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Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Effect of Alkyl Branch Size on Nanoscale Morphology

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Supporting Information

ABSTRACT: Synthesis and morphological characterization are reported for a series of 13 precision branched polyethylene structures, the branch being placed on every 39th carbon and varying in size from methyl to pentadecyl group. A recently established synthetic scheme for preparation of the symmetrical α, ω -diene monomer was employed to increase the number of methylene carbons between the branch points from 20 to 38, yielding polymers with 5.26 mol % α -olefin incorporation. The morphology of these polymers was investigated using differential



scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and transmission electron microscopy (TEM). Methyl branching significantly reduces the melting point and single crystal lamellae thickness of unbranched polyethylene. On the other hand, all further branches from ethyl to pentadecyl produce polymers that have similar melting points and single crystal lamellae thicknesses. A clear change in the morphology of both solution and melt-grown crystals of these polymers was observed from a situation where the methyl branch is incorporated in the polymer's unit cell to one where branches of greater mass are mostly expelled from the unit cell.

INTRODUCTION

The structure of polyethylene has been extensively investigated^{1,2} and is considered as the model for polymer crystallization studies.³⁻⁶ Linear polyethylene (high density polyethylene) crystallized from solution or the melt forms folded chain crystals having the orthorhombic unit cell.⁷ The branched versions of polyethylene (low density and linear low density polyethylene) have attracted more attention due to their wide-ranging thermal and mechanical properties governed by branching.^{8,9} The effect of branching on crystal structure of polyethylene has been examined in chain polymerized ethylene/ α -olefin copolymers with comonomers propylene,^{10,11} 1butene,^{10,12,13} and 1-octene.¹⁴ It is known that the ethylene/ propylene copolymers show evidence for methyl branch inclusion into the crystal unit cell, whereas ethylene/1-butene and ethylene/1-octene polymers display the exclusion of ethyl and hexyl branches due to their larger branch sizes.^{9,15} The validity of this generalization is limited, and partial ethyl branch inclusion is suggested for some of the ethylene/1-butene copolymer systems.^{16,17} For the case of ethylene/1-octene copolymers, X-ray investigations show the existence of a complex multiphase morphology which hinders the deeper examination of hexyl branch placement within the polymer structure.14

The ambiguity in morphology determination of ethylene copolymers is governed by the heterogeneously distributed nature of branches using either Ziegler–Natta,^{18–20} metal-

locene,^{21–23} and late transition metal²⁴ catalytic systems. By its nature, chain-propagation chemistry incorporates structural defects via inevitable chain transfer and chain walking processes which produce alkyl branches of varying lengths randomly spaced along the polyethylene backbone.²⁵

Recently, we have employed step polycondensation chemistry (the ADMET reaction) to generate precisely branched ethylene copolymers.^{26–31} Symmetrical α,ω -diene monomers (having built-in branches) are condensed into unsaturated polymers, which upon saturation generate precision branched polyethylenes.^{32,33} This approach circumvents the random nature of branching in polyethylene with the elimination of chain transfer and chain walking processes. The design of the symmetrical α,ω -diene monomer obviates the ethylene/ comonomer reactivity ratio problems and ensures the precise placement of branches along the polymer backbone. We are now able to prepare polymers where both the identity of the branch and its position are known without equivocation. Systematic alterations in branch identity and position on the polymer backbone can be made during monomer synthesis to yield predictable changes in physical properties.³¹

Linear polyethylene prepared via ADMET by polycondensation of 1,9-decadiene melts at 134 °C. Introduction of branches

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Scheme 2. Synthesis of Precisely Sequenced Polymers



onto the polyethylene backbone disrupts the crystallinity and results in a decrease in melting point.^{26,34} For example, insertion of butyl branches on every 21st carbon (i.e., 20 methylene carbons between consecutive branch points) generates a semicrystalline polymer that melts at 12 °C.²⁹ More frequent butyl branch placement on the polymer backbone can also be achieved with this technique to prepare polymers with lower melting points and, in some cases, amorphous materials (with as few as four methylene groups between branches).³⁵ A recently developed synthetic scheme for preparation of the symmetrical α, ω -diene monomer has been employed to decrease the total concentration of butyl branches by increasing the number of methylene carbons between the branch points from 20 to 38. This synthetic methodology yields a semicrystalline polymer that melts at 75

