Linear Ethylene−Vinyl Ether Copolymers: Synthesis and Thermal Characterization

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ABSTRACT: Linear ethylene-*co*-vinyl ether copolymers were synthesized via a metathesis polymerization−hydrogenation reaction sequence producing a family of well-defined ethylene-based materials. Six high molecular weight macromolecules with desired vinyl ether incorporation levels are reported having methoxy or ethoxy pendant functionality on every 11th, 15th, and 21st carbons in the polymer backbone, and structural characterization of isolated materials via NMR and FT-IR indicates excellent control over copolymer microstructure. Thermal characterization via differential scanning calorimetry (DSC) suggests semicrystallinity for every material under dynamic scanning conditions except one highly functionalized material where subsequent annealing treatments isolated a peak melting temperature deviating from melting trends established by other materials in the study. Variations of physical and spectral properties are discussed as a function of pendant group spacing and overall level of ether incorporation.

Introduction

The copolymerization of ethylene with alkyl vinyl ethers is difficult due to both the large reactivity ratio disparity of the two vinyl monomers[1] and the ability of alkyl vinyl ethers to act as efficient chain-transfer agents during radical and cationic polymerization.[2] A small number of dated U.S. patents[2−10] show that the use of high-pressure, free-radical copolymerization techniques and state-of-the art metal catalysis has yielded structurally diverse (often highly branched) materials ranging from viscous liquids to brittle solids with proposed industrial applications from adhesives to barrier materials (Table 1). While high molecular weight copolymers were reported in some cases, the typically low levels of vinyl ether incorporation lead to marginal differences in bulk properties relative to polyethylene. These early reports indicated successful incorporation of both monomers, but forcing conditions of high temperatures and pressures were required when using either free-radical initiation or what is referred to as Friedel−Crafts polymerization.[2−8] Advancements in late transition metal nickel catalysis have also allowed the preparation of a few examples of ethylene-*co*-vinyl ether (EVE) copolymers at milder conditions with more controllable results.[9,10] Sample characterization data are limited in the patent literature, and reported synthetic methodology and product characterization data are compiled in Table 1 illustrating the range of bulk material properties encountered when applying various chain copolymerization techniques.

As with all polyolefins, bulk EVE properties are highly dependent on polymer microstructure including comonomer ratios, the degree of branching, and especially the presence (or lack thereof) of extended, crystallizable ethylene run lengths in the material.[11,12] Linear high molecular weight EVE copolymers with low vinyl ether content exist as tough, semicrystalline materials resembling high density polyethylene; however, branched, highly functionalized, or low molecular weight EVE materials exist as viscous, adhesive liquids. Although copolymer synthesis can be modified to yield desired materials through proprietary chain copolymerization methodology, reactivity ratio and chain-transfer problems make it virtually impossible to isolate pure copolymer microstructures. The application of metathesis chemistry to the challenge of EVE synthesis allows preparation of linear macromolecules with a priori control over comonomer incorporation and pendant ether branch location, as previously reported in the synthesis of a sequenced ethylene-*co*-methyl vinyl ether copolymer.[13]

Herein, we report the synthesis and thermal characterization of a family of six linear EVE copolymers including three poly(ethylene-*co*-methyl vinyl ether) (EMVE) and three poly(ethylene-*co*-ethyl vinyl ether) (EEVE) materials through a well-known metathesis polymerization−hydrogenation methodology.[14,15] This approach yields sequenced EVE copolymers with monodisperse ethylene run lengths between pendant branches, and structural characterization via NMR and FT-IR techniques illustrates the ability to isolate exact polymer microstructures while evenly spacing pendant ether branches along the polyethylene chain at intervals of 11, 15, and 21 backbone carbons. Thermal analysis via differential scanning calorimetry (DSC) demonstrates the effect of controlled copolymer structure and defined ethylene run lengths on bulk material morphology and polymer crystallization.

Experimental Section

Materials. All reagents were purchased from Aldrich chemical and used as received unless otherwise specified. Ethyl formate was freshly distilled from $MgSO_4$ before use, and 5-bromo-1-pentene, 8-bromo-1-octene, 11-chloro-1-undecene,[16] and Schrock's molybdenum catalyst ($[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i Pr_2)Mo{=}CHC(CH_3)_2\text{-}Ph$)[17] were synthesized according to literature procedures. All reactions were run in flame-dried glassware under argon gas, and tetrahydrofuran (THF) was obtained from an Aldrich keg system with an inline solvent drying column of activated alumina.

Instrumentation and Analysis. All ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Associates Mercury 300 spectrometer. Chemical shifts for ^1H and ^{13}C NMR were referenced to residual signals from $CDCl_3$ ($^1H = 7.27$ ppm and $^{13}C = 77.23$ ppm) with 0.03% v/v TMS as an internal reference. Reaction conversions and relative purity of crude products were monitored by thin-layer chromatography (TLC) performed on EMD silica gel coated (250 μm thickness) glass plates and ^1H NMR.

