

## **Supporting Information**

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## **Precision Ethylene/Vinyl Bromide Polymers**

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## **Supporting Information**

**Chemicals.** Chemicals were purchased from the Aldrich Chemical Company and used as received unless noted. Grubbs' first generation ruthenium catalyst, bis(tricyclohexylphosphine)benzylidine ruthenium (IV)dichloride, was purchased from Strem Chemical and stored in an Argon filled dry box prior to use. Wilkinson's rhodium catalyst RhCl(PPh<sub>3</sub>)<sub>3</sub> was purchased from Strem. Methylene chloride and *o*-xylene were distilled over CaH<sub>2</sub>. The same ADMET PE sample published<sup>1</sup> by our group was used for comparison.

**Instrumentation.** Solution  $^{1}H$  NMR (300 MHz) and  $^{13}C$  NMR (75 MHz) spectra were recorded on a Varian Associates Gemini 300, VXR 300 or Mercury 300 spectrometer. All chemical shifts for  $^{1}H$  and  $^{13}C$  NMR were referenced to residual signals from CDCl<sub>3</sub> ( $^{1}H = 7.27$  ppm and  $^{13}C = 77.23$  ppm) with an internal reference TMS 0.03% v/v.

High-resolution mass spectral (HRMS) data were obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the electron ionization (EI) mode.

Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

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The GPC measurements for samples in THF were taken on a Waters GPCV 2K instrument. Samples were run with HPLC grade THF at 40  $^{\circ}$ C on Waters Styrage1HR 5E columns relative to polystyrene standards.

IR data was obtained using a Perkin-Elmer Spectrum One FTIR outfitted with a  $LiTaO_3$  detector. Measurements were automatically corrected for water and carbon dioxide.

Thermogravimetric analysis (TGA) data was obtained with a Perkin-Elmer 7 series thermal analysis system. The TGA samples (2-5 mg) were heated from 50 °C to 700 °C at 10 °C/min.

Melting and crystallizations were obtained at 10 °C/min in a differential scanning calorimeter TA Instrument DSC-Q1000 V9.6 Build 290 under nitrogen flow and calibrated with indium.

## Synthesis.

General procedure for Grignard reaction. 5-bromopent-1-ene (1), 8-bromooct-1-ene (2), 11-bromoundec-1-ene (3) were synthesized using a published procedure.<sup>2</sup> Bromine compounds 1, 2, 3 were then use as a reagent for Grignard reaction in the presence of Mg and formaldehyde in THF using the same methodology as reported in the literature<sup>3</sup> to yield precursor alcohol compounds undeca-1,10-dien-6-ol (4), heptadeca-1,16-dien-9-ol (5), and tricosa-1,22-dien-12-ol (6). The alcohol precursors were purified with column chromatography on silica gel eluted by a hexane:ether (5:1) mixture (yields 50-55%).

**Undeca-1,10-dien-6-ol (4).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.80 (m, 2H), 4.97 (m, 4H), 3.60 (br, 1H), 2.07 (q, 4H), 1.25-1.62 (br, 8 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

 $\delta$  138.88, 114.75, 71.79, 37.06, 33.89, 25.08. HRMS calcd. for  $C_{11}H_{20}O$  (M+H)<sup>+</sup>, 169.1600; found, 169.1607. Anal. Calcd. for  $C_{11}H_{20}O$ : C, 78.51; H, 11.98; Found: C, 78.58; H, 12.03.

**Heptadeca-1,16-dien-9-ol (5).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.81 (m, 2H), 4.97 (m, 4H), 3.58 (br, 1H), 2.06 (q, 4H), 1.22-1.53 (br, 20 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.33, 114.37, 72.18, 37.68, 33.98, 29.76, 29.31, 29.80, 25.82. HRMS calcd. for  $C_{17}H_{33}O$  (M+H)<sup>+</sup>, 253.2531; found, 253.2534. Anal. Calcd. for  $C_{17}H_{33}O$ : C, 80.88; H, 12.78; Br. Found: C, 80.92; H, 12.83.

Tricosa-1,22-dien-12-ol (6). <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.82 (m, 2H), 4.98 (m, 4H), 3.59 (m, 1H), 2.04 (q, 4H), 1.20-1.50 (br, 32H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.44, 114.30, 72.22, 37.7, 34.03, 29.92, 29.83, 29.77, 29.70, 29.35, 29.15, 25.87. HRMS calcd. for  $C_{23}H_{44}O$  (M)<sup>+</sup>, 336.3314; found, 336.3306. Anal. Calcd. for  $C_{23}H_{44}O$ : C, 82.07; H, 13.18. Found: C, 82.15; H, 13.38.

**General procedure for bromination reaction.** The precursor alcohols **4**, **5**, and **6** were subjected to the same synthetic route which we reported earlier<sup>4</sup> to yield brominated ADMET monomers 6-bromoundeca-1,10-diene (**7**), 9-bromoheptadeca-1,16-diene (**8**), and 12-bromotricosa-1,22-diene (**9**). The brominated ADMET monomers were purified with column chromatography on silica gel eluted by hexane (yield 85%).