°C.³⁶ The thermal and morphological behavior of this polymer was compared to that of an ethylene/1-hexene copolymer having the same net concentration of butyl branches along the polymer backbone but prepared via chain polymerization with a metallocene catalyst.³⁷ Both polymers show the existence of (110) and (200) orthorhombic unit cell reflection planes, with the ADMET polymer having a sharper melting transition and narrower lamella thickness distribution.

Herein, we report the synthesis and the characterization of precisely sequenced polyethylenes containing 13 different branches, each being placed on every 39th carbon on the polymer backbone. This paper extends the scope of the precision polyethylene study to provide a better understanding for the effect of the branch identity on polymer properties.



Figure 1. (A) ¹H 500 MHz NMR spectra of monomer 8h-(hexyl), unsaturated 9h-(hexyl), and saturated 10h-(hexyl) polymers. (B) Olefinic region shown in higher magnification.

RESULTS AND DISCUSSION

A. Synthesis and Primary Structure Characterization of Precisely Branched Polymers. Successful preparation of symmetrical α, ω -diene monomers is the key in this research, where a multistep synthetic route was required for each monomer (8a–m). Scheme 1 illustrates the elaborate synthetic effort, which consisted of a six-step procedure including alkenyl bromide (5) preparation,³⁸ dialkylation of nitriles (6a–m),³⁹ and decyanation of alkylcyano α, ω -dienes (7a–m).⁴⁰

The spacing between the two consecutive branch points along the polyethylene backbone (see structures of polymers 10a-m in Scheme 2) was set in the dialkylation step of nitriles, where the alkenyl bromide run length (in this case 18 methylene units) played a crucial role. Systematic increase of run length from 9 to 18 required challenging purification steps. For example, in the dehydrohalogenation of alkyl dibromide (4) with *t*-BuOK, the crude mixture contained the desired alkenyl bromide (20-bromoicos-1-ene 5), the dielimination product, and unreacted starting material, all with close retardation factors by thin layer chromatography. Consecutive column chromatography passes and the relatively low room temperature solubility of compound 5 in hexane (used as an eluent for the separation) made the purification of the desired compound, 20-bromoicos-1-ene (5), tedious.

Alkenylation of nitriles 6a-m in the presence of lithium diisopropylamide (LDA) and 20-bromoicos-1-ene produced the alkylcyano α,ω -dienes 7a-m in high yields. Decyanation of nitriles 7a-m was achieved with potassium metal via radical chemistry. The resulting tertiary radical after decyanation was further quenched by abstraction of hydrogen from *t*-BuOH to give α,ω -diene monomers **8a-m** in moderate to high yields. Monomers 8a-m were condensed to form the corresponding unsaturated ADMET polymers (Scheme 2). Because of the relatively high melt viscosity of the resulting polymers (9a-m), the polymerization temperature was set to 85 °C. At that elevated temperature, Ru-based catalysts are prone to have low turnover numbers and to generate Ru–H species,⁴¹⁻⁴³ which would cause isomerization problems and disrupt the symmetrical nature of the monomer.^{44,45}

Therefore, monomers 8a-m were condensed to form unsaturated ADMET polymers using Schrock's [Mo] catalyst for clean metathesis chemistry. Because of the oxophilic nature of [Mo] catalysts, all the manipulations prior to polymerization and catalyst addition (catalyst to monomer ratio 1:500) were performed in a glovebox. Polymerization was initiated by melting the monomer at 50 °C, and the temperature was set to 85 °C to be able to stir the viscous polymer melt. After 24 h of reaction, the polymer was cooled to RT, another portion of [Mo] catalyst (catalyst to monomer ratio 1:500) was added in the glovebox, and the temperature was set back to 85 °C.