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Table 1. U.S. Patents Pertaining to Ethylene-*co*-vinyl Ether Materials

U.S. patent	comonomer $CH_2{=}CH{-}O{-}R$ (R=)	mol % vinyl ether in copolymer	polymerization conditions: catalyst[a]	pressure (Kpsi)	temp (°C)	copolymer products[b]
2,467,234 (1949)[3]	C_1, C_2, Ph	not reported	R	0.7−50	20−400	solids
2,748,170 (1956)[4]	C_1–C_{16}	11.2 (C_4)	R, FC	0.4−1.1	150	400−700 g/mol
3,025,267 (1962)[7]	$CH_2(CH_2)_nOH$	2−14	R	15−50	100−200	10−100 kg/mol
3,026,290 (1962)[6]	C_1–C_{16}	5−80	FC	0.500−50	35	liquids and solids
3,033,840 (1962)[2]	CH_3	0.5−10	R	12−30	150−240	solids
3,226,374 (1962)[5]	C_1–C_{10}	1.8−2.6	R	15−80	160−250	solid films
3,560,463 (1971)[8]	C_{15}, C_{18}	0.6−1.3	R	20−30	150−240	solid films
4,906,754 (1987)[9] 4,698,403 (1990)[10]	C_2	1.4	Ni cat.	0.06	65	solids

[a] R = free radical (ROOR and/or O_2 initiators), FC = Friedel−Crafts (Al or Ti catalyst). [b] As published, molecular weight data included when reported.

Developed TLC plates were stained with iodine absorbed on silica or vanillin solution (5 wt % in 50 mL of ethanol with 2 mL of H_2SO_4) to produce a visible signature. Low- and high-resolution mass spectral (LRMS and HRMS) data were obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the chemical ionization (CI) mode.

Differential scanning calorimetry (DSC) analysis was performed using a Perkin-Elmer DSC-7 equipped with a controlled cooling accessory (CCA-7) at a heating rate of 10 °C/min. Calibrations were made using indium and freshly distilled *n*-octane as the standards for peak temperature transitions and indium for the enthalpy standard. All samples were prepared in hermetically sealed pans (4−7 mg/sample) and were run using an empty pan as a reference and empty cells as a subtracted baseline. Annealing treatments for **EEVE11** were performed for 1 h at −25 °C and quench-cooled at 400 °C/min to −100 °C before collecting data at 10 °C/min.

Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector (DRI) and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm ID, 300 mm length) in HPLC grade tetrahydrofuran as the mobile phase at a flow rate of 1.0 mL/min. Injection volumes of 220.5 μL were made at 0.05−0.07% w/v sample concentration, and retention times were calibrated against a minimum of eight narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA).

General Procedure for Grignard Reaction with Alkenyl Chlorides or Bromides. A solution of the 6-bromo-1-hexene (2.2 equiv) in THF (2 M) was added dropwise to freshly scoured magnesium turnings (2.3 equiv) in a flame-dried 250 mL round-bottom flask and allowed to reflux for 1 h under a blanket of argon gas. A solution of ethyl formate (1.0 equiv) in THF (2 M) was added to the flask via addition funnel over 20 min. Upon complete addition, the reaction was brought back to reflux for a period of 16 h. The reaction was quenched via addition of water (50 mL) and dissolved into a biphasic system upon addition of ether (100 mL). The crude reaction mixture was then washed with water (2 × 100 mL) and brine (2 × 50 mL), and the organic layer was concentrated by rotary evaporation to a colorless oil.

1,12-Tridecadiene-7-ol (1). Column chromatography using 4:1 hexane:dichloromethane as the eluent afforded 4.5 g of a colorless oil after solvent evaporation (63% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.24−1.52 (br, 12H), 2.07 (q, 4H), 3.59 (br, 1H), 4.98 (m, 4H), 5.81 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.33, 29.15, 33.94, 37.51, 72.05, 114.57, 139.10. CI/HRMS: $[M + H]^+$ calcd for $C_{13}H_{25}O$, 197.1905; found, 197.1910. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.36; H, 12.44.

1,16-Heptadecadiene-9-ol (2). From 8-bromo-1-octene. Column chromatography using 9:1 hexane:diethyl ether as the eluent afforded 5.1 g of a colorless oil (65% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.22−1.51 (br, 20H), 2.05 (q, 4H), 3.59 (br, 1H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.82, 29.80, 29.31, 29.76, 33.98, 37.68, 72.18, 114.37, 139.33. CI/HRMS: $[M + H]^+$ calcd for $C_{17}H_{33}O$, 253.2531; found, 253.2534. Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.74; H, 12.69.

1,22-Tricosadiene-12-ol (3). From 9-chloro-1-undecene. Column chromatography using 9:1 hexane:diethyl ether as an eluent afforded 15.4 g of a white solid (92% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.50 (br, 32H), 2.04 (q, 4H), 3.59 (m, 1H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.87, 29.15, 29.35, 29.70, 29.77, 29.83, 29.92, 34.03, 37.7, 72.22, 114.30, 139.44. CI/HRMS: $[M]^+$ calcd for $C_{23}H_{44}O$, 336.3392; found, 336.3392. Anal. Calcd for $C_{23}H_{44}O$: C, 82.07; H, 13.18. Found: C, 82.11; H, 13.36.

General Alkylation Procedure for the Preparation of α,ω-Diene Ethers. A solution of **1** (1 equiv) in DMF was added to a slurry of NaH (1.5 equiv) in DMF in a 250 mL three-neck flask. Methyl iodide (1.5 equiv) was added slowly via syringe, and the solution was allowed to stir at room temperature for 1 h. The reaction was heated to 50 °C for 3 h, then cooled and quenched via addition of water (25 mL). Following extraction with diethyl ether and washing with brine, the ether solution was concentrated to a yellow oil.

7-Methoxy-1,12-tridecadiene (4). Column chromatography using 17:3 hexane:dichloromethane as the eluent afforded 2.3 g of a colorless oil (67% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.21−1.52 (br, 12H), 2.05 (q, 4H), 3.13 (m, 1H), 3.31 (s, 3H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.97, 29.37, 33.98, 56.57, 81.05, 114.48, 139.18. CI/HRMS: $[M + H]^+$ calcd for $C_{14}H_{27}O$, 211.2061; found, 211.2067. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.62; H, 12.74.

