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Reducing Branch Frequency in Precision Polyethylene

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Introduction. Recently we have been examining the structure of polyethylene made via polycondensation chemistry (the ADMET reaction), precisely placing a variety of branches along the polymer backbone. This approach generates polymers where both the identity of the branch and its position along the chain are known without equivocation.[1−6] The work has extended well beyond primary structure delineation, in some cases to morphological structure determination. We now can correlate precision changes in primary structure with predictable alterations in morphology, shifting crystal unit cells from orthorhombic to triclinic, for example.[7,9]

An important limitation in our work relates to the synthesis of the symmetrically disposed diene monomers required in this chemistry. Spacing in the symmetrical monomer directly determines precision run lengths in the polymer; prior monomer synthetic schemes have limited the maximum run lengths between branch points along the polymer to 20 methylene carbons (i.e., a branch placed on each and every 21st carbon along polyethylene's backbone).[2,4,6] While we have been able to examine polymers with *more frequent branch placement* (as frequent as every fifth carbon, for example),[8] producing ADMET polyethylene with *less frequent branch placement* had escaped our efforts. Less frequent branching would allow us to generate model polymers more reflective of commercial polyethylene, whose structure has been studied via more conventional methodology for decades.[10,11]

We now report the synthesis and characterization of precision polyethylene possessing a butyl branch on every 39th carbon (38 methylenes between branch points). Complete primary structure characterization is included in this Communication, as is the first morphological examination by wide-angle X-ray diffraction (WAXS) analysis. Success is the result of having devised a reproducible monomer synthesis scheme,[12−14] one that appears to offer potential for stepwise increases of this number (74 methylenes between branch points, 146 methylenes between branch points, and so on). This study will open new horizons in precision polyethylene research in two aspects: the frequency of the branch appearance would be a more realistic mimic of industrially synthesized polyethylene (especially for random ADMET models, easily made by ADMET copolymerization) and will permit the synthesis of polymers with even longer branches than has been done so far. In particular, we are targeting to model metallocene polyethylene[15−20] in this research.

Table 1. DSC Data for Fully Hydrogenated ADMET Polyethylene Butyl Branched Model Polymers

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
ADMET PE	0	134	204

Unbranched ADMET polyethylene, made by polycondensation chemistry, compares well with commercial polyethylene generated by chain polymerization. For example, ADMET polyethylene containing no branches displays thermal behavior virtually the same as that of high-density polyethylene[21] (T_m = 134 °C, ΔH_m = 204 J/g). The crystalline unit cell is orthorhombic. Placing butyl branches on every 21st carbon generates a semicrystalline polymer that sharply melts at 14 °C.[6] In this present research we now see that just increasing the precision run length between butyl branch points from 20 carbons to 38 carbons results in a semicrystalline polymer that melts at 75 °C. Table 1 provides a set of comparable data for a series of precision butyl branched polymers.

Results and Discussion. Establishing a viable synthetic route to the required symmetrical diene monomer is the key to success. Figure 1 shows this synthesis, which consists of a six-step procedure involving alkenyl bromide (**5**) preparation,[12] dialkylation of hexanenitrile (**6**),[13] and decyanation of alkylcyano α,ω-diene (**7**).[14] *What is important to note in this scheme is the flexibility it offers.* For example, if longer precision run lengths are desired, then molecule **5** can be "recycled" in the scheme, replacing molecule **2**; further transformations would then lead to a systematic increase of the spacer length between branch points.

Most of these reactions are almost quantitative, except for the dehydrohalogenation of alkyl dibromide (**4**) and the dialkylation of hexanenitrile (**6**). For the dehydrohalogenation step, 1.4 equiv of base (in this case *t*-BuOK) is used to suppress (but not eliminate entirely) the formation of the dielimination product. Dehydrohalogenation of the dibromide statistically generates mono- and dielimination products and unreacted starting material with close R_f thin layer chromatography values. The desired monoelimination product, 20-bromoicos-1-ene (**5**), is purified via consecutive column chromatography passes. Dialkylation of hexanenitrile (**6**) is a particularly challenging step in this synthetic route. The melting point of compound **5** (T_m = 32 °C) limits the use of cannula wires and syringes, which are techniques needed to fulfill the anhydrous conditions necessary to keep the right stoichiometric ratio of lithium diisopropylamine (LDA) to alkyl bromide during the addition of alkylating agent. The dialkylated premonomer, 2-butyl-2-(icos-19-enyl)docos-21-enenitrile (**7**), is purified from monoalkylated adduct via challenging consecutive column chromatography experiments.

Formation of monoalkylated nitrile and several steps in the purification procedure decreased the yield as low as 19%. In order to increase the yield, the alkylation procedure was modified to fulfill anhydrous conditions. This modification enabled quantitative dialkylation of the nitrile without formation of the monoalkylated adduct (yield = 98%). Only one column chromatography experiment was adequate to purify compound **7**. Finally, decyanation of **7** gave monomer **8** in a quantitative yield.

