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ADMET Modeling of Branching in Polyethylene. The Effect of a Perfectly-Spaced Methyl Group

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Polyethylene is the world's largest volume polymer. It can be synthesized by many routes, including free radical initiation[1] and heterogeneous Ziegler−Natta catalyzed polymerization,[2,3] and more recently using metallocene-based catalyst systems.[4,5] Each of these polymerization techniques operates through chain propagation chemistry, and as a consequence, chain transfer events lead to varying degrees of branching. Branching has a significant influence on the physical properties of polyethylene and similar materials,[6−19] and to date it has been difficult to study the effects of branching in a systematic manner.

While the incorporation of randomly placed branches has been explored previously,[8,12−19] no study has been done describing the perfect control of branching in polyethylene. We now report the first synthesis of polyethylene possessing perfectly spaced methyl branch points along the polymer's backbone, producing macromolecules which we call "perfectly imperfect polyethylene". The synthesis has been done using polycondensation rather than chain techniques, and the synthesis scheme is shown in Figure 1.

The chemistry consists of condensing symmetrical diene hydrocarbon monomers via the ADMET reaction, followed by total hydrogenation at the site of unsaturation via diimide reduction. The procedure offers the potential to control both the number of methylenes between branch points and the length and identity of the substituent R (the branch) as well. Reported herein is work where the "branch" is a methyl substituent appearing on each and every ninth carbon on the polyethylene backbone. Due to the nature of the condensation chemistry applied to this symmetrical monomer, the placement of random branches along the polymer backbone is not possible.

Synthesis of the required monomer is challenging and consists of a six-step procedure involving a one-pot, two-step enolate-driven nucleophilic substitution of ethyl acetoacetate with the appropriate alkyl halide, followed by deacylation via a retro-Claisen condensation. The symmetrically substituted diene ester is then reduced to an alcohol, which is removed by tosylation, followed by a hydride displacement. These steps produce 6-methyl-1,10-undecadiene (**1**) (Figure 1, where $n = 3$ and $R = CH_3$), which is the desired monomer for this study. Other dienes of interest can be made via this synthetic procedure.[20]

Monomer **1** was condensed into its unsaturated ADMET polymer analog via bulk polymerization techniques using the Schrock molybdenum alkylidene, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$, as the catalyst. The polycondensation reaction occurs quite smoothly under mild conditions, producing the expected linear polymer, 6-methylpolynonylene (**2**), and pure ethylene, with no detectable side reactions. Number average molecular weights for the polymer range from 13 000 to 40 000 depending upon the degree of end-group conversion. The polydispersity indices obtained are between 1.4 and 2.4, again depending upon conversion and the nature of the workup. Gel permeation chromatography was performed on both precipitated and unprecipitated samples using both polybutadiene and polystyrene standards. ^{1}H NMR number average molecular weight measurements for the lower molecular weight samples were within 10% of the reported GPC results.[21]

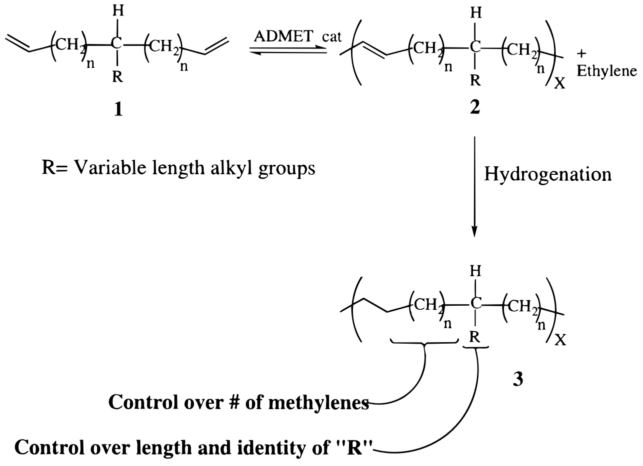

Figure 1. Synthetic scheme for the synthesis of polyethylene with perfectly-spaced alkyl groups.