9-Methoxy-1,16-heptadecadiene (5). From **2**. Column chromatography using 9:1 hexane:dichloromethane as the eluent afforded 3.4 g of a colorless oil (71% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.51 (br, 20H), 2.05 (q, 4H), 3.11 (m, 1H), 3.32 (s, 3H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.44, 29.10, 29.36, 29.93, 33.65, 34.00, 55.58, 81.19, 114.34, 139.37. CI/HRMS: $[M + H]^+$ calcd for $C_{18}H_{35}O$, 267.2687; found, 267.2688. Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 80.95; H, 12.97.

12-Methoxy-1,22-tricosadiene (6). From **3**. Column chromatography using 7:3 hexane:dichloromethane as the eluent afforded 7.3 g of a colorless oil (78% yield). ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.50 (br, 32H), 2.05 (q, 4H), 3.12 (m, 1H), 3.32 (s, 3H), 4.98

(m, 4H), 5.82 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.50, 29.17, 29.37, 29.72, 29.79, 29.86, 30.11, 33.67, 34.04, 56.59, 81.24, 114.30, 139.48. CI/HRMS: $[M + H]^+$ calcd for $C_{24}H_{47}O$, 351.3626; found, 351.3616. Anal. Calcd for $C_{24}H_{46}O$: C, 82.21; H, 13.22. Found: C, 82.10; H, 13.46.

7-Ethoxy-1,12-tridecadiene (7). From **1**. Column chromatography using 17:3 hexane:dichloromethane as the eluent afforded 1.4 g of a colorless oil (62% yield). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19 (t, 3H), 1.21−1.52 (br, 12H), 2.05 (q, 4H), 3.21 (m, 1H), 3.48 (q, 2H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.91, 25.17, 29.36, 34.17, 64.31, 79.44, 114.46, 139.26. CI/HRMS: $[M + H]^+$ calcd for $C_{15}H_{29}O$, 225.2218; found, 225.2223. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.25; H, 12.61.

9-Ethoxy-1,16-heptadecadiene (8). From **2**. Column chromatography using 9:1 hexane:dichloromethane as the eluent afforded 2.3 g of a colorless oil (69% yield). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19 (t, 3H), 1.21−1.52 (br, 20), 2.05 (q, 4H), 3.20 (br, 1H), 3.48 (q, 2H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.92, 25.64, 29.12, 29.36, 29.93, 34.02, 34.37, 64.31, 79.57, 114.34, 139.41. CI/HRMS: $[M + H]^+$ calcd for $C_{19}H_{37}O$, 281.2844; found, 281.2838. Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.32; H, 13.02.

12-Ethoxy-1,22-tricosadiene (9). From **3**. Column chromatography using 9:1 hexane:dichloromethane as the eluent afforded 1.8 g of a colorless oil (67% yield). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19−1.49 (br, 35H), 2.05 (q, 4H), 3.18 (m, 1H), 3.48 (q, 2H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.94, 25.70, 29.18, 29.38, 29.73, 29.81, 29.88, 30.11, 34.06, 34.37, 64.27, 79.59, 114.28, 139.43. CI/HRMS: $[M + H]^+$ calcd for $C_{25}H_{49}O$, 365.3783; found, 365.3792. Anal. Calcd for $C_{25}H_{48}O$: C, 82.34; H, 13.27. Found: C, 82.37; H, 13.48.

General ADMET Polymerization Procedure for Symmetrical Ether Monomers. Purified monomer **4** was distilled onto a potassium metal mirror and allowed to sit for 2 h or until noticeable reaction ceased. Upon vacuum transfer into a 50 mL Schlenk flask, the monomer was taken into an argon-filled glovebox, mixed with Schrock's [Mo] catalyst (2000:1 monomer:catalyst, ∼1.5 g of monomer) in a 50 mL round-bottom flask, and magnetically stirred until ethylene evolution waned and reaction viscosity increased. The polymerization flask was then sealed with a Schlenk adapter and transferred out of the glovebox and onto a high vacuum line. Intermittent vacuum was applied over 4 h at room temperature while the reaction continued to exhibit easily detectable ethylene production and viscosity increase. Once the reaction slowed, the golden amorphous liquid was warmed to 45 °C and allowed to stir for 3 days under high vacuum (10^{-4} Torr). Upon cooling to room temperature, the dark yellow polymerization was quenched by opening the flask to lab atmosphere and adding 25 mL of toluene. The solution was stirred until a dark green color arose (Mo oxides), flashed over a 1" pad of alumina to remove catalyst residue, and concentrated to yield the unsaturated copolymer as viscous oil.

Polymerization of 7-Methoxy-1,12-tridecadiene (10). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.52 (br, 12H), 1.98 (br, 4H), 3.12 (br, 1H), 3.31 (s, 3H), 5.40 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.04, 30.11, 32.82, 33.51, 56.57, 81.10, 130.01 (cis olefin), 130.50 (trans olefin). IR (ν, cm^{-1}): 2930, 2854, 1460, 1369, 1097, 966, 729. GPC data (THF vs polystyrene standards): $M_w = 14\,900$ g/mol. PDI (M_w/M_n) = 1.79.

Polymerization of 9-Methoxy-1,16-heptadecadiene (11). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19−1.52 (br, 20H), 1.97 (q, 4H), 3.12 (m, 1H), 3.32 (s, 3H), 5.39 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.47, 29.39, 29.83, 29.96, 32.80, 33.67, 56.56, 81.18, 130.04 (cis olefin), 130.64 (trans olefin). IR (ν, cm^{-1}): 2928, 2854, 1462, 1367, 1095, 966, 725. GPC data (THF vs polystyrene standards): $M_w = 31\,300$ g/mol. PDI (M_w/M_n) = 1.73.

