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Precisely Controlled Methyl Branching in Polyethylene via Acyclic Diene Metathesis (ADMET) Polymerization

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ABSTRACT: A synthetic approach to attain precisely controlled methyl branching in polyethylene is described. Model polymers based on polyethylene have been created using acyclic diene metathesis (ADMET) chemistry as the mode of polymerization. Differential scanning calorimetry (DSC) was employed to examine the thermal behavior (melting point, heat of fusion, glass transition temperature) of five model polyethylene polymers wherein a methyl branch was placed on each 9th, 11th, 15th, 19th, and 21st carbon respectively along the backbone. Melting points and heats of fusion decrease as the frequency of precise methyl branching increases. On the other hand, the β glass transition and its change in specific heat are independent of branch frequency. Comparisons of these model polymers with industrial polyethylene samples demonstrate that this polycondensation approach will provide the basis for a better understanding of the morphology, crystalline structure, and thermodynamics of the crystallization process of the most abundant synthetic macromolecule in the world, polyethylene.

Introduction

Polyethylene is the highest volume macromolecule produced in the world today, with over 88 billion pounds produced in 1996 and an estimated demand of 109 billion pounds in 2000.[1] Consequently, it is still of interest to study the structure−property relationships, thermal behavior, and morphology of this polymer. The polymer is synthesized via chain propagation chemistry using free-radical initiation,[2] heterogeneous Ziegler−Natta catalysis,[3,4] metallocene-based catalysis,[5,6] and, most recently, late transition metal catalytic systems.[7,8] Inevitably, chain transfer occurs to varying degrees in these polymerization schemes leading to a randomly branched polymer microstructure, a phenomenon which is exploited to create a wider materials response. Branching in polyolefins has been examined for more than 60 years,[9−27] including numerous studies designed to better understand branching in polyethylene.[11,15−27]

Recently, we have found a way to avoid the random nature of branching in polyethylene. This has been accomplished via the elimination of chain transfer during propagation by using step polymerization rather than chain polymerization techniques. The work began by demonstrating that linear ADMET polyethylene[28] (no branches) could be synthesized by condensing linear 1,9-decadiene into its polymer, followed by exhaustive saturation with hydrogen. The use of metathesis polycondensation is important here, for it is mild chemistry that obviates chain transfer and operates via essentially one mechanism. The consequence is that only a single type of repeat unit is formed leading to pure polymer microstructures. This early work was followed by the first known example of introducing a precisely controlled methyl "branch" on each ninth carbon along the polymer backbone.[29] Figure 1 compares the two types of microstructure under discussion, i.e., that with precision branching as compared with random placement.

We now report the synthesis of a series of polyethylenes possessing *precisely controlled* methyl branch points where we have examined the effect of branching on the thermal behavior of these model polymers. The synthetic strategy for this new class of polyethylene involves ADMET polycondensation chemistry and is illustrated in Figure 2.[30,31]

Polymerization of the appropriate methyl-branched α,ω-diene monomer via step polycondensation (ethylene is removed) produces unsaturated polymers, where the microstructure is controlled completely by the symmetrical nature of the monomer. Monomer symmetry is the key to this methodology. Exhaustive hydrogenation produces a fully saturated, precisely branched polymer and these macromolecules, which we term ADMET polyethylene, are described herein.

Results and Discussion

A. Monomer and Polymer Synthesis. Monomer Synthesis and Design. Two synthetic pathways proved useful in the preparation of the symmetrical monomers needed for this work, choosing either an acetoacetate-based route[32] or alkenyl halide/carboxylic acid chemistry;[33,34] this report describes the former route in some detail (Figure 3). Ethyl acetoacetate is reacted with an alkenyl bromide possessing appropriate methylene spacing to produce the disubstituted β-keto product (**4a**−**4f**), which is deacylated by retro-Claisen condensation to yield the ester (**5a**−**5f**). Reduction using lithium aluminum hydride yields the alcohol (**6a**−**6f**), which is tosylated (**7a**−**7f**), then reduced via hydride displacement to produce the symmetrical diene of interest. Six symmetrical monomers were prepared in this manner where $n = 3$, 4, 6, 8, 9, and 2 (Figure 3) (**1a**−**1f**).

ADMET Polymerization And Hydrogenation Chemistry. All six symmetrical monomers in this study were exposed to Grubbs'[35] or Schrock's[36] catalyst under mild ADMET step polymerization conditions. The chemistry proceeds cleanly to produce linear, unsaturated polymers possessing only one type of repeat unit plus the usual small quantity (<1%) of cyclics found in bulk polycondensation conversions. No side reactions are detectable via TLC and NMR analysis. Number-average molecular weights ($\overline{M}_n$'s) range from 8000 to 78 000,

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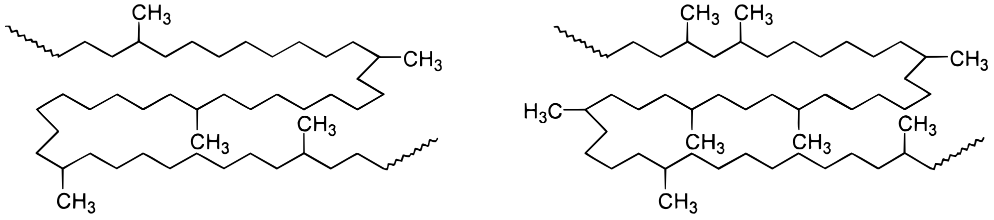


a) Precise Methyl Branch Placement on Every 9th Carbon on the Polyethylene Backbone

b) Random Methyl Branch Placement on the Polyethylene Backbone

Figure 1. Pictorial representation of the difference in branch placement in polyethylene produced by (a) ADMET chemistry and by (b) typical chain processes used to date.

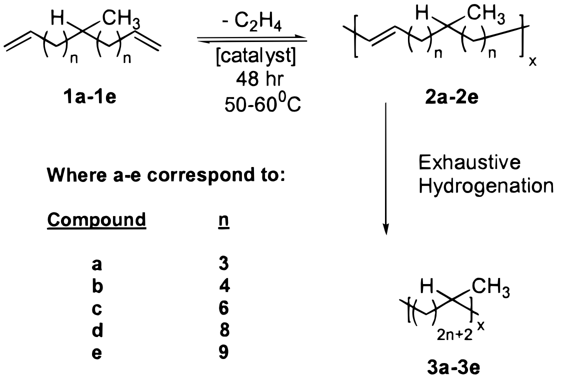


Figure 2. General synthetic scheme for synthesis of symmetrical methyl-branched polyethylene models by ADMET.

typical for polycondensation chemistry as are the polydispersity indices (PDI's), which range from 1.7 to 2.0 (Table 1). Only monomer **1f** failed to produce high polymer due to its propensity to cyclize under bulk reaction conditions, a result of the Thorpe–Ingold effect[37,38] in which thermodynamically favored cyclization is driven by the presence of the methyl group.

These unsaturated polymers were converted to methyl-branched polyethylene via exhaustive hydrogenation, where one of two methods was applied to this procedure. Exhaustive hydrogenation is also key to this examination, for otherwise the comparisons with “chain-made” polyethylene would be incorrect. Consequently two methods for hydrogenation have been examined in this work, one involving a heterogeneous supported hydrogenation catalyst and the other involving homogeneous stoichiometric diimide reduction.

The heterogeneous supported catalysis method uses Grubbs' ruthenium catalysis for both metathesis and hydrogenation.[39] The unsaturated polymer is mixed with dry silica in toluene under inert conditions, pressurized with 125 psi of H_2, stirred for 48 h, and the resultant suspension filtered and concentrated to produce the series of fully saturated polymers (**3a**–**3e**). The fully hydrogenated polymer is dissolved in toluene, then isolated by precipitation into CH_3OH and dried in vacuo for a 24 h period in the melt; molecular weight data for these polymers is also found in Table 1. We find this tandem homogeneous metathesis/heterogeneous hydrogenation procedure to be an efficient method of producing ADMET polyethylene. The stoichiometric diimide method is based on chemistry described by Hahn[40] and also gives excellent results. This is accomplished by successive additions of toluenesulfonylhydrazide (TSH) and tripropylamine (TPA), 3 equiv of each, to the unsaturated polymer in *o*-xylene. The mixture is refluxed; a second equivalent of TSH and TPA are added (3 equiv) and brought to reflux once again. After cooling, the saturated polymer (**3ds**) is recovered by precipitation into CH_3OH.

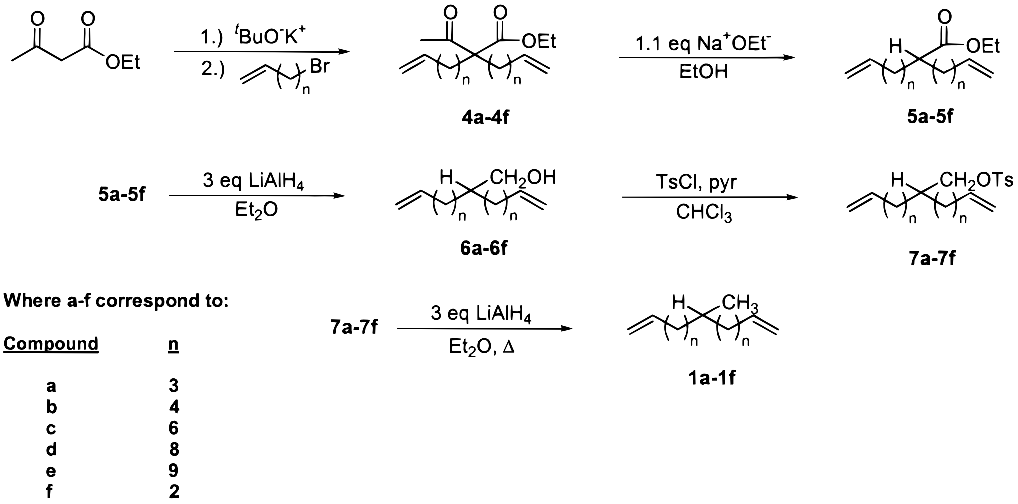
Interestingly, during this study, it was found that combining Mo metathesis catalysis with Ru supported hydrogenation gives very poor saturation results; **2ds** could not be hydrogenated using the heterogeneous catalysis system (silica, Grubbs' catalyst). After exposing **2ds** to these conditions, it was found that only 15–20% hydrogenation had occurred (via NMR integration); consequently, this hydrogenation technique was not pursued further.

Molecular Weight Analysis of Fully Hydrogenated ADMET Polyethylenes. Table 1 shows that hydrogenation does not alter the molecular weight of the unsaturated polymers in this study, an observation noted in our earlier experiments.[29] Polydispersities are somewhat narrower than for the unsaturated analogues principally due to a small degree of fractionation upon precipitation, but the values still reflect a polycondensation scheme. Since the ADMET polyethylene models exhibit polydispersity indices (PDI's) in the range of 2.0, they are excellent models for similar ethylene based polymers produced via metallocene catalysis.[41a]

The molecular weight analysis of these ADMET polyethylenes is an important issue to delineate, for metathesis polycondensation chemistry produces polyethylene samples with lower molecular weights than observed for the usual chain techniques. Clearly there exists a molecular weight dependence of the melting behavior in polymeric materials,[42–45] and because of potential penultimate effects, the question becomes evident whether these macromolecules are of sufficient size to model the thermal behavior of conventional materials.

We have addressed this question in two ways, the data for which is displayed in Table 2. First, linear ADMET polyethylene samples (no branches) were prepared in a range between $\overline{M}_n$ = 2400–15 000. These samples increased in melting point from 130.7 °C to 133.9 °C; further changes in melting behavior with molecular weight were very gradual. The penultimate effect on melting in the $\overline{M}_n$ = 15 000 sample may be present, but only to a small degree, certainly less than is important for comparisons with the methyl-branched samples. Further, this sample's T_m of 133.9 °C and its heat of fusion compare favorably with commercial linear polyethylene prepared using Ziegler–Natta chemistry.