The fully characterized unsaturated polymer (**2**) was subjected to exhaustive homogeneous hydrogenation using diimide chemistry as described previously by Hahn and others,[15,16,22,23] where repetitive treatments with the diimide reagent produces polymer **3**, a completely saturated polymer chain. Proton and carbon NMR spectra are shown in Figure 2; the carbon spectrum for polymer **3** is particularly revealing. Only six carbon signals are present for the polymer, and their chemical shifts (36.3, 30.0, 29.5, 28.8, 26.2, and 18.8 ppm) are in very good agreement with values predicted using the model of Carman, Tarpley, and Goldstein.[24] These data suggest that no side reactions are detectable.

GPC measurements were made before and after hydrogenation, and these data show that hydrogenation has no significant influence on the hydrodynamic volume of the polymer, for the retention times are essentially the same before and after the diimide treatment.[25] This is similar to the observation made earlier where we reported the synthesis of linear polyethylene using ADMET techniques followed by this diimide reduction.[23] Consequently, we have prepared the first samples of linear polyethylene possessing an exact spacing of methyl groups—on each and every ninth carbon—along the polymer backbone (Figure 2B). More significantly, we have developed a synthetic methodology that can produce this branch with a predetermined identity (length) and frequency in order to elucidate the effect of branching on the superstructure of polyethylene-based materials.

Since these polymers are made by step polymerization techniques, the number average molecular weights are lower than that normally reported for polyethylene prepared by chain chemistry. Nonetheless, the size of these polymers is sufficient to model the crystallization

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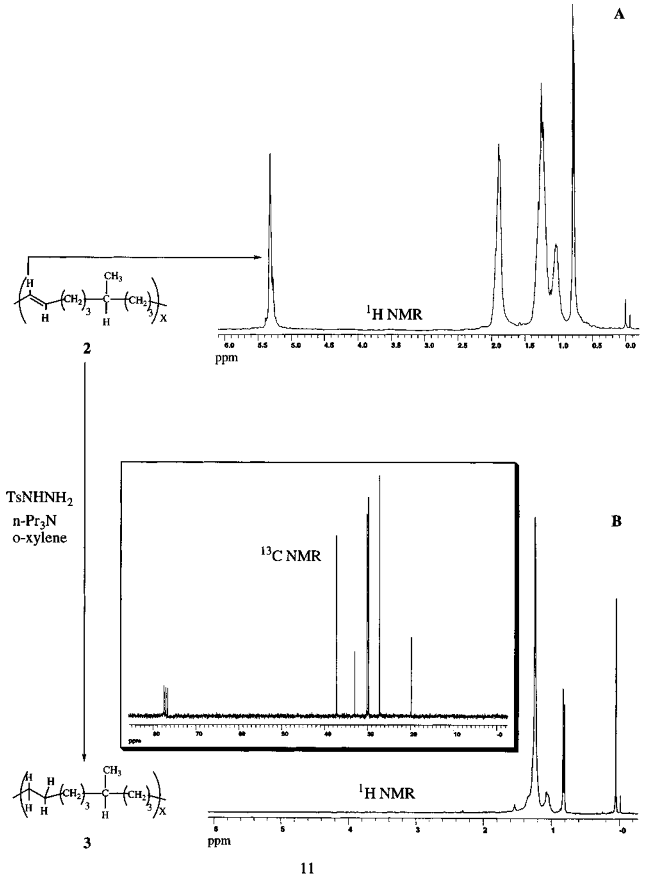

Figure 2. (A) ^{1}H NMR spectrum of the unsaturated polymer **2**. (B) ^{1}H NMR and ^{13}C NMR of polymer **3**.

Table 1. Molecular Weights and Melt Transitions for Perfectly Linear Polyethylene and Polyethylene with a Methyl Group Every Ninth Carbon

	$M_{n(GPC)}$[a]	$M_{w(GPC)}$[a]	M_w/ M_n	ΔH_m/ (J/g)	T_m/ °C[b]
linear polyethylene	15 000	40 000	2.6	204	133.9
methyl-branched PE (polymer **3**)	31 000	42 000	1.4	31.4	−2.01

[a] M_n and M_w determined by GPC using polystyrene standards. [b] DSC analysis, 2.0 °C/min heating and cooling rate.

behavior of saturated polymeric hydrocarbons. We have shown earlier that the melting point of perfectly linear (unbranched) ADMET polyethylene is a function of molecular weight,[23] and in this previous study, the value quickly approaches 134 °C as the number average molecular weight approaches 15 000. In addition, the average polydispersity of 2.0 is similar to that exhibited by polyethylene and similar polymers prepared using metallocene catalysts.[26]