Polymerization of 12-Methoxy-1,22-tricosadiene (12). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19−1.52 (br, 32H), 1.97 (q, 4H), 3.12 (m, 1H), 3.32 (s, 3H), 5.39 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.50, 29.42, 29.75, 29.84, 29.89, 30.13, 32.85, 33.65, 56.58, 81.21, 130.08 (cis olefin), 130.54 (trans olefin). IR (ν, cm^{-1}): 2926, 2853, 1464, 1367, 1097, 966, 721. GPC data (THF vs polystyrene standards): $M_w = 81\,400$ g/mol. PDI (M_w/M_n) = 2.54.

Polymerization of 7-Ethoxy-1,12-tridecadiene (13). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.10−1.52 (br, 15H), 1.98 (br, 4H), 3.12 (br, 1H), 3.47 (q, 2H), 5.40 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.93, 25.24, 30.11, 32.83, 34.22, 64.28, 79.50, 130.02 (cis olefin), 130.51 (trans olefin). IR (ν, cm^{-1}): 2930, 2856, 1460, 1371, 1344, 1101, 966, 731. GPC data (THF vs polystyrene standards): $M_w = 24\,100$ g/mol. PDI (M_w/M_n) = 1.65.

Polymerization of 9-Ethoxy-1,16-heptadecadiene (14). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.50 (br, 23H), 1.97 (q, 4H), 3.20 (m, 1H), 3.47 (q, 2H), 5.39 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.93, 25.64, 29.43, 29.86, 29.97, 32.82, 34.40, 64.28, 79.58, 130.39 (cis olefin), 130.53 (trans olefin). IR (ν, cm^{-1}): 2927, 2854, 1462, 1371, 1344, 1105, 966, 725. GPC data (THF vs polystyrene standards): $M_w = 48\,900$ g/mol. PDI (M_w/M_n) = 1.74.

Polymerization of 12-Ethoxy-1,22-tricosadiene (15). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.19−1.52 (br, 35H), 1.97 (br, 4H), 3.20 (m, 1H), 3.47 (q, 2H), 5.38 (br, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.92, 25.69, 29.41, 29.75, 29.78, 29.84, 29.89, 20.11, 32.84, 34.36, 64.27, 79.60, 130.07 (cis olefin), 130.531 (trans olefin). IR (ν, cm^{-1}): 2927, 2853, 1464, 1371, 1344, 1110, 966, 721. GPC data (THF vs polystyrene standards): $M_w = 9700$ g/mol. PDI (M_w/M_n) = 1.91.

Hydrogenation of Unsaturated ADMET Polymers. The crude polymer solution of **10** was transferred to a Parr Bomb glass sleeve and diluted to ∼200 mL with toluene. Palladium (10% on carbon, 100 mg) was added to the solution, and the sleeve was sealed inside a Parr Bomb equipped with a mechanical stirrer and temperature control. The vessel was purged three times with 1000 psi hydrogen gas, and then filled to 1000 psi and heated to 100 °C for 2 days. Upon depressurization and cooling, the crude reaction mixture was vacuum filtered over a plug of neutral silica, and then concentrated to viscous liquid.

EMVE11 (16). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.52 (br, 20H), 3.12 (br, 1H), 3.32 (s, 3H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.53, 29.87, 29.89, 30.14, 33.71, 56.57, 81.24. IR (ν, cm^{-1}): 2927, 2853, 1464, 1371, 1344, 1110, 721. GPC data (THF vs polystyrene standards): $M_w = 15\,300$ g/mol. PDI (M_w/M_n) = 1.52.

EMVE15 (17). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.22−1.53 (br, 28H), 3.12 (m, 1H), 3.32 (s, 3H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.53, 29.91, 30.14, 33.70, 56.58, 81.25. IR (ν, cm^{-1}): 2920, 2851, 1466, 1369, 1099, 723. GPC data (THF vs polystyrene standards): $M_w = 24\,900$ g/mol. PDI (M_w/M_n) = 1.70.

EMVE21 (18). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.50 (br, 40H), 3.12 (m, 1H), 3.32 (s, 3H). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.51, 29.96, 30.14, 33.66, 56.60, 81.22. IR (ν, cm^{-1}): 2918, 2851, 1470, 1367, 1261, 1097, 804, 719. GPC data (THF vs polystyrene standards): $M_w = 74\,100$ g/mol. PDI (M_w/M_n) = 2.27.

EEVE11 (19). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.50 (br, 23H), 3.20 (m, 1H), 3.48 (q, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.94, 25.73, 29.88, 29.91, 30.13, 34.41, 64.28, 79.62. IR (ν, cm^{-1}): 2926, 2854, 1464, 1372, 1344, 1111, 721. GPC data (THF vs polystyrene standards): $M_w = 25\,600$ g/mol. PDI (M_w/M_n) = 1.64.

EEVE15 (20). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.50 (br, 31H), 3.20 (m, 1H), 3.48 (q, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.94, 25.73, 29.93, 30.13, 34.41, 64.28, 79.62. IR (ν, cm^{-1}): 2926, 2852, 1466, 1371, 1344, 1113, 721. GPC data (THF vs polystyrene standards): $M_w = 43\,100$ g/mol. PDI (M_w/M_n) = 1.75.

EEVE21 (21). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.20−1.50 (br, 40H), 3.12 (m, 1H), 3.32 (s, 3H). ^{13}C NMR (CDCl$_3$): δ (ppm) 15.94, 25.70, 29.94, 30.12, 34.37, 64.27, 79.61. IR (ν, cm^{-1}): 2924, 2853, 1466, 1372, 1344, 1261, 1111, 804, 721. GPC data (THF vs polystyrene standards): $M_w = 11\,600$ g/mol. PDI (M_w/M_n) = 1.58.

