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Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Pushing the Limits toward Longer Run Lengths

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S *Supporting Information*

ABSTRACT: A symmetrical α,ω-diene monomer with a 36 methylene run length was synthesized and polymerized, and the unsaturated polymer was hydrogenated to generate precision polyethylene possessing a butyl branch on every 75th carbon (74 methylenes between branch points). The precision polymer sharply melts at 104 °C and exhibits the typical orthorhombic unit cell structure with two characteristic wide-angle X-ray diffraction (WAXD) crystalline peaks observed at 21.5° and 24.0°, corresponding to reflection planes (110) and (200), respectively.

Polyethylene prepared via step growth polymerization chemistry (the ADMET reaction) has recently proved to generate unique macromolecular structures for morphological examination of polyolefins.[1−4] These polymers, while structurally akin to copolymers made via chain copolymerization of ethylene and vinyl comonomers, have unique properties, because use of symmetrical α,ω-diene monomers ensures the precise spacing of chain branches.[5−8] Systematic alterations in branch identity and position on the polymer backbone are made during monomer synthesis to yield predictable changes in packing behavior and lamella thickness.

ADMET polyethylene prepared by polycondensation of 1,9-decadiene compares well with chain-polymerized commercial high density polyethylene. (Both preparations melt at 134 °C and form orthorhombic unit cells.) Introduction of pendant alkyl moieties onto the polyethylene backbone disrupts the crystallinity and results in a decrease in melting point.[1] For example, insertion of butyl branches on every 39th carbon generates a semicrystalline polymer that melts sharply at 75 °C.[7] The thermal and morphological behavior of this polymer was recently compared to that of a copolymer of ethylene and 1-hexene having the same net concentration of butyl branches along the polymer backbone (although not regularly spaced) prepared via chain polymerization with a metallocene catalyst.[9] Both polymers have orthorhombic unit cells, but the ADMET polymer has a sharper melting transition and narrower lamella thickness distribution. On the other hand, more frequent branch placement in ADMET polyethylene generates polymers with lower melting points and in some cases amorphous materials (with as few as 4 methylene groups between branches). Because this behavior diminishes the possibility of systematic comparisons of ADMET polyethylene with frequent branches with chain-polymerized commercial polyethylene, we are now focusing on the preparation of polymers with less frequent branch placement.

Key to success in this research is the preparation of a symmetrical diene monomer, such that the built-in branch run length strictly dictates the spacing between the two consecutive branch points. Previous publications from our laboratory have reported the successful preparation of polyethylene with precise 38 methylene carbon run lengths (i.e., a branch being placed on every 39th carbon along the polyethylene backbone).[7]

Herein, we report the synthesis and characterization of precision polyethylene possessing a butyl branch on every 75th carbon (74 methylenes between branch points). Primary structure characterization and morphological examination by wide-angle X-ray diffraction (WAXD) analysis are also reported in this communication.

A multistep synthetic route is necessary for the preparation of a symmetrical diene monomer (**11**). Figure 1 illustrates the elaborate synthetic effort, which consists of a nine-step procedure including alkenyl bromide (**8**) preparation[10] from 10-undecenol (**1**), which is a renewable feedstock derived from castor oil,[11] dialkylation of hexanenitrile (**9**),[12] and decyanation of alkylcyano α,ω-diene (**10**).[13] The spacing between the two consecutive branch points along the polyethylene backbone (see structure of polymer **13** in Figure 1) is set in the dialkylation step of hexanenitrile, where the alkenyl bromide run length (in this case 36 methylene units) plays a crucial role. The systematic increase of run length from 9 to 36 requires challenging purification steps. For example, in the dehydrohalogenation of alkyl dibromide (**4**) with *t*-BuOK, the crude mixture contains 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. The situation is even more complicated for dehydrohalogenation of alkyl dibromide (**7**), where the polarity difference within the crude mixture becomes almost unnoticeable as the number of methylene units is doubled. Silica gel with a small particle size distribution (5−20 μm) was selected for the column separation. Consecutive column chromatography passes, and the relatively low room temperature solubility of compound **8** in hexane (used as an eluent for the separation) made the purification of the desired compound, 38-bromooctatriacont-1-ene (**8**), tedious.

