

Feature Article

Precision polyolefin structure: Modeling polyethylene containing alkyl branches

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ABSTRACT

Step-growth acyclic diene metathesis (ADMET) polymerization chemistry followed by exhaustive hydrogenation offers a new modeling approach for the study of polyethylene structures. ADMET controls branch identity and frequency, both of which are predetermined during the monomer synthesis, allowing sequence control in the resultant polymer. This review describes the synthesis and thermal behavior of ADMET polymers that serve as models for copolymers of ethylene with α -olefins such as 1-propene, isobutylene 1-butene, and 1-octene.

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1. Introduction

Polyethylene (PE) is the largest volume polymer produced worldwide with an annual demand of over 60 million tons [1,2]. An average growth rate of 5.2% in terms of demand-production during the present decade is expected [3]. Oligomers of PE were first observed in 1898 by Hans von Pechmann, Eugen Bamberger and Friedrich Tschirner by accident during high pressure experiments with diazomethane [4]. In 1933, Imperial Chemical Industries (ICI) reported the existence of high-molecular-weight polyethylene, and in 1937 ICI obtained the patent for its commercial production [5].

A significant contribution to polymer chemistry was made in the 1950s by Karl Ziegler, when he synthesized high density polyethylene (HDPE) at low pressure and temperature using a heterogeneous titanium catalyst. Inspired by Ziegler's work, in 1954 Giulio Natta applied this technology to synthesize polypropylene. Ziegler and Natta jointly received the Nobel Prize in chemistry for polymerization and the development of these catalysts, which today bear their names [6,7]. Polymerization of ethylene using Ziegler [6–11] and homogenous metallocene-based catalysts [12,13] produces highly crystalline (62–80%) materials. The degree of crystallinity can be controlled by the copolymerization of ethylene with α -olefins; linear-low density polyethylene (LLDPE) is the result. The incorporation of the comonomer, typically 1-propene, 1-butene, 1-hexene, or 1-octene, produces long run lengths of unbranched linear polyethylene with random branched regions. These branched

polyethylenes are known for their enhanced mechanical properties and industrial importance. Diverse types of materials can be obtained by controlling the mode of polymerization, catalyst nature, pressure and temperature [8,11–25].

The physical properties of PE obtained via α -olefin copolymerization depend on the branch content, which is directly related to the amount of comonomer incorporated into the polyethylene backbone. For LLDPE, the physical properties can vary depending on the molecular weight, molecular-weight distribution, branch identity, branch content and branch distribution. Control over LLDPE physical properties can be achieved using diverse methods based on choice of catalyst, initiator, comonomer, as well as types of temperature and pressure [18–20,25–30].

Commercial LLDPE is usually prepared by chain-growth polymerization using Ziegler–Natta or metallocene chemistry. Because of multi-site initiation on the heterogeneous catalyst, Ziegler systems produce primary structures with low-molecular weights and broad molecular-weight distributions. By comparison, metallocenes, which are single-site homogenous catalysts, provide LLDPEs with narrower molecular-weight distributions and higher levels of comonomer incorporation. Both types of catalysts have the disadvantage of generating random errors in the main backbone, causing defects or heterogeneity in the primary structure; the problem is less severe in the case of metallocene-based PE. The frequency of appearance of these defects along the main chain is widely used to manipulate the product to obtain materials with desired physical properties. Studies of model branched PEs can lead to a better understanding of polymer processing and the overall microstructural effects produced by branch perturbations on PE-based materials [17,31,32].

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Chain transfer and/or chain walking can occur if the PE is prepared by free-radical, Ziegler–Natta or metallocene chemistry [17,22,23,33], and attempts to produce model materials with well-defined primary structures have failed using these methods [20,25,28,34–36]. As a result, most of the PE research has focused on the study of short chain branching (SCB) and short chain branch distribution (SCBD) [2,17,19,20,25,28–32,34–40].

Model systems are often employed to study the behavior of these commercial materials. Many of the methods available involve chain propagation chemistry which are still subjected to the incorporation of unwanted defects via head-to-head or tail-to-tail monomer coupling [41–45]. The problems associated with chain-growth polymerization can be overcome using step-growth condensation polymerization. The step-growth acyclic diene metathesis (ADMET) process produces model polyolefins with well-defined primary structures, since the chemistry is controlled by the nature of the monomer rather than the catalyst or comonomer incorporation. Catalyzed copolymerization of ethylene with α -olefins produces ill-defined primary structures; use of a single symmetric monomer in an ADMET polymerization produces PE with a precisely known primary structure [46–50]. Consequently ADMET polymerization chemistry followed by exhaustive hydrogenation offers a new approach to the synthesis of PE backbones either without branches [47] or with specific branches precisely placed along the main backbone [48,49]. While these are not models for industrial ethylene copolymers in the true sense of the word, they represent an excellent starting point for the study of structure property in ethylene-based materials by isolating the effects of specific structural features. These polymers can be seen as benchmarks for industrial copolymers with similar composition.

ADMET chemistry is illustrated in Fig. 1. The driving force of this step-growth polycondensation is the removal of the condensate ethylene, accomplished by applying vacuum under normal polymerization conditions between 25 and 55 °C. As is shown in Fig. 1, an unsaturated polymer is formed and subsequent hydrogenation produces saturated PE models with well-defined primary structures [48–53]. Polyethylene with methyl, *gem*-dimethyl, ethyl and hexyl branches has been synthesized, and their thermal behavior, among other parameters, is being used to model the properties of ethylene/1-propene, ethylene/isobutylene, ethylene/1-butene and ethylene/1-octene random copolymers obtained via typical chain polymerization methods. Below we review the synthesis and thermal behavior of a series of model linear and branched PEs, as well as random ethylene/1-propene copolymers made via the ADMET approach [47–50,53,54].

2. Linear ADMET polyethylene

Synthesis of high-molecular-weight linear PE without undesired defects is important for studies of crystallization behavior [20]. Previous studies of such macromolecules have been limited to large *n*-paraffins (monodisperse ethylene oligomers) up to 390 carbons in length [37,55]. These models have perfect primary structures, but the presence of a high molar concentration of methyl end groups leads to inexact results when morphological behavior is extrapolated to high-molecular-weight systems, because these end groups impede crystallization. Such extrapolations can be useful in studying primary structure, but the results can be ambiguous [1,37–39].

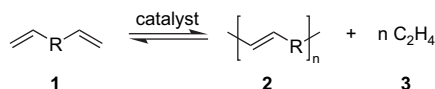


Fig. 1. The ADMET reaction.

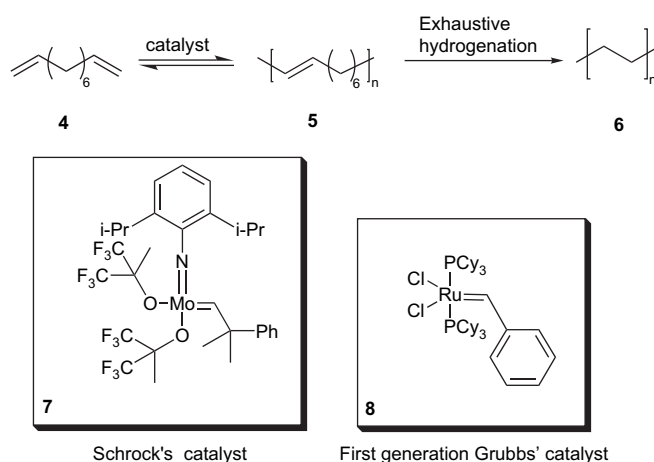


Fig. 2. ADMET polymerization of 1,9-decadiene followed by hydrogenation.