Results and Discussion

Polymer Design and Synthesis. Applying our method of precision polyolefin synthesis[14] to the preparation of EVE materials affords linear copolymers with pendant alkyl ether groups evenly spaced along the polymer backbone.[13,18] To easily describe these materials, we have devised a nomenclature based

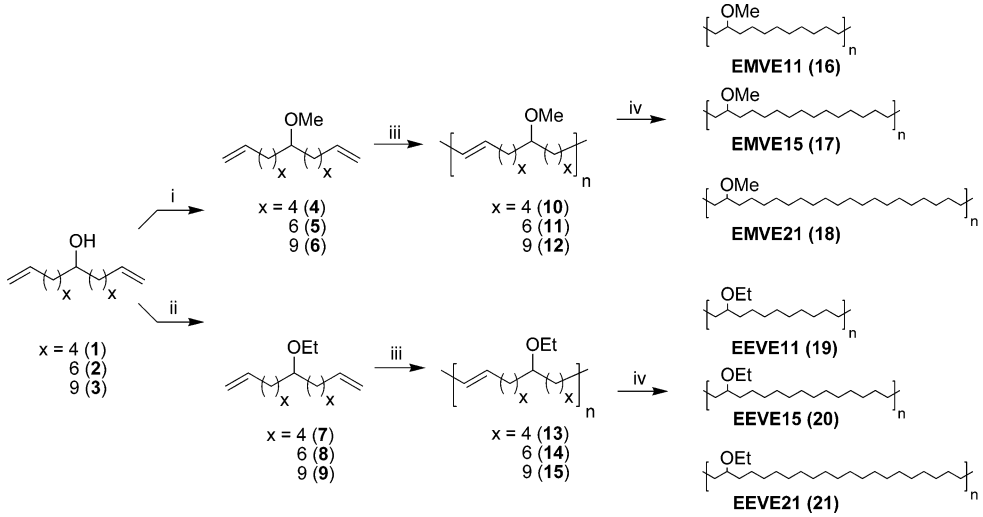

Figure 1. Synthesis of EVE copolymers: (i) NaH, MeI, DMF; (ii) NaH, EtBr, DMF; (iii) Schrock's [Mo] catalyst, high vacuum; and (iv) Pd(C), H_2 (1000 psi), toluene.

Table 2. Characterization Data for Sequenced EVE Copolymers

copolymer name[a]	branch frequency[b]	comonomer (mol %)		unsaturated EVE copolymers[c,d]			saturated EVE copolymers[a,d]		
		vinyl ether	ethylene	M_w	M_n	PDI[e]	M_w	M_n	PDI[e]
EMVE11 (**16**)	11	22	77	14.9	8.3	1.8	15.3	10.0	1.5
EEVE11 (**19**)				24.1	14.6	1.7	25.6	15.7	1.6
EMVE15 (**17**)	15	13	87	39.3	23.1	1.7	41.9	25.2	1.7
EEVE15 (**20**)				48.9	28.1	1.7	43.1	24.6	1.8
EMVE21 (**18**)	21	10	90	81.3	32.0	2.5	74.1	32.7	2.3
EEVE21 (**21**)				9.7	8.5	1.9	11.5	7.3	1.6

[a] See Figure 1. [b] Determined by the number of backbone carbons in central repeat unit. [c] ADMET products **10**−**15**. [d] Molecular weight (kg/mol) determined by GPC performed in THF relative to polystyrene standards. [e] Polydispersity index (M_w/M_n).

on the parent chain addition monomers and ether branch frequency. For example, **EMVE21** stands for ethylene (E) and methyl vinyl ether (MVE), the two comonomers, and the number **21** refers to the branch frequency for each pendant methoxy group. Ethylene-*co*-ethyl vinyl ethers bearing the prefix EEVE were also synthesized for this study, and three examples of each copolymer have been prepared with pendant ether branches every 11, 15, and 21 carbons. These materials can be considered sequenced EVE copolymers at different comonomer ratios with 4.5, 6.5, and 9.5 units of ethylene, respectively, between each vinyl ether monomer in the copolymer.

Synthesis of symmetrical ether bearing α,ω-diene monomers for ADMET polymerization began with the double Grignard addition of various alkenyl bromides onto ethyl formate affording a family of diene alcohols (Figure 1). Once converted to alkyl ethers, diene monomers were polymerized with Schrock's molybdenum catalyst yielding high molecular weight, unsaturated copolymers. Exhaustive hydrogenation of the remaining olefin via Parr techniques affords strictly linear EVE copolymers with exact ether branch frequency along the polymer backbone. Isolated EVE copolymers exist as colorless, viscous liquids at room temperature with the exception of **EMVE21** and **EEVE21**, which are low melting, semicrystalline solids.

Molecular Weight and Structural Analysis. Unsaturated ADMET products and EVE copolymers were analyzed using gel permeation chromatography (GPC), ^{1}H NMR, ^{13}C NMR, and FT-IR to confirm reaction conversions and monitor structural purity throughout the synthesis. Characterization data for the EVE copolymer family are listed in Table 2.

^{13}C and ^{1}H NMR Analysis. Polyolefin analysis via ^{13}C NMR spectroscopy has greatly enhanced the characterization of copolymer microstructure allowing resolution of endgroups and specific branching patterns in sequenced materials[19,20] and random copolymers.[21,22] The resolution of specific C−C and C−H bonding patterns via ^{13}C NMR allows delineation of detailed aliphatic polymer microstructure where FT-IR and ^{1}H NMR analysis can often be vague due to overlapping absorbances or resonances.