Dialkylation of hexanenitrile (**9**) is the other challenging step in this synthesis route. Because of the low solubility of **8** in THF at low temperatures, the traditional procedure (i.e., addition of base at −78 °C and alkylation at 0 °C) for nitrile alkylation was not followed, and 50 °C was selected as the reaction temperature. The elevated temperature increased the likelihood of undesired

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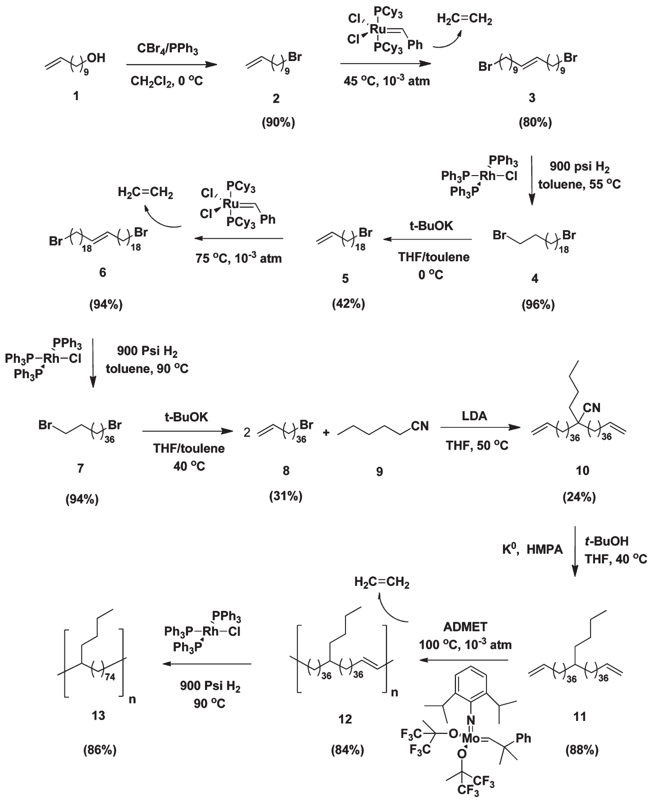


Figure 1. Synthetic scheme for the synthesis of polymer **13**.

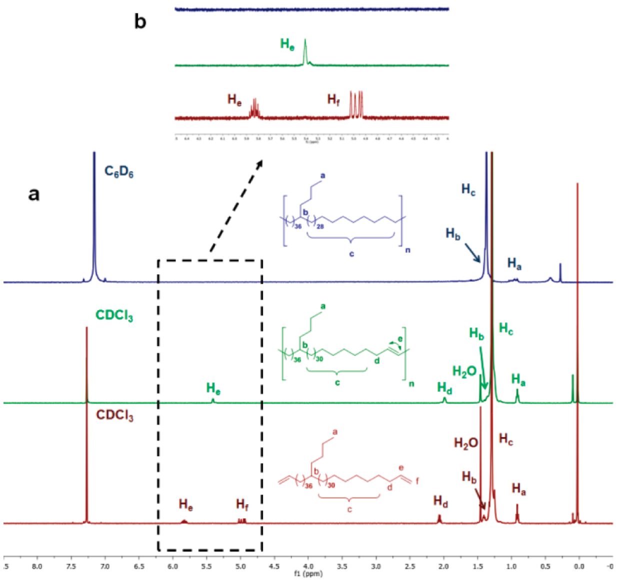
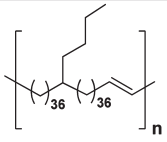
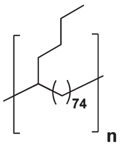


Figure 2. (a) ^{1}H NMR spectra of monomer (**11**), unsaturated (**12**), and saturated (**13**) polymers. (b) Olefinic region shown in higher magnification.

