Functionalized Polyethylene via Acyclic Diene Metathesis Polymerization: Effect of Precise Placement of Functional Groups

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ABSTRACT: The preparation of a variety of model functionalized polyethylenes using step polymerization techniques is described. Specifically, the synthesis and preliminary thermal characterization of sequence-ordered ethylene-*co*-acrylate, -*co*-styrene, and -*co*-vinyl chloride polymers with precisely defined ethylene run lengths is reported. Unsaturated precursor polymers with pendant groups separated by a precise number of carbons are prepared by acyclic diene metathesis (ADMET) polymerization, which upon hydrogenation of the olefin linkages become formally ethylene/polar monomer copolymers. The only variable in the microstructure of these copolymers is the identity of the pendant group allowing the *strict* comparison of various "comonomers" on melting point. The synthesis of the necessary symmetric diene monomers with central pendant alkoxycarbonyl, phenyl, and chloride groups is outlined. Preliminary thermal analysis shows these copolymers to melt sharply with a trend of increased melting point depression with increasing steric bulk of the pendant group.

Introduction

Functionalized polyethylene via transition metal catalyzed polymerization has been an elusive goal of synthetic chemists for more than 50 years now. While catalytic routes offer the promise of microstructural control not possible with the current free-radical techniques, the use of available metallic complexes has been precluded by their susceptibility to poisoning by heteroatoms.[1] Functionalized polyethylene prepared in this manner would significantly broaden utility of this polymer, an opportunity well understood around the world, and recent progress in late transition metal chemistry may indeed present us with chain propagation techniques that will achieve this goal.[2−4] A recent report reveals the ability of late transition metal (nickel) catalysts to polymerize ethylene in the presence of a variety of heteroatom containing additives as well as incorporating functionalized olefins into the polymer.[4] With this in mind, we have exploited a recently developed method[5−9] (Figure 1) for the synthesis of model *functionalized* polyethylenes, in this case including functionalities relevant to polymers produced from commercial vinyl monomer feedstocks. On one hand, these models serve as a preview of what might one day be approached with the use of transition metal mediated chain polymerization. On the other, since metathesis polycondensation allows for a high degree of microstructure control, the effect of structure irregularity can be examined.

Numerous studies have been aimed at delineating the effect of irregularities in chain produced polyethylene random copolymers.[10] These irregularities may be incorporated via side reactions characteristic of the polymerization mechanism or as comomomers. A variety of polymers have served as subjects including ethylene-*co*-α-olefin polymers or branched polyethylene where the branches are alkyl,[11−16] and ethylene polar monomer (EPM) copolymers[17−30] where the pendant groups are polar functionalities. The studies have produced the consensus that the melting point is depressed with increasing frequency and steric bulk of the imperfections. It is well-known that sequence distributions are also a major contributing factor to material properties. Because of differing reactivity ratios of different ethylene/polar monomer pairs, polymers with differing comonomers but precisely the same comonomer composition and sequence distributions are not easily prepared. Interpretation of material studies comparing differing pendant groups must therefore also include some manner of statistical analysis of the sequence distributions.

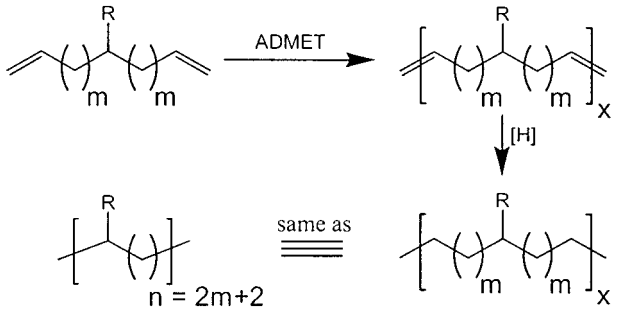

Figure 1. Synthesis of sequence-ordered ADMET functionalized polyethylenes.

The number of variables inherent in these investigations limits the strict comparison of differing comonomers, and therefore, model copolymers with more defined microstructures should prove highly valuable. Ethylene copolymers with strict *mer* sequences (pendant functionality on every fifth carbon) have been prepared indirectly by alternating copolymerization of butadiene with vinyl monomers followed by hydrogenation.[31−35] Model EPM copolymers with a relatively high degree of microstructural purity have also been prepared by the ROMP of substituted cyclooctene derivatives followed by hydrogenation.[36,37] Although the ethylene run lengths vary statistically between 6, 7, and 8 carbons due to the asymmetrical monomers, the mechanism guarantees that the polymers are entirely branch free and that the pendant functionalities are isolated. We have begun an effort to synthesize a number of such

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polymers with commercially relevant substituents in order to provide models with precise placement of these substituents for evaluation of the effect of functionality on polyethylene.

The synthesis of unsaturated precursors for these models is achieved via the acyclic diene metathesis (ADMET) polymerization of symmetric α,ω-dienes with central pendant functionality (Figure 1). If metathesis catalysts with well-defined reactivity are used, the only variable in the repeating structure is the cis/trans distribution of the olefinic linkages. Hydrogenation of the double bonds not only perfects the repeating structure but also converts these to the desired model functionalized polyethylenes with perfectly defined *mer* sequences. Although we also alternately refer to these as ADMET ethylene/polar monomer copolymers (EPM's), a finite structural feature differentiates these models from this designation. Perfect EPM models would contain pendant functionality separated by an odd number of carbons (Figure 1, n = odd number), not an even number as in all the polymers here. Previous examples of model polymers prepared in this way include ethylene/CO,[8] ethylene/propylene,[9] ethylene/vinyl alcohol,[7] and ethylene/vinyl acetate[38] copolymers. In this paper we report our efforts to produce functionalized polyethylene using other commercially relevant comonomers, in this case acrylates, styrene, and vinyl chloride. In addition to strict sequence control, the polymerization mechanism is the same for all polymers, thereby providing models with similar molecular weights and polydispersities regardless of the type of functionality.