ADMET polymerization proceeded smoothly to give the desired unsaturated linear polymers 9a-m with no detectable side reactions. Disappearance of terminal olefin signals in ¹H NMR spectra (Figure 1) proved the complete conversion, which is necessary for any step-growth polymerization. Unsaturated polymers (9a-m) were hydrogenated using Wilkinson's catalyst (catalyst to monomer ratio 1:250) to yield the precision polyethylenes (polymers 10a-m) having branches from methyl to pentadecyl on every 39th carbon.

The polymerization and hydrogenation steps were followed by ¹H nuclear magnetic resonance (NMR) spectroscopy. As an example, Figure 1 illustrates the ¹H NMR spectra of hexyl branched polymer, **10h**-(**hexyl**), and its precursors. ADMET polymerization of monomer **8h-(hexyl)** yielded the unsaturated polymer, **9h-(hexyl)**. Formation of the ADMET polymer resulted in loss of the terminal olefin signals (5.0 and 5.8 ppm) and the appearance of the internal olefin at 5.4 ppm (Figure 1). Exhaustive hydrogenation of the internal olefins with Wilkinson's catalyst generated **10h-(hexyl)**, corresponding to polyethylene with hexyl branches on every 39th carbon, with complete loss of the olefinic signals in ¹H NMR.

Polymerization and hydrogenation of monomer **8h-(hexyl)** was also monitored with ¹³C NMR spectroscopy (Figure 2).



Figure 2. ¹³C 126 MHz NMR spectra of monomer 8h-(hexyl), unsaturated 9h-(hexyl), and saturated 10h-(hexyl) polymers.

Comparison of the ¹³C NMR spectra for the monomer **8h**-(**hexyl**) and unsaturated polymer **9h**-(**hexyl**) indicates the disappearance of the signals belonging to the terminal olefin at 114.31 and 139.44 ppm and formation of the new internal olefin (*cis* olefin at 130.12 ppm, minor product, and *trans* olefin at 130.58 ppm, major product) generated by the metathesis chemistry. Hydrogenation of the internal olefin with Wilkinson's catalyst yielded the saturated polymer **10h**-(**hexyl**) with no detectable trace of olefins.

Infrared (IR) spectroscopy was also used to monitor this transformation (Figure 3). Disappearance of the out-of-plane C-H bend absorption at 969 cm^{-1} indicates the complete



Figure 3. Infrared spectra of the precisely branched polymers 10a-(methyl), 10b-(ethyl), 10c-(propyl), 10d-(iso-propyl), 10e-(butyl), 10f-(iso-butyl), 10g-(pentyl), 10h-(hexyl), 10i-(heptyl), 10j-(octyl), 10k-(nonyl), 10l-(decyl), 10m-(pentadecyl), and ADMET PE.

absence of C=C in the polymer backbone and proves the full conversion for the hydrogenation step.

After hydrogenation, solutions of saturated polymers were concentrated and precipitated into methanol. It is important to note that the solubility characteristics of polymers **10a-m** (soluble in toluene, dichlorobenzene, trichlorobenzene, etc., at high temperatures) are similar to those of polyethylenes prepared by chain polymerization. Molecular weight data were obtained using high temperature gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 135 °C relative to polystyrene standards. Table 1 illustrates the weight-average molecular weights for the precisely branched unsaturated and saturated polymers.

Table 1. Molecular Weights and Thermal Data for Precisely Branched Polymers

			$\overline{M}_{ m w} \; (m kg/mol)^a \; (m PDI^b)$	
branch identity on every 39th carbon	T _m (°C) (peak)	$\frac{\Delta H_{\mathrm{m}}}{(\mathrm{J/g})}$	unsaturated	saturated
no branch	134	211	70.2 (2.7)	70.2 (2.7)
methyl	92	137	33.7 (2.2)	92.7 (2.0)
ethyl	76	93	56.7 (2.2)	53.1 (2.4)
propyl	78	71	217 (3.1)	225 (3.0)
isopropyl	77	74	107 (2.0)	144 (3.5)
butyl	75	66	60.2 (2.3)	66.5 (2.5)
isobutyl	73	51	22.6 (2.5)	54.8 (2.4)
pentyl	74	88	29.3 (2.2)	30.2 (2.0)
hexyl	73	85	30.5 (2.3)	30.5 (1.9)
heptyl	74	85	76.6 (3.0)	74.2 (2.9)
octyl	74	73	200 (3.6)	181 (3.3)
nonyl	73	84	35.9 (2.4)	34.3 (2.2)
decyl	71	76	28.0 (2.4)	27.7 (1.8)
pentadecyl	70	83	58.0 (2.4)	55.9 (2.4)
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"Molecular weight data were collected by GPC in 1,2,4-trichlorobenzene at 135 °C relative to polystyrene standards. ^bPDI, polydispersity index $\overline{M}_w/\overline{M}_n$.