Table 1. Molecular Weight Data for Polymers 12 and 13

polymer	M_n(g/mol)[a]	M_w(g/mol)[a]	PDI[b]
 12	16300	46700	2.86
 13	17700	50200	2.83

[a] Molecular weight data were collected by GPC in 1,2,4-trichlorobenzene at 135 °C relative to polystyrene standards. [b] PDI, polydispersity index (M_w/M_n).

side reactions, such as alkyl bromide elimination. After the purification of 2-butyl-2-(octatriacont-37-en-1-yl)tetracont-39-enenitrile (**10**), the decyanation step gave 39-butylheptahepta-conta-1,76-diene (**11**) in a reasonably high yield.

Because of the relatively high melting point of monomer **11** (T_m = 77 °C), the polymerization temperature was 100 °C where Ru-based catalysts are prone to have low turnover numbers and to generate Ru−H species,[14−16] which would cause isomerization problems and disrupt the symmetrical nature of the monomer.[17,18] Therefore, monomer **11** was condensed to form an unsaturated ADMET polymer using Schrock's [Mo] catalyst for clean metathesis chemistry. The disappearance of terminal olefin signals in ^{1}H NMR spectra (see Figure 2) proves complete conversion, which is necessary for any step-growth polymerization.

The desired unsaturated linear polymer (**12**) was isolated with no detectable side reactions and hydrogenated utilizing Wilkinson's catalyst to yield the precision polyethylene (polymer **13**) possessing a butyl branch on every 75th carbon. Figure 2 illustrates the saturation of internal olefins in an unsaturated polymer (**12**) with complete loss of ^{1}H NMR olefin signals. Total hydrogenation is also evidenced by infrared spectroscopy, as confirmed by the complete loss of the alkene C−H out-of-plane bending peak at 967 cm^{-1}. It is important to note that the solubility characteristics of polymer **13** (soluble in toluene, dichlorobenzene, trichlorobenzene, etc. at high temperatures) are similar to those of polyethylene prepared by chain polymerization. Molecular weight data were obtained using high temperature GPC in 1,2,4-trichlorobenzene (Table 1).

Figure 3 shows the DSC thermograms of the unsaturated and saturated polymers in both the second heating and cooling cycles. The polymers are semicrystalline, having the melting transitions at 95.5 and 104 °C, and as expected, saturation increases both the melting points and the heat of fusion values. The melting transitions of both polymers are sharper than those for chain-polymerized poly(ethylene-*co*-hexene) and other ethylene/α-olefin copolymers, illustrating the importance of precision placement of the branches.[19−21]

Thermal data for polymer **13** and other previously reported precision polyethylenes with more frequent butyl branches[6] (Table 2) clearly demonstrate the effect of precision run length in these materials. As the run length increases between two consecutive branch points, the melting point gradually increases, approaching that of ADMET PE (linear PE without branches, T_m = 134 °C). Experimental data in butyl branched precision polymers were compared with theoretical predictions for infinitely long polyethylene interpreted by Flory.[22] A plot of melting

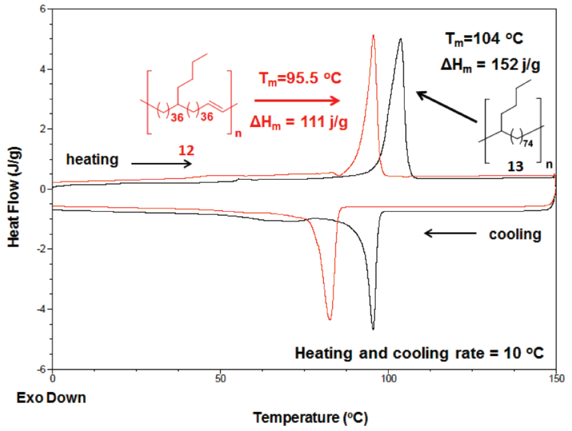


Figure 3. DSC exotherms (down) and endotherms (up) for unsaturated (**12**) and saturated (**13**) polymers.