On the other hand, ADMET polymerization yields defect-free linear PE of molecular weight up to $\bar{M}_n \sim 15,000$ g/mol and a most probable molecular-weight distribution $\bar{M}_w \sim 30,000$ g/mol by bulk polymerization of 1,9-decadiene in the presence of Grubb's or Schrock's catalyst, as shown in Fig. 2. The resulting polyoctanamer is exhaustively hydrogenated to produce completely saturated PE. The ADMET method also allows control of the PE molecular weight by regulating the reaction time, temperature, and monomer/catalyst ratio.

Table 1 shows the melting temperatures and enthalpies for ADMET PEs of varying number-average molecular weights determined by differential scanning calorimetry (DSC). All of these samples, including those with low-molecular weights, show sharp T_m 's at temperatures above 130 °C, even with molecular weight values as low as $\bar{M}_n = 2400$ g/mol. Based on these results, the thermal behavior of lower molecular weight ADMET PE is consistent with that of conventional HDPE [47,51,52].

3. Models of ethylene/ α -propylene copolymers

Methyl-branched ADMET polymers model a large family of statistically random ethylene/ α -olefin copolymers [1,29,51]. For example polypropylene (PP) is crystalline material when the tacticity of the pendant methyl group is highly regular, but it is completely amorphous when the methyl groups are randomly oriented, as in atactic PP. Between the extremes of amorphous PP and defect-free polyethylene lie EP copolymers where the defect is always a methyl group. By varying the number and placement of the incorporated methyl defects, the response of the final material can be significantly altered.

Although numerous methods are available for producing such systems, only those modeled by ADMET have controlled comonomer content and distribution, thereby leading to fewer ambiguities relative to other model systems when relating structure on the molecular level to macroscopic properties. Precisely sequenced EP copolymers can be obtained via ADMET polymerization of a symmetrical α,ω -diene bearing a pendant methyl group, followed by exhaustive saturation. It is important to note

Table 1
Effect of molecular weight on thermal behavior in linear ADMET PE

\bar{M}_n (g/mol)	Polydispersity index (PDI)	T_m (°C) (peak)	Δh_m (J/g)
2400	2.4	130.7	252
7600	2.4	131.3	213
11,000	1.9	132.0	221
15,000	2.6	133.9	204
HDPE	3.1	133.3	210

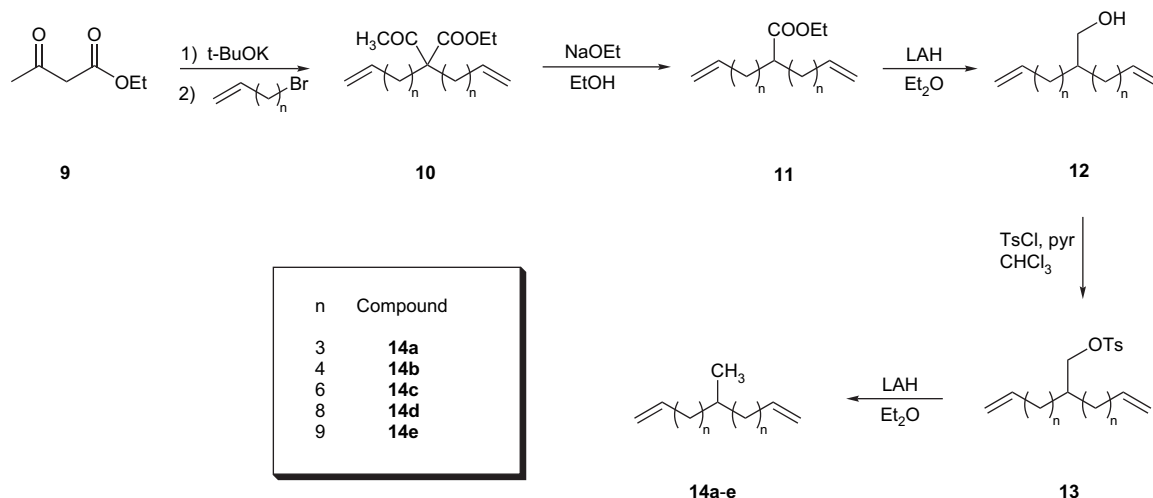


Fig. 3. Synthesis of diverse methyl monomers.

that all polymers obtained by this methodology are atactic with respect to the relative stereochemistry of the alkyl branch. These models are named according to the frequency of the pendant defect. For example EP9 refers to polyethylene containing a methyl branch on every 9th carbon; EP15 has a methyl branch on every 15th carbon, etc.

The α,ω -diene monomers were first prepared by alkylating ethyl acetoacetate [48,51]. Fig. 3 shows the synthetic scheme employed for preparation of diverse methyl α,ω -diene monomers. First, alkylation of ethyl acetoacetate with alkenyl bromide produces a β -alkenyl- β -ketoester, which is then deacylated via a retro-Claisen condensation. The resulting ester is reduced to a primary alcohol, tosylated, followed by displacement with hydride, producing the required methyl-branched diene monomer **14a–e**.

Polymerization of methyl α,ω -diene monomers **14a–e** is carried out with Schrock's catalyst (Fig. 4). The resultant unsaturated ADMET polymer is then exhaustively hydrogenated yielding ADMET PE with methyl groups precisely placed along the PE backbone. This strategy has been used to synthesize a pool of ADMET PE materials containing methyl groups on every 9th, 11th, 15th, 19th, or 21st carbon (EP9 through EP21) [48]. Because ring closing metathesis is observed if the reaction is carried out with 1,6-heptadiene-based structures, synthesis of EP copolymers with higher density of precisely placed CH_3 side groups requires a

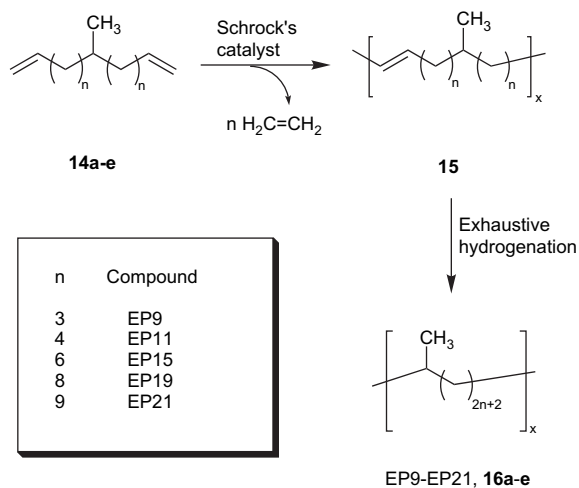


Fig. 4. General synthetic scheme for synthesis of symmetrical methyl-branched polyethylene models by ADMET.

different approach, where polymerization of monomers containing two methyl groups on each monomeric unit is effective. Fig. 5 shows the schemes for synthesizing ADMET monomers containing two methyl groups placed 7 (**23**) and 5 (**26**) carbons apart, respectively [56].

