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Synthesis and Thermal Characterization of Precision Poly(ethylene-*co*-vinyl Amine) Copolymers

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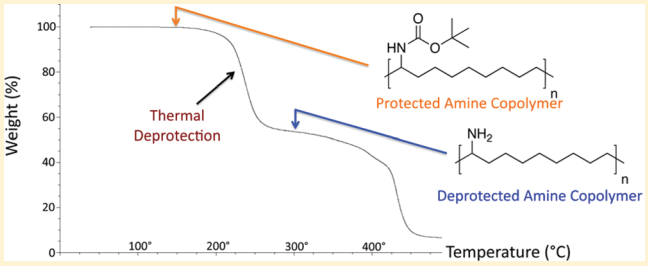
ABSTRACT: A structural investigation of linear ethylene-*co*-vinyl amine (EVAm) copolymers having a primary amine branch on every 9th, 15th, 19th, or 21st carbon along the ethylene backbone has been completed using step polymerization chemistry. Acyclic diene metathesis (ADMET) polymerization has been used with symmetrical α,ω dienes containing protected amine groups to afford polymers with exact primary structures and constant methylene run lengths between branches. The effects of subtle structural changes such as the ethylene run lengths between amine branches can be observed and used to correlate structure property relationships. NMR and FT-IR techniques are used to characterize and verify the excellent structural control this synthetic approach provides over traditional chain polymerization techniques. Thermal decomposition of these copolymers is shown to additionally support polymer structure while differential scanning calorimetry demonstrates crystallinity in the polymers with an amine on every 15th and 21st carbon, whereas the polymer with an amine on every ninth carbon is amorphous. Variations of the physical and spectral properties are discussed as a consequence of the amine branch spacing, protection, and saturation of the ethylene backbone.



INTRODUCTION

Ethylene-*co*-vinyl amine polymers (PEVAm) have several desirable characteristics and numerous commercial applications. The primary amine functionality along the ethylene backbone is a highly reactive site that can be utilized for derivatization and cross-linking. In the protonated form, the cationic charge density of the ammonium ion makes it useful in ionomer applications.[1] In addition, the ability of amines to chelate allow them to form complexes with various metal ions[2,3] and to serve as support scaffolds for enzymes.[4] Considering the many potential applications of these materials, it is important to have an understanding of their primary structure's relationship to physical properties. However, structure−property information of this type has not been readily available or even known.

The lack of fundamental studies can be attributed partly to synthetic difficulties, which have also limited the applications of PEVAm. The copolymerization of ethylene with vinyl amine type monomers is a difficult task due to both the large reactivity ratio disparity of the two vinyl monomers and the tendency of the vinyl amine to act as an efficient chain-transfer agent during radical and cationic polymerization.[5] The simplest precursor monomer for synthesis of polyvinylamine (PVAm), vinyl amine, does not exist in the free state because it tautomerizes to the acetaldehyde imine.[5] This monomer lability necessitates the synthesis of PVAm indirectly from an intermediate polymer, a synthetic approach similar to that used with poly(vinyl alcohol) (PVA).[5]

Although PVAm has been synthesized in numerous ways,[6−8] preparation of PVAm via radical chemistry with minimal structural defects and reasonably high molecular weights has involved two main precursors: *tert*-butyl *N*-vinylcarbamate (TBNVC)[9] and vinylformamide (VFA) monomers.[10,11] BASF, the largest commercial producer of PVAm, has utilized vinylformamide (VFA) with the subsequent hydrolysis of its amide side chains to make PVAm.

Of all the potential copolymers that can be made with vinylamine, those with ethylene as the comonomer are of particular interest. Poly(ethylene-*co*-vinyl amine) (PEVAm) polymers, with ethylene:vinylamine molar ratios of at least 1:1, are ideal for use as flocculants in water clarification. The molar ratio of these copolymers is modified by monomer addition under high-pressure conditions via radical chemistry. The ideal ethylene:vinylamine ratio in these materials is 2:1 to 4:1.[12] Within this preferred range, the desired physical and chemical properties imparted by the amine units are preserved, while the cost of the polymers is markedly lowered by the presence of the more economical ethylene units.[12]

Other than the usual backbone defects elicited by the radical chain polymerization of these materials, irregularities encountered in PEVAm materials come from both the acid and base hydrolysis of the poly(*N*-vinylformamide). Acid hydrolysis can proceed via transiently formed amidine rings, but is unable to surpass the 80% level due to repulsions among the protonated amine side chains.[11] Basic hydrolysis can be carried out completely, but Spange[10] and Bortel[11] have both observed the

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elimination of ammonia as noted by elemental analysis and the perceptible smell during the hydrolysis.

By taking advantage of step polymerization chemistry offered by acyclic diene metathesis (ADMET), our research group has been able to avoid the random nature of addition polymerizations, as well as the unwanted side reactions often observed in radical polymerizations of vinyl monomers. This mild polymerization chemistry also avoids the defects usually imparted by catalysts during chain propagation processes. These defects, in either small or large amounts, can have profound effects on the macromolecule's material behavior and thermal response.

Both Breitenkamp[13] and Masuda[14] have utilized ring-opening metathesis polymerization (ROMP) to prepare amine-functionalized polymers. Herein, we report the synthesis and thermal characterization of a family of four linear EVAm copolymers with amine branches precisely spaced along the polyethylene backbone at intervals of every 9th, 15th, 19th, or 21st carbon. Their preparation has been accomplished using ADMET chemistry, which assures that the branches are set at specific, not random, intervals along the backbone, generating polymers incapable of being made by other methodologies.[15−21] Primary structural analysis has been achieved by ^{1}H and ^{13}C NMR and FT-IR techniques, and detailed calorimetry data are presented to demonstrate the morphological differences arising from the combined effects of branch frequency and the regular distribution of amine branches.

EXPERIMENTAL SECTION

Materials. Reagents and chemicals were used as received from Aldrich Chemical Co. unless otherwise noted. Diethyl ether and THF were used as dry solvents from the Aldrich keg system and dried over 4 Å sieves. The second generation Grubbs catalyst (tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) dichloride) was synthesized and used as previously described by Grubbs et al.[22]

Instrumentation and Analysis. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Associates Mercury 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR were referenced to residual signals from $CDCl_3$ (^{1}H = 7.24 ppm and ^{13}C = 77.23 ppm) with 0.03% v/v TMS as an internal reference. High resolution mass spectra (HRMS) were obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the chemical ionization mode. IR data was obtained using a Perkin-Elmer Spectrum One FT-IR outfitted with a $LiTaO_3$ detector, measurements were automatically corrected for water and carbon dioxide. FT-IR polymer samples were prepared by solution-casting a thin film from THF onto a KBr salt plate.

Gel permeation chromatography (GPC) of polymers 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-4E columns (10 μm PD, 7.8 ID, 300 mm length) using 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 concentrations. Retention times were calibrated against a minimum of nine narrow molecular weight polystyrene standards purchased from Polymer Laboratories (Amherst, MA).