Table 2. DSC Data for Precision Polyethylenes Possessing Butyl Branch

butyl branch on every *n*th carbon, *n*	butyl branches per 1000 carbon atoms	T_m (°C)	ΔH_m (J/g)
5	200	amorphous	--
15	67	−33	13
21	48	14	47
39	26	75	66
75	13	104	152
ADMET PE	0	134	204

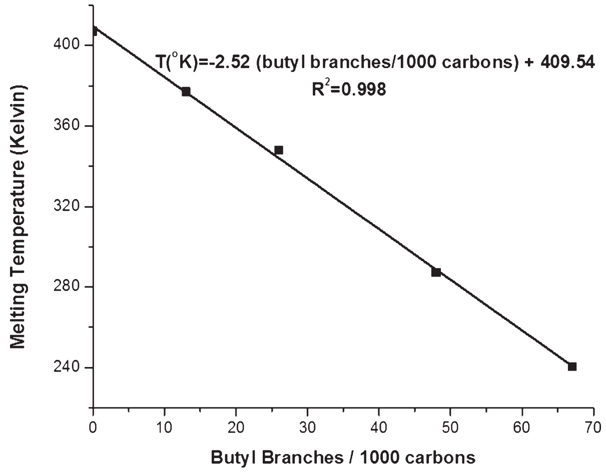


Figure 4. Plot of melting temperature vs butyl branch frequency in precision polyethylenes.

point vs number of butyl branches per 1000 carbons in butyl branched precision polymers (Figure 4) shows good linearity, an indication of the similarity in thermal behavior between ADMET PE and infinitely long PE.

Morphological examination by WAXD is illustrated in Figure 5 for polymer **13**, ADMET PE, and commercial High Density Polyethylene (HDPE) made with Ziegler−Natta catalyst. The similarity of polymer **13** to ADMET PE and HDPE is obvious: all three polymers exhibit the typical orthorhombic unit cell structure with two characteristic crystalline peaks observed at 21.5° and 24.0°, corresponding to reflection planes (110) and (200), respectively. Orthorhombic packing suggests the exclusion of the butyl branch from the unit cell, consistent with the previously documented measurements on the chain-polymerized poly(ethylene-*co*-hexene) copolymer.[9] Transmission Electron Microscope (TEM) measurements are underway to better understand the morphology of polymer **13**.

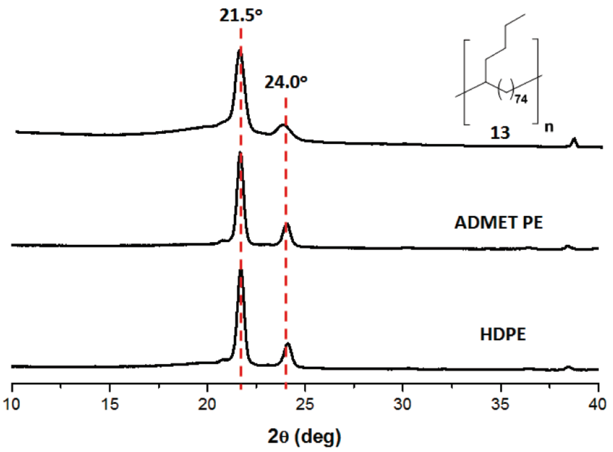


Figure 5. WAXD diffractograms of precision polymer (**13**), ADMET PE, and commercially available High Density Polyethylene (HDPE) prepared with Ziegler−Natta catalyst. Data were collected at 30 °C for all polymer samples.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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