Both the schemes are based on diethyl malonate chemistry. Dialkylation of either 1,6-dibromohexane or 1,4-dibromobutane with diethyl alkenyl malonate yields a tetraester diene, which is converted to the respective tetraacid diene after saponification and decarboxylation. Reduction to the diol is achieved with lithium aluminum hydride. Subsequent double-mesylation of the respective diol followed by reductive cleavage with hydride yields the desired monomer **23** or **26** [56].

Polymerization of monomers **23** and **26** is carried out in the bulk with Schrock's catalyst under high vacuum, as is shown in Fig. 6 for EP7. High-molecular-weight unsaturated polymers EP5u ($\bar{M}_n = 26,000$ g/mol) and EP7u ($\bar{M}_n = 12,700$ g/mol) were isolated, and exhaustive hydrogenation yielded EP5 and EP7, respectively.

Table 2 presents thermal analysis data for ADMET polymers EP5–EP21. The effects of branch distribution are obvious. The peak melting temperatures and heats of fusion of ADMET EPs increase as the branch content decreases, a clear indication of increasing crystalline content [48,51]. Due to the highly organized primary microstructure, these precise models are semicrystalline even at branch contents high enough to render random EP copolymers completely amorphous. Only when methyl groups are placed on every 5th carbon do these precise ADMET EP copolymers lose the ability to crystallize.

Semicrystalline polymers EP9–EP21 show sharp and well-defined endothermic transitions, as shown in Fig. 7 [29]. In contrast EP copolymers obtained via Ziegler–Natta polymerization exhibit a broad and indistinct melting behavior when the percentage of propylene incorporated in the final material exceeds 15% [57,58].

It is also interesting to compare the DSC data for ADMET EPs with the results for ADMET PE, where $T_m = 134$ °C and $\Delta h_m = 204$ J/g are significantly higher than T_m and Δh_m for any of the EP products. The data in Table 2 show that the amorphous contribution can be tuned by the frequency of the methyl branches producing totally amorphous or semicrystalline materials.

Two versions of ADMET EP19 copolymers were prepared with significantly different number-average molecular weights, $\bar{M}_n = 17,400$ g/mol and $\bar{M}_n = 72,000$ g/mol to investigate the effect of molecular weight. A sharp melting endotherm of 57 °C is observed for both the polymers, indicating that a number-average molecular weight of approximately 17,400 is sufficient for the

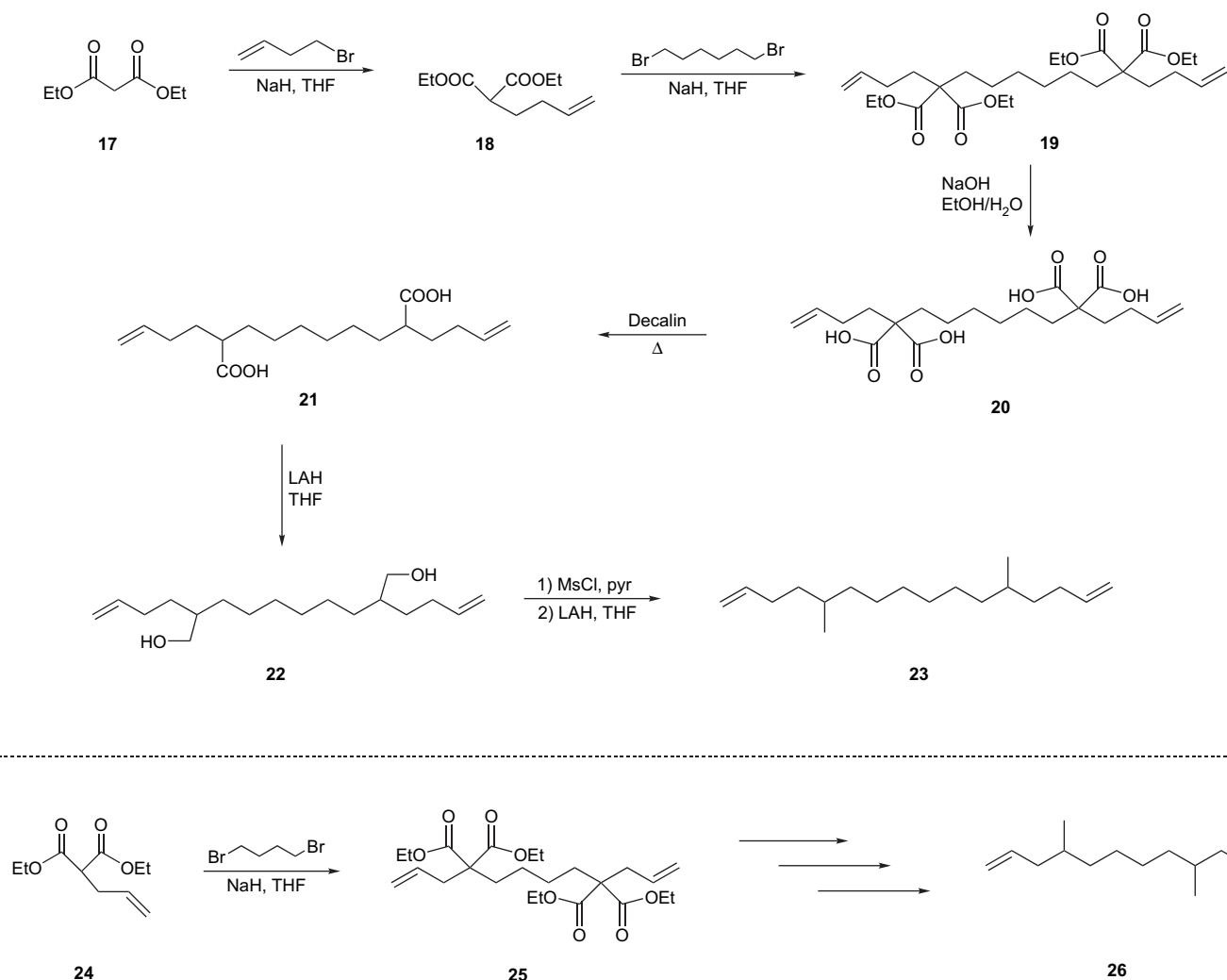


Fig. 5. General synthetic scheme for short ethylene run length monomers for ADMET.

thermal comparison of this model with commercial EP copolymers [48,55,59].