Spectral data from the EVE copolymers demonstrate the ability of metathesis chemistry to produce linear, sequenced copolymers as shown in Figure 1. Figure 2 displays the evolution of ^{13}C NMR spectral data from diene monomer **4** to **EMVE11** (**16**), chosen for the high concentration of functional groups, although the interpretation is similar for all reported EMVE materials. Starting at the top, monomer identity is confirmed by signals corresponding to terminal olefin (114.5 and 139.2 ppm), ether carbons (56.6 and 81.1 ppm), and various alkyl signals (25−35 ppm). Polymerization affords the unsaturated copolymer **10** confirmed by disappearance of the terminal olefin signals from the monomer and emergence of two new signals attributed to trans (130.5 ppm, major) and cis (130.0 ppm, minor) 1,2-disubstituted olefins in the polymer backbone. The presence of low intensity signals identical to the monomer verifies α-olefin end group identity for all unsaturated EVE copolymers (**10**−**15**). After saturation with hydrogen, the bottom spectrum for **EMVE11** suggests the successful preparation of the target molecule by absence of all allylic and olefinic signals along with the simplification of the alkyl region revealing the symmetric nature of the copolymer.

At a molecular weight of over 14 kg/mol, **EMVE11** exhibits only five unique ^{13}C NMR signals (A−E, Figure 2) due to an axis of symmetry between the α and ϵ carbons creating degenerate chemical shifts for most carbons in the material and greatly simplifying the spectral data. Carbons A and B

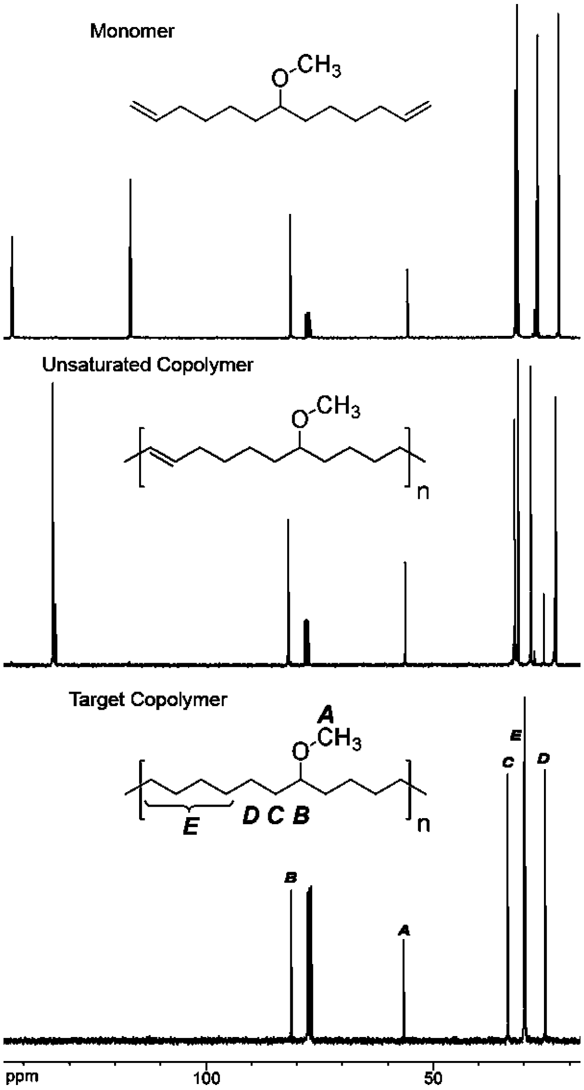

Figure 2. ^{13}C NMR progression from monomer to target EVE copolymer for EMVE11.

correspond to the methyl (56.6 ppm) and methine (81.2 ppm) carbons in the ether and, importantly, remain intact throughout the synthesis of **EMVE11**. Signals marked C and D represent α and *β* carbons to the branch point, respectively, that exist in higher molar concentration than A and B as indicated by greater signal intensity. The final resonance E at 30 ppm corresponds to the remaining six methylenes in the polymer backbone furthest from the alkoxy branches as one broad composite resonance exhibiting multiple maxima. Methylene signal overlap is compounded for longer run length copolymers such as **EMVE15** and **EMVE21** where higher methylene concentrations lead to a greater intensity signal near 30 ppm relative to branch point and ether carbon resonances.

Analysis of EEVE ^{13}C NMR data follows a rationale similar to the structural analysis presented above and also reveals the single structural difference between the two EVE copolymer families, the alkyl ether substitution. A downfield shift of the primary ether carbon to 64.3 ppm and a signal at 15.9 ppm verify the presence of ethoxy substitution unlike the single resonance displayed by the EMVE series at 56.6 ppm. Otherwise, minor differences of 0.2 ppm result in some cases, but overlap of extended methylene signals occurs in EEVE materials near 30 ppm, as expected. This overlap represents one limitation of ^{13}C NMR analysis where determination of ethylene run length is difficult, but quantitative ^{1}H NMR analysis allows calculation of molar concentration of methylene units in the material.

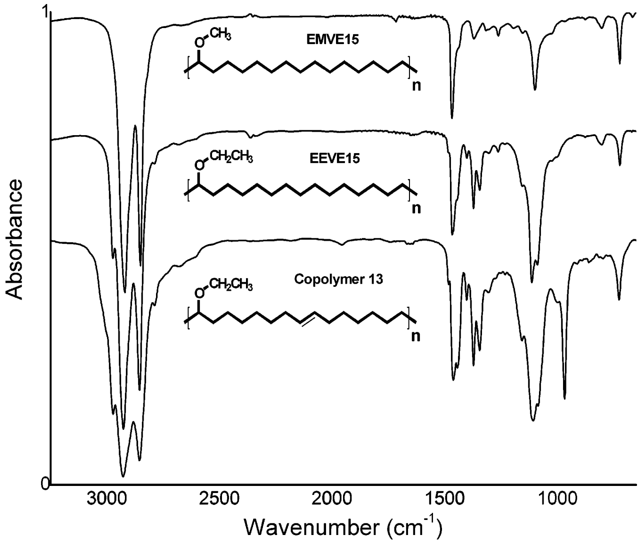

Figure 3. FT-IR analysis of EVE copolymers.