Second, we prepared two samples possessing dramatically different molecular weights of polyethylene which contain a methyl branch precisely placed on each 19th carbon along the chain (the chemistry used to



Compound	n
a	3
b	4
c	6
d	8
e	9
f	2

Figure 3. Synthetic pathway to produce methyl-branched diene with symmetrical methylene spacing for both alkenyl substituents.

Table 1. Molecular Weight Data for Unsaturated and Saturated Branched ADMET Polymerization Polyethylene Polymers

		unsaturated polymer		saturated polymer	
methyl-branched ADMET polyethylene	methyl branch on every *n*th carbon, *n*	$10^3\overline{M}_n$[a]	polydispersity index (PDI)	$10^3\overline{M}_n$[a]	polydispersity index (PDI)
3a	9	22.8	2.0	17.5	1.7
3b	11	8.0	1.7	8.5	1.8
3c	15	15.7	1.7	17.1	1.7
3d	19	11.3	1.9	17.4	1.6
3ds	19[b]	78.1	1.9	72.0	1.9
3e	21	20.2	1.7	20.2	1.7

[a] Molecular weight data was taken using chloroform as solvent and is relative to polystyrene standards. [b] Polymerized using Schrock's [Mo] alkylidene.

Table 2. Effect of Molecular Weight on Thermal Properties for Linear and Methyl-Branched ADMET Polyethylene Polymers

ADMET polyethylene	methyl branch on every *n*th carbon, *n*	$\overline{M}_n$	polydispersity index (PDI)	T_m (°C) (peak)	Δh_m (J/g)
linear ADMET PE[a]		2400	2.4	130.7	252
linear ADMET PE[a]		7600	2.4	131.3	213
linear ADMET PE[a]		11000	1.9	132.0	221
linear ADMET PE[a]		15000	2.6	133.9	204
branched ADMET PE[b] **3d**	18	17400	1.6	57	96
branched ADMET PE[c] **3ds**	18	72000	1.9	57	84

[a] Synthesized by ADMET of 1,9-decadiene. GPC analyses performed in 1,2,4-trichlorobenzene at 135 °C with respect to polyethylene standards.[28] [b] Polymerized with Grubbs' [Ru] benzylidene. GPC analysis performed in chloroform with respect to polystyrene standards. [c] Polymerized with Schrock's [Mo] alkylidene. GPC analysis performed in chloroform with respect to polystyrene standards.

accomplish this is described in the Experimental Section), both with an $\overline{M}_n$ greater than 15 000 (samples **3d** and **3ds**, Table 2). A sharp melting endotherm of 57 °C is observed for both of them, one with an $\overline{M}_n$ = 17 400 and the other with one of 72 000. These data suggest that a minimum number-average molecular weight of approximately 15 000 is sufficient for comparison between samples in this study.

Structural Determination Data. Figure 4 shows the ^{1}H NMR spectra for a typical conversion of monomer **1e**, 12-methyl-1,22-trieicosadiene, to its unsaturated polymer **2e**, and then to its saturated ADMET polyethylene methyl branch polymer **3e**. The olefin region illustrates the conversion of monomer to unsaturated polymer with the disappearance of the terminal olefin at 4.96 and 5.81 ppm in the monomer and the subsequent growth of internal olefin resonance at 5.37 ppm in the unsaturated polymer **2e**. Upon exhaustive hydrogenation, these olefin resonances completely disappear. The ^{13}C NMR spectra (Figure 5) further supports the conclusion of exhaustive hydrogenation; note that the sp^2 resonances in the unsaturated polymer (trans, 130.36 ppm, cis, 129.90 ppm) completely disappear after hydrogenation giving **3e**. These spectra are typical for all the ADMET polyethylenes synthesized in the series, and they illustrate the degree of structure control that is possible.

Further, the ^{13}C NMR data exhibited in Figure 5 reveal that six sp^3 carbon signals are present in this polymer, which contains a methyl branch on every 21st carbon, an observation made earlier for the ADMET polyethylene sample possessing a methyl branch every 9th carbon.[29] The chemical shifts observed for polymer **3e** were 19.73, 27.11, 29.73, 30.05, 32.75, and 37.11 ppm, values which are in very good agreement with the values predicted by Carman, Tarpley, and Goldstein for a series of branched alkanes.[46] Resolution of chemical shifts apparently extends only to this point since the entire series of saturated polymers produced in this study, regardless of the number of methylene spacers,

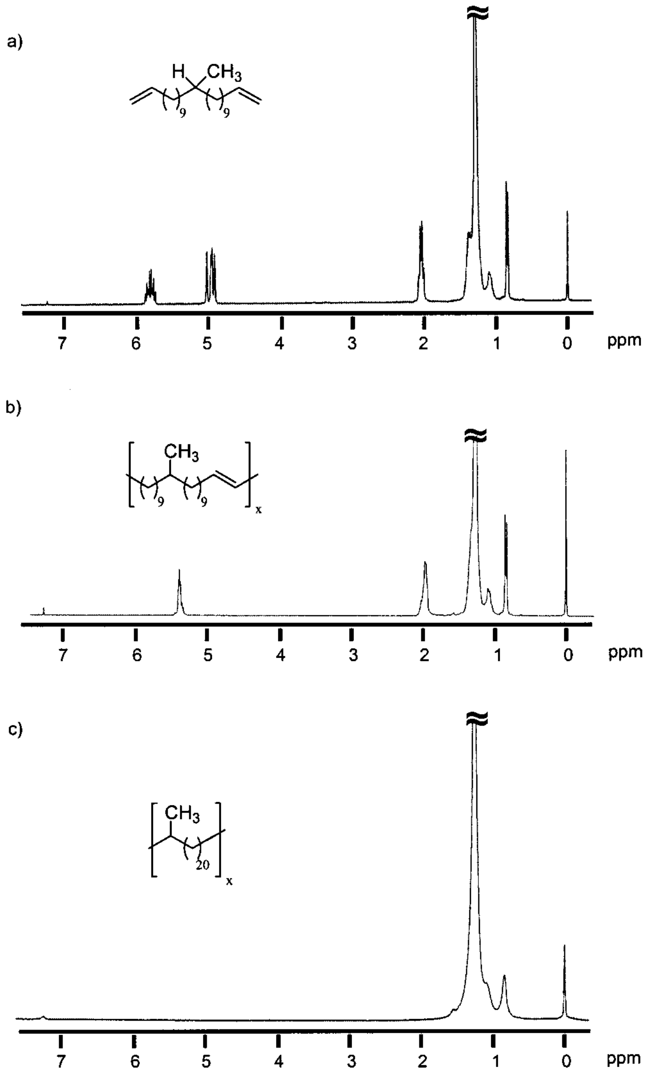


Figure 4. ^{1}H NMR: (a) monomer, **8f**; (b) unsaturated polymer, **2e**; (c) saturated polymer, **3e**.

yields the same six chemical shifts. Higher field NMR experiments which may resolve these signals further is presently being investigated.

These spectral data not only support the primary structure of the repeat unit but also suggest that no side reactions are detectable within the limitations of the NMR instrument. Elemental analysis results also show good agreement between theoretical and experimental values, as do bromine uptake experiments, sensitive to the presence of any unsaturation.

Do these methyl-branched ADMET polyethylenes possess tacticity? Traditionally, tacticity in synthetic polymers describes the nature of successive stereocenters placed on every second or third carbon in the polymer backbone. In this work, the methyl branches are widely spaced from one another (from 9 to 21 carbons apart) and so the issue of tacticity is less important. Even so, strictly speaking the tacticity issue applies; however, the nature of the ADMET polymerization mechanism yields a completely random distribution of *R* and *S* stereocenters which makes these model systems atactic by definition. Nevertheless, as the thermal data demonstrates, the regular placement of the methyl branch has given these materials a level of order which does allow for crystallization to occur. Again, higher field ^{13}C NMR as well as X-ray crystallography should allow for a better understanding of the imposed order in these model systems.

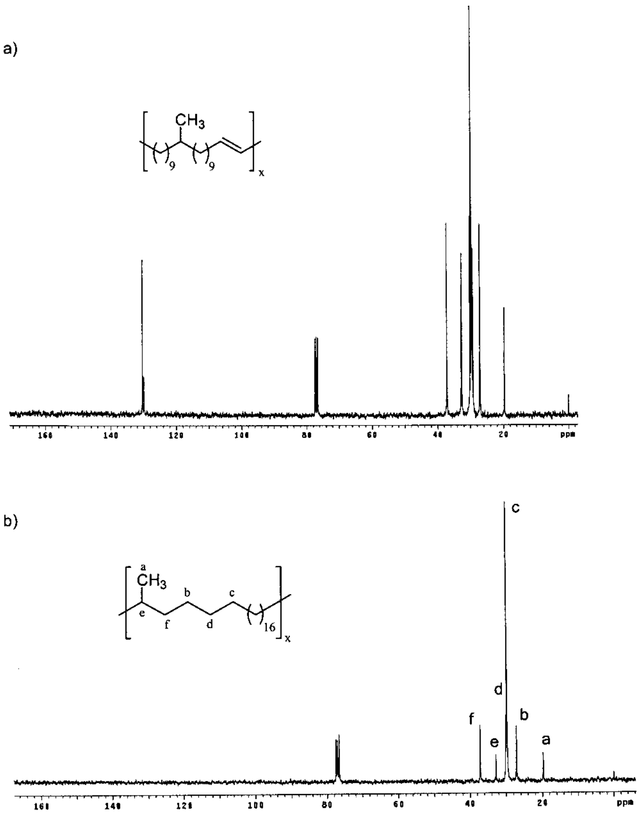


Figure 5. ^{13}C NMR spectra: (a) unsaturated polymer, **2e**; (b) saturated polymer, **3e**.

B. Thermal Analysis. Comparative Polyethylene Thermal Data. Many different types of polyethylene have been produced since its commercial inception in the 1930s; however, each type has a unique mode of initiation that leads to distinct differences in branch identity and branch content. This variation in branching gives rise to striking differences in the thermal properties of these materials which in turn becomes very important in materials processing. For the sake of comparison, Table 3, vide infra, compares these various types of polyethylenes descending from the theoretical (infinitely long chain, no branching) to varying degrees of branching. Included in this table are two types of ADMET polyethylene, linear and methyl branched.

Differences in melting points are quite interesting to compare. Hoffman's[47a] theoretical polyethylene melt is the highest, followed by linear versions (no branching, or nearly so), then followed by materials possessing low quantities of random branches (metallocene PE, high density polyethylene (HDPE), Brookhart PE), and then to purposely branched polymers such as ethylene/propylene copolymers and low density polyethylene. Finally, precisely methyl-branched ADMET polyethylene appears in the table. While the Brookhart polyethylenes are new, the others have been examined extensively, and in general, the endotherm for a branched polyethylene made by chain techniques is broadened in shape and melts at lower temperatures as the methyl branch content increases.

The situation is decidedly different for precisely branched, ADMET polyethylene. By comparison, all these endotherms are considerably sharper—some very sharp. Further, while linear ADMET polyethylene melts

Table 3. Data for a Number of Polyethylene Systems

type of polyethylene	$10^3\overline{M}_n$	methyl branches per 1000 carbon atoms	T_m (°C)	Δh_m (J/g)
theoretical PE[e]	24–114	0	141.5–146.5	293
ADMET PE[c]	2–15	0	131–134	204–252
metallocene PE[d]	30–1500	0.9–1.2	137–140	
HDPE[e]	50–250	1–6	133–138	219–245
Brookhart PE[a]	14–65	1.2–74	97–132	
ethylene/propylene copolymers[b]	20–70	2–100	80–133	
LDPE[e]	20–100	30–60	105–115	95–141
MB ADMET PE[f]	8–72	48–111	−14–62	28–103

[a] See ref 8c: M. Brookhart's new late transition metal systems using Pd and Ni. [b] See ref 26: ethylene/propylene copolymers from the work of Wunderlich. [c] See ref 28: J. E. O'Gara and K. B. Wagener; PE produced by ADMET polycondensation. [d] See ref 41: Kaminsky, Cecchin, and Zucchini's work reviews on metallocene PE catalysis. [e] See ref 47: J. D. Hoffman's equilibrium values derived for an infinitely long PE chain. [f] Work in this study—PE model polymers made by ADMET with precise placement of methyl branches along the backbone.