**6-bromoundeca-1,10-diene (7).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.80 (m, 2H), 5.00 (m, 4H), 4.05 (p, 1H), 2.05 (m, 4H), 1.82 (m, 4H), 1.77-1.41 (br, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 138.48, 115.14, 58.39, 38.72, 33.28, 26.98. HRMS calcd. for C<sub>11</sub>H<sub>19</sub>Br (M+Br)<sup>-</sup>, 380.9848; found, 380.9856. Anal. Calcd. for C<sub>11</sub>H<sub>19</sub>Br: C, 57.15; H, 8.28; Br, 34.56. Found: C, 57.24; H, 8.26; Br, 34.72.

**9-bromoheptadeca-1,16-diene (8).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.81 (m, 2H), 4.97 (m, 4H), 4.05 (p, 1H), 2.05 (m, 4H), 1.80 (m, 4H), 1.61-1.30 (br, 16H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.29, 114.45, 59.11, 39.37, 33.96, 29.17, 29.12, 29.04, 27.74. HRMS calcd. for C<sub>17</sub>H<sub>31</sub>Br (M<sup>+</sup>), 314.1609; found, 314.1595. Anal. Calcd. for C<sub>17</sub>H<sub>31</sub>Br: C, 64.75; H, 9.91; Br, 25.34. Found: C, 64.97; H, 9.92; Br, 25.16.

**12-bromotricosa-1,22-diene** (**9**). <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 5.81 (m, 2H), 4.97 (m, 4H), 4.05 (p, 1H), 2.05 (m, 4H), 1.81 (m, 4H), 1.61-1.00 (br, 28H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.44, 114.33, 59.23, 39.40, 34.03, 29.72, 29.69, 29.67, 29.34, 29.28, 29.16, 27.80. HRMS calcd. for C<sub>23</sub>H<sub>43</sub>Br (M+Br)<sup>-</sup>, 417.1726; found, 417.1728. Anal. Calcd. for C<sub>23</sub>H<sub>43</sub>Br: C, 69.15; H, 10.85; Br, 20.00. Found: C, 69.16; H, 10.88; Br, 20.01.

General procedure for bulk polymerization. Monomer and Grubbs' first generation catalyst were combined in a ratio of 500:1 under argon atmosphere. The polymerization was conducted at 35-40 °C under vacuum with stirring for 5 days. The reaction was then stopped and 5 ml of toluene was added to dissolve the polymer with stirring. The reaction was allowed to cool to room temperature. The polymers were then precipitated by dripping the toluene solution into cold acidic methanol. They were then isolated by filtration and dried. Polymers were then redissolved in 50 ml of toluene and treated with THP (tris(hydroxymethyl)phosphine)) in order to remove any residual catalyst. The polymers were then reprecipitated into acidic methanol, filtered and dried.

**Polymerization of 6-bromoundeca-1,10-diene (UPE9Br).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>)  $\delta$  **5**.80 (b, 0.02H), 5.41 (m, 2H), 5.00 (b, 0.06 H), 4.03 (p, 1H), 2.00 (m, 4H), 1.80 (m, 4H), 1.75-1.4 (b, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ ?130.47, 129.96, 58.70, 58.63,

38.91, 38.83, 32.13, 27.83, 27.68, 26.81.  $M_{\rm w}$  (GPC vs. PS) = 18,400 g/mol. PDI =  $(M_{\rm w}/M_{\rm n})$  = 1.99.

**Polymerization of 9-bromoheptadeca-1,16-diene (UPE15Br).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>)  $\delta$  **5**.81 (b, 0.02H), 5.39 (m, 2H), 4.97 (b, 0.04 H), 3.89 (p, 1H), 1.97 (m, 4H), 1.71 (m, 4H), 1.6-1.1 (b, 16 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ ?130.55, 130.07, 64.58, 38.76, 32.77, 29.88, 29.77, 29.38, 29.28, 29.24, 27.39, 26.71.  $M_{\rm w}$  (GPC vs. PS) = 35,300 g/mol. PDI =  $(M_{\rm w}/M_{\rm n})$  = 1.75.

**Polymerization of 12-bromotricosa-1,22-diene (UPE21Br).** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>)  $\delta$  **5**.81 (b, 0.01H), 5.39 (m, 2H), 5.00 (b, 0.02 H), 4.03 (p, 1H), 1.97 (m, 4H), 1.80 (m, 4H), 1.65-1.0 (b, 28 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ ?130.58, 130.12, 59.26, 39.63, 32.84, 29.89, 29.78, 29.53, 29.40, 29.32, 27.83, 27.44.  $M_{\rm w}$  (GPC vs. PS) = 75,800 g/mol. PDI =  $(M_{\rm w}/M_{\rm p})$  = 2.19.