Solid-State NMR (SS-NMR) spectra were performed at the Max Planck Institute for Polymer Research (MPIP) in Mainz, Germany using a Bruker DSX 7.05 T instrument at 21.7 MHz for ^{15}N employing a magic angle spinning (MAS) frequency of 10 kHz. The ^{15}N cross-polarization from ^{1}H was conducted using a contact angle of 7 ms and a high-power ^{1}H decoupling two-pulse phase modulation (TPPM) of 100 kHz. The ^{15}N spectra were referenced to the $^{15}NO_3$ in ^{15}N-enriched NH_4NO_3. All spectra were acquired from a 4 mm rotor at room temperature. Because of the low natural abundance of nitrogen-15 (0.37%), long time scans from these nonlabeled materials were conducted in order to achieve good signal-to-noise ratios.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q1000 equipped with a liquid nitrogen cooling accessory and calibrated using sapphire and high purity indium metal. All samples were prepared in hermetically sealed pans (4−7 mg/sample) and were referenced to an empty pan. A scan rate of 10 °C per minute was used. Melting temperatures were taken as the peak of the melting transition, glass transition temperatures as the midpoint of a step change in heat capacity. Thermal experiments were conducted as follows: samples were heated through the melt to erase thermal history, followed by cooling at 10 °C per minute to −150 °C, and then heated through the melt at 10 °C per minute. Data reported reflects this second heating scan.

Premonomer Amine Diene Synthesis. Magnesium (4.89 g, 0.20 mol) was added to a 500 mL three-necked flask equipped with a reflux condenser and an addition funnel. The reaction vessel was backfilled three times with Ar and flame-dried after each backfill. Dry THF (100 mL) was added, followed by the addition of 5-bromo-1-pentene (25.0 g, 0.17 mol) dropwise via syringe. The solution was refluxed for 2 h to completely form the Grignard. Ethyl formate (5.64 g, 0.076 mol) in 30 mL THF was added dropwise to the cooled mixture (0 °C), and the solution was allowed to warm slowly to room temperature and then refluxed for 21 h. Hydrochloric acid (1M, 100 mL) was added, and the solution was extracted with ether (3 × 25 mL), washed with 1 M HCl (1 × 30 mL), and washed with brine (3 × 20 mL). The solution was dried over $MgSO_4$, followed by evaporation of the solvent to yield 14.18 g of the crude alcohol.

To a 500 mL round-bottom flask equipped with an addition funnel were added pyridinium chlorochromate (PCC) (26.0 g, 0.12 mol), Celite (equal weight to crude alcohol), and methylene chloride (100 mL) followed by the addition of the crude alcohol (1 equiv). The reaction was stirred for 4 h at room temperature, diethyl ether (200 mL) was added, and the mixture was filtered through a pad of silica gel. Solvent evaporation yielded 13.0 g of the crude ketone.

To a 500 mL round-bottom flask was added the crude ketone, dry methanol (225 mL), ammonium acetate (60 g, 0.78 mol), sodium cyanoborohydride $NaCNBH_3$ (25 g, 0.40 mol), and a spatula tip of crushed 4 Å molecular sieves; the mixture was refluxed for 48 h under N_2. The crushed molecular sieves were filtered via Büchner filtration and deionized water (200 mL) was added to the filtrate, followed by extraction with diethyl ether (3 × 50 mL). The organic layer was washed with 1 M NaOH (2 × 50 mL) and brine (2 × 30 mL) and dried over $MgSO_4$. The solution was concentrated to a brown viscous oil, which was purified by flash column chromatography using a 3:1:1 (hexane:ethyl acetate:methanol) mobile phase yielding 9.28 g of the desired **3,3NH$_2$** product for an overall yield of 73%.

1-Undec-10-enyl-dodec-11-enylamine (3,3NH$_2$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15−1.70 (m, 8H), 2.01−2.15 (br,4H), 2.65−2.76 (br, 1H), 4.90−5.10 (m, 4H), 5.75−5.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.87, 34.29, 37.84, 51.45, 114.95, 139.19.

Heptadeca-1,16-dien-9-amine (6,6NH$_2$). This premonomer was in limited supply and is extremely valuable so it was used *in situ* to directly make the Boc-protected monomer.

Tricosa-1,22-dien-12-amine (9,9NH$_2$). The 9,9NH$_2$ was synthesized as described above using 11-bromo-1-undecene (25.0 g, 0.106 mol) instead of 5-bromo-1-pentene. After purification, a final yield of 48% (13.0 g) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15−1.45 (br, 32H), 2.05 (q, 4H), 2.65−2.75 (br, 1H), 4.88−5.05 (m, 4H), 5.72−5.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.39, 29.20, 29.41, 29.76, 29.84, 29.90, 30.07, 34.08, 38.02, 51.50, 114.36, 139.50.

1-Dec-9-enyl-undec-10-enylamine (8,8NH$_2$). Synthesis was performed using a modified procedure by Zantour and co-workers.[39] To a 500 mL three-neck round-bottom flask equipped with a reflux condenser and an addition funnel was added 10-undecenoyl chloride (20.27 g, 100 mmol) and dry diethyl ether (150 mL). The solution was cooled to 0 °C, and triethylamine (18.21 g, 180 mmol) was added dropwise, instantly forming white triethylamonium chloride salts. The reaction mixture was warmed to room temperature and stirred for 24 h, followed by Büchner filtration of the salts and evaporation to yield

the liquid intermediate β-lactone. Deionized water (100 mL) and NaOH (8.80 g, 2.10 mol) were added, and the mixture was refluxed for 12 h. The solution was acidified with 1 M HCl and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with 1 M HCl (2 × 20 mL) and brine (2 × 20 mL). After drying over $MgSO_4$ and recrystallizing from MeOH, 13.15 g of the pure ketone was obtained. The ketone was converted to the amine using the same methodology as described with the $3,3NH_2$ and $9,9NH_2$ syntheses. The overall yield for the two steps was 58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18−1.62 (br, 28H), 2.04 (q, 4H), 2.80−2.94 (m, br, 1H), 4.03−4.54 (br, 2H), 4.88−5.07 (m, 4H), 5.71−5.91 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.52, 29.34, 29.54, 29.88, 30.01, 30.20, 34.21, 38.18, 41.61, 114.46, 139.50.

General Fmoc Protection of the Amine Dienes. To a dry 500 mL round-bottom flask were added 150 mL of dry THF, 50 mL of dry pyridine, and Fmoc−Cl (1.0 g, 3.90 mmol) under argon. Then, $9,9NH_2$ (1 g, 3.25 mmol) was slowly added over 0.5 h and the reaction was allowed to stir at room temperature for an additional 2 h. After 2 h, 100 mL of ether was added to the reaction and it was extracted with 1 M HCl (2 × 50 mL) and brine (2 × 50 mL). The protected amine solution was dried over $MgSO_4$ followed by rotary evaporation to yield the 9,9NHFmoc product. The 9,9NHFmoc was purified via column chromatography using ethyl acetate:hexane (3:2).

(9H-Fluoren-9-yl)methyl Henicosa-1,20-dien-11-ylcarbamate (9,9NHFmoc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, 2H), 7.61 (d, 2H), 7.40 (t, 2H), 7.28 (t, 2H), 5.82 (m, 2H), 4.94 (m, 4H), 4.40 (d, 2H), 4.23 (t, 1H), 2.04 (m, 4H), 1.15−1.45 (br, 28H). EI/HRMS [M + 1]: calcd for $C_{36}H_{51}NO_2$, 530.3998; found, 530.4006.

General Boc Protection of the Amine Dienes. To a dry 500 mL round-bottom flask was charged 150 mL dry THF and the appropriate amine (2.5 g) under argon. A syringe was used to add the Boc anhydride (1 M in THF, 1 equiv) over 15 min at room temperature. The reaction was allowed to stir for 24 h and was monitored by TLC (ethyl acetate: hexane, 1:19) for disappearance of the starting material amine. At the end of the 24 h reaction period, 100 mL of ether was added and the solution was extracted with water (1 × 50 mL), $NaHCO_3$ (2 × 50 mL), and brine (2 × 50 mL). The washed solution was dried over $MgSO_4$ followed by rotary evaporation to yield the Boc protected product. The monomer was purified via column chromatography using ethyl acetate:hexane (1:19).