Control over the primary structure of the final precision polymer is governed by the precision established on the molecular level. The purity of the monomers and the absence of any side reactions during the polymerization ensure the successful polycondensation chemistry and the level of control. Upon close inspection of the ¹³C NMR data for the polymers, it can be concluded that the branches are precisely placed along the polyethylene backbone with none of the undesired branches due to chain transfer typically observed during chain-growth chemistry. As an example, Figure 4 shows a portion (10-55 ppm) of the ¹³C NMR spectra for precise polymers having branches from methyl to propyl. All spectra are dominated by a singlet at 29.99 ppm corresponding to methylenes on the main polyethylene chain. Note that the presence of alkyl branches precisely placed along the main chain affects the chemical shifts of carbons located within three CH₂ units from an individual branch.²⁶

In the spectrum for **10a**-(**methyl**), which is polyethylene containing methyl branches on every 39th backbone carbon (Figure 4A), the resonances belonging to the methyl branch, 19.84 ppm, as well as main chain carbons, 37.45, 27.98, 30.34, and 29.99 ppm and the carbon at the branch point (33.12 ppm) indicate that only methyl branches are present, in good agreement with previously reported²⁶ experimental data and predicted values.⁴⁶



Figure 4. Comparison of ¹³C NMR spectra for precision polymers (A) 10a-(methyl), (B) 10b-(ethyl), and (C) 10c-(propyl).

Introduction of ethyl branches changes the chemical shifts of both backbone and side chain carbons (Figure 4B). The terminal methyl carbon is now more shielded by the presence of a methylene unit, which results in a predictable shift upfield (11.19 ppm). On the other hand, the methine carbon is deshielded with more electron delocalization and shifts downfield (39.41 ppm) compared to the methyl branched polymer. All the chemical shifts shown in Figure 4B for the polymer **10b**-(ethyl) are in good agreement with previously reported ethylene/1-butene and hydrogenated polybutadiene systems.

In the spectrum for **10d-(propyl)** (Figure 4C), the resonances belonging to the propyl branch, 14.55, 20.20, and 36.66 ppm, as well as main chain carbons, 34.25, 27.16, 30.49, and 29.99 ppm and the methine carbon (37.70 ppm) indicate that only propyl branches are present, in good agreement with previously reported data on chain-growth polymers obtained by copolymerization of ethylene with 1-pentene.^{51–53}

B. Melting Behavior of Precisely Branched Polymers. Figures 5 and 6 present the differential scanning calorimetry



Figure 5. Differential scanning calorimetry thermograms for second heating cycles of ADMET PE, 10a-(methyl), 10b-(ethyl), 10c-(propyl), 10d-(iso-propyl), 10e-(butyl), and 10f-(iso-butyl) with 10 °C/min heating rate.



Figure 6. Differential scanning calorimetry thermograms for second heating cycles of precision polymers 10g-(pentyl), 10h-(hexyl), 10i-(heptyl), 10j-(octyl), 10k-(nonyl) and 10l-(decyl), and 10m-(pentadecyl) with 10 °C/min heating rate.

(DSC) thermograms of linear **ADMET PE** and precise polymers having branches from methyl to pentadecyl increasing in both length and bulkiness.