Experimental Section

General Considerations. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Gemini series NMR superconducting spectrometer system or a Varian VXR-300 in $CDCl_3$. Resonances are referenced to residual protio solvent and reported in δ units downfield from TMS at 0.0 ppm. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. Low-resolution mass spectrometry data were recorded on a Finnigan MAT 95Q gas chromatograph/mass spectrometer utilizing electron ionization. Gel permeation chromatography (GPC) was performed by the Department of Materials Science and Engineering (University of Florida) using a Waters Associates liquid chromatograph with THF as eluting solvent. Retention times were calibrated against eight narrow (PDI < 1.07) polystyrene with $M_p = 1.350 \times 10^3 - 8.6 \times 10^5$ g/mol.

Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) data were obtained with a Perkin-Elmer 7 series thermal analysis system. DSC samples (5−10 mg) were analyzed with ice or liquid nitrogen as coolant and under a helium flow rate of 25 mL/min. All samples were predried at 40−50 °C under reduced pressure (<0.1 mmHg) for at least 24 h. The instrument was calibrated for peak onset temperature transitions and peak area using indium and ultrapure water as standards. Samples were scanned at a heating/cooling rate of 5 °C/min from −80 to 100 °C with data collection during the second cycle in the appropriate temperature ranges to include observed thermal transitions. TGA samples (5−10 mg) were heated from room temperature at 20 °C/min under N_2 with a flow rate of 30 mL/min, until complete combustion.

Materials. The ruthenium catalyst $Cl_2(Cy_3P)_2RuCHPh$ (**1**) was prepared according to the literature.[39] Diethyl ether, toluene, and THF were distilled from Na/K alloy under argon and degassed. Ph_3P was dried in the molten state under reduced pressure prior to use and CCl_4 was distilled from P_2O_5. HMPA and diisopropylamine were distilled under reduced pressure from NaH and CaH_2, respectively, and stored under argon. Acetone was stirred over $CaSO_4$, decanted to fresh $CaSO_4$, and freshly distilled before use. Ketone diene (**7**), hydroxy diene (**9**), 11-dodecenoic acid, 13-tetradecenoic acid, 9-decenyl bromide, and 11-dodecenyl bromide were prepared as published.[38] All other reagents were used as received. All monomers were purified by flash chromatography on silica gel-60.[40]

Synthesis. 2-(9-Decenyl)-11-dodecenoic Acid (2). Diene **2** was prepared by C-alkylation of the dianion (enolate, generated by reaction with 2 equiv of LDA) of 11-dodecenoic acid with 9-decenyl bromide. All manipulations were conducted using standard Schlenk techniques under argon atmosphere. Butyllithium (74.4 mL 2.5 M in hexanes, 0.186 mol, 2.05 equiv) was added slowly via syringe to diisopropylamine (26.2 mL, 0.186 mol, 2.05 equiv) in 100 mL of THF while maintaining the temperature at $-15\ °C \geq T \geq -30\ °C$. The solution was stirred 5 min at −20 °C and then 15 min at RT. 11-Dodecenoic acid (18 g, 90.8 mmol, 1.0 equiv) was added slowly via syringe while maintaining the temperature at $-15\ °C \geq T \geq$ -30 °C, and then the mixture was stirred at 50 °C for 2 h. The solution was cooled to 0 °C, and HMPA (15.8 mL, 90.8 mmol, 1.0 equiv) was added via syringe followed by rapid addition of 9-decenyl bromide (19.9 g, 90.8 mmol, 1.0 equiv) via syringe. After stirring 12 h the reaction was chilled to 0 °C, quenched with 500 mL of ice cold 3 N HCl, and concentrated under reduced pressure. The heterogeneous aqueous mixture was extracted with pentane, and the organic layer washed with 3 N HCl, water, and brine, then dried over Na_2SO_4, and concentrated to ∼38 g of pale yellow oil. The oil was further purified by flash chromatography (15% EtOAc/pentane) to render pure **2** in 71% isolated yield as a white solid. ^{1}H NMR: δ (ppm) 5.7 (m, 2H); 4.94 (m, 4H); 2.33 (m, 1H); 2.01 (q, 4H); 1.63 (m, 2H); 1.48 (m) + 1.27 (br) = 26H. ^{13}C NMR: δ 183.26, 139.15, 114.11, 45.57, 33.79, 32.12, 29.51, 29.39, 29.09, 28.89, 27.34.

2-(11-Dodecenyl)-13-tetradecenoic Acid (3). Diene **3** was prepared by C-alkylation of the dianion (enolate) of 13-tetradecenoic acid with 11-dodecenyl bromide, as described for diene **2**. The carboxylic acid was isolated as a white powder in 82% yield. ^{1}H NMR: δ (ppm) 5.7 (m, 2H); 4.94 (m, 4H); 2.33 (m, 1H); 2.01 (q, 4H); 1.63 (m, 2H); 1.48 (m) + 1.27(br) = 34H. ^{13}C NMR: δ 183.34, 139.10, 114.105, 45.63, 33.82, 32.11, 29.49, 29.38, 29.11, 28.80, 27.32.

Methyl 2-(11-Dodecenyl)-13-tetradecenoate (6). Diene **6** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **3** with MeI. Anhydrous K_2CO_3 (1.32 g, 9.6 mmol, 2.5 equiv) and **3** (1.5 g, 3.8 mmol, 1 equiv) were combined with 50 mL of dry acetone in a Schlenk flask fitted with a water-cooled (15 °C) condenser under argon. MeI (1.9 mL, 30.5 mmol, 8 equiv) was added via syringe. The mixture was heated with a 60−70 °C oil bath for 24 h with vigorous stirring. Two additional aliquots of MeI (2 mL) were added at intervals via syringe during this period. The acetone was evaporated under reduced pressure, and the concentrate was taken up in 50 mL of pentane and deionized water. The organic layer was washed with saturated $NaHCO_3$, 3 N HCl, and brine, dried over Na_2SO_4, and concentrated to 1.57 g of pale yellow oil. The oil was further purified by flash chromatography (5% EtOAc/hexanes) to 1.45 g (93.5%) of **6** as a clear colorless oil (100% GC). LRMS (EI): 406 (m+). Elem. Anal. Calcd for $C_{27}H_{50}O_2$: C, 79.74; H, 12.39. Found: C, 79.79; H, 12.54. ^{1}H NMR: δ (ppm) 5.80 (m, 2H); 4.94 (m, 4H); 3.70 (s, 3H) 2.35 (m, 1H); 2.04 (q, 4H); 1.61 (m, 2H); 1.39 (m) + 1.23 (br) = 34H. ^{13}C NMR: δ 177.06, 139.18, 114.06, 51.24, 45.70, 33.80, 32.49, 29.54, 29.46, 29.13, 28.91, 27.46.