*tert-Butyl Undeca-1,10-dien-6-ylcarbamate 3,3NHBoc (**1**).* Monomer is a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20−1.46 (br, m, 8H), 1.48 (s, 9H), 2.01 (m, 4H), 3.52 (br, 1H), 4.22 (br, d, 1H), 4.93 (m, 4H), 5.76 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.33, 27.60, 28.62, 33.79, 35.25, 50.57, 79.00, 114.78, 138.83, 155.89. FT-IR (KBr pellet): 3348, 3077, 2978, 2934, 2860, 1814, 1692, 1641, 1522, 1457, 1443, 1416, 1391, 1366, 1284, 1249, 1174, 1120, 1056, 1026, 944, 910, 868, 773, 637 cm^{-1}. ESI/HRMS [2M +1]: calcd for $C_{16}H_{29}NO_2$, 535.4469; found, 535.4463. Anal. Calcd for CHNO: C, 71.86; H, 10.93; N, 5.24. Found: C, 71.91; H, 11.06; N, 5.23.

*tert-Butyl Heptadeca-1,16-dien-9-ylcarbamate 6,6NHBoc (**2**).* Monomer is a waxy white solid that melts at 38 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23−1.40 (br, m, 8H), 1.41 (s, 9H), 2.01 (q, 4H), 3.50 (br, 1H), 4.20 (br, d, 1H), 4.91 (m, 4H), 5.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.01, 28.65, 29.05, 29.27, 29.63, 33.97, 35.79, 50.83, 79.00, 114.37, 139.35, 155.92. FT-IR (KBr pellet): 3444, 3346, 3077, 2977, 2928, 2856, 1821, 1703, 1693, 1641, 1522, 1455, 1441, 1415, 1390, 1365, 1248, 1174, 1092, 1057, 993, 909, 869, 778, 750, 725, 636, 555 cm^{-1}. EI/HRMS [2M +1]: calcd for $C_{22}H_{41}NO_2$, 703.6347; found, 703.6327. Anal. Calcd for CHNO: C, 75.16 ; H, 11.75 ; N, 3.98. Found: C, 75.26 ; H, 11.99 ; N, 3.93.

*tert-Butyl Henicosa-1,20-dien-11-ylcarbamate 8,8NHBoc (**3**).* Monomer is a waxy white solid that melts at 43 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21−1.41 (br, m, 28H), 1.42 (s, 9H), 2.01 (q, 4H), 3.50 (br, 1H), 4.20 (br, d, 1H), 4.93 (m, 4H), 5.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.06, 28.67, 29.14, 29.33, 29.64, 29.76, 29.80, 34.02, 35.82, 50.87, 78.95, 114.31, 139.42, 155.94. FT-IR (KBr pellet): 3348, 3077, 2977, 2926, 2855, 1701, 1641, 1503, 1456, 1390, 1365, 1245, 1173, 1046, 993, 909, 865, 723, 640 cm^{-1}. EI/HRMS [2M +1]: calcd for $C_{26}H_{49}NO_2$, 815.7599; found, 815.7466. Anal. Calcd for CHNO: C, 76.60; H, 12.11; N, 3.44. Found: C, 76.58; H, 12.26; N, 3.47.

*tert-Butyl Tricosa-1,22-dien-12-ylcarbamate 9,9NHBoc (**4**).* Monomer is a waxy white solid that melts at 46 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22−1.40 (br, m, 32H), 1.41 (s, 9H), 2.01 (q, 4H), 3.49 (br, 1H), 4.20 (br, d, 1H), 4.91 (m, 4H), 5.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.07, 27.63, 28.66, 29.15, 29.34, 29.68, 29.74, 29.80, 34.02, 35.84, 50.90, 78.95, 114.30, 139.43, 155.94. FT-IR (KBr pellet): 3446, 3349, 3077, 2977, 2927, 2855, 1820, 1705, 1641, 1503, 1456, 1415, 1390, 1365, 1247, 1174, 1049, 992, 909, 867, 780, 750, 722, 636, 552, 464 cm^{-1}. EI/HRMS [2M +1]: calcd for $C_{28}H_{53}NO_2$, 871.8225; found, 871.8195. Anal. Calcd for CHNO: C, 77.18; H, 12.26; N, 3.21. Found: C, 77.24; H, 12.27; N, 3.25.

General ADMET Polymerization Procedure for Symmetrical Boc Amine Monomers. Monomer was transferred into a dry 25 mL Schlenk tube equipped with a stir bar and glass stopcock and dried by heating the vessel in an oil bath at 50 °C under full vacuum (10^{-3} mmHg) for 24 h. After 24 h, the reaction vessel was backfilled with argon and first-generation Grubbs' Ru catalyst (200:1/monomer:-catalyst) was added. The full vacuum was placed back on the polymerization reaction after 0.5 h. Additional catalyst was added 60 h into the polymerization to ensure maximum possible couplings. The polymerization reaction was monitored closely by ^{1}H NMR to confirm that no remaining terminal olefin was present. Upon completion, the reaction was quenched by opening the flask and adding 25 mL of toluene and 1 mL of ethyl vinyl ether. The polymer was purified by precipitation of the polymer solution into 1.5 L of cold methanol. The polymer was then filtered and dried for characterization.

*Polymerization of tert-Butyl Undeca-1,10-dien-6-ylcarbamate 3,3NHBoc (**5**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18−1.48 (br, 17H), 1.92 (br, 4H), 3.48 (br, 1H), 4.26 (br, 1H), 5.24−5.40 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.01, 27.26, 28.63, 29.18, 29.85, 32.64, 35.31, 50.63, 78.92, 129.95, 130.43, 155.88. FT-IR (KBr pellet): 3443, 3341, 2977, 2931, 2857, 2248, 1691, 1523, 1456, 1391, 1365, 1248, 1174, 1056, 968, 912, 867, 779, 734, 647, 462 cm^{-1}.

*Polymerization of tert-Butyl Heptadeca-1,16-dien-9-ylcarbamate 6,6NHBoc (**6**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (br, 14H), 1.41 (s, 9H), 1.96 (br, 4H), 3.49 (br, 1H), 4.21 (br, 1H), 5.28−5.5.37 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ26.04, 27.39, 28.64, 29.03, 29.25, 29.33, 29.47, 29.67, 29.90, 32.76, 33.95, 35.79, 50.85, 78.91, 130.03, 130.49, 155.93. FT-IR (KBr pellet): 3445, 3344, 2977, 2927, 2855, 1692, 1525, 1456, 1390, 1365, 1248, 1174, 1090, 1013, 967, 909, 867, 778, 728, 646, 463 cm^{-1}.

*Polymerization of tert-Butyl Henicosa-1,20-dien-11-ylcarbamate 8,8NHBoc (**7**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21−1.40 (br, m, 28H), 1.41 (s, 9H), 1.91−1.99 (br, 4H), 3.49 (br, 1H), 4.22 (br, d, 1H), 5.29−5.39 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.10, 27.44, 28.67, 29.37, 29.70, 29.81, 29.88, 29.98, 32.82, 35.85, 50.93, 78.95, 130.53, 155.93. FT-IR (KBr pellet): 3443, 3344, 2975, 2927, 2854, 1691, 1523, 1456, 1390, 1365, 1247, 1174, 1093, 1019, 967, 914, 864, 778, 724, 645, 464 cm^{-1}.