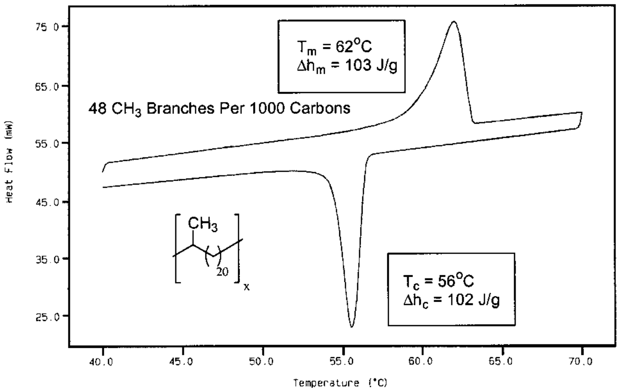


Figure 6. Typical DSC plot illustrating melting endotherm and crystallization exotherm. DSC for **3e** (methyl branch every 21st carbon).

Table 4. DSC Data for Fully Hydrogenated ADMET Polyethylene Methyl-Branched Model Polymers

ADMET polyethylenes[a]	methyl branch on every *n*th carbon, *n*	methyl branches per 1000 carbon atoms	T_m (°C) (onset)	T_m (°C) (peak)	Δh_m (J/g)
3a	9	111	−18	−14	28
3b	11	91	−3	11	66
3c	15	67	35	39	82
3d	19	53	53	57	96
3ds	19	53	49	57	84
3e	21	48	57	62	103
linear ADMET polyethylene[b]		0		134	204

[a] **3a**–**3e** polymerized with Grubbs' [Ru] benzylidene; however, **3ds** was prepared using Schrock's [Mo] alkylidene. [b] Made by ADMET of 1,9-decadiene.[28]

in a manner similar to metallocene and HDPE materials, methyl-branched ADMET polyethylene melts at dramatically lower temperatures, clearly lower than any of the commercially produced polymers. This change in behavior is attributed to its significantly different, precisely controlled microstructure where only methyl branches are present; these methyl branches are precisely—exactly—placed along the backbone. Of course, polyethylene made by chain propagation possesses randomly placed branches of differing identity (methyls, longer alkyls, vinyls, allyls, etc.).

Methyl-Branched ADMET Polyethylene Melting Behavior. DSC analyses were performed using a Perkin-Elmer DSC 7 at a heating rate of 2 °C/min. Calibrations were accomplished using indium and *p*-nitrotoluene as standards for both peak temperature transitions and heats of fusion. To erase thermal history, each sample was annealed for 5 h at 50 °C above the peak melting point found in initial scans. Complete details of exact scanning procedures can be found in the Experimental Section.

Differential scanning calorimetry was employed to determine the melting behavior of the ADMET polyethylene series, since a great deal of DSC data is present in the literature for comparison. The random copolymers, such as those made from ethylene and propylene via Ziegler–Natta catalysis,[26] exhibit a broad, indistinct melting behavior when the percentage of propylene exceeds approximately 15%.[25,26] In comparison, the exact placement of a methyl group in methyl-branched ADMET polyethylene produces both sharp melting endotherms and recrystallization exotherms; as illustrated in Figure 6 for polymer sample **3e**. This sample possesses a methyl branch on each 21st carbon along the polyethylene backbone (48 methyl branches per 1000 carbon atoms), and it is important to emphasize that all of the ADMET polyethylenes in this series show similar endotherm and exotherm shapes.

Table 4 lists the DSC data obtained for the methyl-branched ADMET polyethylene model polymers studied to date. Note that the melting temperatures (Table 4) are reported as onsets and peak maxima, and enthalpy values are quantitative thermodynamic measurements and are reported in relation to the unit weight.

Several interesting results are observed concerning the melting point behavior of these precisely placed methyl-branched polymers. While the T_m for perfectly linear ADMET PE approaches that of other highly linear polyethylenes made by commercial routes,[49,50] the precisely placed methyl group on every 9th carbon, polymer (**3a**), depresses the peak melting point to −14 °C with a Δh_m of 28 J/g. This polymer melts approximately 150 °C lower than linear ADMET polyethylene and exhibits a heat of fusion approximately approximately 1 order of magnitude smaller.[28]

As the methylene spacing increases between branch points for the methyl-branched ADMET polyethylene series, melting points and heats of fusion increase. This is to be expected, for as the frequency of comonomer content (methyl/methine mole fraction) decreases, the percent crystallinity of the polymer sample should increase. The increase in T_m and Δh_m with a decrease in comonomer content indicates that the crystallinity is increasing but still quite distant from the corresponding values for linear ADMET polyethylene.

The mere presence of a distinct melting point for any of the methyl-branched polymers, and particularly for sample **3a**, is a surprising result. Alamo and Mandel-

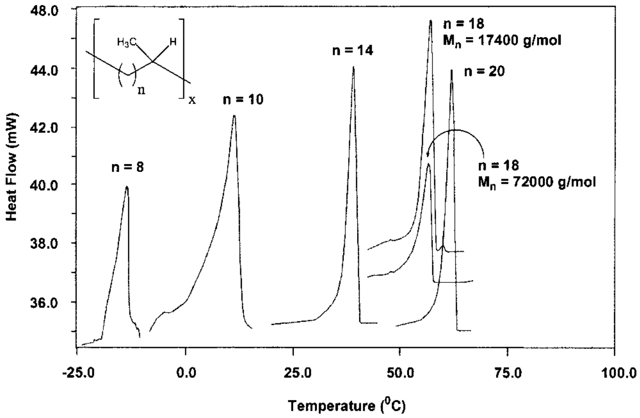


Figure 7. DSC visual overlay of melt transitions for ADMET polyethylene with precisely placed methyl branches presented in Table 4.

kern have shown that the lack of regularity in ethylene run lengths impacts the nature of the melting temperature transition,[27] and model studies by others using chain propagation techniques illustrate that a completely amorphous polymer is formed when the frequency of methyl branch is an average of 150 or greater branches per 1000 carbon atoms.[17,26] However, in the case of ADMET polyethylene possessing precise spacing, a branch frequency of 111 methyl branches per 1000 carbon atoms (sample **3a**) yields a material possessing a distinct, sharp melting point. In fact, the breadth of all melt transitions for the entire series of polymers in Table 4 are narrower than those reported for poly(ethylene-copropylene) samples with comparable comonomer content.[26,51] Figure 7 provides a DSC visual overlay for all of the polymer samples described herein.

This trend in melting point behavior for methyl-branched ADMET polyethylene illustrates the dependence of melting point on comonomer composition, and these data are plotted in Figure 8 using the Flory equation.[52]

$$T_{\mathrm{m}} = T_{\mathrm{m}}^{\circ}\left(1 - \frac{RT_{\mathrm{m}}^{\circ}}{\Delta H_{\mathrm{m}}^{\circ}}[\chi_{\mathrm{CHCH_3}}]\right) \qquad (1)$$

The equilibrium melting point T_{m}° of theoretical polyethylene is assumed to be 145.5 °C; the equilibrium enthalpy of melting, $\Delta H_{\mathrm{m}}^{\circ}$ is taken as 4.1 kJ/mol of methylene groups; and $X_{\mathrm{CHCH_3}}$ is the mole fraction of the methyl branch moiety in the polymer. Theoretical data are plotted in comparison with the ADMET polymer data.

Just as the theoretical model predicts, the methyl-branched ADMET polyethylene models give a linear relationship when plotting the melting point depression versus the increase in comonomer content ($\mathrm{CHCH_3}$). However, the slope of the line for methyl-branched ADMET polyethylene samples studied here is distinctly different when compared to the theoretical model for random branching. The discrepancy between experimental and theoretical data can be expected, for the Flory equation accounts not for the chemical nature of the comonomer units but only the number of these units in the polyethylene chain. Nevertheless, the correlation coefficient of 0.998 indicates that these ADMET polyethylene polymers provide an effective tool for modeling precise methyl branch placement along the backbone of polyethylene.

The Glass Transition Behavior of Methyl-Branched ADMET Polyethylene. While the relaxation spectra of linear and branched polyethylene have been extensively examined,[53−60] debate continues on the exact transitions which can be called the glass transition temperature for this polymer.[54,60] Thermal expansion, calorimetric, and dynamic mechanical measurements on branched polyethylene all have shown three distinct loss regimes termed α, β, and γ respectively.

Work completed by various researchers have reported the α relaxation[56,57] at 70 ± 10 °C, the β relaxation[58] at −30 ± 15 °C and the γ relaxation[54,59] at −125 ± 5 °C. Most investigators agree that these three transitions exist but cannot agree on the true T_{g} for polyethylene. The α relaxation is thought to arise from motions in the crystalline regions of the polymer (growth of longspacing), while the β transition is attributed to the relaxation of chain branch regions of the polymer. The γ relaxation origin is a topic of considerable debate; however, it is often described as the consequence of a crankshaft type motion along a small number of methylene units in the amorphous domains of PE. A study concerning the relative magnitudes of the β and γ relaxation in dynamic mechanical measurements showed a marked increase in the intensity of the β relaxation as the number of chain branches increased.[53] This and other observations on ethylene containing copolymers led experimentalists

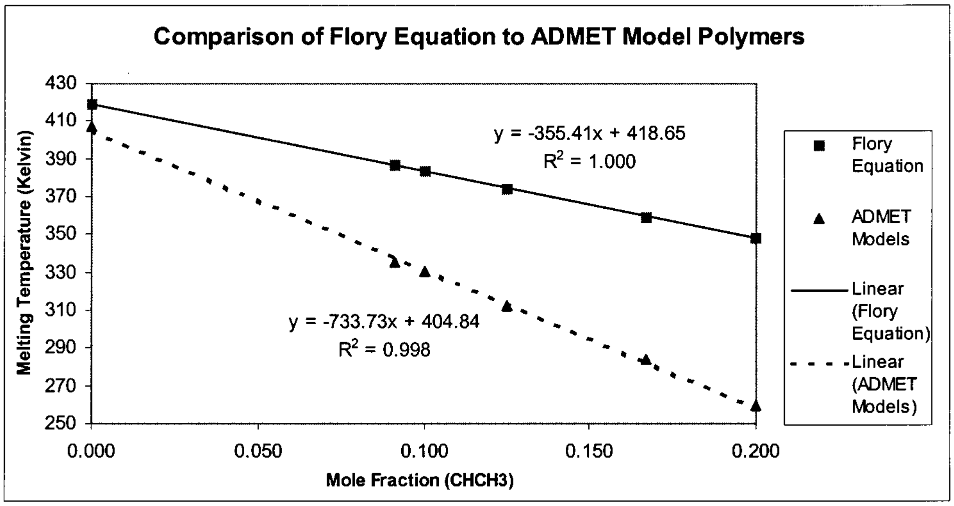


Figure 8. Flory equation treatment for the impact of comonomer content on the melting point.