Methyl 2-(9-Decenyl)-11-dodecenoate (4). Diene **4** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **2** with MeI, as described for **6** (100% GC). Yield: 88%. LRMS (EI): 351 (m+). Elem. Anal. Calcd for $C_{23}H_{42}O_2$: C, 78.80; H, 12.08. Found: C, 78.90; H, 12.26. ^{1}H NMR: δ (ppm) 5.77 (m, 2H); 4.92 (m, 4H); 3.63 (s, 3H) 2.29 (m, 1H); 2.00 (q, 4H); 1.55 (m, 2H); 1.33 (m) + 1.23 (br) = 26H. ^{13}C NMR: δ 177.01, 139.12, 114.06, 51.21, 45.67, 33.76, 32.47, 29.49, 29.35, 29.05, 28.86, 27.42.

Ethyl 2-(9-Decenyl)-11-dodecenoate (5). Diene **5** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **2** with EtI, as described for **4** (100% GC). Yield: 83%.

LRMS (EI): 365 (m+). Elem. Anal. Calcd for $C_{24}H_{44}O_2$: C, 79.06; H, 12.16. Found: C, 79.10; H, 12.26. ^{1}H NMR: δ (ppm) 5.77 (m, 2H); 4.92 (m, 4H); 4.13 (q, 2H); 2.34 (m, 1H); 2.04 (q, 4H); 1.55 (m, 2H); 1.33 (m) + 1.23 (br) = 29H. ^{13}C NMR: δ 176.51, 139.13, 114.06, 59.85, 45.72, 33.76, 32.47, 29.50, 29.36, 29.06, 28.89, 27.39, 14.32.

11-Phenyl-1,20-heneicosadiene (8). Diene **8** was prepared via nucleophilic attack of phenyllithium on ketone diene **7**, followed by in situ deoxygenation. Bromobenzene (2.0 mL, 19.6 mmol, 2 equiv) in 20 mL of ether was added slowly to lithium foil (1.087 g, 157 mmol, 16 equiv) in 40 mL of ether under argon. After refluxing 1 h, ketone diene **7** (3 g, 9.79 mmol, 1 equiv) in 20 mL of ether was added slowly, and the mixture was stirred for 1 h. The mixture was chilled to −50 °C, and ~50 mL of NH_3 was condensed into the flask at which time the reaction turned blue. After 10 min, the reaction was quenched via addition of 11 g of NH_4Cl_{anh}. The ammonia was evaporated, the mixture was filtered, and the ether solution was washed with brine and deionized water. Pure (100% GC) diene **8** was obtained after flash chromatography (pentane) as a clear, colorless liquid; 2.2 g, 61% yield. LRMS (EI): 368 (m+). Elem. Anal. Calcd for $C_{27}H_{44}$: C, 87.97; H, 12.03. Found: C, 88.00; H, 12.06. ^{1}H NMR: δ (ppm) 7.25 (m, 2H); 7.20 (m, 3H); 5.79 (m, 2H); 4.95 (m, 4H); 2.45 (m, 1H); 2.01 (q, 4H); 1.54 (m, 4H); 1.34 (m) + 1.21 (br) = 24H. ^{13}C NMR: δ 146.37, 139.18, 128.10, 127.63, 125.66, 114.06, 46.06, 36.97, 33.79, 29.73, 29.47, 29.10, 28.91, 27.60.

11-Chloro-1,20-heneicosadiene (10). Diene **9** (2.0 g, 65 mmol, 1 equiv) in 10 mL of CCl_4 was added via cannula under argon to Ph_3P (5.5 g, 21 mmol, 3.2 equiv) in 20 mL of CCl_4, and the vessel was heated in an 80 °C oil bath for 16 h. The mixture was filtered, and the solids were washed with pentane. Repeated dissolution in minimal pentane, chilling, and filtration followed by concentration yielded 2.17 g of a slightly cloudy liquid. Pure (100% GC) diene **10** was obtained after flash chromatography (pentane) as a clear, colorless liquid. Yield: 1.8 g, 85%. LRMS (EI): 326 (m+). Elem. Anal. Calcd for $C_{21}H_{39}Cl$: C, 77.14; H, 12.02. Found: C, 77.07; H, 12.13. ^{1}H NMR: δ (ppm) 5.79 (m, 2H); 4.94 (m, 4H); 3.86 (m, 1H); 2.02 (q, 4H); 1.69 (m, 4H); 1.50 (m) + 1.36 (m) + 1.27 (br) = 24H. ^{13}C NMR: δ 139.13, 114.12, 64.29, 38.50, 33.80, 29.45, 29.40, 29.16, 29.09, 28.90, 26.48.

General Procedure for Polymerization and Hydrogenation. Polymerization and hydrogenation were conducted as previously reported.[38]

ADMET/Hydrogenation of Methyl 2-(9-Decenyl)-11-dodecenoate (HP4). Elem. Anal. Calcd for $[C_{21}H_{40}O_2]$: C, 77.72; H, 12.42. Found: C, 77.44; H, 12.43. ^{1}H NMR: δ (ppm) 3.63 (s, 3H) 2.29 (m, 1H); 1.54 (m) + 1.40 (m) + 1.21 (br) = 36H. ^{13}C NMR: δ 177.06, 51.22, 45.71, 32.50, 29.67, 29.57, 29.47, 27.47. M_n (GPC vs Sty) = 4.8×10^4 (PDI = 1.9).