*Polymerization of tert-butyl tricosa-1,22-dien-12-ylcarbamate 9,9NHBoc (**8**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21−1.41 (br, m, 32H), 1.42 (s, 9H), 2.01 (br, 4H), 3.49 (br, 1H), 4.21 (br, d, 1H), 5.30−5.38 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.10, 27.45, 28.67, 29.42, 29.55, 29.74, 29.81, 29.84, 29.90, 30.00, 32.84, 35.84, 50.92, 78.93, 130.10, 130.56, 155.94. FT-IR (KBr pellet): 3445, 3346, 3136, 2975, 2925, 2854, 2248, 1693, 1523, 1456, 1390, 1365, 1247, 1174, 1097, 1048, 1024, 966, 910, 865, 778, 723, 647, 463 cm^{-1}.

Hydrogenation of Unsaturated ADMET Polymers. The crude polymer solution was transferred to a Parr Bomb glass sleeve and diluted to ∼200 mL with toluene. Argon was bubbled through the solution for 30 min, after which a spatula tip of Wilkinson's catalyst ($RhCl(PPh_3)_3$) 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 600 psi hydrogen gas, then filled to 600 psi with hydrogen gas and left for 4 days at room temperature. Upon depressurization, argon was bubbled through the crude reaction mixture for 30 min. The solution was concentrated to ∼50 mL and slowly dripped into 1 L of cold

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methanol. The precipitated polymer was filtered and dried for characterization.

*Polysat3,3NHBoc (**9**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (br, 16H), 1.41 (s, 9H), 3.48 (br, 1H), 4.21 (br, d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.24, 22.82, 25.72, 26.09, 27.89, 28.66, 29.79, 29.91, 32.03, 35.85, 50.90, 78.95, 155.95. FT-IR (KBr pellet): 3446, 3342, 3134, 2928, 2855, 2248, 1692, 1524, 1456, 1390, 1365, 1248, 1175, 1098, 1048, 1020, 909, 865, 802, 733, 667, 647, 556, 463 cm^{-1}.

*Polysat6,6NHBoc (**10**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (br, 24H), 1.41 (br, s, 13H), 3.49 (br, 1H), 4.21 (br, d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.33, 22.89, 26.10, 28.67.29.48, 29.86, 29.91, 32.10, 35.84, 50.92, 78.94, 155.95. FT-IR (KBr pellet): 3446, 3346, 3137, 2977, 2924, 2854, 2249, 1695, 1525, 1456, 1390, 1365, 1247, 1175, 1060, 1013, 909, 866, 778, 734, 646, 465 cm^{-1}.

*Polysat8,8NHBoc (**11**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21−1.41 (br, m, 36H), 1.42 (s, 9H), 3.49 (br, 1H), 4.21 (br, d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.32, 22.88, 26.06, 28.64, 29.83, 29.89, 32.10, 35.80, 50.87, 78.92, 155.93. FT-IR (KBr pellet): 3445, 3348, 3135, 2925, 2854, 2248, 1693, 1526, 1457, 1390, 1365, 1248, 1175, 1096, 1019, 909, 865, 801, 732, 647, 464 cm^{-1}.

*Polysat9,9NHBoc (**12**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15−1.34 (br, 40H), 1.41 (s, 9H), 3.49 (br, 1H), 4.21 (br, d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.33, 22.90, 26.08, 28.66, 29.56, 29.84, 29.94, 32.13, 35.82, 50.88, 78.92, 155.93. FT-IR (KBr pellet): 3446, 3346, 3136, 2925, 2854, 1696, 1523, 1465, 1457, 1390, 1365, 1248, 1175, 1058, 1019, 866, 783, 753, 721, 650, 462 cm^{-1}.

Removal of the Boc Protection Group from the Polymers. Each saturated, protected polymer was readily dissolved in THF and transferred to a 10 mL screw-cap vial. The solution was rotovapped with rapid spinning to create a thin film along the walls of the vials. The vial was attached to a vacuum vial adapter and placed under high vacuum (10^{-3} mmHg) for 1 day to dry. After the polymer was dry, the vial was submerged in 275 °C sand in an aluminum foil lined heating mantle and left under heat and vacuum for 2 h. Upon submersion into the hot sand, each polymer began to slowly melt and then bubble. Each sample melted and went from a light beige color to a dark brown color within the first 5 min of heating under vacuum.

RESULTS AND DISCUSSION

Polymer Design and Synthesis. The preparation of linear, precisely branched, ethylene-*co*-vinyl amine (EVAm) polymers requires the synthesis of a symmetrically branched α,ω-diene monomer for the ADMET reaction. In light of the recent successes of other groups performing ROMP on free amines,[13,14] and with the development of more nitrogen tolerant metathesis catalysts,[23] an initial attempt was made to polymerize the free amine diene. However, the reaction was unsuccessful due to the tendency of the amine to facilitate catalyst decomposition. As a result, a protection strategy was required to polymerize the amine dienes.

Use of the 9-fluorenyl carbamate (Fmoc) group as an amine protection strategy was previously developed in our group by Leonard et al.[24] for the synthesis of amino acid containing polyolefins. Because of the ease with which the Fmoc group is removed under mild basic conditions, this same methodology was attempted for EVAm. The synthesis of the 9,9NHFmoc monomer was readily accomplished by protecting the corresponding amine diene with 9-fluorenylmethyl chloroformate (Fmoc−Cl) to yield a white fluffy powder with a sharp melting point. However, polymerization of this monomer in THF led to the formation of dimers and trimers almost immediately upon addition of catalyst, as observed by the precipitation of these oligomers from solution (Figure 1). Attempts to characterize these oligomers failed due to lack of solubility in any known solvent.

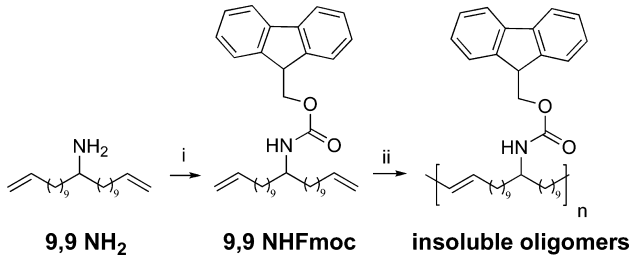

Figure 1. Initial protection strategy for amine monomers: (i) FmocCl, DMAP, THF; (ii) first-generation Grubbs' catalyst.

As an alternative protection strategy, the *tert*-butyl oxycarbonyl (Boc) group was employed, because it can be readily removed using acid or heat. Figure 2 details the synthetic approach employed to conduct the metathesis polymerization, hydrogenation, and deprotection. Monomer **1** is a colorless viscous oil while monomers **2**, **3**, and **4** are white crystalline solids that melt at 38, 43, and 46 °C, respectively. As a result, all four monomers can be polymerized neat in the melt with no solvent. The ADMET polymerization of the Boc-protected monomers proceeded normally under vacuum. The molecular weight and thermal data for the unsaturated polymers are presented in Table 1. Subsequent hydrogenation was performed in toluene with Wilkinson's catalyst under hydrogen pressure in a Parr reactor. These hydrogenations were done at room temperature; there was no spectroscopic evidence that any Boc protection groups were removed during this step.

Structural Analysis with ^{13}C and ^{1}H NMR and IR. Primary structural analysis by ^{1}H- and ^{13}C NMR revealed the kind of pristine primary structure that can be obtained when using ADMET polymerizations and hydrogenation reactions.[17,25,26] Confirmation of the branch precision and knowledge of methylene run lengths between branches allows confident determination of molar ratios of ethylene and vinyl amine. These proton and carbon spectra are the best techniques to determine primary structure of monomer, unsaturated polymer, and saturated polymer.