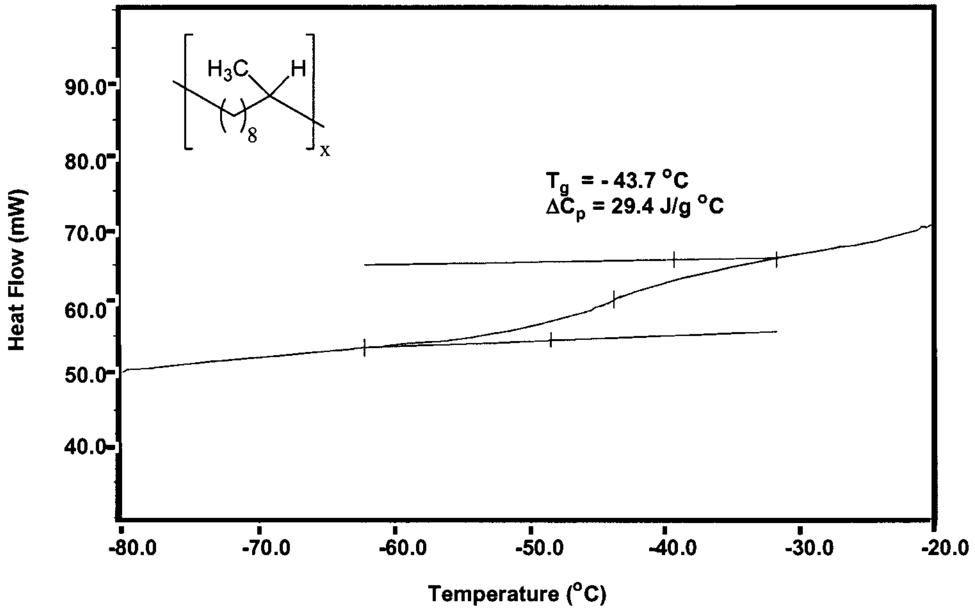


Figure 9. Glass transition curve for methyl-branched ADMET polyethylene with a methyl branch on each and every 9th carbon.

Table 5. Glass Transition Data for ADMET Polyethylene Model Polymers

polymer	methyl branch on every *n*th carbon, *n*	T_g (°C)	ΔC_p (J/g °C)
3a	9	−44	29
3b	11	−44	28
3e	21	−43	27

to view the β relaxation as the primary T_g of branched, semicrystalline polyethylene, a result supported by work done by Stehling and Mandelkern in 1970.[54]

Given that methyl-branched ADMET polyethylene likely possesses a high amorphous content, three such polymers—**3a**, **3b**, and **3e**—ranging from 48 methyls to 111 methyl branches per 1000 carbon atoms were examined for their glass transition behavior in the β relaxation region, and the results are displayed in Table 5.

The T_g's and changes in specific heat average are −44 °C and 29 J/g°C respectively, and are the same *for all three samples* regardless of running length of the methylene units between branch points. This β relaxation is particularly evident in the DSC plots of these precisely spaced methyl-branched polyethylenes. Figure 9 shows one of the DSC curves, which is essentially identical to what is observed for the other two. The likely explanation for this behavior relates to the probability that relaxation about the branch point is quite local in scope such that running methylene lengths are not a factor. These initial glass transition findings are indeed intriguing.

Conclusions

The perfect control of methyl branch placement along the backbone of polyethylene has a profound influence on the thermal behavior of these PE model materials. As the methylene spacing between branch points increases, the melting point and heat of fusion increase. The data correlate well with the Flory relationship, suggesting that the ADMET polycondensation approach to model branching in polyethylene offers a sound analytical basis, despite the lower molecular weight ranges for these step polymers. Initial glass transition data show the β relaxation for polyethylene is independent of the frequency of branching.

Presently we are continuing this research by gathering X-ray and other scattering data for these methyl-substituted polymers. Our intention is to better understand the secondary and tertiary structure of these models. We also are preparing other ADMET polyethylenes possessing longer branches (ethyl, butyl, hexyl, etc.) in order to model other common materials such as linear low-density PE, metallocenes and the like. Furthermore, we are probing the glass transition data in more detail.

ADMET chemistry represents the only method to precisely control the identity and distribution of branches along the backbone of polyethylene. *This research will provide the basis for a better understanding of the morphology, crystalline structure, and thermodynamics of the crystallization process of the most abundant synthetic macromolecule in the world, polyethylene.*

Experimental Section

1.1. Instrumentation and Analysis. All ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on either a General Electric QE-Series NMR Superconducting spectrometer system or Varian Associates Gemini 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMRs were referenced to residual signals from $CDCl_3$ with 0.03% v/v TMS as an internal reference. Reaction conversions and relative purity of crude reactions were monitored by chromatography. Gas chromatography (GC) was performed on a Hewlett-Packard HP5880A gas chromatograph equipped with a methyl silicone capillary column and flame ionization detector. Thin-layer chromatography (TLC) was performed on Watman aluminum backed, 250 mm silica gel coated plates. TLC plates were developed with mixtures of hexanes and ethyl acetate as the mobile phase. TLC plates for UV inactive olefin monomers were stained with either potassium permanganate (2%) in an aqueous solution of sodium bicarbonate (4%) or phosphomolybdic acid (10%) in ethanol after development to produce a visible signature. Low and high-resolution mass spectral (LRMS and HRMS) data were obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the electron ionization (EI) mode. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

Ester and alcohol intermediates were purified by vacuum distillation from calcium hydride. Initial purification of monomer was accomplished by simple short path vacuum distillation. Final purification to yield pure monomer was accomplished by either flash chromatography[61] using 100% hexanes as the eluent or high performance liquid chromatography (HPLC) using 99.5% hexanes and 0.5% ethyl acetate as the mobile phase. HPLC was accomplished using a Ranin instrument equipped with Dynamax SD1 pumps, Dynamax UV-1 variable wavelength UV/vis absorbance detector and a Varian Star 9042 Refractive Index (RI) detector in series, and Dynamax FC-1 fraction collector. Two columns were utilized: (1) analytical or scout scale column with dimensions of 10.0 mm (inner diameter) by 250.0 mm; (2) preparative scale with dimensions of 41.4 mm (inner diameter) by 250.0 mm. Both columns were silica packed with a particle size of 8 μm and a pore size of 60 Å. Crude samples were diluted in a 25% solution (w/v) of HPLC grade hexanes and filtered before injection.

Gel permeation chromatography (GPC) was performed using a Waters Associates liquid chromatography U6K equipped with a tandem ABI Spectroflow 757 UV absorbance detector and a Perkin-Elmer LC-25 RI detector. All molecular weights are relative to polystyrene standards. Polymer samples were dissolved in HPLC grade $CHCl_3$ (approximately 0.1% w/v) and filtered before injection (a volume of 20−40 μL). The GPC was equipped with a Ultrastyragel linear mixed-bed column. HPLC grade chloroform was used as the eluent at a constant flow rate of 1.0 mL/min. Retention times were calibrated against narrow molecular weight polystyrene standards (Scientific Polymer Products, Inc.). All standards were selected to produce M_p or M_w values well beyond the expected polymer's range. A minimum of five data points were acquired for a calibration curve.

Differential scanning calorimetry (DSC) analyses were performed on two separate instruments. Initial results were obtained on a TA Instruments model 2910 DSC and model 2850 TGA equipped with a model 2000 data analysis software program. DSC analyses were obtained at a heating rate of 2 °C/min. Calibrations were made using indium as the standard for both peak temperature transitions and the heats of fusion. All samples were prepared in hermetically sealed pans. Attempts were made to keep a small range on the weight for all polymer samples (approximately 10 mg/sample). Initial scans were performed to determine the onset and peak melting position for each unannealed polymer sample. All samples were run using an empty pan as reference and empty cells as a subtracted baseline. The two lowest melting samples were analyzed from −80 to +30 °C, (**3a**, **3b**) and the remainder of the samples (**3c**−**3e**) were analyzed from 0 to 80 °C. These melting points were used as guides for annealing in the subsequent DSC study. Initial melting point and heat of fusion data is given in the experimental for each polymer. Thermogravimetric analysis (TGA) was also performed. All samples were heated from room temperature to 800 °C in nitrogen at a scan rate of 10 °C/min. The onset of weight loss was taken as the initial value.

After initial values for peak melting points were found, a second set of samples were prepared in a fashion similar to the first set. DSC analyses were performed using a Perkin-Elmer DSC 7 at a heating rate of 2 °C/min. Thermal calibrations were done using indium and *p*-nitrotoluene as standards for both peak temperature transitions as well as for heats of fusion. To destroy all thermal history, each sample was annealed for 5 h at 50 °C above the peak melting point found in the initial scans. Subsequently, the samples were then cooled at 2 °C/min to approximately one degree below the onset melt temperature found in the initial DSC measurements. Each sample was then annealed at this point for 5 h. Then, the sample was cooled at 2 °C/min to a point which was approximately 30 °C below the observed recrystallization temperature, followed by isothermal cooling at 30 °C below the crystallization temperature for 5 min. After cooling, the sample was heated at 2 °C/min until reaching approximately 30 °C above the observed melting point, followed by isothermal heating for 5 min. Finally, the samples were scanned for multiple cycles through the same range to verify the results obtained on the first run. Data collection was taken on the first run. The results are listed in the experimental and in tabular form within the text. Reported values are given as T_m (peak) (melting, first-order transition peak position), T_m (onset), T_c (peak) (recrystallization, first-order transition peak position). Glass transition temperatures (T_g's) were taken in the following manner. Each sample was loaded and annealed for 5 h at 50 °C above the observed melting temperature. Next the sample was rapidly quenched to −80 °C (from +50 °C above the melt to −80 °C in approximately 4 s) and isothermally cooled for 15 min. Finally, the sample was heated at 2 °C/min from −80 to 0 °C. Reported values are given as T_g (glass transition)(second-order transition) and C_p (heat capacity in J/g °C).

1.2. Materials. Grubbs' benzylidene ruthenium catalyst, $RuCl_2({=}CHR)(PCy_3)_2$, where Cy = cyclohexyl, and R = phenyl, was synthesized using the literature procedure.[35] Schrock's molybdenum catalyst $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ was also synthesized via literature procedure.[36] Acrôs 60 mesh silica gel was dried under vacuum ($<10^{-3}$ mmHg) at 100 °C for 24 h and stored in an argon atmosphere drybox prior to use in the hydrogenation reactions.

Dimethoxyethane (DME), toluene, and diethyl ether (Et_2O) were freshly distilled from Na/K alloy using benzophenone as the indicator. *p*-Toluenesulfonohydrazide (TSH) was purchased from Aldrich and recrystallized from CH_3OH prior to use. Tripropylamine (TPA) and *o*-xylene were purchased from Aldrich and distilled from CaH_2 prior to use. A solution of 2 M potassium *tert*-butoxide (KO*t*-Bu) was prepared in a flame-dried, argon-purged Schlenk tube by combining the salt (Aldrich) with DME freshly distilled from Na/K alloy. 5-bromo-1-pentene, 6-bromo-1-hexene, 8-bromo-1-octene (Aldrich), 10-bromo-1-decene (Alfa Aesar, Avocado), and 11-bromo-1-undecene were distilled from CaH_2 prior to use. The 11-bromo-1-decene was synthesized from 10-undecen-1-ol (Alfa Aesar, Avocado) via literature method (see Experimental Section).[61] Ethyl acetoacetate (Aldrich) was also distilled from CaH_2 prior to use. ^1H NMR and ^{13}C NMR spectra for ethyl acetoacetate and all alkenyl bromides are provided under the listing of starting materials. All other reagents mentioned in the experimental were used as received.

1.3. Characterization of Starting Materials. Ethyl acetoacetate (Aldrich): ^1H NMR ($CDCl_3$) δ 1.29 (t, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 2.29 (s, 3H, $-C(O)\ \boldsymbol{CH_3}$), 3.46 (s, 2H), 4.21 (q, 2H, $-C(O)OCH_2\boldsymbol{CH_3}$), 12.17 (s, 0.06H, enol contributor); ^{13}C NMR ($CDCl_3$) δ 14.12 ($-C(O)OCH_2\boldsymbol{C}H_3$), 30.10 ($-C(O)$-$\boldsymbol{C}H_3$), 50.10, 61.30 ($-\boldsymbol{C}(O)OCH_2CH_3$), 167.22 ($-\boldsymbol{C}(O)OCH_2$-$CH_3$), 200.74 ($-\boldsymbol{C}(O)CH_3$).