ADMET/Hydrogenation of Ethyl 2-(9-Decenyl)-11-dodecenoate (HP5). Elem. Anal. Calcd for $[C_{22}H_{42}O_2]$: C, 78.05; H, 12.50. Found: C, 77.81; H, 12.49. ^{1}H NMR: δ (ppm) 4.05 (q, 2H); 2.38 (m, 1H); 1.61 (m) + 1.39 (m) + 1.22 (br) = 39H. ^{13}C NMR: δ 176.43, 59.89, 45.67, 32.47, 29.50, 29.36, 29.06, 28.92, 27.43, 14.32. M_n (GPC vs Sty) = 6.4×10^4 (PDI = 1.8).

ADMET/Hydrogenation of Methyl 2-(11-dodecenyl)-13-tetradecenoate (HP6). Elem. Anal. Calcd for $[C_{25}H_{48}O_2]$: C, 78.88; H, 12.71. Found: C, 78.92; H, 12.78. ^{1}H NMR: δ (ppm) 3.71 (s, 3H); 2.33 (m, 1H); 1.61 (m) + 1.39 (m) + 1.23 (br) = 44H. ^{13}C NMR: δ 177.06, 51.24, 45.70, 32.49, 29.52, 29.37, 29.10, 28.91, 27.43. M_n (GPC vs Sty) = 4.7×10^4 (PDI = 1.9).

ADMET/Hydrogenation of 11-Phenyl-1,20-heneicosadiene (HP8). Elem. Anal. Calcd for $[C_{25}H_{42}]$: C, 87.64; H, 12.36. Found: C, 87.39; H, 12.46. ^{1}H NMR: δ (ppm) 7.25 (m, 2H); 7.20 (m, 3H); 2.43 (m, 1H); 1.60 (m, 4H); 1.21 (br, 32H). ^{13}C NMR: δ 146.43, 128.10, 127.64, 125.64, 46.07, 37.00, 29.79, 29.71, 29.67, 29.57, 27.63. M_n (GPC vs Sty) = 1.8×10^4 (PDI = 1.7).

ADMET/Hydrogenation of 11-Chloro-1,20-heneicosadiene (HP10). Although the ADMET polymerization proceeded in fashion similar to all others, analysis of the polymer after attempted hydrogenation showed very little conversion (virtually unchanged olefin signals in ^{1}H and ^{13}C NMR). The polymerization was repeated, and the reaction was quenched by exposure to air. The unsaturated polymer (483 mg) was combined with Pd/C (10 wt %/wt, 500 mg) and 15 mL of dry, degassed toluene under argon in a pressure tube. The mixture was exposed to a constant 80 psig H_2 at room temperature with vigorous stirring. After 8 h, the polymer was seen to precipitate as evidenced by gelatinous particles, and the Pd/C was no longer freely dispersing. The mixture was heated to 40 °C at which time stirring resumed and the gelatinous particles disappeared. After 24 h, the mixture was filtered through a medium glass frit (while heated) and then passed through a 0.2 μm syringe filter to ensure complete removal of fine Pd/C particles. The white solid polymer was obtained in quantitative yield after precipitation into methanol. Elem. Anal. Calcd for $[C_{19}H_{37}Cl]$: C, 75.83; H, 12.39; Cl, 11.78. Found: C, 75.74; H, 12.51; Cl, 11.68. ^{1}H NMR: δ (ppm) 3.86 (m, 1H); 2.02 (q, 4H); 1.68 (m, 4H); 1.47 (m) + 1.38 (m) + 1.23 (br) = 32H. ^{13}C NMR: δ 64.39, 38.53, 33.80, 29.70, 29.59, 29.53, 29.21, 26.51. M_n (GPC vs Sty) = 5.4×10^4 (PDI = 1.8).

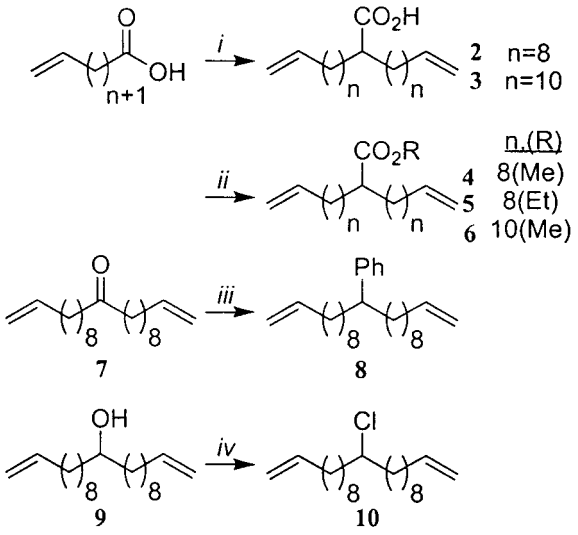

Figure 2. Syntheses of diene monomers. (i) ① 2 LDA, −15 °C ② HMPA, RBr; (ii) K_2CO_3, RI, acetone, Δ; (iii) ①PhLi, XS Li° ②NH_3/NH_4Cl; (iv) Ph_3P, CCl_4, Δ.

Results and Discussion

Monomer Synthesis. Monomers with Pendant Alkoxy−Carbonyl Moieties. The preparation of functionalized dienes with the functional group symmetrically disposed leads to the various types of functionalized polyethylene reported in this paper. Dienes with central pendant alkoxy−carbonyl groups (Figure 2) were synthesized as monomers for model ethylene/acrylate copolymers. One of the most useful organic transforms for constructing carbon skeletons of this type is the dialkylation of enolate ions with alkyl halides, and this method has previously been shown[9] to be effective in the synthesis of similar dienes.