The proton spectra in Figure 3 shows the clean and complete transformation of the 9,9 monomer (**4**) to unsaturated polymer (**8**) and then to the saturated polymer (**12**). The resonances from the terminal olefins of **4**, at roughly 4.8 and 5.8 ppm, condense to one peak, at 5.3 ppm in **8**, while the chemical shifts of the other peaks are maintained and slightly broadened. From the unsaturated (**8**) to saturated polymer (**12**), the internal olefin and its alpha proton peak at 2.0 ppm are completely removed from the sample through the hydrogenation step. The hydrogenation of the unsaturated polymer also leads to the formation of methyl end groups resonating at 0.9 ppm. The final hydrogenated polymer (**12**) shows five proton shifts relating to the polymer: (1) methyl end groups at 0.8 ppm; (2) backbone protons at 1.23 ppm; (3) nine Boc group protons at 1.41 ppm; (4) proton on the carbon with the amine branch at 3.48 ppm; (5) carbamate nitrogen's proton at 4.21 ppm.

The same trends are observed in the carbon spectra of the corresponding 6,6 molecules (**2**, **6**, **10**), shown in Figure 4. The terminal olefin resonances at 130 and 156 ppm in **2** are condensed to an internal olefin peak in **6**, (two peaks due to *cis*/*trans* isomers). This internal olefin peak is then eliminated from the sample upon hydrogenation.

Compound structure and purity was also confirmed with FT-IR throughout the EVAm copolymer synthesis. The analysis for all of these copolymers is essentially identical due to the

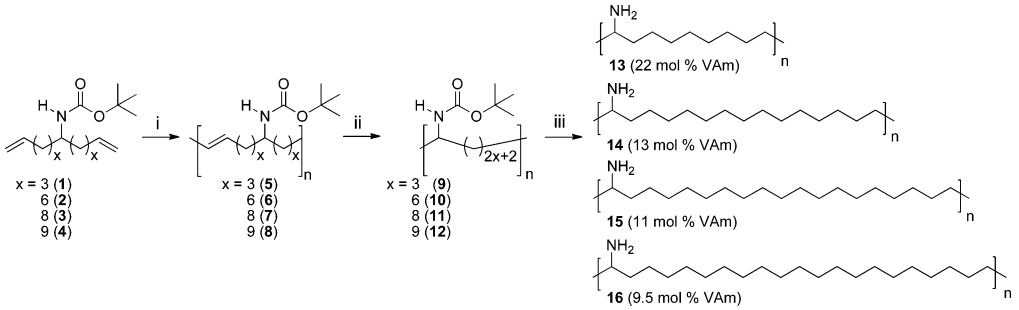

Figure 2. Ethylene-*co*-vinyl amine copolymer synthesis: (i) first-generation Grubbs' catalyst; (ii) H_2 (600 psi), $RhCl(PPh_3)_3$, toluene, room temperature; (iii) 250 °C under vacuum.

Table 1. Molecular Weight and Thermal Data for Unsaturated Ethylene Vinyl Amine Copolymers:

polymer	mol % vinylamine[a]	T_g[b] (°C)	M_W[c]	PDI[c]	D_p[c]
5	22	19.1	7.4	1.45	21
6	13	−5.4	11.4	1.43	25
7	10.5	−8.5	14.7	1.99	20
8	9.5	−24.2	13.3	1.67	20

[a]Calculated from theoretical repeat unit, confirmed by NMR. [b]10 °C/min scan rate, values determined from second scan data. [c]Reported in kg/mol and performed in THF at 40 °C with calibration vs polystyrene standards.

identical functional groups contained in each material. The polymerization was 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 polymerization.[27] The elimination of the olefinic band at 967 cm^{-1} corresponding to the out-of-plane C−H bend confirms complete hydrogenation of the ethylene backbone. Strong absorbance bands present at 2925 and 2854 cm^{-1} for these copolymers correspond to the asymmetric and symmetric methylene C−H stretching motions of the backbone carbons. The carbonyl stretch of the Boc's carbamate functionality is observed at 1692 cm^{-1} with additional carbamyl bands at 1524 and 1248 cm^{-1}. Scissoring bands from the methylene C−H vibrations are also readily observed at 1457 cm^{-1}.

Thermal Analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on each of the three groups of polymer samples: the unsaturated protected, the saturated protected, and the saturated deprotected polymers. Table 2 summarizes the thermal properties exhibited while Figures 5, 6, 7, 10, and 11 show thermograms which detail the decomposition, glass transition, and melting points of these materials. It is apparent from this thermal data that the molar ratio of incorporated vinyl amine has a dramatic effect on the material behavior.

The decomposition traces of both the unsaturated and saturated protected amine polymers (Figure 5) are predictable. Yamamoto[28] and Ahn[29] have shown in their research that the Boc group can be removed thermally at about 175 °C.[28,29] A sharp loss in weight occurs at this temperature for each of the

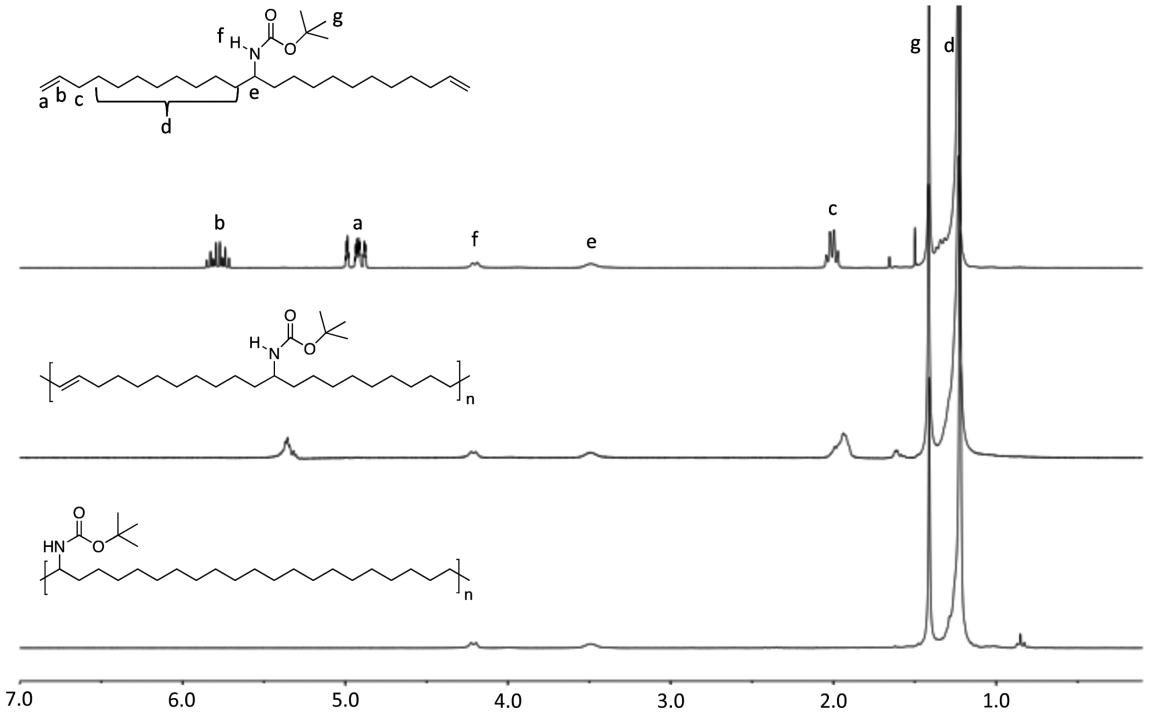

Figure 3. Progression of monomer to polymer monitored by ^1H NMR.

