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Modeling Ethylene/Methyl Methacrylate and Ethylene/Methacrylic Acid Copolymers Using Acyclic Diene Metathesis Chemistry

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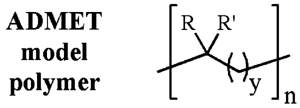
ABSTRACT: The synthesis, characterization, and thermal behavior of ADMET models of ethylene/methyl methacrylate (EMMA) and ethylene/methacrylic acid (EMAA) copolymers are described. These model copolymers exhibit sharper melting transitions and lower melting points relative to random copolymers made using chain-growth polymerization methods. The EMMA and EMAA model copolymers are compared with ADMET ethylene-based model copolymers reported previously, comparisons which support the earlier finding that melting points decrease with an increase in the steric bulk of the pendant group.

Introduction

Researchers have long sought to make functionalized hydrocarbon polymers via transition-metal-catalyzed copolymerization of ethylene with polar monomers. Such catalytic routes would provide a greater control of the polymer's microstructure than the current free radical techniques allow and could significantly broaden the utility and range of properties of ethylene-based copolymers. Generally, the use of available catalysts has been precluded by their susceptibility to poisoning by heteroatoms.[1] Recent research by Brookhart[2] and Grubbs[3] offers promise and suggests that nickel-based catalysts might lead to chain polymerization chemistry to generate commercial scale functionalized polyethylene. The preparation of such polymers would represent an important advance for polyolefin chemistry.

The preparation of copolymers with precisely the same comonomer compositions and sequence distributions is rarely possible due to the nature of chain-growth polymerization mechanisms and the differing reactivity ratios of ethylene/comonomer pairs. Irregularities in polymer microstructure result from random branching, induced by either chain transfer reactions or inconsistent (random) placement of pendant groups in the copolymer. Many studies have been aimed at delineating the effect of these irregularities in polyethylene random copolymers.[4] Melting points are depressed with increasing frequency and/or steric bulk of the imperfections (branches or polar pendant groups). Since the sequence distribution of the comonomers is a major contributing factor to material properties, preparing model copolymers with more precise microstructures would be valuable for the strict comparison of different types of comonomers in these ethylene-based copolymers.

With this in mind, we have exploited a step polymerization technique (the ADMET reaction) to synthesize model versions of ethylene copolymers with precisely placed pendant groups on the polymer backbone. We are examining the effect of precise placement of alkyl branches and functional groups on the crystallization and thermal behavior of this commercially important class of polymers. This work began with the synthesis of perfectly linear polyethylene by the exhaustive hydrogenation of polyoctenamer made by ADMET (**1** in Figure 1), a polymer which melts sharply at temperatures comparable to industrially produced high-density polyethylene.[5] Subsequent studies illustrated precise placement of branches along the polyethylene backbone has a significant effect on the polymer's crystallization and melting behavior, phenomena never observed previously. One such study involved the synthesis of a series of methyl branched ADMET polyethylenes (**2a**−**e**), where the methyl group was placed precisely on every 9th, 11th, 15th, 19th, and 21st carbon atom of the backbone, respectively.[6] As expected, the melting temperature (T_m) of the polymer decreases with an increase in the frequency of methyl branches. However, in contrast to their ethylene/propylene copolymer chain polymerization counterparts, these ADMET polymers exhibit sharp melting endotherms in their DSC traces at substantially lower T_m ranges than observed for the copolymer equivalents made via chain propagation, addition type polymerization.



1	R, R' = H (linear polyethylene)
2a-e	R = CH_3, R' = H; y = 8, 10, 14, 18, and 20
3	R = (=O); y = 18
4a-d	R = OAc, R' = H; y = 18, 20, 22, and 26
5a-b	R = CO_2CH_3, R' = H; y = 18 and 22
6	R = $CO_2CH_2CH_3$, R' = H; y = 18
7	R = C_6H_6, R' = H; y = 18
8	R = Cl, R' = H; y = 18
9	R, R' = CH_3; y = 8, 14, 20

Figure 1. ADMET model polymers studied previously.

Other studies focused on the preparation of model copolymers of ethylene with carbon monoxide (**3**), vinyl acetate (**4a**−**d**), methyl acrylate (**5a,b**), ethyl acrylate (**6**), styrene (**7**), vinyl chloride (**8**), and isobutylene (**9**). These ADMET polymers were made using symmetric α,ω-diene monomers followed by hydrogenation of the unsaturated polymer (see Figure 1);[7−12] several hydro-

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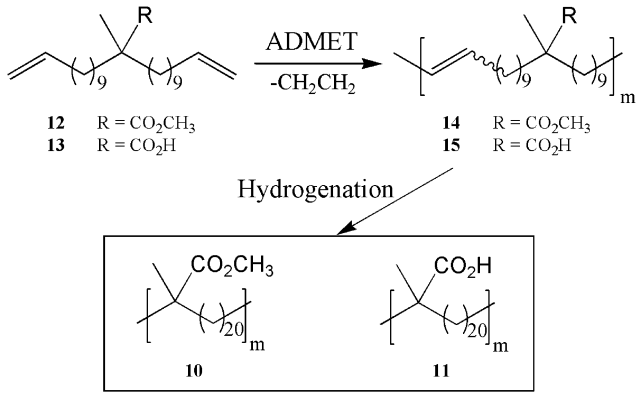


Figure 2. Synthetic scheme for the ADMET-made EMMA and EMAA model copolymers.

genations were done using a tandem ADMET polymerization/heterogeneous hydrogenation method developed by Watson.[7] Consistent with the methyl branch study mentioned above, the model functionalized polyethylenes (**3**−**9**) exhibit sharper, more defined melting endotherms and T_m's lower than their chain-made counterparts (except for **9a**, which is completely amorphous). Further, an analogous series of ethylene-based model copolymers were prepared possessing perfectly spaced pendant groups on every 19th carbon atom.[9] Significantly, the width of the melting point range spanned nearly 150 °C within the series, where the melting points decreased with increasing steric bulk in the pendant groups. Steric size alone does not dictate melting point; for example, model copolymers possessing chloro and methyl groups (**8** and **2d**, respectively) have similar steric requirements, yet their melting endotherms differ by more than 20 °C. Understanding the melting behavior of this polymer series is a challenging subject.

