapered flange plug. The reaction was cooled to room temperature and quenched with 6M HCl until neutralized (approx. 4 mL). Organic solvents were removed in vacuo and solid product was isolated via filtration, rinsing with water. Attempts to remove residual boric acid byproducts were conducted with three repeats of dissolving material in 5 mL methanol and rotovapping at 40 °C. Isolated product was dried in a vacuum oven overnight at 60 °C.

### OxyCPDT-PBN2VN-b-PS

 $\delta$  c (500 MHz, solid state): 151.49 – 140.99, 133.99 – 117.50, 73.69 – 61.8, 55.52 – 30.31

ATR-IR Spectroscopy (cm<sup>-1</sup>): 456, 537, 696, 753, 907, 1028, 1062, 1369, 1451, 1492, 1601, 2849, 2921, 3025, 3059, 3081, 337

### Additional Figures, Schemes, and Spectra



Scheme S1. Conversion of a BN2VN block adjacent to the trithiocarbonate in the presence of hydrogen peroxide could result in gem-diol, aldehyde, or carboxylic acid end groups in an aqueous acidic workup.

### **Molecular Weight Data**

Table S2. Molecular weight data for RB block conversion study.								
$ \begin{array}{c}                                     $								
Time	Technique	Retention Time (min)	M <sub>n</sub> (g/mol)	M <sub>w</sub> (a/mol)	M <sub>w</sub> /M <sub>n</sub>	DP from M <sub>n</sub> 's	Yield (mg)	% Conversion
3h	GPC RI	5.29	4065	5031	1.24	24	85.6	16.7
	GPC RI	5.31	3949	4834	1.22	23	90.3	17.7
	LALS		3938	7877	1.24	23		
	LALS		5723	7378	1.29	35		
4.5h	GPC RI	5.21	4823	6257	1.30	29	121.7	23.8
	GPC RI	5.14	5798	7736	1.33	35	169.5	33.1
	LALS		10236	8770	1.32	64		
	LALS		9130	12699	1.4	57		
6h	GPC RI	5.12	5587	7936	1.42	34	154.4	30.2
	GPC RI	5.04	6901	10093	1.46	42	261.3	51.1
	LALS		9358	12915	1.38	58		
	LALS		9880	15396	1.56	62		
9h	GPC RI	5.01	6909	11073	1.60	42	268.8	52.6
	GPC RI	4.95	7437	13620	1.83	46	315	61.6
	LALS		12260	20574	1.68	77		
	LALS		10331	23533	2.28	64		
12h	GPC RI	5.02	6663	10938	1.64	41	293.4	57.4
	GPC RI	4.98	7289	13186	1.81	45	345.4	67.5
	LALS		15094	26014	1.7	95		
	LALS		11963	25329	2.12	75		
24h	GPC RI	4.96	7384	14594	1.98	45	397.7	77.8
	GPC RI	4.93	8751	15817	1.81	54	385.5	75.4
	LALS		12364	25683	2.08	78		

	LALS		19773	38691	1.96	125		
48h	GPC RI	4.94	7962	15957	2.00	49	410.2	80.2
	GPC RI	4.76	8163	17258	2.11	50	421.2	82.3
	LALS		10629	22833	2.15	66		
	LALS		12973	29449	2.27	188		



Figure S13. Failed chain-extension of RB with styrene as evidenced by raw bimodal full spectrum GPC RI curves (THF, 1.0 mg mL<sup>-1</sup>, RT). Overlays are RB (black) and chain extension attempts with radical initiator AIBN (dark grey) and with thermally initiated conditions (light grey). RB block comes from Ouchi-like ratios: [BN2VN]:[CPDT]:[AIBN] = 100:1:0.9.



Figure S14. Failed chain-extension of RB with styrene as evidenced by raw bimodal full spectrum GPC RI curves (THF, 1.0 mg mL<sup>-1</sup>, RT). Overlays are RB (black) and chain extension attempts with radical initiator AIBN (dark grey) and with thermally initiated conditions (light grey). RB block comes from typical RAFT ratios: [BN2VN]:[CPDT]:[AIBN] = 100:1:0.1.