5-Bromo-1-pentene (Aldrich): ^1H NMR ($CDCl_3$) δ 1.95 (m, 2H), 2.21 (m, 2H), 3.41 (t, 2H), 5.05 (m, 2H), 5.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 31.80, 32.06, 33.06, 115.91, 136.74.

6-Bromo-1-hexene (Aldrich): ^1H NMR ($CDCl_3$) δ 1.52 (m, 2H), 1.87 (m, 2H), 2.09 (m, 2H), 3.40 (t, 2H), 5.03 (m, 2H), 5.82 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 27.25, 32.07, 32.65, 33.35, 114.82, 137.93.

8-Bromo-1-octene (Aldrich): ^1H NMR ($CDCl_3$) δ 1.38 (m, br, 6H), 1.86 (m, 2H), 2.05 (m, 2H), 3.40 (t, 2H), 4.97 (m, 2H), 5.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 28.21, 28.77, 28.91, 32.84, 33.82, 33.88, 114.20, 139.08.

10-Bromo-1-decene (Alfa Aesar, Avocado): ^1H NMR ($CDCl_3$) δ 1.38 (m, br, 10H), 1.86 (m, 2H), 2.05 (m, 2H), 3.41 (t, 2H), 4.98 (m, 2H), 5.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.19, 28.81, 28.94, 29.10, 29.42, 32.87, 33.84, 33.85, 114.19, 139.14.

10-Undecene-1-ol (Alfa Aesar, Avocado): ^1H NMR ($CDCl_3$) δ 1.24 (m, br, 12H), 1.58 (m, 2H), 1.82 (s, s, 1H, alcohol), 2.09 (m, 2H), 3.67 (t, 2H), 5.03 (m, 2H), 5.84 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 25.72, 28.90, 29.06, 29.37, 29.50, 32.78, 33.72, 62.94, 114.04, 139.11.

Synthesis and Characterization of Starting Material. 11-Bromo-1-undecene.[62] To a flame-dried and Ar-purged 500 mL three-neck flask equipped with a magnetic stir bar were added 20.0 g (117 mmol) of 10-undecen-1-ol and 200−250 mL of anhydrous Et_2O. To this solution was added 77.9 g (235 mmol) CBr_4. The stirring solution was then cooled to 0 °C, and 65.4 g PPh_3 (235 mmol) was added in small increments over a period of 30 min. The solution was allowed to warm to room temperature and stir for 6 h. The solution had manifested a yellow tint at this point. The solution was then filtered and the solvent removed under reduced pressure. The resultant residue was dissolved in pentane and filtered. The solution was then flash filtered through a short bed of silica gel and the pentane removed under reduced pressure. The resultant solution was distilled under vacuum to yield the alkenyl bromide. Yield of 11-bromo-1-undecene: 82.7% (isolated). The following spectral properties were observed. ^1H NMR ($CDCl_3$): δ 1.35 (m, br, 12H), 1.85 (m, 2H), 2.04 (m, 2H), 3.39 (t, 2H), 4.96 (m, 2H), 5.80 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 28.20, 28.79, 28.94, 29.11, 29.41, 32.87, 33.83, 33.87, 114.16, 139.13.

2. Symmetrical Monomer Synthesis and Characterization. The following set of five monomers were synthesized using an extension of a methodology presented previously.[32] A sample procedure is given for the first monomer in the series. *Note: Results for **4**−**8f** are not listed since a high polymer was not obtained*.

2.1. Step 1 (One-Pot, Two-Step Synthesis) (Dialkylation of Ethyl Acetoacetate). Synthesis and Characterization of Ethyl-2-acetyl-2-(4-pentenyl)-hept-6-enoate (4a). A 10.9 g (84 mmol) sample of ethyl acetoacetate and 200−250 mL of dry DME were placed in a flame-dried, argon-purged 500 mL three-neck flask equipped with a magnetic stirbar and condenser. A 42 mL portion of a 2 M solution of potassium *tert*-butoxide in DME was then added with stirring. Upon addition, the solution turned lime-green in color. Because of the exothermic nature, the reaction mixture was allowed to stand for 30 min to cool. Next, 12.5 g (84 mmol) of dry 5-bromo-1-pentene was slowly added via syringe over the course of 5−6 min. The reaction mixture was slowly raised to reflux becoming an orange-brown in color with salt formation. After 18 h (longer halides in this series require up to 24 h of reaction time as shown by GC), the reaction was allowed to cool to room temperature in preparation for the second addition of halide. At this point, the reaction mixture was pale yellow in color with a white precipitate. The second addition of 42 mL of a 2 M solution of potassium *t*-butoxide in DME and 12.5 g (84 mmol) of dry 5-bromo-1-pentene was administered in the same manner as described above. The reaction was taken to reflux for a period of 26 h (monitored by GC, note that longer halides in this series require up to 36 h of reaction time for completion). The reaction mixture is cooled to room temperature, quenched with 3 N HCl, and extracted three times with Et_2O. The combined ether extracts were washed with DI H_2O, dried over $MgSO_4$, filtered, and finally evaporated under reduced pressure to yield a yellow-tinted product. **Note:** the disubstituted β-keto product was not purified before proceeding with the next reaction. Yield of **4a**: 80.0% (crude). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.17 (m, br, 4H), 1.26(t, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 1.85 (m, br, 4H), 2.05 (q, 4H), 2.11 (s, 3H, $-C(O)\boldsymbol{CH_3}$), 4.19 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.99 (m, 4H, vinyl CH_2), 5.76 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.11, 23.22, 26.67, 30.73, 33.62, 33.89, 61.17, 63.38, 115.14 (vinyl CH_2), 138.01 (vinyl CH), 172.57 ($-\boldsymbol{C}(O)OCH_2CH_3$), 205.26 ($-\boldsymbol{C}(O)CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{16}H_{26}O_3$, 267; found, 267.

Synthesis and Characterization of Ethyl-2-acetyl-2-(5-hexenyl)-oct-7-enoate (4b). Synthesized as above. Yield of **4b**: 81.2% (crude). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.01 (m, br, 4H), 1.26(t, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 1.42 (m, br, 4H), 1.85 (m, br, 4H), 2.03 (q, 4H), 2.16 (s, 3H, $-C(O)\ \boldsymbol{CH_3}$), 4.20 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.98 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) not obtained. EI/LRMS: $[M + 1]^+$ calcd for $C_{18}H_{30}O_3$, 295; found, 295.

Synthesis and Characterization of Ethyl-2-acetyl-2-(7-octenyl)-dec-9-enoate (4c). Synthesized as above. Yield of **4c**: 80.1% (crude). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.09 (m, br, 4H), 1.20(t, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 1.34 (m, br, 12H), 1.84 (m, br, 4H), 2.03 (q, 4H), 2.10 (s, 3H, $-C(O)\ \boldsymbol{CH_3}$), 4.19 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.95 (m, 4H, vinyl CH_2), 5.78 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.13, 23.81, 26.63, 28.87, 29.88, 31.22, 33.80, 61.06, 63.50, 114.32 (vinyl CH_2), 138.96 (vinyl CH), 172.69 ($-\boldsymbol{C}(O)OCH_2CH_3$), 205.33 ($-\boldsymbol{C}(O)CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{22}H_{38}O_3$, 351; found, 351.

Synthesis and Characterization of Ethyl-2-acetyl-2-(9-decenyl)-dodec-11-enoate (4d). Synthesized as above. Yield of **4d**: 96.2% (crude). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.06 (t, br, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 1.30 (m, br, 24H), 1.79 (m, 4H), 2.07 (q, 4H), 2.11 (s, 3H, $-C(O)\boldsymbol{CH_3}$), 4.19 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.96 (m, 4H, vinyl CH_2), 5.80 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.12, 23.75, 26.65, 27.38, 28.90, 29.28, 29.38, 29.95, 31.10, 33.79, 61.06, 63.49, 114.15 (vinyl CH_2), 139.16 (vinyl CH), 172.75 ($-\boldsymbol{C}(O)OCH_2CH_3$), 205.62 ($-\boldsymbol{C}(O)CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{26}H_{46}O_3$, 407; found, 407.

Synthesis and Characterization of Ethyl-2-acetyl-2-(10-undecenyl)-tridec-12-enoate (4e). Synthesized as above. Yield of **4e**: 90.3% (crude). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.34 (m, br, 31H), 1.84 (m, br, 4H), 2.03 (q, 4H), 2.10 (s, 3H, $-C(O)\ \boldsymbol{CH_3}$), 4.19 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.97 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.13, 23.81, 26.62, 27.47, 28.99, 29.17, 29.37, 29.52, 30.02, 31.21, 33.86, 61.01, 63.50, 114.18 (vinyl CH_2), 139.10 (vinyl CH), 172.72 ($-\boldsymbol{C}(O)OCH_2CH_3$), 205.35 ($-\boldsymbol{C}(O)CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{28}H_{50}O_3$, 435; found, 435.

2.2. Step 2 (Retro-Claisen Condensation). Synthesis and Characterization of Ethyl-2-(4-pentenyl)-hept-6-enoate (5a). A 21.81 g sample of crude **4a** (82 mmol) and 125 mL of anhydrous EtOH (Aldrich) were placed in flame-dried, Ar-purged 500 mL three-neck round-bottom flask equipped with a condenser and stirbar. Then, 125 mL (1.1 mol) of a 21% w/w NaOEt/EtOH solution (Aldrich) was added via cannula to the solution. The reaction mixture was refluxed 4−6 h (dependent on the monomer). After cooling the solution to room temperature, the reaction was quenched with water (slowly) and 3 N HCl. The quenched reaction mixture was extracted three times with Et_2O, washed with DI H_2O, and dried over $MgSO_4$. Finally, the combined organics were distilled and evaporated under reduced pressure. The product was then placed over CaH_2 and stirred overnight. The crude ester over CaH_2 was then placed into a Vigreux distillation apparatus, placed under vacuum, and stirred overnight ($<10^{-1}$ mmHg). Crude ester (**5a**) was then distilled with a boiling point of 79−80 °C at 1 mm Hg. Yield of ester **5a**: 96.2% (crude); 62.3% (isolated). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H, $-C(O)OCH_2\boldsymbol{CH_3}$), 1.40 (m, br, 6H), 1.61 (m, br, 2H), 2.04 (q, 4H), 2.32 (m, 1H), 4.14 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.98 (m, 4H, vinyl CH_2), 5.76 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.36, 26.68, 31.93, 33.61, 45.47, 60.02 ($-C(O)O\boldsymbol{C}H_2CH_3$), 114.65 (vinyl CH_2), 138.48 (vinyl CH), 176.29 ($-\boldsymbol{C}(O)OCH_2CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{14}H_{24}O_2$, 225; found, 225; Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.94; H, 10.79. Found: C, 74.97; H, 10.77.

Synthesis and Characterization of Ethyl-2-(5-hexenyl)-oct-7-enoate (5b). Synthesized as above. Crude ester (**5b**) was distilled with a boiling point of 93−94 °C at 1 mm Hg. Yield of **5b**: 73.5% (crude); 48.3% (isolated). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.28 (m, br, 11H), 1.65 (m, 4H), 2.02 (q, 4H), 2.31 (m, 1H), 4.15 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 5.01 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.02, 14.10, 24.64, 26.67, 28.35, 28.40, 28.45, 28.64, 32.08, 33.30, 34.12, 45.46, 59.84 ($-C(O)O\boldsymbol{C}H_2CH_3$), 114.12 (vinyl CH_2), 138.54 (vinyl CH), 173.35 ($-\boldsymbol{C}(O)OCH_2CH_3$). EI/HRMS: $[M + 1]^+$ calcd for $C_{16}H_{28}O_2$, 252.2089; found, 252.2089. Anal.s Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.16; H, 11.20.