Table 1 presents the DSC melting points and heats of fusion for ADMET linear polyethylene compared with the same polymer (**3**) possessing a methyl "branch" every ninth carbon.[27] While the T_m value of 134 °C for linear polyethylene approaches the theoretical maximum,[28,29] *the regularly spaced methyl group found at every ninth carbon on the chain in polymer **2** plunges the peak melting point to −2 °C, a drop of more than 130 deg with respect to the unsubstituted linear polymer.*

Figure 3a shows the endotherms for ADMET-prepared linear polyethylene and polymer **3**, while Figure 3b gives the DSC data for the "methyl-branched" polymer only (structure **3**). This methyl-branched polymer recrystallizes at −16 °C, and the sample easily cycles back and forth through the melt and recrystallization curves. Heats of fusion are about 1 order of magnitude lower than for linear polyethylene.[23]

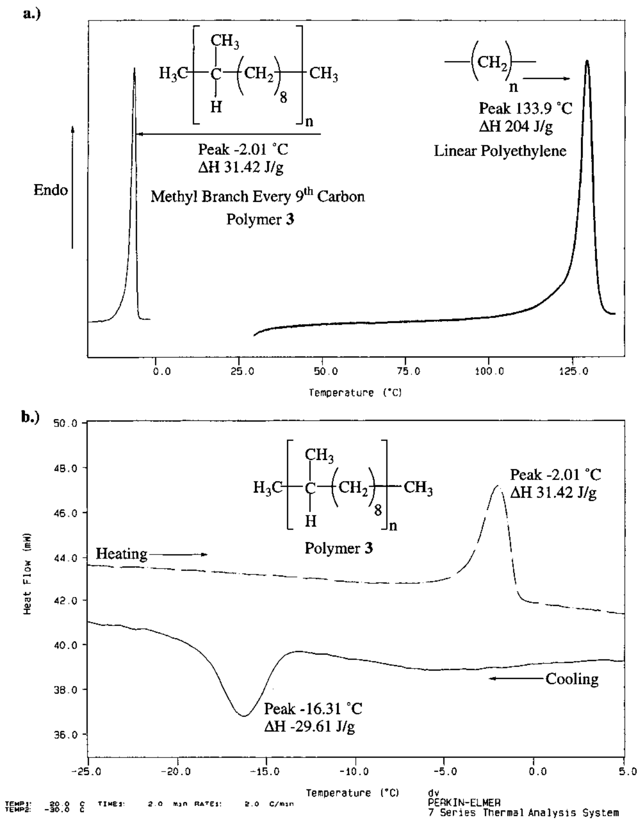

Figure 3. (A) Thermal analysis of perfectly linear polyethylene and methyl substituted polyethylene. The heat flow scale is arbitrary. (B) Reproducible heating and cooling cycle at 2 °C/min of methyl-substituted polyethylene showing the melt and recrystallization temperatures and heats of fusion.

The breadth of melting transition for polymer (**3**) is quite narrow compared to that reported for conventionally prepared poly(ethylene-*co*-propylene) samples.[30,31] Random copolymerization of ethylene and propylene provides a distribution of ethylene run lengths and thus a distribution of crystallite sizes and melting temperatures. Perfect control of the placement of the methyl group has a profound influence on crystallization behavior by controlling exactly the number of contiguous methylenes in the polymer backbone. Model studies by others using chain addition mechanisms have shown that frequent methyl branching (an average of 15 methyl branches per 100 carbon atoms or greater) results in a completely amorphous polymer.[14,31] Alamo and Mandelkern[32] also have shown that the melting temperature of such random copolymers depends on the details (regularity or lack thereof) of the ethylene run lengths.

We consider these to be particularly exciting results and currently are both lengthening the distance along the chain between branch points as well as increasing the size of the branch itself. We also are completing copolymerization work with unbranched hydrocarbon dienes to dilute the concentration of branch points further. Polymers prepared by this synthetic approach may allow for systematic determination of the effect of branch placement and branch identity on crystallite structure, morphology, and the thermodynamics of crystallization processes. We will also be able to probe the effect of these parameters on the glass transition temperature of ethylene-based materials.

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