Review of the literature indicated that this process is decreasingly productive with increasing length of the alkyl bromide.[41] However, the dianions (enolates) of carboxylic acids are very effective carbon nucleophiles in such schemes.[42] The needed long chain ω-unsaturated carboxylic acids were available in our laboratories, and their preparation is published elsewhere.[38] Construction of the diene skeleton in this manner proved to be high yielding, and the acid functional intermediates are easily purified by simple flash chromatography. The acid groups of these dienes were O-alkylated in near quantitative yields by mild base-promoted esterification with excess methyl or ethyl iodide.[43]

Chloro- and Phenyl-Substituted Dienes. Intermediates used in the previously published[8,38] syntheses of other diene monomers were also converted to symmetric dienes with central pendant chloro and phenyl substituents (Figure 2). Dienes substituted by a phenyl ring can be used to prepare model ethylene/styrene copolymers, and to this end, a phenyl-substituted monomer (**8**) was easily obtained from the ketone diene (**7**). The phenyl ring is attached via nucleophilic attack on the carbonyl carbon by phenyllithium, and the resulting benzylic tertiary alkoxide is deoxygenated in situ under Birch reduction-like conditions.[44] The combination of excess Ph_3P in refluxing CCl_4 is effective in converting the alcohol-functionalized diene (**9**) to the chloride (**10**) in good yield.

Realization of high molecular weight via the ADMET reaction, just as for any condensation polymerization, requires high-purity monomers, and this requirement is further emphasized if the polymers are to serve as models with "perfect" microstructure. As in our previous studies with other sequence-ordered copolymers, the monomers utilized here were obtained in sufficient purity that no contaminants could be detected by GC or GC-MS, NMR, and HPLC (UV and RI detectors).

Polymerization and Hydrogenation. With the exception of the chloro-functional polymer (**HP10**), all the ADMET model polymers reported here were prepared utilizing our recently published[8,38] tandem homogeneous ADMET/heterogeneous hydrogenation procedure. Monomer and catalyst ($Cl_2(Cy_3P)_2RuCHPh$) **1** were combined inside an argon-purged drybox, and the ADMET polymerization was conducted at 45−65 °C under reduced pressure to remove ethylene, driving the condensation to high conversion. Addition of silica gel to adsorb the catalyst residue, toluene to aid dispersion, and exposure to hydrogen pressure results in quantitative olefin hydrogenation. Mechanical separation of the heterogeneized catalyst residue and evaporation of toluene yielded the colorless polymers in near-quantitative yields.

As previously published,[8] secondary alkyl chlorides have been found to inhibit the hydrogenation stage of this procedure. In concord with this observation, the unsaturated linkages of the chloride functional precursor polymer could not be effectively reduced by this method. Investigation of the ^{1}H NMR spectrum of the incompletely reduced product indicated that no chloride functionality was lost. Alternately, hydrogenation over Pd/C at 80 psig H_2 in toluene proved quantitative within spectroscopic detection limits. The reduction was conducted at 40 °C as the polymer begins to precipitate from room temperature toluene during the course of the reaction as evidenced by the formation of gelatinous particles in the mixture. Subsequent observations showed the final fully saturated product to be poorly soluble in toluene, benzene, methylene chloride, 1,2-dichloroethane, and THF but more highly soluble in chloroform at room temperature. Analytical data for the polymers are collected in Table 1.

Polymer Characterization. As shown in Table 1, all the polymers reported have molecular weights in the range $(2-6) \times 10^4$ g/mol. The GPC trace for **HP6** (Figure 3) illustrates the typical product distribution obtained as a consequence of the equilibrium condensation polymerization. The major fraction is monomodal with PDI ~ 2, along with a minor fraction of oligomers. As was seen previously for analogous ADMET EVA polymers,[38] the distribution of (cyclic) oligomers is apparently partially resolved as indicated by the series of small peaks following the major peak. The inset shows that, for polymers with the same ethylene run length, the series of peaks overlap.

Table 1. Characterization of ADMET Functionalized Polyethylenes⟨*tgr*⟩

polymer	"*n*"	R	$M_n \times 10^4$ [PDI][a]	T_m (°C)
HP4	18	CO_2Me	4.8 [1.9]	14.4
HP5	18	CO_2Et	6.4 [1.8]	12.5[b]
HP6	22	CO_2Me	4.7 [1.9]	37
HP8	18	Ph	1.8 [1.7]	−12[b]
HP10	18	Cl	5.4 [1.8]	77

[a] GPC versus polystyrene. [b] Average of two observed endotherms.

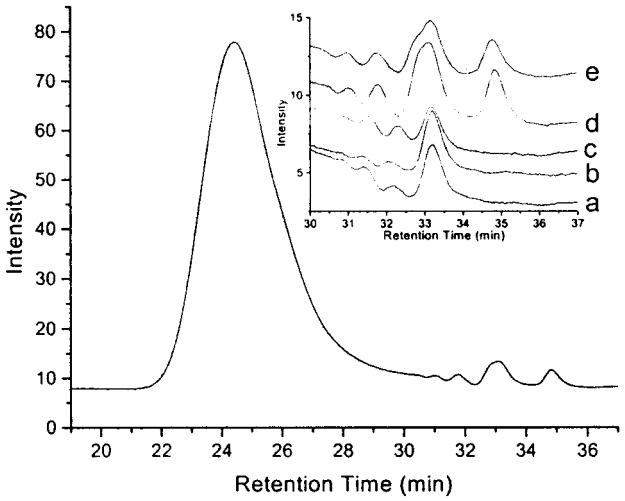

Figure 3. GPC trace of **HP6**. Inset shows selected partial GPC traces illustrating overlapping peaks for oligomers with the same ethylene run lengths ("*n*" in Figure 1): a, **HP4**; b, **HP5**; c, **HP10**; d, **HP6**; e, ADMET EVA (Figure 1: $n = 22$, R = OAc).[38]

Typical ^{1}H and ^{13}C spectra are shown in Figure 4 (**HP4**). The absence of signals in the region between 5 and 6 ppm (^{1}H) from the olefinic protons of the unsaturated precursor polymer indicates that hydrogenation is complete, as is the case for all the polymers reported here. The ^{13}C spectra are notably simple due to the high microstructural purity. The pattern of peaks is general: a partially resolved cluster of peaks (~30 ppm) due to the polyethylene segments; peaks due to the pendant group and the methine carbon; and one signal downfield and upfield, relative to the cluster at 30 ppm, corresponding to the carbons β and γ, respectively, to the pendant group. The inset in the proton spectra will be discussed in the section describing this particular polymer.