EP21 and EP15 polymers have been characterized further by X-ray diffraction, wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) as well as transmission electron microscopy (TEM), and Raman spectroscopy to further understand their structure and morphology [60]. According to the TEM results, the lamellar thickness far exceeds the inter-branch distance along the backbone, indicating that the methyl group is included within

the crystal. This finding was verified by crystallography, which shows that the chains pack into a triclinic lattice that allows inclusion of methyl branches as lattice defects. Further, the methylene sequences between defects participate in a hexagonal sublattice. In order for the chains to pack in this way, the defects must all be contained within planes oblique to the chain stems, leading to conformationally distorted crystals. This is more prevalent in the case of EP15 than in EP21 due to the greater defect content, a result confirmed by Raman spectroscopy, as well as the

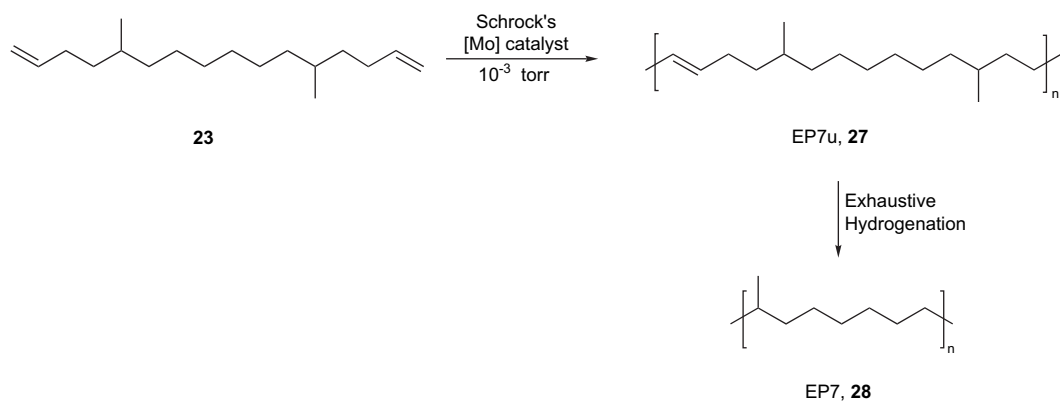


Fig. 6. Synthesis of EP7 copolymer.

Table 2
Precise short chain branch distribution and its effect on thermal behavior

ADMET PE	Methyl branches per 1000 carbon atoms	T_m (°C) (peak)	Δh_m (J/g)	\bar{M}_n (g/mol)
EP5	200	Amorphous		28,400
EP7	143	-60	19	12,900
EP9	111	-14	28	17,500
EP11	91	11	66	8500
EP15	67	39	82	17,100
EP19	53	57	96	17,400
EP19	53	57	84	72,000
EP21	48	62	103	20,200
Linear ADMET PE	0	134	204	15,000

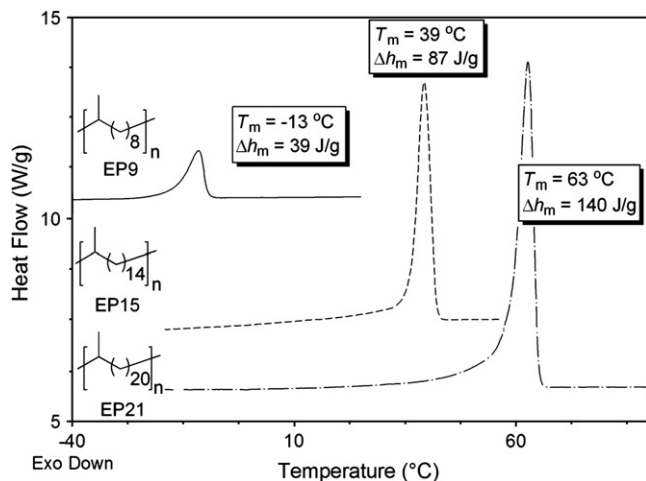


Fig. 7. DSC profiles for EP9, EP15 and EP21 copolymers.

melting temperature data in Table 2. Scattering and DSC experiments performed on EP21 led to the same conclusion [61]. The defects are concentrated in planes between stacks of hexagonally packed methylene sequences; the unit cell which houses the defected planes and hexagonal sublattice is described as monoclinic, rather than triclinic [61].

Additional differential scanning calorimetry studies of EP5 and EP7 copolymers illustrate the effects of the short run length on thermal behavior, as is shown in Fig. 8. ADMET EP copolymers from EP9 to EP21 exhibit semicrystalline behavior, whereas EP5 exhibits fully amorphous behavior. While a β glass transition temperature for semicrystalline ADMET EP9–EP21 copolymers is observed at -43 °C [48], EP5 shows a T_g at -65 °C, 20 °C lower. The dramatic

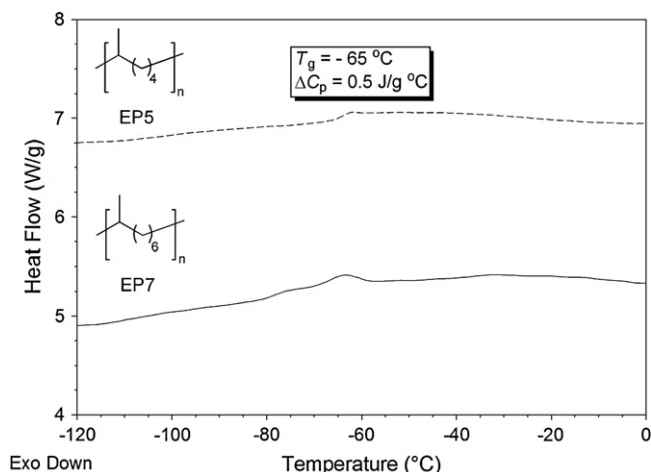


Fig. 8. DSC profiles of EP5 and EP7.

shift to a lower temperature of the observed T_g is attributed to the high methyl branch density. Similar effects have been observed in random EP copolymers when the propylene content exceeds 50 wt% [21]. However, when propylene content exceeds 84 wt%, the polymer exhibits residual crystallinity resembling homopolypropylene, and the material can be classified as ethylene-poor ethylene/propylene copolymer [21,56]. Copolymer EP5 is the first example of fully amorphous material within the family of sequenced EP copolymers.

4. Irregularly placed methyl branches

Copolymers with irregularly placed methyl branches can be synthesized by copolymerization of ADMET EP monomers with an unbranched α,ω -diene. For example, copolymerization of a methyl-substituted α,ω -diene with 1,9-decadiene, followed by exhaustive hydrogenation, yields ADMET EP copolymers with irregular branch placement [50]. Fig. 9 shows six copolymers, which model their industrial EP copolymer analogs.

The melting temperatures for irregularly placed methyl branching EP copolymers follow a pattern similar to that of commercial materials obtained via chain propagation chemistry. As the methyl branch content increases, the peak melting, percent crystallinity, and heat of fusion decrease, as is shown in Table 3 [50].

Polymers with the highest amount of propylene incorporation (43.3 and 55.6 branches per 1000 carbons) show broad and indistinct DSC profiles as commercial materials do. However, lowering the amount of propylene results in sharp and well-defined endotherms similar to those obtained for precisely sequenced EP copolymers. Fig. 10 shows the DSC thermograms for two polymers with 45 methyl branches per 1000 carbons [50,51]. The top trace, corresponding to the polymer with equally spaced methyl groups, has a sharp well-defined endotherm; this is in contrast with the thermogram of the irregularly sequenced analog, which shows a broad and ill-defined melting transition. The difference in thermal behaviors may be attributed to microstructural characteristics of the two polymers.