It is immediately obvious that methyl branching significantly reduces the melting point of ADMET polyethylene. On the other hand, all further branches, from ethyl to pentadecyl, produce polymers that have very similar (in some cases identical) melting points. As discussed further below, this behavior may be attributed to a change in morphology from a situation where the methyl branch is incorporated into the polymer crystal to one where larger branches are expelled from the crystal. It is important to note that the ethyl branch is incorporated into the polymer crystal when the branches are placed on every 21st carbon.³¹ Increasing the distance between two consecutive branches from 20 carbons (10.0 mol % α olefin incorporation) to 38 carbons (5.26 mol % α -olefin incorporation) expels the ethyl branches from the crystal lattice into the amorphous phase. Similar observations were also reported for chain polymerized ethylene/1-butene copolymers, where the ethyl branch is mostly found in the amorphous region.9,54

As shown in Figure 5, unbranched **ADMET PE** displays thermal behavior virtually the same as that of high density polyethylene ($T_{\rm m} = 134$ °C, $\Delta H_{\rm m} = 211$ J/g). Incorporation of

methyl branches precisely placed on every 39th carbon, polymer 10a-(methyl), disrupts the crystal structure and decreases the melting temperature to 92 °C and the enthalpy of fusion to 137 J/g. A similar trend is observed when the branch is an ethyl group, 10b-(ethyl); the melting point decreases below that of 10a-(methyl) $(T_m = 76 \text{ }^\circ\text{C} \text{ with a heat})$ of fusion $\Delta H_{\rm m}$ = 93 J/g). Depression of both the melting temperature and the heat of fusion suggests a reduction of crystal thickness for polymer 10b-(ethyl). Transmission electron microscopy (TEM) measurements of solution-grown single crystals for polymer 10b-(ethyl) also support this observation (see section C). Extension of the branch size from ethyl to propyl, 10c-(propyl), does not lead to further decreases in melting temperature and enthalpy of fusion ($T_m =$ 78 °C and $\Delta H_{\rm m}$ = 71 J/g). Similar melting behavior is observed for precision polyethylene possessing longer branches (Figure 7).



Figure 7. Effect of branch identity on melting point and heat of fusion.

Incorporation of defects in polyethylene crystal along with the melting behavior of chain-polymerized ethylene copolymers has been extensively studied.^{9,15,54} Alamo et al. reported that only small groups, such as CH₃, Cl, O, and OH, are incorporated into the crystal lattice, whereas the bigger defects are expelled from the crystal.⁹ Hosoda et al. prepared various ethylene/ α -olefin copolymers with a vanadium catalyst system.⁵⁴ They determined that the probability of branch inclusion into the crystal is strongly dependent on branch identity and is in the order of methyl > ethyl > butyl = hexyl = decyl > isobutyl. Interestingly, ethylene/1-octene and ethylene/ 1-dodecene copolymers reported by the same group with 5.14 and 4.54 mol % α -olefin incorporation ratios exhibit melting points (70-75 °C) very similar to those of precision polymers 10h-(hexyl) and 10l-(decyl) with 5.26 mol % α -olefin incorporation. More recently, Hosoda et al. compared the melting behavior of precision polymer 10e-(butyl) with the ethylene/1-hexene copolymer having the same net concentration of butyl branches along the polymer backbone but prepared via chain polymerization with a metallocene catalyst.³⁷ The melting profile of polymer 10e-(butyl) displays a melting curve at 75 °C with width less than 20 °C. Even though the two polymers have the same net concentration of butyl branches, ethylene/1-hexene copolymer melts over a broader range from 50 to 105 °C with a melting point of 99 °C. The distinctly different melting behavior of these polymers was attributed to

the broader lamella thickness distribution of chain-polymerized ethylene/1-hexene copolymer due to random positioning of butyl branches along the polymer backbone.³⁷

C. Morphology and Crystal Structure Determination of Precisely Branched Polymers. Wide-angle X-ray and selected area electron diffraction measurements further support the observation of a change in unit cell as a function of branch size. WAXD diffractograms of precision polymers having branches from methyl to pentadecyl are shown in Figures 8 and 9.