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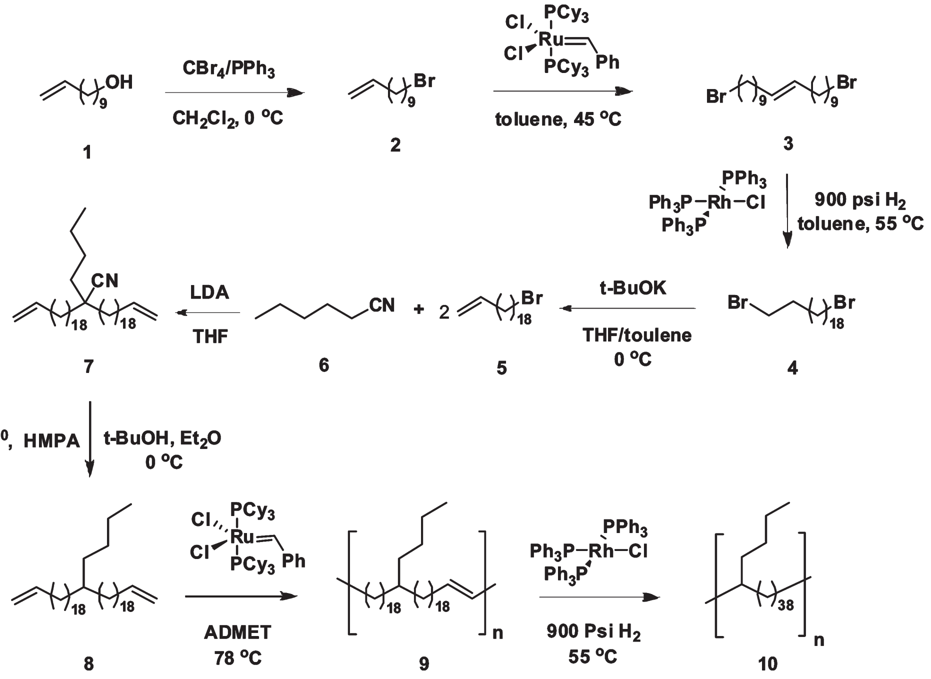

Figure 1. Synthetic scheme for the synthesis of precision ethylene/1-hexene polymer.

Monomer **8** was condensed to form unsaturated ADMET polymer utilizing Grubbs' first-generation catalyst. ADMET polymerization proceeded smoothly to give the desired unsaturated linear polymer **9** with no detectable side reactions. The resulting unsaturated polymer is soluble in chloroform and THF. The M_n for unsaturated polymer **9** is 46 000 with a PDI of 1.44 (GPC, polystyrene standards), values which are appropriate to mimic the crystallization behavior of chain-made polyethylene. Figure 2 shows the ^{1}H NMR spectra of unsaturated polymer **9** with no detectable terminal olefin signals (functional group conversion is greater than 99%). Important to note is that ADMET polycondensation chemistry is best done under bulk conditions using mechanical stirring under vacuum. These are typical conditions for any polycondensation reaction.

Fully characterized unsaturated polymer **9** was hydrogenated via Wilkinson's catalyst to produce saturated polymer **10**, which is precision polyethylene possessing a butyl branch on every 39th carbon.

The solubility characteristics of **10** are similar to that of chain-made polyethylene, being resistant to most organic solvents. Figure 2 also displays the NMR trace for the saturated (**10**) polymer; loss of the unsaturated proton signal confirms hydrogenation. Infrared spectroscopy, a more sensitive technique, also confirms total hydrogenation, as evidenced by the complete loss of alkene C−H out-of-plane bending peak at 967 cm^{-1}.

DSC profiles are depicted in Figure 3 comparing the unsaturated and saturated polymer on heating and cooling. The breadth of melting transitions for both polymers is narrower than typically observed for chain-made poly(ethylene-*co*-hexene), for example, a reflection of precision placement of the branch. As expected, the melting point of the saturated polymer (T_m = 75 °C) is higher than that of the unsaturated one (T_m = 52 °C).

The effect of branch frequency on thermal behavior is easily seen by comparing these data with ADMET polyethylene possessing butyl branches on every 5th, 15th, and 21st carbon (Table 1).[6]

As the branch frequency decreases, the melting point increases, approaching that of HDPE (T_m = 134 °C). Further evidence for the similarity of polymer **10** to commercial versions of polyethylene is found in wide-angle X-ray diffraction (WAXS) patterns (Figure 4), which suggest the presence of an orthorhombic crystal lattice. The (110) and (200) reflections are clearly observed at 21.5° and 23.7°, respectively. Other precision-branched ADMET polyethylenes with a shorter branch interval display a WAXS peak around 19°−20° assigned to a monoclinic, triclinic, or hexagonal phase.[9,22]