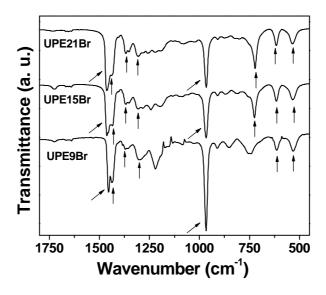
General Procedure for hydrogenation. The bromine containing polymers (UPE9Br), (UPE15Br), and (UPE21Br) were hydrogenated using a 150 ml Parr high-pressure reaction vessel equipped with a glass liner and Teflon stirbar. Unsaturated polymer (1.0g) and Wilkinson's catalyst (0.02g) were added to the glass liner under a nitrogen blanket. Finally, 20 ml of toluene were added. The vessel was sealed and attached to a grade 5 hydrogen tank and purged with hydrogen several times. The bomb was charged with 550 psi of H<sub>2</sub> and stirred for 5 days at room temperature °C. The hydrogenated polymer was dissolved in toluene, and precipitated into methanol. The polymer was then filtered and dried under reduced pressure.

**PE9Br.** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 4.03 (p, 1H), 1.81 (m, 4H), 1.65-1.2 (bm, 12H), 0.9 (t, 0.12H). <sup>13</sup>C NMR (75 MHz,CDCl<sub>3</sub>) δ 59.23, 39.41, 29.62, 29.25, 27.80,

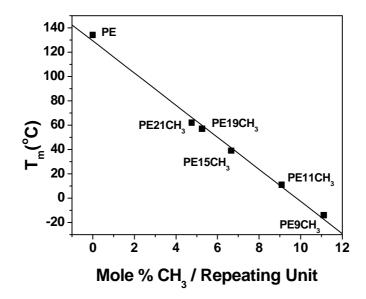
1.24. Anal. Calcd.: C, 52.70; H, 8.35; Br, 38.95. Found: C, 52.86; H, 8.36; Br, 38.72.  $M_{\rm w}$  (GPC vs. PS) = 23,600 g/mol. PDI =  $(M_{\rm w}/M_{\rm n})$  = 1.75.

**PE15Br.** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 4.04 (p, 1H), 1.82 (m, 4H), 1.65-1.2 (bm, 24H) 0.9 (t, 0.20H). <sup>13</sup>C NMR (75 MHz,CDCl<sub>3</sub>) δ 59.29, 39.42, 29.89, 29.87, 29.82, 29.74, 29.32, 27.83, 1.24. Anal. Calcd.: C, 62.28; H, 10.10; Br, 27.62. Found: C, 61.61; H, 10.09; Br, 27.26.  $M_{\rm w}$  (GPC vs. PS) = 27,600 g/mol. PDI =  $(M_{\rm w}/M_{\rm n})$  = 1.68.

**PE21Br.** <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 4.04 (p, 1H), 1.81 (m, 4H), 1.7-1.2 (bm, 36H), 0.9 (t, 0.11H). <sup>13</sup>C NMR (75 MHz,CDCl<sub>3</sub>) δ 59.27, 39.42, 29.94, 29.88, 29.82, 29.74, 29.32, 27.82, 1.24. Anal. Calcd.: C, 67.54; H, 11.07; Br, 21.40. Found: C, 67.64; H, 11.06; Br, 21.39.  $M_{\rm w}$  (GPC vs. PS) = 94,100 g/mol. PDI =  $(M_{\rm w}/M_{\rm n})$  = 2.23.



**Figure S-1.** IR spectra of **UPE9Br**, **UPE15Br**, **UPE21Br**. Indicated peaks correspond those in Figure 1b, with the exception of the intense peak found at 967 cm<sup>-1</sup> corresponding to the out of plane olefin C-H wag in the unhydrogenated samples **UP21Br**, **UP15Br**, and **UP9Br** shown here.



**Figure S-2.**  $T_m$  vs number of moles of  $CH_3$  in repeating unit for PE9CH<sub>3</sub>, PE11CH<sub>3</sub>, PE15CH<sub>3</sub>, PE19CH<sub>3</sub>, PE21CH<sub>3</sub>, and PE. All data collected from our group publication.<sup>6</sup>

**Table S-1.** Summary of thermal properties measured via DSC for the family of ethylene/vinyl bromide polymers.

J J F J							
Sample	M <sub>o</sub> (g/mol)	$\mathrm{DH_f(J/g)^{(b)}}$	$\mathrm{DH_f(J/mol)}^{(c)}$	Tm(°C)	Tm(K)	$DS_f(J molK)^{(d)}$	DS <sub>f</sub> \bond <sup>(e)</sup>
PE9Br	205.14	20.71	4248	-14.81	258.35	16.44	1.83
PE15Br	289.29	35.05	10140	48.84	322.00	31.49	2.10
PE19Br <sup>(a)</sup>	345.40	43.35	14973	63.89	337.05	44.42	2.34
PE21Br	373.45	48.17	17989	69.63	342.79	52.48	2.50

(a) ref 12 in manuscript, ref 4 in supporting information. The Tm and  $\Delta H$  values listed were obtained in a new specimen for baseline consistency within the series.

(b), (c), (d), (e). From observed DSC values

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