Figure S15. Raw data SEC traces of successful chain extension of RS with BN2VN.



Figure S16. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for  $\rm RS_{48}.$ 



Figure S17. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for  $RS_{48}$ -*b*- $RB_{10}$ .



Figure S18. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for  $PS_{48}$ -*b*-PVA<sub>10</sub>.



Figure S19. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 16.7%).



Figure S20. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 17.7%).



Figure S21. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 23.8%).



Figure S22. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 30.2%).



Figure S23. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 33.1%).



Figure S24. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 51.1%).



Figure S25. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 52.6%).



Figure S26. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 57.4%).



Figure S27. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 61.6%).



Figure S28. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 67.5%).



Figure S29. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 75.4%).



Figure S30 Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 77.8%).



Figure S31. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 80.2%).



Figure S32. Raw data SEC trace stacks of GPC RI, UV-Vis (254 nm), and low-angle light scattering (LALS) modes for RB (Conversion 82.3%).

### **UV-Vis Data**



Figure S33. Chain extension of CPDT-PS with BN2VN at varying reaction times. The BN2VN and TTC absorbance handle 310 nm is indicated.



**NMR Data** 



Figure S35. <sup>1</sup>H NMR of an unsuccessful attempt to RAFT polymerize BN2VN with a nonconjugated monomer compatible RAFT agent, CMCD.



Figure S36. Solution phase <sup>1</sup>H and <sup>13</sup>C NMR spectra of CPDT-PS taken in CDCI<sub>3</sub>.



Figure S37. Solution phase <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra of RB.



Figure S38. Solution phase <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra of block copolymer RS-*b*-RB.



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 13C ppm

Figure S39. Solid state <sup>13</sup>C NMR of resubjected chain-extension of RS to RS-*b*-RB to achieve longer and longer BN2VN blocks.



Figure S40. Full solid state <sup>13</sup>C NMR spectra of oxidized block copolymers. Peaks > 200 ppm have been assigned as spinning side bands.

### **IR Data**



Figure S41. ATR-IR spectra of macro-RAFT RS, chain extension to block copolymers RS-*b*-RB, and oxidized block copolymer PS-*b*-PVA.

### DSC and TGA Data

Table S3. DSC data for macro-RAFT starting block, block copolymer, and oxidized block copolymer.

Compound	T <sub>g</sub> (°C)
RS <sub>48</sub>	84.07
RS <sub>48</sub> -b-RB <sub>10</sub>	101.15
PS <sub>48</sub> -b-PVA <sub>10</sub>	102.36



Figure S42. Non-deconvoluted TGA data for  $RS_{48}$  showing two degradation peaks for loss of RAFT end groups and PS block.



Figure S43. Overlay of TGA (black) and deconvoluted TGA curve (red) using Igor 8 multi-peak function with fitted ExpModGauss peak type (gray, dashed) for RS<sub>48</sub>.



Figure S44. Non-deconvoluted TGA data for RS<sub>48</sub>-*b*-RB<sub>10</sub> showing a RAFT end-group degradation peak and a bimodal degradation peak for PS and PBN2VN blocks.



Figure S45. Non-deconvoluted overlay of TGA data for RS<sub>48</sub>-*b*-RB<sub>10</sub> and its precursor RS<sub>48</sub>.



Figure S46. Non-deconvoluted TGA data for PS<sub>48</sub>-b-PVA<sub>10</sub>



Figure S47. Overlay of TGA (black) and deconvoluted TGA curves (dashed) using Igor 8 multipeak function with fitted ExpModGauss peak type (gray, dashed) shows three major pyrolysis events (assigned end-group, PS block, and PVA block) for PS<sub>48</sub>-b-PVA<sub>10</sub>.