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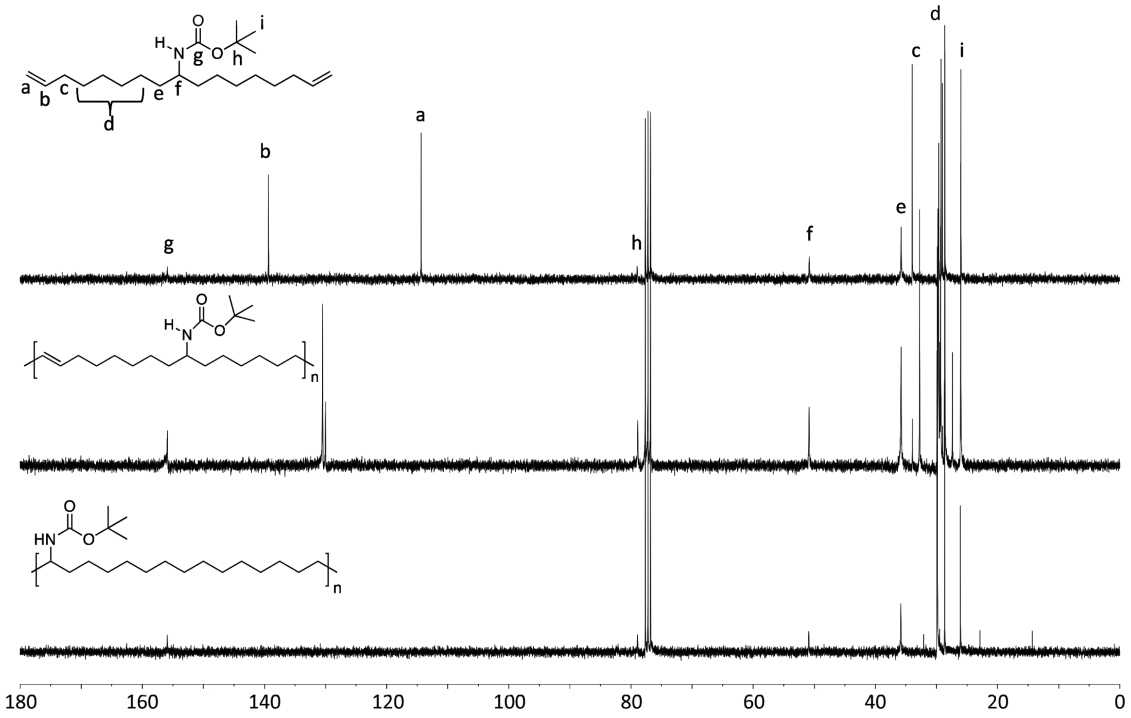

Figure 4. Progression of monomer to polymer monitored by ^{13}C NMR.

Table 2. Thermal Data for the Protected and Deprotected Polymers

polymer	mol % vinylamine[a]	T_g[b] (°C)	T_m[b] (°C)
9	22	4	N/A
10	13	2	N/A
11	10.5	−8	N/A
12	9.5	2	N/A
13	22	10	N/A
14	13	N/A	49
16	9.5	N/A	44

[a]Calculated from theoretical repeat unit, confirmed by NMR. [b]10 °C/min scan rate, values determined from second scan data.

eight protected polymers; the shoulder or plateau area of each curve represents the stable deprotected amine polymer. The percent weight losses experimentally observed in these decomposition curves were 45, 32, 29, and 25% as measured to the inflection point of the plateau. These percent weight losses correspond to the Boc protection group being cleaved from the amine releasing carbon dioxide and isobutene from each repeat unit. The calculated predictive weight loses of 42, 31, 26, and 25% are in excellent agreement with these experimental values. The TGA traces for both the unsaturated and saturated polymer families are nearly identical which prove that the addition of hydrogen to the internal alkene has a minimal net effect on the weight loss. It can be determined from these weight loss profiles that the thermally deprotected polymer is stable and exists over a 100° range, indicating that these materials are excellent candidates for a single thermal deprotection step.

Figure 6 shows the DSC data (second heating scan) for the series of unsaturated and saturated protected polymers. All four unsaturated polymers are amorphous, but the T_g's are consistent with ADMET sequenced materials.[27] Amorphous sequenced copolymers occur as a consequence of steric congestion along the polymer backbone, thus preventing the ethylene run lengths between branches to crystallize. The

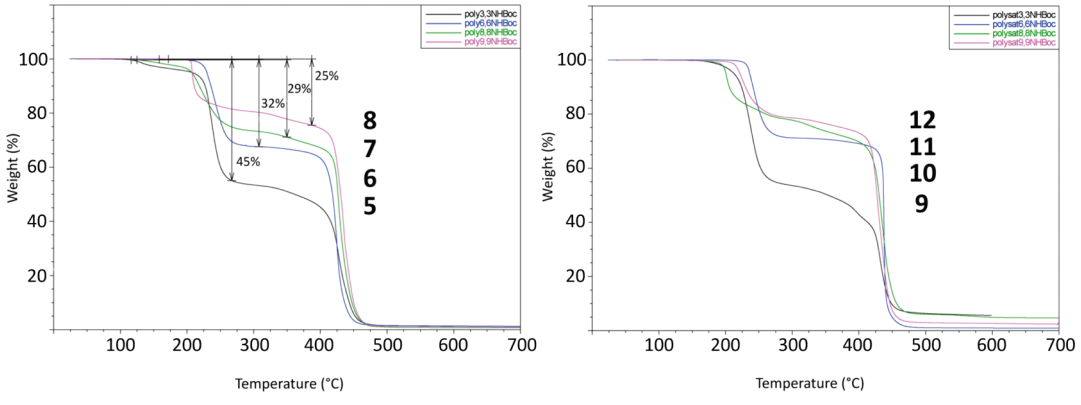

Figure 5. TGA traces for (left) unsaturated protected polymers (right) saturated protected polymers.

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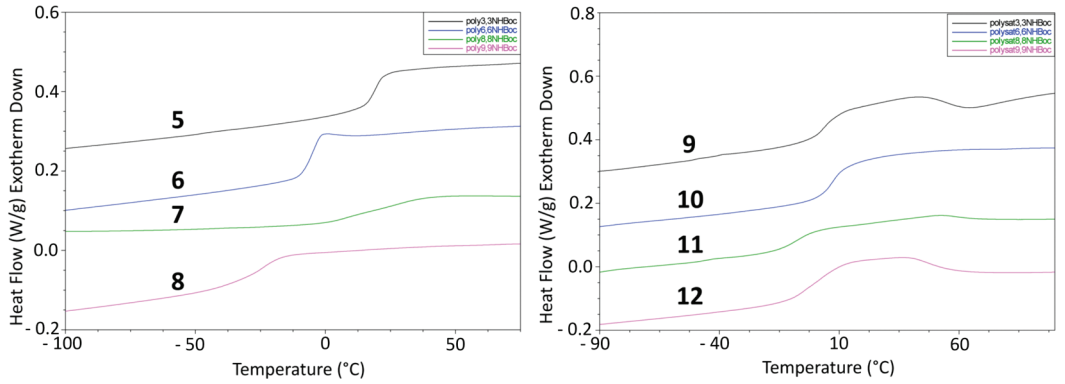

Figure 6. DSC of ADMET (left) unsaturated protected polymers (right) saturated protected polymers.