The polymer with precise branch spacing has a unique lamellar thickness and a sharp well-defined endotherm. The irregular branch spacing system exhibits broad thermal response and a lower heat of fusion due to the variable lamellar thickness imparted by uneven ethylene run length. These facts illustrate the effect of irregular and uniform SCBD on EP copolymers. ADMET has proven to impart control over the branch content, and more importantly, branch regularity, allowing formation of model polymers which cannot be made in any EP copolymerization via conventional chain-growth chemistry [50–52].

5. Precise models of ethylene/ α -olefin copolymers

Polyethylene with precisely placed alkyl branches larger than methyl groups has also been prepared via ADMET, where such materials are models for copolymers of ethylene and α -olefins larger than propylene. ADMET models with precisely placed *gem*-dimethyl, ethyl, and hexyl branches have been examined to further understand the morphology of these precise materials and to investigate the size limit for inclusion of defects within the crystal.

6. Polyethylene containing geminal dimethyl branches

Polyethylene containing *gem*-dimethyl branches can be regarded as an ethylene/isobutylene (EIB) copolymer. While these structures have proven to be elusive via chain propagation techniques due to the vastly differing reactivities of the comonomers [62], EIB models have been prepared in high yields via ADMET polymerization [53].

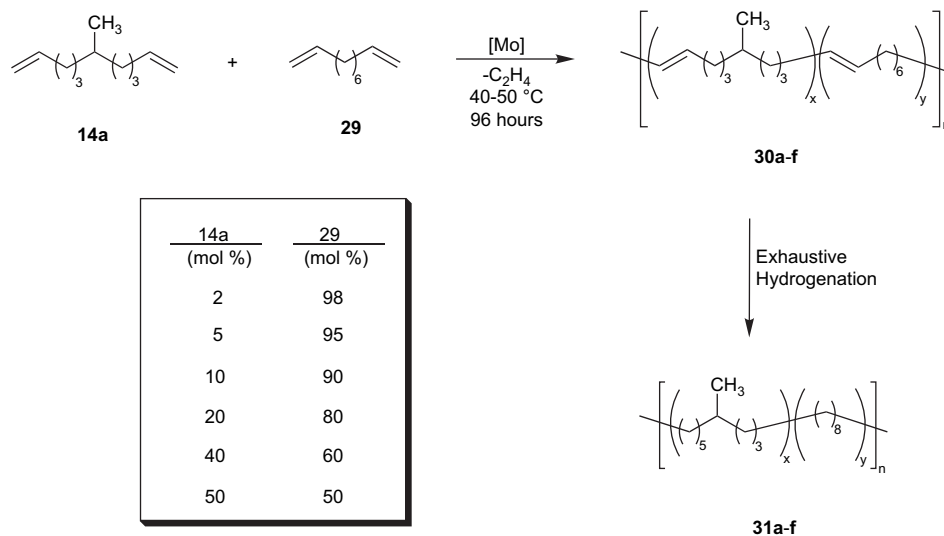


Fig. 9. Synthesis of irregularly placed methyl branching PE copolymers by varying diene comonomer ratios.

Table 3

The effect of increasing branch content on thermal behavior and crystallinity in random EP copolymers

Polymer	Methyl branches per 1000 carbon atoms	T_m (°C) (peak)	Δh_m (J/g)	% Crystallinity
Linear ADMET PE	0	133.0	230.0	78.5
31a	1.5	129.0	207.6	71.3
31b	7.1	123.2	183.4	62.1
31c	13.6	119.0	165.8	56.3
31d	25.0	111.6	137.3	47.6
31e	43.3	80.7	87.0	29.6
31f	55.6	52.1	85.0	29.0

Fig. 11 illustrates the chemistry used to synthesize three symmetrical *gem*-dimethyl-substituted α,ω -diene monomers. Sequential addition of two equivalents of alkenyl bromide to ethyl propionate using lithium diisopropyl amide (LDA) to form the enolate intermediate, leads to the carboxylic acid intermediate **33**. Reduction with LiAlH_4 generates the alcohol **34**, which is converted to the tosylate **35**. Finally, the tosylate is reduced with LiAlH_4 to give the symmetrical *gem*-dimethyl-substituted α,ω -diene **36**. Polymerization of *gem*-dimethyl α,ω -diene monomers is carried out with Schrock's catalyst. The resulting unsaturated ADMET polymer is then exhaustively hydrogenated yielding EIB models of

polyethylene with geminal dimethyl groups precisely placed on every 9th, 15th and 21st carbon [53].

Precision *gem*-dimethyl ADMET EIBs serve as models to show the effect of increasing steric bulk. The DSC data for EIB9, EIB15, and EIB21 are presented in Fig. 12 and Table 4. These results can be compared with the data of EP9, EP15, and EP21 in Fig. 7 and Table 2. In the case of EIB9, the addition of the second methyl group disrupts the polymer's ability to pack into crystals resulting in a totally amorphous material, compared to semicrystalline EP9. Extending the inter-defect sequence length to 14 or 20 carbons renders the polymer semicrystalline, with depressed melting temperature when compared to the analogous EP models.

Interestingly, the difference between the T_m s for EIB15 and EP15 is only 7 °C, compared to a 17 °C decrease between EP21 and EIB21. Extensive DSC studies on this polymer have revealed that much of this behavior is dependent on thermal history. The rather broad hysteresis between the melting and crystallization transitions suggests that these polymers crystallize fairly slowly. This possibility is supported by the finding that the samples undergo a "cold crystallization" [53]. Wide-angle X-ray diffraction (WAXD) studies show reflections associated with hexagonal, monoclinic, and triclinic packing, pointing towards polymorphism as a possible cause of this complex behavior. The melting behavior was found to be very similar with the melting of a 20-carbon *n*-paraffin, suggesting that the crystallization behavior of EIB21 is strongly related to the branch-to-branch distance [61].

7. Polyethylene containing ethyl branches

Copolymers of ethylene with 1-butene are obtained industrially by copolymerization via Ziegler–Natta and metallocene chemistry [17,31,32]. While many studies deal with modification of the catalyst and optimization of the reaction's conditions, precise models of LLDPE are more important for understanding the morphology and thermal behavior of these materials [20,25,28,30,34–36,40]. Inspired by the success in modeling EP and EIB copolymers via ADMET polymerization, we have synthesized ethylene/1-butene (EB) copolymers featuring precisely placed ethyl branches, thus extending behavioral studies moving from two single-carbon defects (EIB copolymers) to a single two-carbon defect (EB copolymers).

Multiple synthetic procedures were attempted in order to obtain perfectly spaced ethyl-branched LLDPE materials. The first strategy to produce ethyl-branched α,ω -diene monomers was based on alkenylation of ethyl acetoacetate, as shown in Fig. 13.