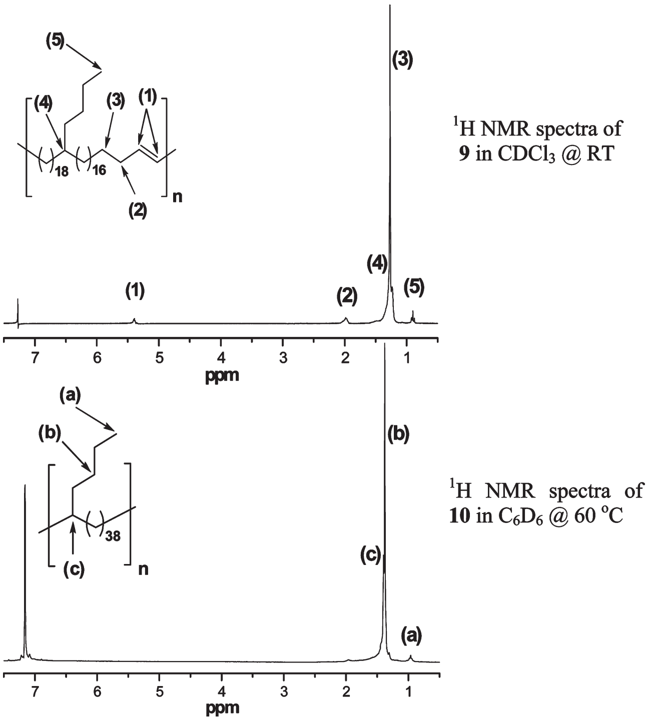

Figure 2. ^{1}H NMR spectra of unsaturated (**9**) and saturated (**10**) polymers.

An interesting aspect of the WAXS profile is that the 19.8° peak, which is sharper than that of the amorphous halo of commercial polyethylene, suggests the possible coexistence of a dominant orthorhombic crystal and other crystalline polymorphisms as a minor component overlapping the broad amorphous

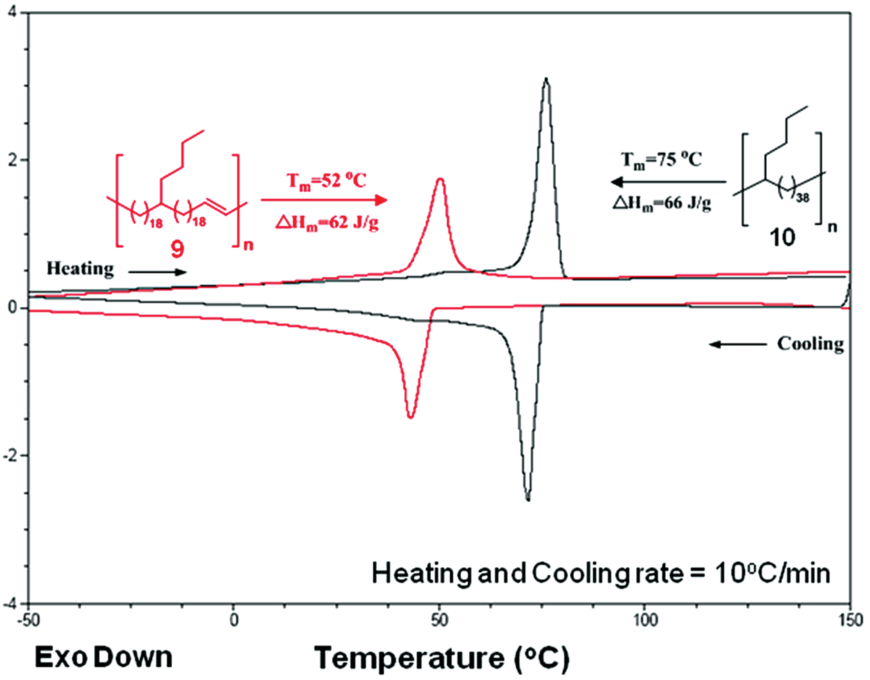

Figure 3. DSC exotherms and endotherms for unsaturated (**9**) and saturated (**10**) polymers.

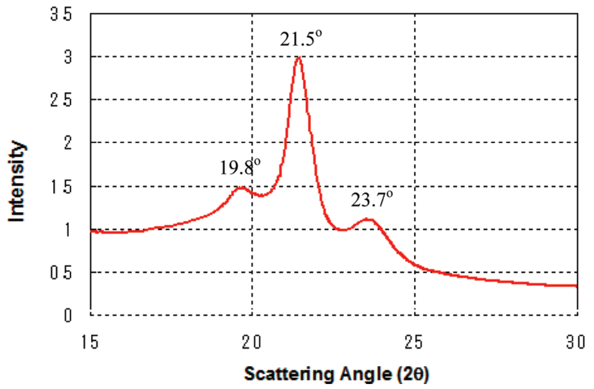

Figure 4. WAXS diffractogram of saturated polymer **10**.

halo. Time-resolved WAXS measurements during crystallization are underway to better understand these observations.

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

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