Figure 8. Wide-angle X-ray diffraction (WAXD) patterns for precision polymers **10a-(methyl)**, **10b-(ethyl)**, **10c-(propyl)**, **10d-(iso-propyl)**, **10e-(butyl)**, **10f-(iso-butyl)**, and **ADMET PE** obtained at RT. Prior to data acquisition, all samples were heated to 20 °C above the melting temperature of each polymer to remove the thermal history and then cooled to room temperature at a rate of 50 °C/min.

WAXD data were collected using the Cu K α radiation (λ = 0.154 17 nm) induced by a generator operating at 40 kV and 150 mA. Diffraction patterns were recorded for 2(theta) values ranging from 10° to 40°. The peak at 38.5° observed in all WAXD diffractograms is the (111) reflection of the Al cubic closed packed structure. Aluminum foil was used to sandwich the polymer sample between copper holders.

For the sake of comparison, **ADMET PE** is displayed at the bottom of Figure 8. It exhibits the typical orthorhombic crystal structure (lattice parameters a = 7.40 Å, b = 4.93 Å, and c = 2.54 Å) with two characteristic crystalline peaks, exactly the same as for high density polyethylene made by chain propagation chemistry.⁵⁵ The more intense peak at scattering angle 21.7° and the less intense one at 24.0° correspond to reflection planes (110) and (200), respectively.

Introduction of precisely placed methyl branches on every 39th carbon (see polymer 10a-(methyl) in Figure 8) disturbs



Figure 9. Wide-angle X-ray diffraction patterns for precision polymers 10g-(pentyl), 10h-(hexyl), 10i-(heptyl), 10j-(octyl), 10k-(nonyl), 10l-(decyl), and 10m-(pentadecyl) obtained at RT. Prior to data acquisition, all samples were heated to 20 °C above the melting temperature of each polymer and then cooled to room temperature at a rate of 50 °C/min.

the unit cell of ADMET PE and shifts the two strong scattering peaks to 21.1° and 23.0°, corresponding to (110) (d = 4.19 Å) and (200) (d = 3.87 Å) reflection planes with lattice parameters a = 7.74 Å and b = 5.00 Å. An expansion of the unit cell by 4.6% and 1.4% along the *a*- and *b*-axes proves the distortion in the orthorhombic unit cell governed by the incorporation of the methyl branches in the unit cell. A similar expansion in unit cell parameters was also reported for ethylene/propylene copolymers prepared via chain polymerization, thus confirming the methyl branch inclusion into the unit cell.¹¹ In the case of the ethyl branched polymer 10b-(ethyl), WAXD and electron diffraction data suggest the existence of the orthorhombic crystal structure with lattice parameters of a = 7.58 Å and b =4.98 Å. WAXD diffractograms of precision polymers having branches larger than ethyl (from propyl to pentadecyl) show nearly identical scattering patterns, indicating the formation of the orthorhombic crystal structure.

To better understand these observations, the scattering angles of two strong diffraction peaks are plotted as a function of branch identity in Figure 10. The decrease of scattering angles for methyl branched polymer **10a-(methyl)** indicates the larger *d*-spacing between the diffraction planes, suggesting the inclusion of the methyl branches into the unit cell. A clear structural change for polymers ranging from **10b-(ethyl)** to **10l-(decyl)** is evidenced by the increase of scattering angles, confirming the exclusion of branches from the unit cell. It is important to note that precision polymer **10m-(pentadecyl)**



Figure 10. Scattering angles of two strong reflections for alkyl branched precision polymers. The blue line corresponds to reflection at higher angle, while the black line corresponds to reflection at lower angle.

exhibits a distinct morphological behavior, in which the relatively long pentadecyl branch presumably cocrystallizes with the main polymer chain, thereby increasing the *d*-spacing between the diffraction planes. Cocrystallization of branches longer than 10 carbon atoms in length with the main chain was previously reported for chain polymerized polyolefins.⁵⁶

An interesting aspect of the WAXD patterns for the precision polymers ranging from 10b-(ethyl) to 10m-(pentadecyl) is that the 19.6° peak, which is sharper than that of the amorphous halo, suggests the possible coexistence of a dominant orthorhombic crystal and another metastable crystal structure as a minor component. Selected area electron diffraction (SAED) measurements on solution-grown polymer 10b-(ethyl) crystals confirm the formation of a monoclinic crystal with lattice parameters of a = 8.04 Å, c = 4.80 Å, and $\beta =$ 109.4°. The metastable monoclinic polyethylene structure was previously reported by Seto⁵⁷ with unit cell parameters a = 8.08Å, b = 2.54 Å, c = 4.79 Å, and $\beta = 107.9^{\circ}$. Please note that the notation of crystallographic directions for the monoclinic crystal structure differs from the orthorhombic case. Here the crystalline *b*-direction is the direction parallel to the polymer chain.