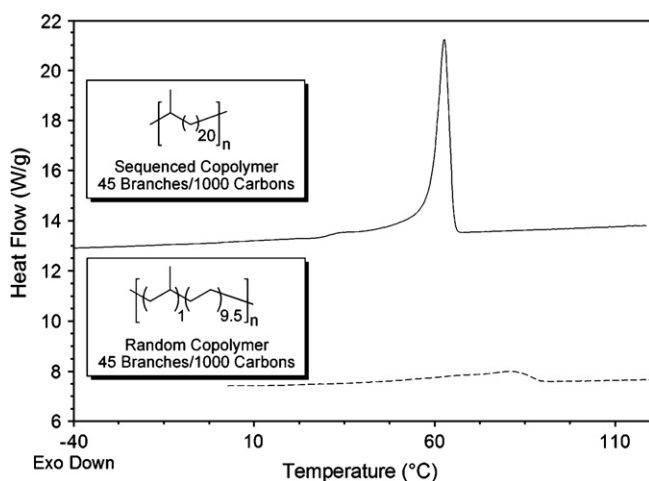


Fig. 10. DSC traces of precise sequenced EP (top) and irregularly sequenced EP (bottom) polymers having similar branch content.

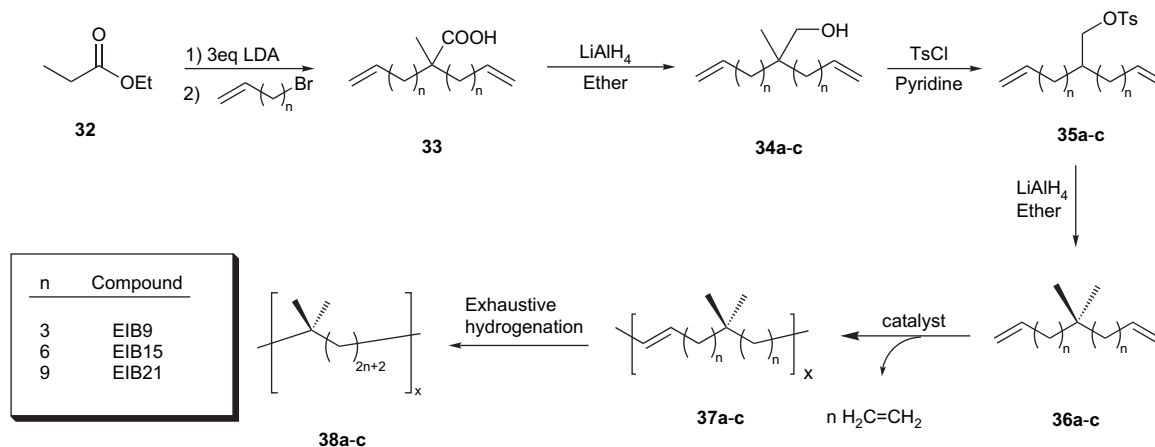


Fig. 11. Synthesis of symmetrical *gem*-dimethyl-substituted α,ω -diene monomers and their ADMET polymers.

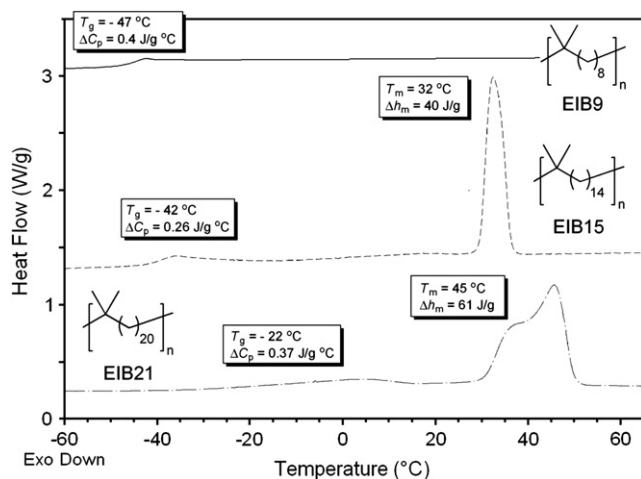


Fig. 12. DSC traces of precise *gem*-dimethyl polyethylene: EIB9 (top), EIB15(center) and EIB21 (bottom).

Table 4

Thermal transitions of the ADMET *gem*-dimethyl-branched and methyl-branched model polyethylenes

Branches per 1000 carbon	<i>gem</i> -Dimethyl polymer	T_m (°C)	T_g (°C)	Methyl polymer	T_m (°C)	T_g (°C)
111	EIB9	Amorphous	-47	EP9	-14	-44
67	EIB15	32	-42	EP15	39	-
48	EIB21	45	-22	EP21	62	-43

However, problems during reduction of tosylate **42** impeded the application of this methodology to longer chain lengths. The preferred approach for synthesizing monomers with longer spacers between ethyl groups is shown in Fig. 14. Diethyl malonate is alkenylated in the presence of sodium hydride to give diester **45**. Saponification of compound **45** followed by decarboxylation, reduction, and bromination yields bromo alkyl α,ω -diene **48**. A single-carbon homologation is then achieved by addition of CO_2 to the respective Grignard of **50** [49,51]. Using this scheme, monomers with $n = 3, 6,$ and 9 were produced.

The thermal data for EB copolymers are presented in Table 5. Similar to EP copolymers, precisely sequenced EB copolymers show an increase in peak melting temperature, enthalpy, and crystallinity with increasing run length. Like EP copolymers, SCB influences the thermal behavior of ADMET EB copolymers, but the final physical properties seem to depend mostly on the identity of the branch [49]. Fig. 15 shows the DSC thermograms for the polymers with a variety of branch types, in all cases with the branch occurring on every 9th carbon. Polyethylene with a methyl branch on every 9th carbon (EP9) shows a peak melt at -14°C , while the ethyl branch version (EB9) is fully amorphous with only a glass transition temperature of -76°C and no apparent melting behavior. The only viable explanation for this change in thermal behavior is the difference in branch size. In the case of EP9, the pendant methyl branches are too small to inhibit crystallization [48–51,60]. On the other hand, the ethyl branches on EB9 are large enough to completely prevent crystallization. An increment of one carbon unit in

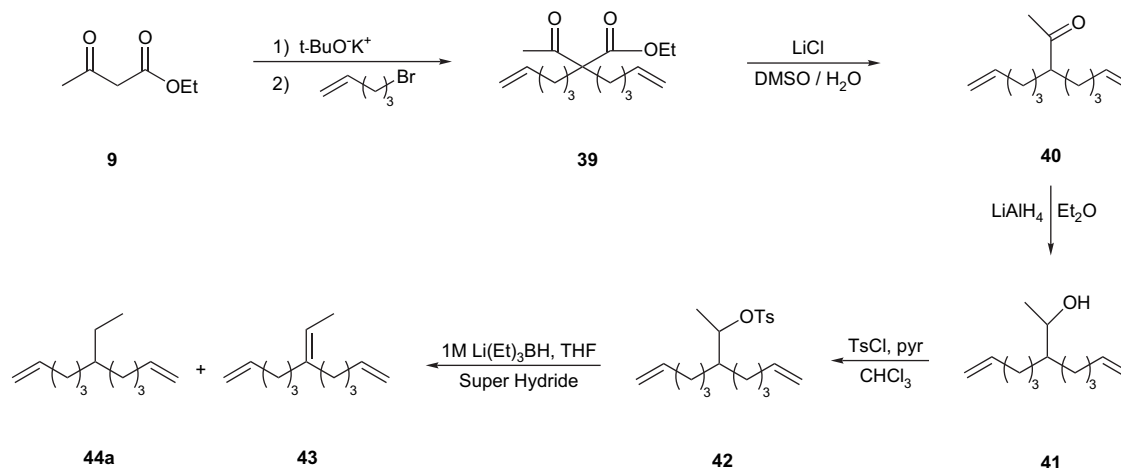


Fig. 13. Ethyl-branched monomer synthesis via alkylation of acetoacetate.