Synthesis and Characterization of Ethyl-2-(7-octenyl)-dec-9-enoate (5c). Synthesized as above. Crude ester (**5c**) was distilled with a boiling point of 155−156 °C at 1 mm Hg. Yield of **5c**: 79.5% (crude); 49.9% (isolated). The following spectral properties were observed: ^1H NMR ($CDCl_3$) δ 1.14 (m, br, 21H), 1.60 (m, br, 2H), 2.02 (q, 4H), 2.31 (m, 1H), 4.14 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 5.04 (m, 4H, vinyl CH_2), 5.83 (m, 2H, vinyl

CH); ^{13}C NMR ($CDCl_3$) δ 14.31, 27.33, 28.83, 28.91, 29.35, 32.44, 33.69, 45.72, 59.82 ($-C(O)O\boldsymbol{C}H_2CH_3$), 114.10 (vinyl CH_2), 139.03 (vinyl CH), 176.33 ($-\boldsymbol{C}(O)OCH_2CH_3$). EI/HRMS: $[M + 1]^+$ calcd for $C_{20}H_{36}O_2$, 308.2715; found, 308.2728. Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.85; H, 11.77. Found: C, 78.00; H, 11.70.

Synthesis and Characterization of Ethyl-2-(9-decenyl)-dodec-11-enoate (5d). Synthesized as above. Crude ester (**5d**) was distilled with a boiling point of 170−171 °C at 1 mm Hg. Yield of **5d**: 87.2% (crude); 56.4% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.33 (m, br, 29H), 1.58 (m, br, 2H), 2.02 (q, 4H), 2.27 (m, 1H), 4.13 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.96 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.37, 27.44, 28.94, 29.13, 29.43, 29.55, 32.54, 33.83, 45.78, 59.92 ($-C(O)O\boldsymbol{C}H_2CH_3$), 114.13 (vinyl CH_2), 139.19 (vinyl CH), 176.62 ($-\boldsymbol{C}(O)OCH_2CH_3$). EI/HRMS: $[M + 1]^+$ calcd for $C_{24}H_{44}O_2$, 365.3419; found, 365.3397. Anal. Calcd for $C_{20}H_{36}O_2$: C, 79.05; H, 12.17. Found: C, 79.11; H, 12.05.

Synthesis and Characterization of Ethyl-2-(10-decenyl)-tridec-12-enoate (5e). Synthesized as above. Crude ester (**5e**) was distilled with a boiling point of 90−91 °C at 0.03 mmHg. Yield of **5e**: 85.9% (crude); 77.5% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.37 (m, br, 33H), 1.59 (m, br, 2H), 2.03 (q, 4H), 2.28 (m, 1H), 4.13 (q, 2H, $-C(O)O\boldsymbol{CH_2}CH_3$), 4.96 (m, 4H, vinyl CH_2), 5.81 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 14.37, 25.01, 27.47, 28.97, 29.17, 29.29, 29.51, 29.55, 32.57, 33.85, 45.81, 59.92 ($-C(O)O\boldsymbol{C}H_2CH_3$), 114.13 (vinyl CH_2), 139.22 (vinyl CH), 176.63 ($-\boldsymbol{C}(O)OCH_2CH_3$). EI/LRMS: $[M + 1]^+$ calcd for $C_{26}H_{48}O_2$, 393; found, 393.

2.3. Step 3 (Ester Reduction to the Alcohol). Synthesis and Characterization of 2-(4-Pentenyl)-hept-6-en-1-ol (6a). An 18.1 g (81 mmol) sample of distilled **5a** and 200 mL of dry ether were combined in a flame-dried, Ar-purged three neck 500 mL round-bottom flask equipped with a stir bar and condenser. This mixture was then cooled to 0 °C and stirred for 30 min. To this stirring, cooled solution was added 61 mL (3 equiv of hydride) of 1.0 M lithium aluminum hydride (LAH) in Et_2O over a period of 5−10 min. Bubbling was observed during addition. The reaction was allowed to come to room temperature and stirred for a period of 6−12 h. After transferring to a beaker, DI H_2O was added (***Caution!*** dropwise initially) with stirring to quench the reaction. Upon formation of a gellike solution that hinders stirring, 3 N HCl was added to complete the quenching, dissolving all precipitated salts. The reaction mixture was extracted three times with Et_2O, washed with DI H_2O, and dried over $MgSO_4$. The combined organic extracts were filtered and evaporated under reduced pressure. The product was then placed over CaH_2, stirred overnight, and distilled under reduced pressure using a Vigreux column($<10^{-1}$mmHg). Crude alcohol (**6a**) was distilled with a boiling point of 97−98 °C at 2.2 mm Hg. Yield of alcohol **6a**: 99.8% (crude); 58.9% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.38 (m, br, 9H), 1.74 (s, 1H, $-CH_2O\boldsymbol{H}$), 2.04 (q, 4H), 3.53 (d, 2H, $-C\boldsymbol{H_2}OH$), 4.98 (m, 4H, vinyl CH_2), 5.81 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 26.23, 30.40, 34.16, 40.36, 65.48 ($-\boldsymbol{C}H_2OH$), 114.46 (vinyl CH_2), 138.90 (vinyl CH) EI/HRMS: $[M + 1]^+$ calcd for $C_{12}H_{22}O$, 183.1749; found, 183.1796. Anal. Calcd for $C_{12}H_{22}O$: C, 79.05; H, 12.17. Found: C, 79.11; H, 12.19.

Synthesis and Characterization of 2-(5-Hexenyl)-oct-7-en-1-ol (6b). Synthesized as above. Crude alcohol (**6b**) was distilled with a boiling point of 89.5−90.5 °C at 1.5 mm Hg. Yield of alcohol **6b**: 93.0% (crude); 80.2% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.30 (m, br, 13H), 1.83 (s, s, 1H, $-CH_2O\boldsymbol{H}$), 2.08 (q, 4H), 3.54 (d, 2H, $-C\boldsymbol{H_2}OH$), 5.06 (m, 4H, vinyl CH_2), 5.84 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 26.37, 29.30, 30.89, 33.64, 40.61, 65.71 ($-\boldsymbol{C}H_2OH$), 114.20 (vinyl CH_2), 138.96 (vinyl CH). EI/HRMS: $[M + 1]^+$ calcd for $C_{14}H_{26}O$, 211.2062; found, 211.2070. Anal. Calcd for $C_{14}H_{26}O$: C, 79.92; H, 12.47. Found: C, 79.90; H, 12.47.

Synthesis and Characterization of 2-(7-Octenyl)-dec-9-en-1-ol (6c). Synthesized as above. Crude alcohol (**6c**) was distilled with a boiling point of 138−139 °C at 1.2 mm Hg. Yield of alcohol **6c**: 90.2% (crude); 76.6% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.31 (m, br, 22H), 2.04 (q, 4H), 3.53 (d, 2H, $-C\boldsymbol{H_2}OH$), 4.97 (m, 4H, vinyl CH_2), 5.81 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 26.88, 28.96, 29.16, 29.95, 30.93, 33.83, 40.54, 65.66 ($-\boldsymbol{C}H_2OH$), 114.18 (vinyl CH_2), 139.18 (vinyl CH). EI/HRMS: $[M + 1]^+$ calcd for $C_{18}H_{34}O$, 266.2610; found, 266.2629. Anal. Calcd for $C_{18}H_{34}O$: C, 81.12; H, 12.87. found: 81.20; H, 12.91.

Synthesis and Characterization of 2-(9-Decenyl)-dodec-11-en-1-ol (6d). Synthesized as above. Crude alcohol (**6d**) was distilled with a boiling point of 173−174 °C at 1.0 mm Hg. Yield of alcohol **6d**: 90.8% (crude); 64.3% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.37 (m, br, 30H), 2.04 (q, 4H), 3.52 (d, 2H, $-C\boldsymbol{H_2}OH$), 4.96 (m, 4H, vinyl CH_2), 5.81 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 26.91, 28.96, 29.17, 29.52, 29.61, 30.08, 30.93, 33.85, 40.54, 65.67 ($-\boldsymbol{C}H_2OH$), 114.13 (vinyl CH_2), 139.22 (vinyl CH). EI/HRMS: $[M + 1]^+$ calcd for $C_{22}H_{42}O$, 323.3314; found, 323.3315. Anal. Calcd for $C_{22}H_{42}O$: C, 81.91; H, 13.13. Found: C, 82.05; H, 13.21.

Synthesis and Characterization of 2-(10-Undecenyl)-tridec-12-en-1-ol (6e). Synthesized as above. Crude alcohol (**6e**) was then distilled with a boiling point of 205−206 °C at 1.0 mm Hg. Yield of alcohol **6e**: 94.3% (crude); 60.7% (isolated). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.30 (m, br, 33H), 1.91 (s, s, 1H, $-CH_2O\boldsymbol{H}$), 2.03 (q, 4H), 3.54 (d, 2H, $-C\boldsymbol{H_2}OH$), 4.96 (m, 4H, vinyl CH_2), 5.81 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$) δ 15.25, 26.94, 28.99, 29.20, 29.57, 29.67, 30.14, 30.98, 33.88, 40.57, 65.61 ($-\boldsymbol{C}H_2OH$), 114.13 (vinyl CH_2), 139.21 (vinyl CH). EI/LRMS: $[M + 1]^+$ cald. for $C_{24}H_{46}O$, 351; found, 351. EI/HRMS: $[M + 1]^+$ calcd for $C_{24}H_{46}O$, 351.3627; found, 351.3630. Anal. Calcd for $C_{24}H_{46}O$: C, 82.20; H, 13.23. Found: C, 82.15; H, 13.20.

2.4. Step 4 (Tosylation of the Alcohol). Synthesis and Characterization of 6-*p*-Toluenesulfonyl Methyl-1,10-undecadiene (7a). In a flame-dried and Ar-purged 300 mL three-neck flask equipped with a stir bar, 13.04 g (72 mmol) of distilled **6a** and 100 mL of $CHCl_3$ were added. This solution was cooled to 0 °C followed by the addition of 11.6 mL (11.3 g, 143 mmol) of pyridine. After stirring 20 min, 20.49 g (107 mmol) of *p*-toluenesulfonyl chloride (TsCl) was added with constant stirring. The solution changed from colorless to a yellow-brown hue after the addition. The solution was then allowed to warm to room temperature and stirred 12−24 h. (depending on the size of the diene). The reaction was stopped and washed with 3 N HCl to neutralize any excess pyridine and dissolve pyridinium salts. The organic layer was washed with DI H_2O and saturated K_2CO_3 solution in order to remove unreacted tosyl chloride. The aqueous layers were extracted three times by $CHCl_3$, washed with DI H_2O, and combined with the original organic layer. The organic layer was dried with $MgSO_4$, filtered, and evaporated under reduced pressure to yield the crude tosylate (**7a**). The resulting product was a viscous yellow oil. Attempts to isolate the product were not pursued for fear of elimination of tosic acid. Therefore, yields for this reaction were not calculated. The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.26 (m, br, 9H), 1.95 (d, br, 4H), 2.43 (s, 3H, methyl), 3.90 (d, 2H, $-C\boldsymbol{H_2}OTs$), 4.94 (m, 4H, vinyl CH_2), 5.72 (m, 2H, vinyl CH), 7.33 (dd, 2H), 7.77 (dd, 2H); ^{13}C NMR ($CDCl_3$) δ 21.63, 25.70, 33.79, 37.41, 72.59 ($-\boldsymbol{C}H_2OTs$), 114.62 (vinyl CH_2), 127.02, 127.90, 129.84, 130.27, 138.45 (vinyl CH), 144.67. EI/LRMS: $[M]^+$ calcd for $C_{19}H_{28}SO_3$, 336; found, 336.