In the sections that follow, the preliminary thermal characterization of these polymers will be discussed. Before proceeding, two points should be addressed. There is no doubt that in this molecular weight range the concentration of end groups affects morphology. However, it has been shown[9] for two related model polymers (Figure 1: R = Me, $n = 18$) that a change in M_n from 1.74×10^4 to 7.2×10^4 did not change the T_m, which is the measurement we are concerned with here. Further, the question of tacticity is often raised when discussing these model polymers. As the achiral, branched centers of the symmetrical diene monomers are highly displaced from the reactive sites and the only

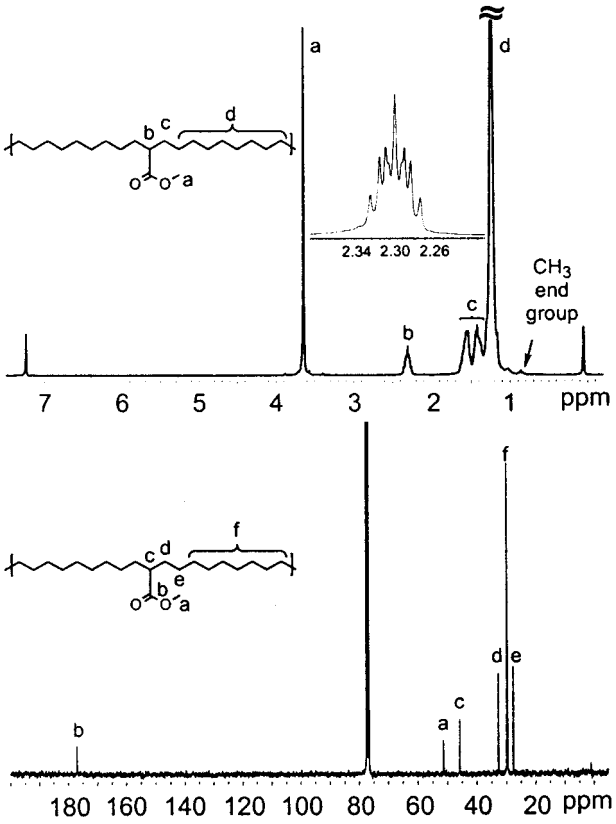

Figure 4. ^{1}H and ^{13}C NMR spectra of **HP4**. Inset: multiplet from proton "b" (500 MHz).

selectivity displayed by the catalyst is in relation to the olefinic cis−trans ratio, the immediate reply is *atactic*. We do however perceive the *possibility* of generating tacticity in the bulk state through equilibration during later stages of the reaction. Should rearrangement to a tactic polymer be thermally favored for packing reasons at a given polymerization temperature, this could occur simply by chain−chain equilibration of the repeating units (postcondensation exchange reactions).

Ethylene/Acrylate Copolymers. Commercial ethylene/methyl acrylate (EMA) copolymers are currently produced by high-pressure, free radical processes and generally contain approximately 20 wt % methyl acrylate.[45] The monomer reactivity ratios for methyl acrylate and ethylene differ substantially ($r_1 \gg 1$, $r_2 \ll 0.2$, M_1 = methyl acrylate),[46] and small changes in feed ratio have a significant effect on copolymer composition in the range 10−40 wt % comonomer. Copolymers with differing MA content are not as easily attainable as ethylene/vinyl acetate (EVA) copolymers, and therefore detailed studies of the effect of this pendant ester group are lacking in comparison to EVA's. The two classes of polymers exhibit similar physical properties, which is not surprising considering that the pendant groups in the polar repeat units are merely isomers, differing only in the orientation of the ester group. Reported melting points for EMA resins[47] are within 15 °C of the analogous EVA resins[48] with approximately the same weight percent comonomer.

We previously reported[38] the preparation of a series of ADMET EVA's for comparison to their commercial analogues and found a linear relation between the frequency of the pendant acetoxy groups and the melting point. In order that the isomeric methoxycarbonyl group may be compared to these, we have prepared the

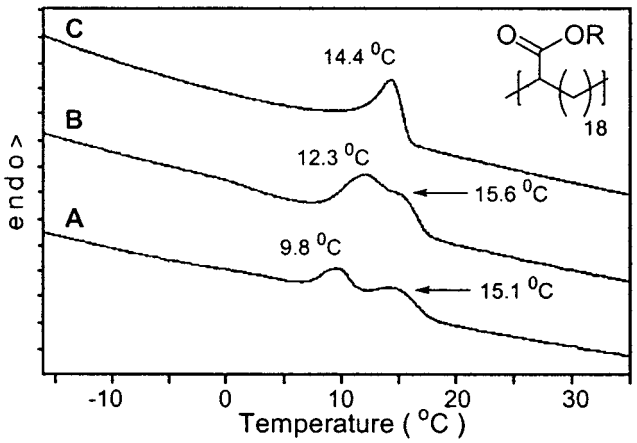

Figure 5. DSC heating traces for ADMET EMA and EEA polymers: A, **HP5**; B, **HP5** (annealed 3 °C, 1 h); C, **HP4**.

first two examples of analogous ADMET EMA's as well as one example of an ethylene/ethyl acrylate (EEA) copolymer. ADMET/hydrogenation of monomers **4** and **6** to polymers **HP4** and **HP6** yielded polyethylenes with a pendant methoxycarbonyl on every 19th and 23rd carbon, respectively. **HP5** was prepared in the same manner to compare the larger ethoxycarbonyl on every 19th carbon. **HP4** and **HP5** are rubbery solids at room temperature while **HP6** forms tough translucent or transparent films from the melt or from solution.