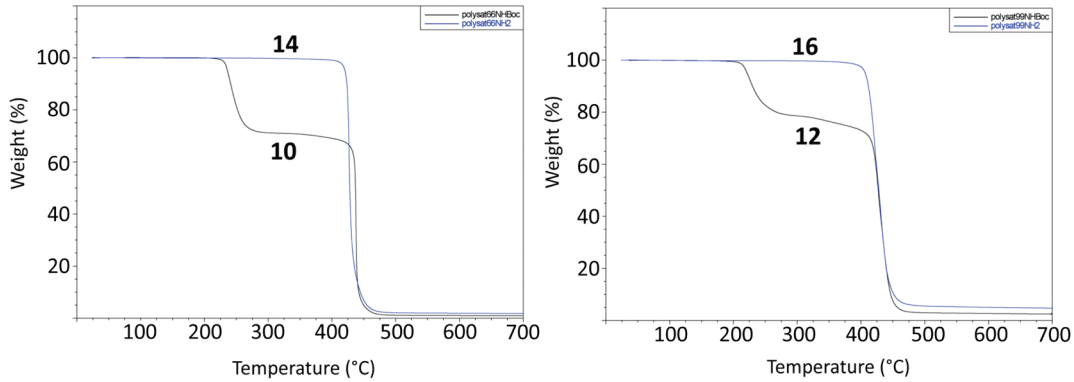

Figure 7. TGA traces of (left) polysat6,6NHBoc (**10**) and polysat6,6NH_2 (**14**) (right) polysat9,9NHBoc (**12**), and polysat9,9NH_2 (**16**) polymers.

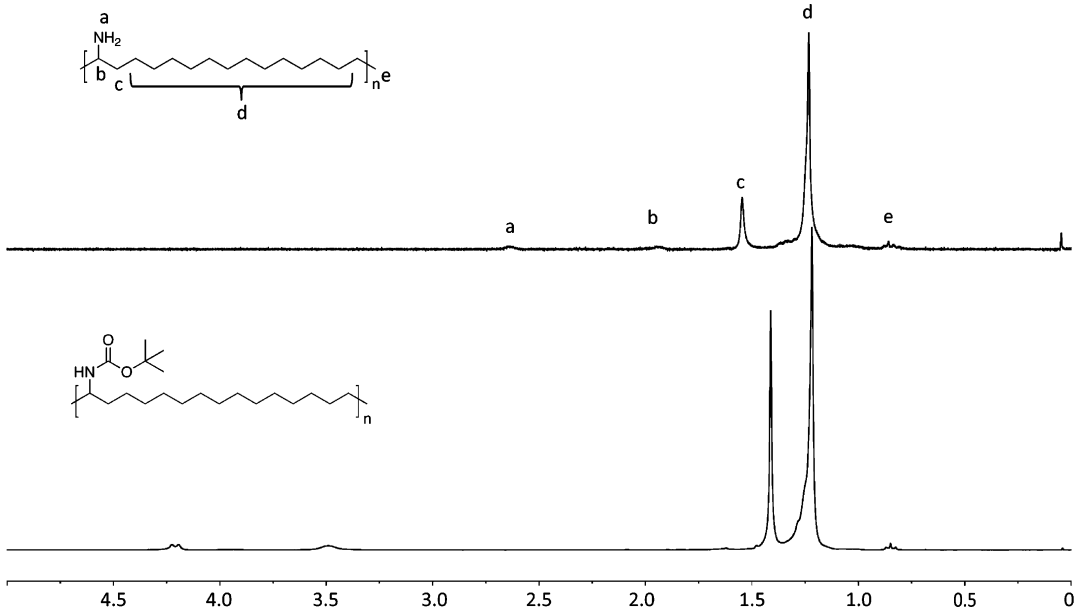

Figure 8. ^{1}H NMR of (top) polysat6,6NH_2 (**14**) and (bottom) polysat6,6NHBoc (**10**).

tert-butyl carbamate protection group explains the general trend of a decreasing T_g with decreasing branch frequency, since it allows for hydrogen bonding with other such protecting groups. This hydrogen bonding allows branches to become associated with each other to form a physically cross-linked structure. As the number of H-bond cross-links decreases in the compounds **5**, **6**, **7**, and **8**, the polymer chain has greater flexibility and a lower T_g. The DSC traces for the saturated protected polymers each shows a complicated transition, which resembles the start of a T_g but then appears to lead directly into a melt. The general trend observed in precision polymers previously synthesized in this group demonstrates that increasing the pendant branch frequency yields materials with less and less crystalline character, until a critical threshold is met and the material becomes amorphous.[15,25,26] This threshold is not obvious in the present data, because the polymer with the

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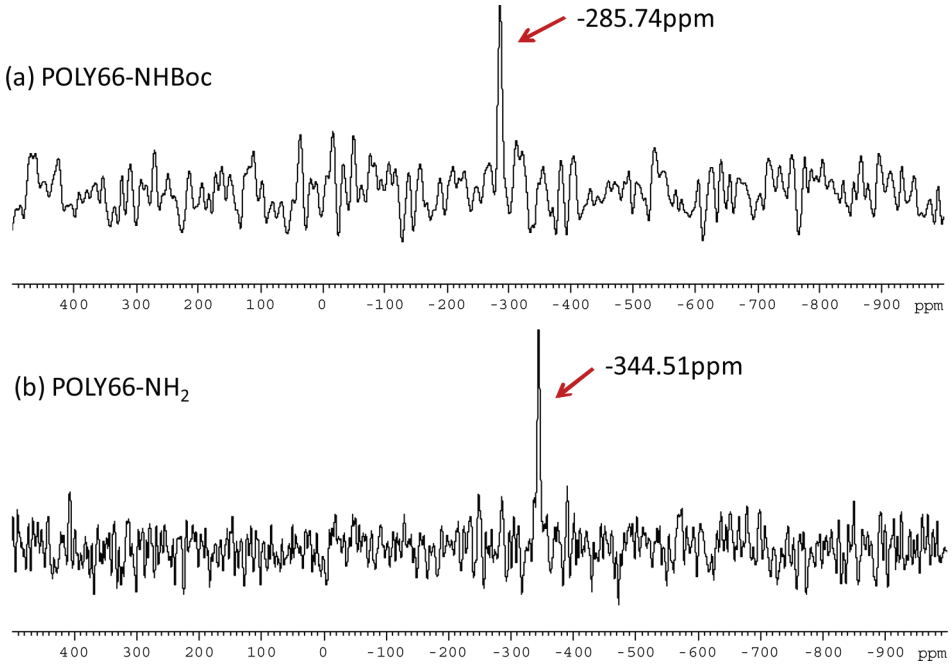

Figure 9. ^{15}N CP/MAS spectra of (a) protected precision polymer POLY-NHBoc, and (b) deprotected precision polymer POLY66-NH_2.

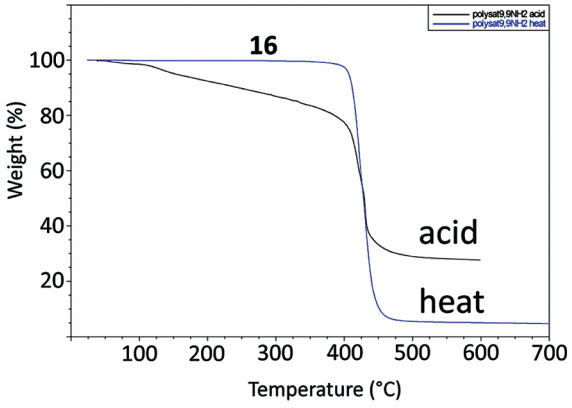

Figure 10. TGA traces of polysat9,9NH_2 polymers deprotected from heat and acid.