Formation of monoclinic crystalline phase is known for chain-polymerized ethylene/ α -olefin copolymers (having branches larger than methyl) with high comonomer content.⁵ Hu et al. reported ethylene/1-butene and ethylene/1-octene copolymers with α -olefin concentrations ranging from 7.50 to 19.7% prepared with single site metallocene catalyst.⁵⁸ Monoclinic crystals were found to coexist with the dominant orthorhombic crystalline phase for polymers having comonomer content higher than 9.00 mol %. The authors proposed that the formation of monoclinic crystals is strongly dependent on the nature of the crystalline-amorphous interface.58 Polymers with high comonomer content display low crystallinity by populating the crystalline-amorphous interfacial area and favor the formation of monoclinic crystals. It is interesting that the precision polymers discussed here also exhibit monoclinic crystals even with 5.26 mol % comonomer incorporation. Because the defects larger than methyl are expelled from the crystal, they presumably "agglomerate" at the fold surface of the crystal. This might lead to a packing problem

Table 2. Observed WAXD and SAED Lattice Plane Distances for 10a-(methyl) and Their Corresponding Allocation to Orthorhombic and Monoclinic Crystal Planes ^a					
$WAXD_{obs} d [Å]$	SAED _{obs} d [Å]	intensity _{obs} WAXD/SAED	index (<i>hkl</i>)	$d_{(hkl)calc}$ [Å]	

$WAXD_{obs} d [A]$	$SAED_{obs} d [A]$	intensity _{obs} WAXD/SAED	index (<i>hkl</i>)	$d_{(hkl)calc} [A]$
4.58	4.61	w/s	(001)mono	4.58
4.19	4.19	vs/vs	(110)ortho	4.20
3.87	3.88	s/s	(200)ortho/(200)mono	3.88/3.87
3.58	3.62	w/s	(-201)mono	3.60
2.50	2.52	w/s	(020)ortho/(201)mono	2.50/2.57
^a Abbreviations: obs, observed; calc, calculated; mono, monoclinic; ortho, orthorhombic; w, weak; s, strong; vs, very strong.				

with too high a density of bulky defects and finally cause the crystal lattice to shear to a metastable, in this case, monoclinic lattice. There should be a limit in metastable crystal phase formation for precisely branch polyethylene structures. That limit was recently reached by positioning branches on every 75th carbon (2.70 mol % comonomer incorporation) where the butyl branches are fully expelled from the crystalline phase, yielding pure orthorhombic crystals with none of the metastable crystal structure formation.⁵⁹

SAED measurements were performed for solution-grown crystals of precision polymer **10a-(methyl)**. Along with the orthorhombic crystalline phase, monoclinic crystals were also found with lattice parameters a = 8.22 Å, c = 4.85 Å, and $\beta = 109.3^{\circ}$. Table 2 illustrates WAXD and SAED analysis of polymer **10a-(methyl)**. A strong reflection corresponding to a *d*-spacing of 4.19 Å indicates that the orthorhombic crystal structure is the dominant form. However, some of the single crystals show a nonorthorhombic electron diffraction pattern which can be indexed as a monoclinic unit cell. Methyl branches in chain-polymerized ethylene/1-propene copolymers drive the change of orthorhombic crystal toward a hexagonal/rotator crystalline phase instead of monoclinic phase.¹⁰ Observation of this unusual behavior in precision polymer **10a-(methyl)** is subject to further investigation.