Polymers **HP4** and **HP6** correspond to EMA's with ∼26% and ∼23% MA by weight and melt at 14.4 and 37 °C, respectively. It should be noted that the commercial relatives with similar comonomer incorporation melt considerably higher, in the range of 70−90 °C.[47] The same relation was seen for the ADMET EVA's[38] as well as methyl-substituted polmers[9] when compared to their commercial counterparts, but the underlying physical factors are yet to be elucidated. However, in agreement with the commercial relatives, DSC melting points for the ADMET EMA's do not show drastic (<10 °C) differences in peak melting temperatures from the analogous ADMET EVA's. Distinction is seen in the *shape* of the endotherms (see Figure 5, **HP4**) where the EMA peaks appear narrower and do not exhibit a high-temperature shoulder as seen in the latter. While no attempts were made to measure second-order transitions here, it has been shown that commercial EVA's and EMA's exhibit significantly different second-order transitions attributed to flexible side-group reorientation. These studies, both empirical[19−21] and theoretical,[22−24] reach the general consensus that the cause is greater hindrance to rotation in the vicinity of the pendant ester group of MA relative to VA repeat units.

Comparison of the ^{1}H NMR resonances from the methine protons of **HP4** (Figure 4, inset, 500 MHz) and the analogous ADMET EVA (acetoxy group on every 19th carbon) reveals the differing chemical environments exerted by the two groups on the proximal backbone atoms. The methine proton of the EVA gave rise to the expected pentet due to splitting by four equivalent geminal protons. However, in the case of the EMA, these four protons are not equivalent due to anisotropy induced by the attached carbonyl, giving rise to the triplet of triplets seen in the inset. Further, the protons labeled "c" produce two partially resolved multiplets, each with an integral value of ∼2H. These observations agree with the aforementioned theoretical

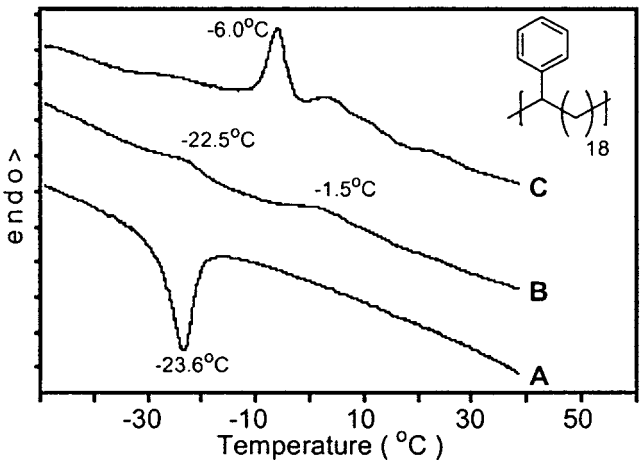

Figure 6. DSC traces for **HP8**: A, cooling; B, heating; C, heating (annealed −15 °C, 1 h).

calculations indicating different degrees of hindrance to rotation. Perhaps the differing mobilities of these two pendant groups affect crystal packing in these periodic polymers as well, leading to the small observed differences in melting behavior.

The larger ethoxycarbonyl group of **HP5** (ethylene/ethyl acrylate, EEA) causes a significant change in the profile of the DSC melting endotherm (Figure 5) relative to the analogous EMA. Two maxima are seen, and the position of the higher temperature maxima is within 1 °C of the peak seen for the analogous EMA model. Annealing at 3 °C (1 h) shifts the lower temperature maxima by nearly 4 °C toward the higher temperature peak, creating greater overlap and eliminating visible premelting as evidenced by flattening of the slope of the baseline prior to the endotherm. It is tempting to attribute this difference in melting behavior to greater disruption of polyethylene crystalline segments by the larger ethoxycarbonyl groups, but this of course awaits detailed study.

ADMET Ethylene/Styrene Copolymer. Due to the extremely high reactivity of styrene relative to ethylene, copolymers with even moderate levels of ethylene incorporation are unattainable by free radical copolymerization. Alternately, traditional Ziegler−Natta copolymerization of ethylene and styrene typically produced polymers that contain less than 1% styrene.[49] Recent reports disclose the use of homogeneous half-sandwich and metallocene catalysts, activated by MAO, to successfully prepare random ethylene/styrene copolymers with varied levels of styrene content.[50−52] It may be expected that as time goes on these polymers will also become convenient subjects for studying the effect of pendant groups on polyethylene, in this case the bulky phenyl group.

To compare the effect of a regularly spaced phenyl group on crystallization, an ADMET ethylene/styrene copolymer (**HP8**) was prepared with a phenyl ring on every 19th carbon. As predicted, the phenyl group induces the greatest melting point depression observed so far for ADMET model polymers with the same ethylene run length. This polymer is a viscous liquid at room temperature. Although the polymer shows a distinct first-order transition on cooling (DSC trace, Figure 6), the heating trace appears to contain two broad but apparently separate endotherms with low ΔH relative to the other polymers. Annealing at a temperature between the two small maxima resulted in a new relatively sharp peak (−6 °C) below the higher temperature peak and an undulating baseline up to 15−20 °C. Although it is not clear at this point, comparison of the shapes of the heating traces, annealed and unannealed, in the range of the lower temperature transition suggests that this is in fact a second-order transition.

ADMET Ethylene/Vinyl Chloride Copolymer. Chlorinated polyethylene (CPE) may be prepared from polyethylene via various chlorination techniques resulting in polymers that are formally ethylene/vinyl chloride (EVC) copolymers.[53] These materials have significant technical possibilities and have proven convenient subjects for microstructure/morphology studies.[26,27,29,30] In particular, morphological studies have been aimed at determining whether the chloride groups are included into crystal lattices as defects or excluded in amorphous regions. In a thorough study by Wegner,[29] EVC's were prepared by several chlorination techniques from polyethylene and partially hydrogenated polyoctenamers. The different methods produced polymers with varying incorporation of isolated and vicinal chloro substituents. X-ray studies in concert with DSC measurements indicated that the chloro groups were incorporated as defects in the crystals. As the chloride content of the polymers increased, the lateral dimensions of the unit cell were shown to increase relative to the unit cell of pure polyethylene. Polymers with vicinal chloro groups showed greater melting point depression as a result of the larger defects. EVC's with a broad range of chlorine content have also been prepared by partial reduction of PVC with trialkyl tin hydrides and equally thoroughly studied.[30] In both cases, specific note was made of the *importance of the sequence distribution of pendant groups* on the crystallization behavior.