Synthesis and Characterization of 7-*p*-Toluenesulfonyl Methyl-1,12-tridecadiene (7b). Synthesized as above. The following spectral properties were observed: ^{1}H NMR ($CDCl_3$) δ 1.25 (m, br, 13H), 1.98 (q, 4H), 2.47 (s, 3H, methyl), 3.91 (d, 2H, $-C\boldsymbol{H_2}OTs$), 4.95 (m, 4H, vinyl CH_2), 5.76 (m, 2H, vinyl CH), 7.37 (dd, 2H), 7.85 (dd, 2H); ^{13}C NMR ($CDCl_3$) δ 14.71, 21.61, 25.91, 28.97, 30.40, 33.60, 37.56, 72.68 ($-\boldsymbol{C}H_2OTs$), 114.47 (vinyl CH_2), 127.05, 127.93, 129.80, 130.25, 133.12, 138.77 (vinyl CH), 144.66. EI/LRMS: $[M]^+$ calcd for $C_{21}H_{32}SO_3$, 364; found, 364.

Synthesis and Characterization of 9-*p*-Toluenesulfonyl Methyl-1,16-heptadecadiene (7c). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 1.26 (m, br, 21H), 2.02 (q, 4H), 2.45 (s, 3H, methyl), 3.91 (d, 2H, $-\mathrm{C}\boldsymbol{H_2}$OTs), 4.97 (m, 4H, vinyl CH$_2$), 5.78 (m, 2H, vinyl CH), 7.37 (dd, 2H), 7.79 (dd, 2H); ^{13}C NMR (CDCl$_3$) δ 21.63, 26.42, 28.88, 29.02, 29.64, 30.60, 33.79, 37.61, 72.81 ($-\boldsymbol{C}$H$_2$OTs), 114.24 (vinyl CH$_2$), 127.06, 127.95, 129.80, 130.24, 133.10, 139.09 (vinyl CH), 144.66. EI/LRMS: [M]$^+$ calcd for $C_{25}H_{40}SO_3$, 420; found, 420.

Synthesis and Characterization of 11-*p*-Toluenesulfonyl Methyl-1,20-uneicosadiene (7d). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 1.24 (m, br, 29H), 2.04 (q, 4H), 2.47 (s, 3H, methyl), 3.91 (d, 2H, $-\mathrm{C}\boldsymbol{H_2}$OTs), 4.97 (m, 4H, vinyl CH$_2$), 5.83 (m, 2H, vinyl CH), 7.34 (dd, 2H), 7.79 (dd, 2H); ^{13}C NMR (CDCl$_3$) not obtained. EI/LRMS: [M]$^+$ calcd for $C_{29}H_{48}SO_3$, 476; found, 476.

Synthesis and Characterization of 12-*p*-Toluenesulfonyl Methyl-1,22-trieicosadiene (7e). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 1.26 (m, br, 33H), 2.04 (q, 4H), 2.44 (s, 3H, methyl), 3.91 (d, 2H, $-\mathrm{C}\boldsymbol{H_2}$OTs), 4.96 (m, 4H, vinyl CH$_2$), 5.81 (m, 2H, vinyl CH), 7.37 (dd, 2H), 7.86 (dd, 2H); ^{13}C NMR (CDCl$_3$) not obtained. EI/LRMS: [M]$^+$ calcd for $C_{31}H_{52}SO_3$, 504; found, 504.

2.5. Step 5 (Reduction of the Tosylate To Yield the Methyl Branch). Synthesis and Characterization of 6-Methyl-1,10-undecadiene (1a). In a flame-dried and Ar-purged 500 mL three-neck flask equipped with a stirbar, 20.50 g (61 mmol) of crude **7a** and 200 mL of anhydrous Et$_2$O were added. This mixture was then cooled to 0 °C and stirred for 30 min. To this stirring, cooled solution, was added 91 mL (6 equiv of hydride) of 1.0 M LAH in Et$_2$O slowly over a period of 15−20 min; bubbling was observed during the addition. The reaction was brought to reflux for a period of 24−36 h, cooled, and quenched with DI H$_2$O (***Caution!*** dropwise initially). Upon formation of a viscous gel, 3 N HCl was used to complete quenching, dissolving all precipitated salts. The reaction mixture was extracted three times with Et$_2$O, washed with DI H$_2$O, and dried over MgSO$_4$. Finally, the combined organic extracts were filtered and evaporated under reduced pressure. The crude monomer was distilled before performing flash column chromatography or HPLC (see section 1.1). The crude monomer was placed over CaH$_2$, stirred overnight, and distilled by Vigreux distillation apparatus (3 mmHg). Crude monomer (**1a**) was distilled with a boiling point of 55−60 °C at 3.4 mm Hg. Yield of monomer **1a** (based on two steps from the isolated alcohol) 97.3% (crude); 43.4% (isolated). The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 0.86 (d, 3H, methyl), 1.13 (m, 2H), 1.36 (m, br, 7H), 2.04 (q, 4H), 4.97 (m, 4H, vinyl CH$_2$), 5.81 (m, 2H, vinyl CH); ^{13}C NMR (CDCl$_3$) δ 19.66, 26.44, 32.59, 34.16, 36.53, 114.18 (vinyl CH$_2$), 139.22 (vinyl CH). EI/HRMS: [M]$^+$ calcd for $C_{12}H_{22}$, 166.1722; found, 166.1740. Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.70; H, 13.30.

Synthesis and Characterization of 7-Methyl-1,12-tridecadiene (1b). Crude monomer (**1b**) was distilled with a boiling point of 77−78 °C at 1.2 mm Hg. Yield of monomer **1b** (based on two steps from the isolated alcohol): 76.7% (crude); 36.0% (isolated). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 0.83 (d, 3H, methyl), 1.20 (m, 13H), 2.04 (q, 4H), 4.96 (m, 4H, vinyl CH$_2$), 5.80 (m, 2H, vinyl CH); ^{13}C NMR (CDCl$_3$) δ 19.70, 26.59, 29.32, 32.72, 33.89, 36.91, 114.15 (vinyl CH$_2$), 139.22 (vinyl CH). EI/HRMS: [M]$^+$ calcd for $C_{14}H_{26}$, 194.2035; found, 194.2019. Anal. Calcd for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.70; H, 13.39.

Synthesis and Characterization of 9-Methyl-1,16-heptadecadiene (1c). Crude monomer (**1c**) was distilled with a boiling point of 115−116 °C at 1.2 mm Hg. Yield of monomer **1c** (based on two steps from the isolated alcohol): 89.5% (crude); 61.1% (isolated). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 0.83 (d, 3H, methyl), 1.23 (m, br, 21H), 2.04 (q, 4H), 4.96 (m, 4H, vinyl CH$_2$), 5.81 (m, 2H, vinyl CH); ^{13}C NMR (CDCl$_3$) δ 19.71, 27.04, 29.01, 29.21, 29.88, 32.80, 33.81, 37.11, 114.07 (vinyl CH$_2$), 139.21 (vinyl CH). EI/HRMS: [M]$^+$ calcd for $C_{18}H_{34}$, 250.2661; found, 250.2666. Anal. Calcd for $C_{18}H_{34}$: C, 86.31; H, 13.69. Found: C, 86.43; H, 13.63.

Synthesis and Characterization of 11-Methyl-1,20-uneicosadiene (1d). Crude monomer (**1d**) was distilled with a boiling point of 158−160 °C at 0.5 mm Hg. Yield of monomer **1d** (based on two steps from the isolated alcohol): 80.4% (crude); 57.2% (isolated). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 0.83 (d, 3H, methyl), 1.13 (br, 2H), 1.27 (br, 27H), 2.03 (q, 4H), 4.96 (m, 4H, vinyl CH$_2$), 5.81 (m, 2H, vinyl CH); ^{13}C NMR (CDCl$_3$) δ 19.73, 27.11, 28.99, 29.20, 29.57, 29.70, 30.05, 32.78, 33.86, 37.12, 114.10 (vinyl CH$_2$), 139.22 (vinyl CH). EI/LRMS: [M]$^+$ calcd for $C_{22}H_{42}$, 306; found, 306. EI/HRMS: [M]$^+$ calcd for $C_{22}H_{42}$, 306.3287; found, 306.3295. Anal. Calcd for $C_{22}H_{42}$: C, 86.18; H, 13.82. Found: C, 86.16; H, 13.84.

Synthesis and Characterization of 12-Methyl-1,22-uneicosadiene (1e). Crude monomer (**8f**) was distilled with a boiling point of 170−172 °C at 0.5 mm Hg. Yield of monomer **8f** (based on two steps from the isolated alcohol): 89.7% (crude); 47.8% (isolated). Synthesized as above. The following spectral properties were observed: ^{1}H NMR (CDCl$_3$) δ 0.83 (d, 3H, methyl), 1.13 (br, 2H), 1.26 (br, 31H), 2.03 (q, 4H), 4.96 (m, 4H, vinyl CH$_2$), 5.81 (m, 2H, vinyl CH); ^{13}C NMR (CDCl$_3$) δ 19.73, 27.12, 28.99, 29.20, 29.57, 29.67, 29.75, 30.07, 32.77, 33.86, 37.12, 114.09 (vinyl CH$_2$), 139.22 (vinyl CH). EI/HRMS: [M]$^+$ calcd for $C_{24}H_{46}$, 334.3599; found, 334.3564. Anal. Calcd for $C_{24}H_{46}$: 86.13; H, 13.87. Found: C, 86.08; H, 13.92.

3. ADMET Polymerizations of Symmetrical Methyl-Branch Monomers 1a−1e. General Metathesis Conditions for All Polymerizations Shown Below. All glassware was thoroughly cleaned and flame-dried under vacuum prior to use. The monomers were degassed and distilled from CaH$_2$ prior to polymerization. All metathesis reactions were initiated in the bulk, inside an argon atmosphere glovebox. Monomers were placed in 25 or 50 mL round-bottomed flasks equipped with a magnetic Teflon stirbar. The flasks were then fitted with an adapter equipped with a Teflon vacuum valve. The adapter allows direct attachment to the vacuum line or Schlenk hose (depending on attachment design). Monomer-to-catalyst ratios typically used were 200−500:1. After addition of catalyst, slow to moderate bubbling of ethylene was observed. The sealed reaction vessel was removed from the drybox and immediately placed on the vacuum line. The reaction vessel was then exposed to intermittent vacuum while stirring in an oil bath at 40−50 °C until the viscosity increases. Generally after 4 h, the polymerization was exposed to full vacuum ($<10^{-1}$ mmHg) and then high vacuum ($<10^{-3}$ mmHg) for a period of 48 h at 60 °C. The reaction vessel is then cooled to room temperature. The unsaturated polymer is hydrogenated using one of two methods (vide infra).

3.1. Polymerization of 6-Methyl-1,10-undecadiene (2a) Monomer **1a** was synthesized as previously described. A 1.4 g (8.4 mmol) sample of monomer **1a** was combined with 0.028 g (3.41×10^{-5}mol) of Grubbs benzylidene catalyst. The reaction was not quenched before proceeding to the hydrogenation reaction (246:1). The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR (CDCl$_3$) δ 0.84 (d, 3H, methyl), 1.11 (br, 2H), 1.30 (br, 7H), 1.97 (br, 4H), 5.36 (m, br, 2H, internal olefin); ^{13}C NMR (CDCl$_3$) δ 19.69, 27.12, 27.23, 27.53, 32.59, 32.95, 36.58, 36.70, 129.92 (cis olefin), 130.39 (trans olefin). ^{13}C NMR (CDCl$_3$) integration of cis:trans peaks gives: 23:77. GPC data: $M_n = 22\,800$; PDI (M_w/M_n) = 2.0.