Figure 11 shows the TEM images of solution-grown single crystals for precision polymers and ADMET PE. Lozenge-



Figure 11. Transmission electron microscopy (TEM) micrographs of (1) ADMET PE, (2) 10a-(methyl), (3) 10b-(ethyl), (4) 10c-(propyl), (5) 10e-(butyl), (6) 10g-(pentyl), (7) 10h-(hexyl), (8) 10i-(heptyl), (9) 10j-(octyl), (10) 10k-(nonyl), (11) 10l-(decyl), and (12) 10m-(pentadecyl). ADMET PE crystals were grown from 0.03 wt % C₂Cl₄ solution, and all the other polymer single crystals were grown from 0.03% *o*-xylene solution.

shaped rhombohedral single crystals were observed for all polymers, consistent with previous reports on solution-grown HDPE single crystals.^{3,4} It is noteworthy that, although the crystallization conditions were similar for all the branched polymers, the morphology of solution-grown crystals changed based on the branch size.

Besides the ADMET PE single crystals, which clearly show secondary nucleation via screw dislocations, only the single crystals of polymer **10a-(methyl)** exhibit secondary nucleation. This may be an indication of a well-defined crystalline fold surface and hence the incorporation of methyl branches into the polymer crystal.

The lamella thicknesses of the solution-grown single crystals were determined using energy-filtered TEM measurements.^{60,61} Taking two consecutive images from the same TEM sample, one with the slit positioned at the zero-loss peak and one without the slit, yielded two images, the elastically filtered image I_0 and the inelastic image I_t . After aligning both images for possible sample drift, the relative thickness, t, at each point of the images was given by $t/\lambda = \ln(I_0/I_t)$, in which λ is the mean free path of the respective material for the respective electron energy (200 kV). Calculation of the mean free path scales the image to an absolute thickness mapping.⁶¹ Table 3 illustrates such single crystal lamella thicknesses of **ADMET PE** and precision polymers.

Table 3. Lamellae Thicknesses of ADMET PE and Precision Polymers Determined by TEM

polymer	thickness (nm)	polymer	thickness (nm)
ADMET PE	9.75	10i-(heptyl)	4.39
10a-(methyl)	7.09	10j-(octyl)	4.06
10b-(ethyl)	4.79	10k-(nonyl)	4.67
10e-(butyl)	4.25	10l-(decyl)	4.16
10g-(pentyl)	5.03	10m-(pentadecyl)	5.33
10h-(hexyl)	4.17		

Methyl branching reduces the lamella thickness of unbranched polyethylene; on the other hand, all further branches produce polymers that have very similar lamella thicknesses. Single crystal thickness data provide good evidence for the positioning of branches. Assuming the all-trans conformation of methylene units in the crystalline phase (lattice constant c = 2.54 Å), the distance between the two consecutive branch points (38 methylene units) can be estimated to be 4.8 nm. The length matches quite well with the observed crystal thickness of polymer **10b**-(**ethyl**) and precision polymers having branches longer than ethyl, suggesting the exclusion of such branches from the crystal phase. However, the single crystal thickness of polymer **10m**-(**pentadecyl**) is slightly increased to a value of ~5.3 nm, which

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onto the crystal surface. Solution-grown single crystal lamella thickness measurements provide additional evidence of a clear change in the morphology of these polymers from a situation where the methyl branch is incorporated into the solution-grown single crystal to one where branches of greater mass are mostly expelled from the crystal.

CONCLUSIONS

Metathesis polycondensation chemistry has been employed to control the crystalline morphology of a series of 13 precision branched polyethylene structures, the branch being placed on every 39th carbon and varying in size from methyl to pentadecyl. The primary structures of both monomers and polymers have been confirmed via ¹H NMR, ¹³C NMR, and IR spectroscopy to prove the purity of the monomers and the absence of any undesired side reactions during polycondensation and hydrogenation steps. Methyl branches, being incorporated into the polymer crystal, decrease the melting point and the heat of fusion of ADMET PE. On the other hand, increasing the size of the branch to ethyl and larger yields a set of polymers with a completely different morphology, with the branches mostly expelled from the polymer crystal. WAXD patterns of melt-grown crystals and lamella thicknesses of the solution-grown single crystals also support this argument.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for all monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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