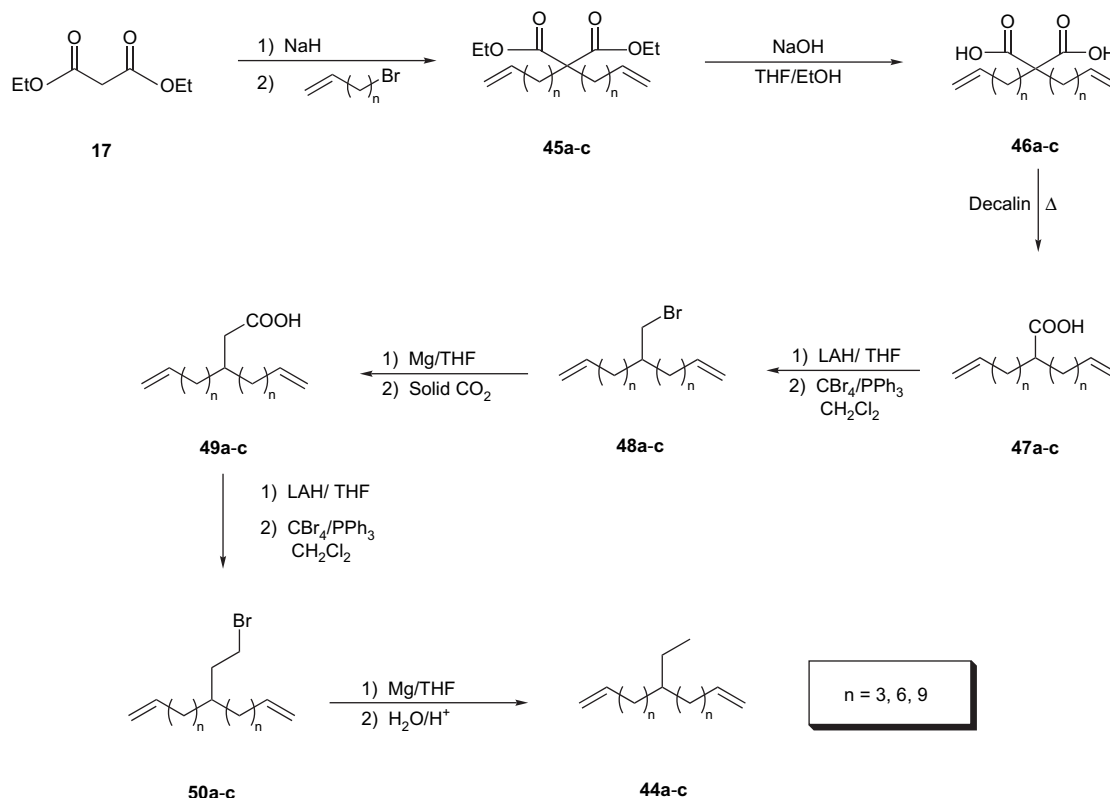


Fig. 14. Synthetic pathway to ethyl-branched monomers via malonate modification.

Table 5
Thermal transitions of the ADMET ethyl-branched model polyethylenes

Ethyl branches per 1000 carbon	Ethyl polymer	T_m (°C)	T_g (°C)
111	EB9	Amorphous	-76
67	EB15	-33 and -6	NA
48	EB21	35	NA

the branch length results in a significant change in the thermal behavior.

Similar to EP copolymers, crystal formation and crystallization kinetics of EB copolymers are directly affected by the branch spacing, as is shown in Fig. 16. Increasing the spacing from every 9th carbon to every 21st carbon results in a change from fully amorphous EB9 to semicrystalline EB21. However, EB15 produces

a bimodal profile with a melting temperature of -33 °C and -6 °C, unlike the corresponding polymer with methyl branches on every 15th carbon (EP15, shown in Fig. 7), which shows only a single melting endotherm.

WAXD investigations as well as extensive DSC analysis explain this behavior. Like EIB21, the melting behavior of EB21 can be correlated to that of eicosane, indicating a high dependence on the branch-to-branch distance. The WAXD results show some lattice expansion implying the partial inclusion of ethyl groups into the crystal, but to a much lesser extent than in EP21. This suggests that polymorphism resulting from inclusion and exclusion of the ethyl defect may be responsible for these observations. Comparing the WAXD results for EIB21 and EB21 suggests that much of the melting behavior is attributed to crystallization of methylene sequences between defects. The inclusion of these crystallized segments into

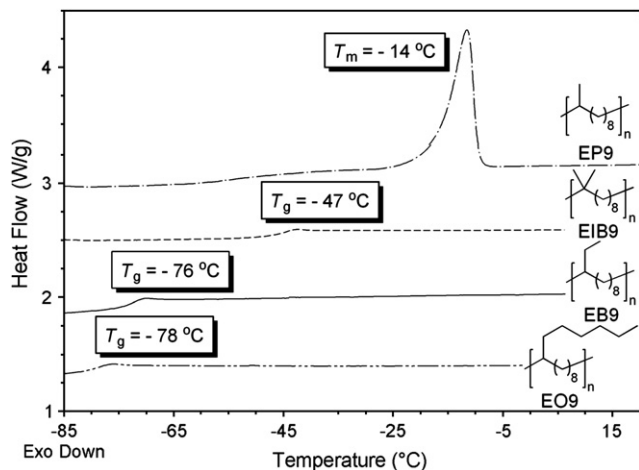


Fig. 15. Comparison of EP9, EIB9, EB9, and EO9 DSC traces.

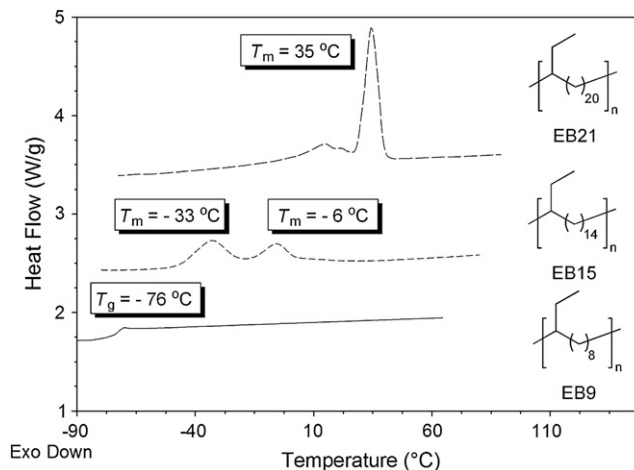


Fig. 16. DSC profiles of EB9, EB15 and EB21.