To compare the effect of a periodic chloro group to the other pendant groups in this study, an ADMET ethylene/vinyl chloride (EVC) copolymer was prepared. Based purely on steric arguments, a model ethylene/vinyl choride copolymer with pendant chloride every 19th carbon would be expected to have a higher melt than any of the analogues reported here with the same ethylene run length. This was indeed found to be the case as **HP10** shows a $T_m = 77$ °C. The melting trace is sharp and well-defined much like the ADMET model methyl-substituted polymers.[9] The DSC melting points of random EVC's have been compared to analogous ethylene/propylene (EP) copolymers as a function of counit content, and the two data sets fell on the same line.[26] The researchers concluded that the melting behavior was the same due to the similar size of the chloro and methyl groups. Perhaps the smaller van der Waals radius[54] of chloride(1.75 Å) relative to methyl (2.0 Å) may be offset somewhat by the longer C−Cl bond length (1.78 Å) relative to C−C (1.54 Å). However, in stark contrast to these studies, the analogous ADMET EP polymer with a pendant methyl every 19th carbon melts 20 °C lower ($T_m = 57$ °C)[9] than this ADMET EVC.

Subsequent observations showed the final product to be poorly soluble in a variety of organic solvents at room temperature. The low solubility compared to those of the other polymers is no doubt a consequence of the greater crystallinity which might be expected from a copolymer with the smallest pendant group. Preliminary X-ray analysis indicate that the chloro groups of **HP10** organize in a highly ordered array and that the distance between chloro groups may be observed.[55] A number of

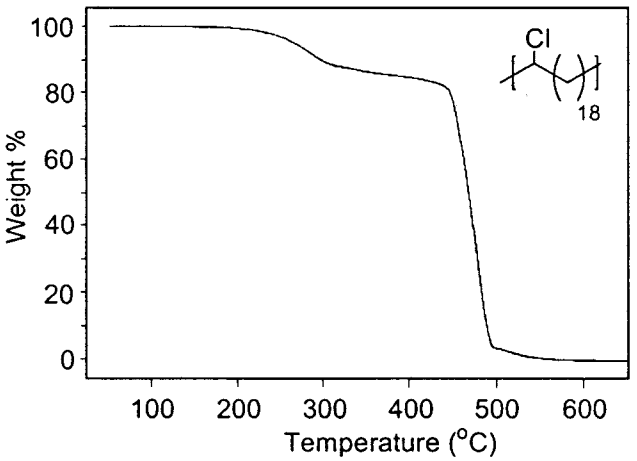

Figure 7. TGA trace of **HP10** showing thermal elimination of HCl followed by catastrophic decomposition.

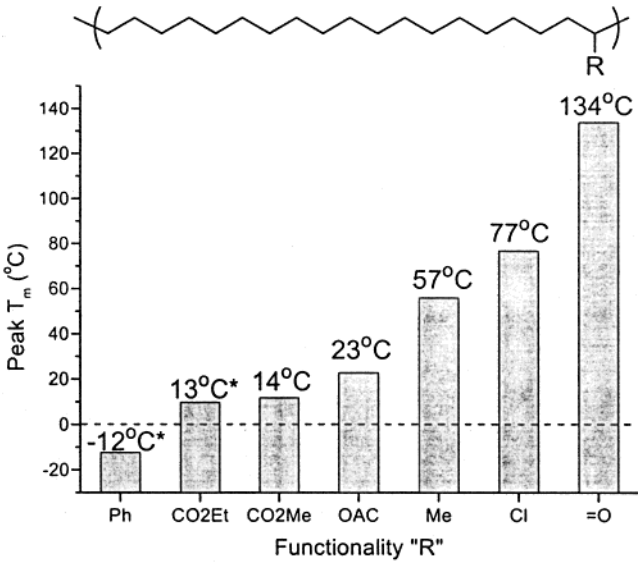

Figure 8. Peak melting points of ADMET ethylene copolymers (prepared to date) with regular pendant functionality separated by 18 carbons. Asterisk: average of two observed endotherms.

bulk crystal habits were observed, including spherulites and dendrites, by optical microscopy after cooling a heated dilute toluene solution to room temperature.

PVC and chlorinated polyethylenes are known to be thermally unstable due to facile elimination of HCl from the polymer backbone.[56] The TGA trace for **HP10**, shown in Figure 7, shows stepwise weight loss due to thermal elimination of HCl prior to catastrophic decomposition. The measured weight loss due to elimination of HCl (11.54%) is in reasonable agreement with that predicted from the known structure (12.11%).

The number of ADMET polymers with varied pendant functionality and identical ethylene run lengths (n = 18) has now been expanded sufficiently to allow comparisons of the effect of a variety of moieties on the melting point of functionalized polyethylene (Figure 8). First, one should note that the melting point of polyethylene with regularly spaced functional groups (on every 19th carbon) can be varied over a range of nearly 150 °C. Further, it is no surprise that melting points are progressively more depressed with increasing steric bulk of the pendant functionality. In the most extreme case presented, a pendant phenyl group, crystallization under the conditions studied is almost completely suppressed in the absence of annealing. However, it is obvious from the comparison of the chloro- and methyl-substituted polymers that size is not the most important factor.

Conclusions

The scope of the ADMET/hydrogenation procedure for producing model sequence-ordered ethylene polymers has now been expanded to include a variety of functionalized polyethylene macromolecular structures. In concord with the previously reported[8] observation, our one-pot homogeneous ADMET/heterogeneous hydrogenation procedure is not effective for hydrogenation of chlorofunctional polymers, but these may be easily obtained by alternate hydrogenation conditions. The preparation of polymers with varied substituents as the only variable in microstructure should allow the strict comparison of the effect of these substituents as more applied studies follow. For the polymers prepared to date, good correlation between the size and frequency of the pendant group and melting point depression is observed. Contrary to previous studies involving random copolymers, significant differences are seen between the melting points of methyl- and chloro-substituted polymers with the same repeating sequence. We are continuing to expand the number of precise models through homologous series of those polymers prepared already as well as with new pendant functionality. Future work will also include crystallographic and morphological studies.

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