^{1}H NMR was performed on all synthesized materials for basic structural analysis and verification of comonomer ratios for all EVE copolymers. Determination of comonomer ratios is possible by comparison of downfield integral ratios from ether protons with integral values from overlapping methine, methylene, and methyl resonances, but specific polyolefin bonding patterns are difficult to resolve without the compilation of structural analysis data from multiple analytical techniques.

FT-IR Analysis. Compound structure and purity was confirmed throughout EVE copolymer synthesis using FT-IR spectroscopy. Metathesis polymerizations were verified by the coalescence of two absorbance bands from α-olefins in monomers at 991 and 908 cm^{-1} into a single band at 967 cm^{-1}, indicating a mostly trans 1,2-disubstituted olefin and successful polymerizations.[14] Figure 3 displays FT-IR absorbance traces for **EMVE15**, **EEVE15**, and unsaturated copolymer **13**, all possessing equimolar ether incorporation allowing direct structural comparison of the two families of alkyl vinyl ether copolymers. Nevertheless, identical analysis follows for all sequenced EVE materials in this report with minor changes in relative peak intensity due to varying comonomer ratios.

The bottom traces in Figure 3 track the hydrogenation of the unsaturated ADMET polymer to copolymer **EEVE15** through the elimination of the olefinic band at 967 cm^{-1}. Also observed in ^{1}H and ^{13}C NMR analysis, FT-IR spectral data confirm quantitative saturation of metathesis products within experimental error yielding target EVE copolymers. Structural differences between **EMVE15** and **EEVE15** are easily discernible upon juxtaposition of the IR data in the top two absorbance traces in Figure 3. Strong absorbance bands present at 2926 and 2854 cm^{-1} for both copolymers correspond to the asymmetric and symmetric methylene C−H stretching motions from backbone carbons. For **EEVE15**, an absorbance maximum at 2972 cm^{-1} is also observed corresponding to the methyl C−H stretch of the pendant ethyl ether branch, unique to the EEVE materials in this study. This absorbance is not observed for **EMVE15** due to the shift of the methyl ether C−H stretching bands to 2850 cm^{-1}, overlapping with the previously mentioned backbone methylene vibrations.

Moving to lower wavenumbers, aliphatic methyl and methylene C−H vibrations are observed for both copolymers.

Table 3. Thermal Analysis Data for Sequenced EVE Copolymers[a]

copolymer name[b]	branch frequency[c]	comonomer (mol %)		observed thermal transitions[d] (10 °C/min)			
		vinyl ether	ethylene	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔC_p (J/g °C)
EMVE11 (**16**)	11	22	77	−40	35	−62	0.6
EEVE11 (**19**)				−4[e]	33[e]	−65	0.8
EMVE15 (**17**)	15	13	87	−10	62	*	*
EEVE15 (**20**)				−33	36	*	*
EMVE21 (**18**)	21	10	90	40	78	*	*
EEVE21 (**21**)				28	79	*	*

[a] * = not observed at 10 °C/min. [b] See Figure 1, **16**−**21**. [c] Determined by the number of backbone carbons in central repeat unit. [d] Measured at midpoint of transition. [e] Values from annealed sample (**EEVE11***, Figure 4); no melt observed in dynamic scanning.

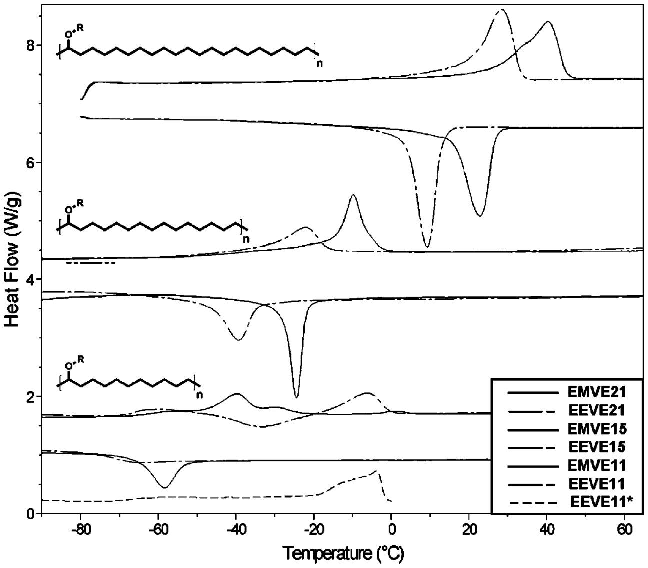

Figure 4. DSC second heating and cooling scans for six sequenced EVE copolymers and a one heating scan labeled **EEVE11*** annealed at −25 °C and quench-cooled prior to analysis.