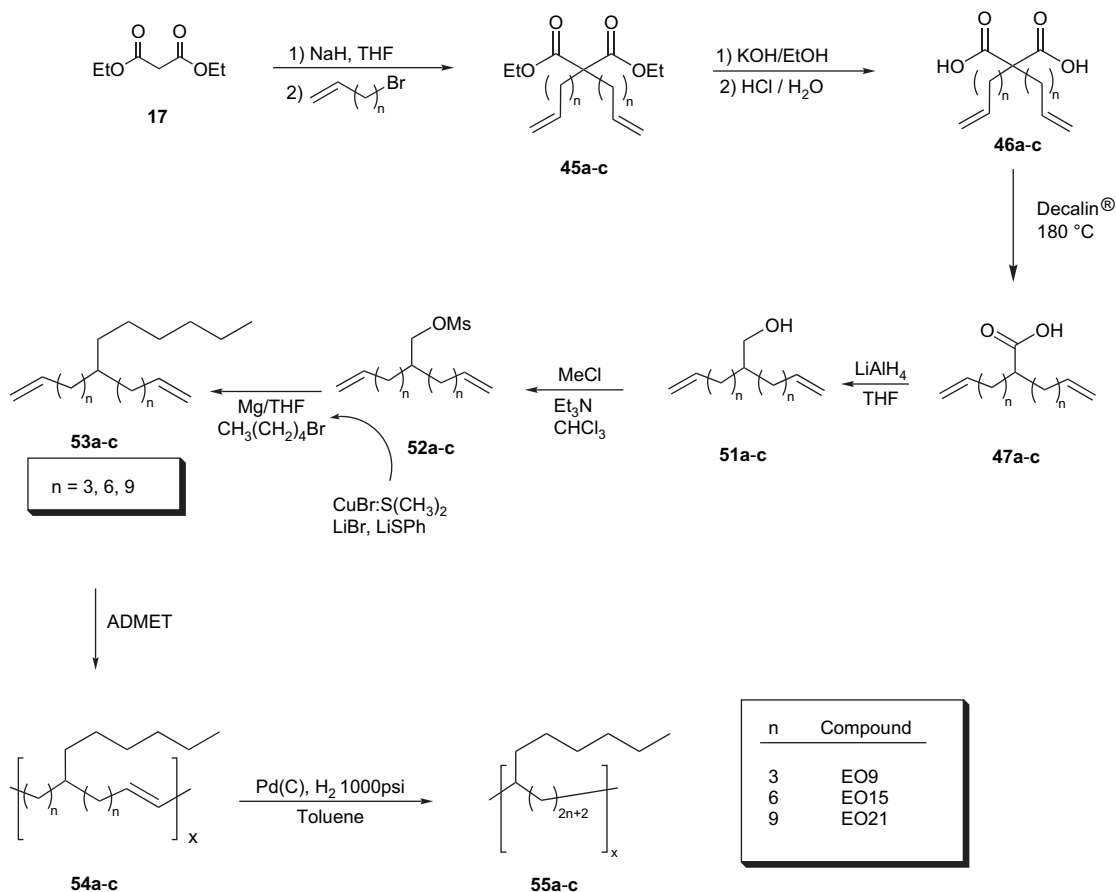


Fig. 17. Synthesis of symmetrical hexyl substituted α,ω -diene monomers and their ADMET polymers.

higher melting crystals results in bimodal thermal behavior in both the cases. Regardless of whether the branch is included or excluded from the crystal, there is very obvious effect of the increased volume requirements resulting from addition of a single methylene group [60,61].

8. Polyethylene containing hexyl branches

ADMET can also be used to prepare polymers with precisely placed branches longer than two carbons. Fig. 17 shows the scheme for such polymers containing hexyl branches, which serves as a model for ethylene/1-octene (EO) copolymers; in fact the method can be applied to alkyl branches of any length. Initial steps to prepare carboxylic acid **47** are explained above in relation to Fig. 14. The acid is reduced to the primary alcohol and directly converted to the sulfonic acid ester **52** using mesyl chloride. A modified Grignard/Gilman reaction was developed for insertion of a branch functionality of any length to form symmetrical α,ω -diene monomers, as shown in Fig. 17 for a hexyl substituent.

Thermograms for EO model polymers are shown in Fig. 18. The trends are similar to those observed for the families discussed above. The melting temperatures and heat of fusion decrease with increasing branch content. EO9 is totally amorphous, which is no surprise considering that the ethyl branch is able to completely disrupt crystallinity at the same branch concentration. A semicrystalline morphology is observed for EO15, which is quite surprising since all other known EO copolymers with similar branch content are amorphous [63]. Semicrystalline behavior is also noted for EO21, where the low melting temperature is indicative of small crystallites. Interestingly, the heat of fusion of EO21 (53 J/g) is

similar to that of EB21 (57 J/g). This observation is unexpected considering the notable decrease in heat of fusion from EP21 (103 J/g) to EIB21 (61 J/g) and EB21 (57 J/g). The melting profile of the EO21 closely mimics that of EP21, rather than either EIB21 or EB21. This implies a uniform crystal structure for EO21, rather than the apparent polymorphism displayed by EIB21 and EB21. One possible explanation is that the hexyl branch is large enough to be completely excluded from the crystal, with the result that the observed behavior is due solely to crystallization of inter-defect methylene units. Another possible explanation is that the branch is included to give a single crystalline form as seen in EP21.

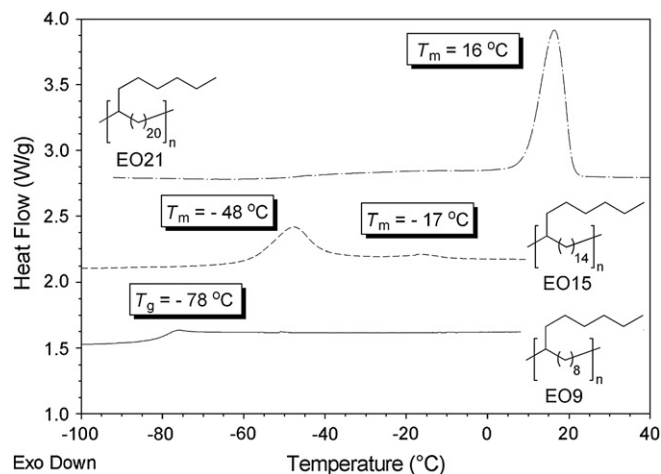


Fig. 18. DSC profiles of EO9, EO15 and EO21 copolymers obtained via ADMET.

9. Conclusions

Acyclic diene metathesis polymerization is useful in modeling precisely and irregularly sequenced ethylene/ α -olefin copolymers.

Considering the results for the entire precise alkyl branch ADMET family, it is clear that both defect placement and identity have a definitive effect on the overall properties of the resulting polymers. Small alkyl branches are included within the crystal lattice. The limits have been delineated regarding the amount of alkyl defects that can be incorporated into these precise systems before crystallinity is completely disrupted. In addition, relative to irregularly sequenced systems, precise models can endure a much higher defect concentration without destroying the ability of the chains to pack into lamellae. Our work in this area continues, focusing on much longer defect-to-defect spacing and a variety of branch identities. By creating a complete catalogue of polymers with precise alkyl branch placement, we aim to fully understand the intriguing behavior of these precision model materials.

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