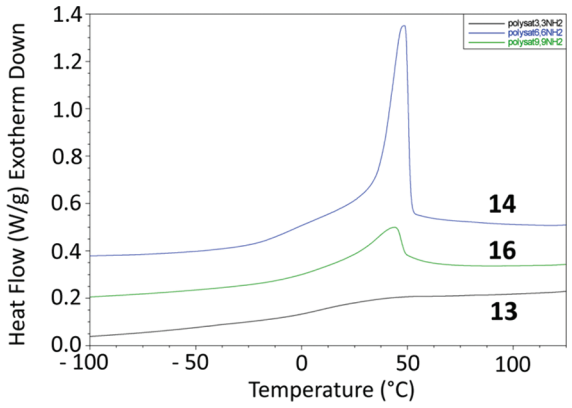

Figure 11. DSC of the deprotected amine branch every 9th, 15th, and 21st carbon on polymer.

most closely spaced pendant groups (every ninth carbon, **9**) exhibits a melt peak. Additional work on polymers with more frequent branches is needed to determine if the trend holds for precision PEVAm.

Deprotection Strategy. Initial attempts to deprotect these polymers were carried out in solution with hydrochloric acid. The protected polymer was readily dissolved in a minimum amount of a 1:1 THF/dioxane solvent mixture, and 10 vol equiv of 4 M HCl in dioxane were added at room temperature. Within minutes, a dark brown polymer started to precipitate onto the sides of the round-bottom flask. After 1 h the solution was extracted with ether, but no polymer was obtained upon rotary evaporation of the organic layer. Multiple attempts to remove the polymer remaining on the walls of the flask were unsuccessful due to lack of solubility. The polymer was finally removed from the flask by physically scraping it from the sides, placing the dark brown scrapings into a vial, and drying them.

It is believed that the negligibly soluble polymer on the flask walls was the ammonium chloride salt of the amine. Upon protic acid deprotection in solution, the corresponding ammonium salt branches are attracted to each other and likely cluster together tightly with the polymer backbone coil around them, thus preventing any further solvation of the material.

In order to prevent this strong ionic aggregation, the thermal degradation information gathered from the TGA thermograms shown in Figure 5 was advantageously used. To employ this deprotection technique, the polymer was cast as a thin film in a 10 mL vial and placed in a 275 °C sand bath under vacuum. For each of these materials, the protected, tan-colored polymer films turned dark brown within minutes upon heating with bubbles, presumed to be carbon dioxide and isobutene, eliminated from the viscous melted polymer. Since this deprotection is performed under vacuum, the isobutene is removed upon elimination with no further need of purification. Figure 7 shows the overlapping TGA traces of the saturated protected 6,6 polymer and 9,9 polymer with their respective deprotected counterparts. The weight loss corresponding to the Boc group no longer exists in the TGA trace from the polymer recovered from the vial. These thermally deprotected polymers,

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like the chemically deprotected ones, have negligible solubility in all solvents tested. However, a small amount of the deprotected 6,6 saturated polymer dissolved in $CDCl_3$, and the corresponding ^1H NMR spectra are shown in Figure 8. No ^{13}C NMR spectra was observed due to this lack of copolymer solubility.

To better elucidate both the protected and deprotected 6,6 amine polymer's chemical structures and demonstrate the success of synthesis, natural-abundance ^{15}N solid state NMR (SS-NMR) spectra were collected at Max Planck Institute for Polymer Research in Mainz, Germany. The SS-NMR spectroscopy when coupled with cross-polarization magic angle spinning (CP-MAS) provides excellent sensitivity and narrow line widths. Moreover, this technology also eliminates possible errors arising from the partial solubility of the deprotected precision amine polymer samples.

Compared to commonly seen ^{13}C SS-NMR, ^{15}N CP-MAS NMR offers generally simple and readily interpretable ^{15}N spectra in terms of probing a polymer's structure. Figure 9 shows the spectra of both a protected and deprotected ADMET amine polymer: POLY66-NH_2 (**14**) and POLY66-NHBoc (**10**), each of which exhibits a single resonance at −344.51 ppm and −285.74 ppm, respectively. The signal at −344.51 ppm in Figure 9b falls within the resonance range of primary amine NH_2 groups[30−32] and can be readily assigned to the amine groups on the deprotected POLY66-NH_2 (**14**) side chains. Considering the single peak at −285.74 ppm from the protected sample as shown in Figure 9a, this peak should be the only nitrogen resonance arising from the amide groups in POLY66-NHBoc (**10**), if the deprotection step is successful, which is indeed the case herein. It is known that amide isotropic chemical shifts are highly sensitive to both hydrogen bonds and protonation at the carbonyl oxygen.[33] The single resonance at −285.74 ppm in Figure 9a is quite close to the reported ^{15}N isotropic chemical shifts from amides and urethanes.[34−36] The introduction of the electron-withdrawing Boc group causes the nitrogen nuclei in POLY66-NHBoc (**10**) to shift downfield exhibiting a significantly more positive chemical shift.

In short, ^{15}N solid-state NMR analysis has demonstrated that the deprotection step is successful based on the significant isotropic chemical shift changes between the protected and deprotected precision polymers. The synthetic route employed in this study is applicable to offer precise amine polymers.

Figure 10 contains the TGA traces of both the saturated 9,9 polymer (**16**) deprotected by heat and (**16**) deprotected by acid. These overlapping thermograms demonstrate the biggest advantages of thermal over acid deprotection—solvent and counterion contamination. The weight loss on the acid deprotected polymer begins below 100 °C, and this weight loss continues until the main chain decomposes at 400 °C. However, the thermally deprotected polymer shows no solvent contamination or other impurity associated weight loss upon TGA analysis and is immediately ready for further analysis.

The final deprotected polymers with amine groups on every 15th, and 21st carbon polymers exhibit crystallinity. The DSC traces in Figure 11 show that the polymer with an amine on every 15th carbon (**14**) has a sharp melt at 49 °C, whereas **16** (an amine on every 21st carbon) has a broader melt at 44 °C. Although the every 15th polymer exhibits a sharper melting point than the 21st material, we believe the hydrogen bonding of the branches may induce different chain packing and alter the crystallinity of this material relative to the other copolymers. This is contrary to the trend observed in the series of precision ethylene copolymers prepared in our laboratory, in which the melting points usually increase as the number of CH_2 groups between branches increases.[26] In previous polymer families made in our group,[25] the polymer substituted on every ninth carbon is amorphous. This trend is upheld for the PEVAm materials, Figure 11, as the polymer with an amine branch on every ninth carbon appears completely amorphous. Unfortunately, a lack of copolymer with an amine on every 19th carbon prevented thermal analysis for this material.

■ CONCLUSIONS

Reported for the first time, a family of four sequenced copolymers of ethylene with vinyl amine has been prepared with predetermined comonomer ratios. Although metathesis catalysts are evolving to become more tolerant of amine and nitrogen functionality, the amine functionalized dienes synthesized here must be protected prior to ADMET polymerization. The Boc protected monomers provided soluble polymers while the Fmoc protected analogues did not. These polymers possess exact ethylene run lengths between pendant primary amine branches on every 9th, 15th, 19th, or 21st carbon along the backbone. Spectroscopic analysis via NMR and FT-IR affirms the microstructural control achieved via metathesis polymerization. The pristine nature of these copolymers' primary structures imparts marked effects on thermal behavior. Mass losses observed by TGA verify that the thermal deprotection reactions yielded the expected amine copolymers. Both thermal and chemical deprotection approaches yielded minimally soluble product but the thermal approach provided less contamination to the sample. Although this poor solubility of the deprotected PEVAm polymer hampered characterization efforts, a combination of ^{15}N solid-state NMR, ^1H NMR, and TGA confirmed quantitative deprotection. The polymers with an amine branch on every 15th and 21st carbon were shown to be crystalline, whereas the polymer with an amine on every ninth carbon is amorphous.

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