EMVE15 and **EEVE15** both display similar scissoring bands at 1466 cm^{-1} due to identical copolymer backbones and ethylene sequence lengths. **EEVE15** exhibits two specific absorbances arising from multiple methylene bonding arrangements in the polymer backbone and the pendant ethyl ether group leading to bands at 1371 and 1344 cm^{-1}, respectively, whereas **EMVE15** exhibits only one lower intensity band at 1369 cm^{-1} once again due to overlap of methyl ether and methylene stretching bands. Analysis of the ether C−O−C stretching at lower wavenumbers allows direct comparison of alkyl substitution patterns from carbon−oxygen bonding rather than indirect analysis via secondary effects on C−H aliphatic vibrations described above. A single asymmetric ether stretch can be observed in **EMVE15** at 1097 cm^{-1} arising from the methyl−isopropyl ether bonding arrangement, while the ethyl−isopropyl ether arrangement in **EMVE15** results in vibronic coupling within the copolymer and a split in the absorbance to wavenumbers of 1088 and 1112 cm^{-1}. Verification of sequenced copolymer structures through FT-IR data supports NMR and GPC observations, indicating successful synthesis of strictly linear polyethylene with controlled incorporation of two different alkyl vinyl ethers.

Thermal Analysis. Thermal analysis of the ethylene copolymers has demonstrated the general correlation of increased branch content to decreased melting points and heats of fusion for this diverse family of macromolecules. Notably, sharp melting profiles exhibited by high-density polyethylene become broad transitions in random α-olefin copolymers with increasing levels of the comonomers propylene,[23,24] vinyl chloride,[25] and acrylic acid[26] due to variable lamellar thickness induced by a distribution of ethylene sequence lengths until substitution renders copolymer amorphous. Thermal analysis of random EVE materials reported in Table 1 either was not performed or not disclosed in the patent literature.[2−10]

Thermal analysis of the family of EVE copolymers was performed by differential scanning calorimetry. DSC thermograms from second heating and cooling scans at 10 °C/min and peak melting temperatures and heats of fusion values for the series of EVE sequenced copolymers are displayed in Figure 4, and data are compiled in Table 3.

Every example in the family of EVE materials exhibits semicrystallinity regardless of the high levels of ether incorporation into the copolymer. For the EMVE copolymers, melting temperatures ranging from −40 to 40 °C and heats of fusion from 35 to 78 J/g suggest a similar relationship between comonomer content and thermal response as random ethylene copolymers, but lower heat of fusion values may indicate lower overall crystallinity relative to α-olefin copolymers assuming similar crystal forms. As ethylene sequence length decreases and branch density increases, polymer crystallization is inhibited by both conformational disorder and the presence of short ethylene run lengths, which are less likely to crystallize into chain folded lamellae, resulting in low melting copolymers.[20]

EEVE copolymers display the same melting point trend as EMVE materials with systematically lower melting point values for ethoxy polymers relative to the methoxy materials with only one exception. Interestingly, **EEVE21** melts at 28 °C with a heat of fusion of 79 J/g and **EEVE15** melts at −33 °C with a heat of fusion of 36 J/g, roughly 12 °C lower than their EMVE analogues, but **EEVE11** breaks this trend, displaying a cold crystallization not observed with any other copolymer in this study. **EEVE11** displays an initial relaxation at −65 °C, followed by a cold crystallization peak at −34 °C, and crystal melting at −6 °C. Evidence of a glass transition temperature and no recrystallization is observed during cooling, unlike other copolymers that all reveal uniform melting and recrystallization profiles under dynamic scanning conditions but do not exhibit glass transition temperatures. The lack of **EEVE11** crystallization during cooling at 10 °C/min may arise from steric congestion of ethoxy branches and kinetic factors, but observation of polymer crystallization is possible upon annealing at −25 °C for 1 h followed by quench cooling. Upon heating the annealed sample, a melting profile indicating polymer crystallization can be observed with a peak melting temperature of −4 °C, surprisingly higher than **EMVE11** at −40 °C and comparable to **EMVE15** at −10 °C. The heat of fusion of 33 J/g for **EEVE11** also deviates from this trend, yielding little difference from **EEVE15** at 36 J/g and **EMVE11** at 35 J/g. In this sense, the thermal behavior of **EEVE11** is not well understood in this study or upon comparison with previously synthesized sequenced materials,[14,20] and these results may indicate a different crystal structure for **EEVE11** as compared to the other five EVE materials.

Glass transition temperatures for the EVE copolymers were only observed for the two most highly functionalized copolymers, **EMVE11** and **EEVE11**, with a midpoint value at −65 °C. Figure 4 illustrates all thermal responses observed when scanning from −150 to 140 °C, although data have been clipped to highlight melting endotherms. The lack of observation of this relaxation in other EVE copolymers is likely due to the semicrystalline nature of the materials known to inhibit resolution of thermal relaxation in DSC analysis.

Conclusion

A family of six sequenced copolymers of ethylene with both methyl and ethyl vinyl ether have been prepared at targeted comonomer ratios, creating materials possessing exact ethylene run lengths between pendant ether branches. To our knowledge, this is the first report of the structure−property relationship for strictly linear EVE copolymers exhibiting no branching defects. Spectroscopic analysis via NMR and FT-IR reveals the microstructural control available via metathesis polymerization, indicating no detectable side reactions during polymerization or hydrogenation. The pristine nature of isolated copolymer structures has marked effects on thermal behavior, and all sequenced EVE copolymers exhibit semicrystalline morphologies with peak melting temperatures and heats of fusion proportional to the comonomer ratio in all but one case where **EEVE11** underwent cold crystallization exhibiting an unexpectedly high peak melting point. The ability to retain sequence length control and a high degree of structural regularity permits copolymer crystallization, giving peak melting points between −40 and 40 °C for the family of EVE materials. Although one copolymer fails to correlate the trend of increasing ethylene run lengths to higher peak melting points, we believe the level of ether incorporation and the size of the ethoxy pendant group may possibly induce different chain packing and alter the crystal structure in this material relative to the other EVE copolymers in the study.

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