Polymerization of 7-Methyl-1,12-tridecadiene (2b). Monomer **1b** was synthesized as previously described. 1.6 g (8.2 mmol) of monomer **1b** was combined with 0.018 g (2.2×10^{-5} mol) of Grubbs benzylidene catalyst (372:1). The reaction was not quenched before proceeding to the hydrogenation reaction. The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR (CDCl$_3$): δ 0.83 (d, 3H, methyl), 1.19 (br, 13H), 1.97 (br, 4H), 5.36 (m, br, 2H, internal olefin); ^{13}C NMR (CDCl$_3$): δ 19.72, 27.08, 29.26, 29.70, 29.81, 29.92, 32.65, 32.75, 37.11, 129.89 (cis olefin), 130.36 (trans olefin). ^{13}C NMR ($CDCl_3$) integration of cis:trans peaks gives: 25:75. GPC data: $M_n = 8000$; PDI (M_w/M_n) = 1.7.

Polymerization of 9-Methyl-1,16-heptadecadiene (2c). Monomer **1c** was synthesized as previously described. 1.3 g (5.0 mmol) of monomer **1c** was combined with 0.021 g (2.6×10^{-5} mol) of Grubbs' benzylidene catalyst (192:1). The reaction was not quenched before proceeding to the hydrogenation reaction. The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.84 (d, 3H, methyl), 1.08 (br, 2H), 1.26 (br, 19H), 2.03 (br, 4H), 5.38 (m, br, 2H, internal olefin); ^{13}C NMR ($CDCl_3$) δ 19.72, 27.08, 27.23, 29.26, 29.38, 29.70, 29.81, 29.92, 32.65, 32.75, 37.11, 129.89 (cis olefin), 130.36 (trans olefin). ^{13}C NMR ($CDCl_3$) integration of cis:trans peaks gives: 26:74. GPC data: M_n = 15 700; PDI (M_w/M_n) = 1.7.

Polymerization of 11-Methyl-1,20-uneicosadiene (2d). Monomer **1d** was synthesized as previously described. 2.1 g (6.8 mmol) of monomer **1d** was combined with 0.026 g (3.2×10^{-5} mol) of Grubbs benzylidene catalyst (215:1). The reaction was not quenched before proceeding to the hydrogenation reaction. The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.07 (br, 2H), 1.26 (br, 27H), 2.01 (br, 4H), 5.38 (m, br, 2H, internal olefin); ^{13}C NMR ($CDCl_3$) δ 19.72, 27.11, 27.21, 29.22, 29.34, 29.58, 29.72, 30.05, 32.63, 32.77, 37.12, 129.89 (cis olefin), 130.36 (trans olefin). ^{13}C NMR ($CDCl_3$) integration of cis:trans peaks gives: 17:83. GPC data: M_n = 11 300; PDI (M_w/M_n) = 1.9.

Polymerization of 11-Methyl-1,20-uneicosadiene (2ds). Monomer **1d** was synthesized as previously described. 2.2 g (7.1 mmol) of monomer **1d** was combined with 0.011 g (1.4×10^{-5} mol) of Schrock's catalyst (507:1). The reaction was quenched by exposing to the air before proceeding to the hydrogenation reaction. The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.08 (br, 2H), 1.26 (br, 27H), 2.02 (br, 4H), 5.37 (m, br, 2H, internal olefin); ^{13}C NMR ($CDCl_3$) δ 19.72, 27.09, 27.21, 29.21, 29.34, 29.57, 29.72, 30.05, 32.63, 32.76, 37.12, 129.89 (cis olefin), 130.36 (trans olefin). ^{13}C NMR ($CDCl_3$) integration of cis:trans peaks gives: 21:79. GPC data: M_n = 78 100; PDI (M_w/M_n) = 1.9.

Polymerization of 12-Methyl-1,22-trieicosadiene (2e). Monomer **1e** was synthesized as previously described. 1.6 g (4.8 mmol) of monomer **1e** was combined with 0.028 g (3.4×10^{-5} mol) of Grubbs benzylidene catalyst (141:1). The reaction was not quenched before proceeding to the hydrogenation reaction. The following spectral properties were obtained for the unsaturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.08 (br, 2H), 1.26 (br, 31H), 2.02 (br, 4H), 5.37 (m, br, 2H, internal olefin); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.14, 29.22, 29.35, 29.58, 29.70, 29.76, 30.08, 32.65, 32.78, 37.14, 129.90 (cis olefin), 130.36 (trans olefin).^{13}C NMR ($CDCl_3$) integration of cis:trans peaks gives: 20:80. GPC data: M_n = 20 200; PDI (M_w/M_n) = 1.7.

4.1. Hydrogenation of Polymers 2a–2e. Supported Catalyst System.[39] Synthesis and Characterization of 3a. **2a** was taken into an argon atmosphere drybox. The tacky, rubbery polymer was removed from its original flask, sliced into smaller pieces, and placed into a high-pressure glass wall reactor with a threaded top and equipped with a disposable magnetic stir bar. The unsaturated polymer and 2.8 g (100 times the weight of catalyst is typical) of silica gel were added. The three substances were then kneaded, mixed, and formed into a ball-like structure using a spatula. Finally 20 mL of dry toluene was added. The reaction vessel was then sealed with a Teflon cap affixed with a high-pressure valve attachment and pressure gauge. The reaction vessel was removed from the drybox, connected to a hydrogen tank, and charged with 125 psi of H_2. The reaction was then stirred and heated at 80–85 °C for 48 h, then cooled to room temperature. The hydrogenated polymer **3a** was obtained by filtration of the silica and other particulate matter, and finally evaporation of the reaction solvent under reduced pressure. The polymer was then dried in vacuo overnight. **2a** was then dissolved in toluene and precipitated into cold CH_3OH. Yield: 65% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.08 (br, 2H), 1.26 (br, 15H); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.11, 29.78, 30.07, 32.77, 37.12. Anal. Calcd for repeat unit $(C_{10}H_{20})_n$: C, 85.62; H, 14.38. Found: C, 85.58; H, 14.41. GPC data: M_n = 17 500; PDI (M_w/M_n) = 1.7. Initial DSC results (samples not annealed): T_m(peak) = −12 °C, ΔH_f = 37 J/g. DSC results (annealed samples): T_m(onset) = −18 °C, T_m(peak) = −14 °C, ΔH_f = 28 J/g; T_c(onset) = −22 °C, T_c(peak) = −24 °C, ΔH_f = 25 J/g. Glass transition temperature data: T_g = −44 °C, ΔC_p = 28 J/g°C. Thermogravimetric analysis (TGA) (onset of weight loss) = 416.52 °C.

4.2. Synthesis and Characterization of 3b. Synthesized as above. Yield: 69% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.08 (br, 2H), 1.26 (br, 19H); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.12, 29.76, 30.07, 32.77, 37.12. Anal. Calcd for repeat unit $(C_{12}H_{24})_n$: 85.62; H, 14.38. Found: C, 85.57; H, 14.38. GPC data: M_n = 8500; PDI (M_w/M_n) = 1.8. Initial DSC results (samples not annealed): T_m(peak) = 14 °C, ΔH_f = 51 J/g. DSC results (annealed samples): T_m(onset) = −3 °C, T_m(peak) = 11 °C, ΔH_f = 66 J/g; T_c(onset) = 0 °C, T_c(peak) = −2 °C, ΔH_f = 63 J/g. Glass transition temperature data: T_g = −44 °C, ΔC_p = 28 J/g°C. Thermogravimetric analysis (TGA) (onset of weight loss) = 435.27 °C.

4.3. Synthesis and Characterization of 3c. Synthesized as above. Yield: 73% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.07 (br, 2H), 1.29 (br, 27H); ^{13}C NMR ($CDCl_3$) δ 19.75, 27.12, 29.75, 30.08, 32.77, 37.14. Anal. Calcd for repeat unit $(C_{16}H_{32})_n$: 85.62; H, 14.38. Found: C, 85.43; H, 14.30. GPC data: M_n = 17 100; PDI (M_w/M_n) = 1.7. Initial DSC results (samples not annealed): T_m(peak) = 39 °C, ΔH_f = 71 J/g. DSC results (annealed samples): T_m(onset) = 35 °C, T_m(peak) = 39 °C, ΔH_f = 82 J/g; T_c(onset) = 32 °C, T_c(peak) = 31 °C, ΔH_f = 83 J/g. Thermogravimetric analysis (TGA) (onset of weight loss) = 447.32 °C.

4.4. Synthesis and Characterization of 3d. Synthesized as above. Yield: 71% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.82 (d, 3H, methyl), 1.24 (br, 37H); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.12, 29.73, 30.06, 32.78, 37.13. Anal. Calcd for repeat unit $(C_{20}H_{40})_n$: 85.62; H, 14.38. Found: C, 85.39; H, 14.38. GPC data: M_n = 17 400; PDI (M_w/M_n) = 1.6. Initial DSC results (samples not annealed): T_m(peak) = 57 °C, ΔH_f = 107 J/g. DSC results (annealed samples): T_m(onset) = 53 °C, T_m(peak) = 57 °C, ΔH_f = 96 J/g; T_c(onset) = 53 °C, T_c(peak) = 51 °C, ΔH_f = 99 J/g. Thermogravimetric analysis (TGA) (onset of weight loss) = 444.64 °C.

4.5. Synthesis and Characterization of 3e. Synthesized as above. Yield: 77% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^{1}H NMR ($CDCl_3$) δ 0.84 (s, br, 3H, methyl), 1.25 (br, 41H); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.11, 29.73, 30.05, 32.75, 37.11. Anal. Calcd for repeat unit $(C_{22}H_{44})_n$: C, 85.62; H, 14.38. Found: C, 85.26; H, 14.32. GPC data: M_n = 17 500; PDI (M_w/M_n) = 1.7. Initial DSC results (samples not annealed): T_m(peak) = 63 °C, ΔH_f = 100 J/g. DSC results (annealed samples): T_m(onset) = 57 °C, T_m(peak) = 62 °C, ΔH_f = 103 J/g; T_c(onset) = 60 °C, T_c(peak) = 56 °C, ΔH_f = 102 J/g. Glass transition temperature data: T_g = −42 °C, ΔC_p = 27 J/g°C. Thermogravimetric analysis (TGA) (onset of weight loss) = 448.35 °C.

5. Hydrogenation of Polymer 2ds. Modified Diimide Reaction.[18,19,39–40] Synthesis and Characterization of 3ds. The hydrogenation was performed in a flame-dried, Ar-purged 100 mL three-neck round-bottom flask equipped with a reflux condenser and Teflon magnetic stirbar. To this flask was added 400 mg (1.3×10^{-3}mol) of **2ds**, 40 mL of dry *o*-xylene, 608 mg (2.5 equiv) of TSH, and 467 mg (or 0.62 mL, 2.5 equiv) of TPA. The solution was heated to reflux and maintained for 6 h with vigorous stirring. Gas evolution was observed upon heating. The solution was then cooled to room temperature and an additional 2.5 equiv of TSH and TPA were added. The solution was brought to reflux for an additional 6 h period and then cooled to room temperature. Finally, the reaction mixture was precipitated directly into cold CH_3OH giving a rubbery white solid. The polymer was placed in a flask under vacuum overnight at 60 °C. The resultant product was cooled and isolated as a hard, milky film. Yield: 92% (after precipitation). The following spectral properties were obtained for the saturated polymer: ^1H NMR ($CDCl_3$) δ 0.83 (d, 3H, methyl), 1.24 (br, 37H); ^{13}C NMR ($CDCl_3$) δ 19.73, 27.11, 29.73, 30.07, 32.78, 37.12. Anal. Calcd for repeat unit $(C_{20}H_{40})_n$: C, 85.62; H, 14.38. Found: C, 85.41; H, 14.26. GPC data: $M_n = 72\,000$; PDI (M_w/M_n) = 1.9. Initial DSC results (samples not annealed): T_m(peak) = 57 °C, ΔH_f = 84 J/g. DSC results (annealed samples): T_m(onset) = 49 °C, T_m(peak) = 57 °C, ΔH_f = 86 J/g; T_c(onset) = 51 °C, T_c(peak) = 49 °C, ΔH_f = 82 J/g. Thermogravimetric analysis (TGA) (onset of weight loss) = 447.50 °C.

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