The advent of well-defined metathesis catalysts, some of which are tolerant of the presence of such functional groups as alcohols, ketones, esters, etc., has made studies of this nature possible. Often the ADMET reaction operates by essentially one mechanism with no branch-forming side reactions, where the only variable in the repeat unit is the cis/trans distribution of the olefinic link. Hydrogenation removes this variable and generates the desired ethylene-based model copolymer with perfectly spaced pendant groups. The only difference between the chain structure of ADMET ethylene-based model copolymers and a perfect copolymer model is that the pendant functionality is separated by an even number of carbon atoms in the ADMET polymers instead of an odd number.

This paper reports the preparation and examination of ADMET models of ethylene/methyl methacrylate (EMMA) (**10**) and ethylene/methacrylic acid (EMAA) (**11**) copolymers (Figure 2). These polymers, each of which possesses precisely placed pendant groups on every 21st carbon atom of the polymer backbone, provide additional models for evaluation of the effect of functionality and regular branch placement on polyethylene.

Results and Discussion

Monomer Synthesis. The synthesis of the carboxylic acid monomer (**13**) used to make the ethylene/methacrylic acid (EMAA) model copolymer has been reported elsewhere.[11,12] Prior to polymerization, the monomer (**13**) was rigorously purified by column chromatography followed by two successive recrystallizations from hexanes. The methyl ester monomer (**12**) was synthesized by simple esterification of the carboxylic acid monomer (**13**). See the Experimental Section for the details of this reaction.

Polymerization and Hydrogenation. Figure 2 illustrates the scheme for the synthesis of EMMA (**10**) and EMAA (**11**) model copolymers. The ester and carboxylic acid functional monomers (**12** and **13**) were polymerized in the bulk (no solvent) using Grubbs' ruthenium benzylidene catalyst $Cl_2[P(C_6H_{11})_3]_2RuCH\text{-}C_6H_5$ (**16**). These are equilibrium polycondensation reactions, driven by the removal of ethylene under reduced pressure, which produce the unsaturated polymers (**14** and **15**) with precise microstructures. Details of the polymerization and hydrogenation reactions are provided in the Experimental Section.

The ester functional monomer (**12**) was cleanly converted to the unsaturated ester functional polymer (**14**) using Grubbs' catalyst (**16**). Although very faint traces of the terminal olefin end groups were visible in the ^{1}H NMR spectrum at about 5.0 and 5.8 ppm, GPC analysis indicated reasonably high molecular weight (M_n = 26 000, PDI = 1.9). In contrast, the polymerization of the carboxylic acid functional monomer (**13**) was considerably more challenging. An initial attempt to make the unsaturated carboxylic acid functional polymer (**15**) using the Ru catalyst (**16)** resulted in low molecular weight oligomers averaging six repeat units by ^{1}H NMR analysis. Premature catalyst decomposition during the 5 day reaction is the probable explanation, possibly caused by the carboxylic acid group.

A second attempt to synthesize this carboxylic acid polymer was more successful. A lower initial monomer-to-catalyst ratio (440:1) was employed, followed by the addition of more catalyst periodically during the reaction, bringing the total monomer-to-catalyst ratio to about 150:1. Unlike the first attempt, there were no terminal olefin end groups visible in the ^{1}H NMR spectrum of the polymer made in the second attempt, which suggests that a high molecular weight polymer was obtained. ^{13}C NMR spectra in both deuterated chloroform and DMSO could not be obtained due to the low solubility of the polymer in these solvents. This low solubility of the polymer in such common NMR solvents indicates a high degree of interchain interaction, likely hydrogen bonding between chains. GPC analysis of this polymer also proved difficult for the same reason.

IR spectra of the low- and high-M_n unsaturated polymers (**15**) provide additional evidence for the high molecular weight of the polymer made using the repetitive catalyst addition procedure. Monomer **13** exhibits two IR absorptions, one at 1822 cm^{-1} and one at 3078 cm^{-1}, which reflect the presence of terminal olefins. The low molecular weight version of polymer **15** displays two IR absorptions at these positions due to the high concentration of vinyl end groups. These IR absorptions vanish when using the repetitive catalyst addition procedure, suggesting that the concentration of vinyl end groups is either nonexistent or very low. We believe these model polymers are of sufficient size to model commercial EMAA copolymers.

Quantitative hydrogenations of the unsaturated polymers **14** and **15** to give the EMMA model copolymer (**10**) and the EMAA model copolymer (**11**), respectively, were accomplished using Wilkinson's catalyst ($ClRh(PPh_3)_3$).

The saturated EMMA model copolymer (**10**) was obtained as a clear, colorless, highly viscous liquid after a purification sequence consisting of column chromatography, precipitation, column chromatography again, and vacuum-drying at 60 °C. GPC analysis of the saturated polymer (**10**) gave an M_n of 27 000 g/mol and a PDI of 2.0. The complete disappearance of the olefin resonances in the NMR spectra and the absence of the alkene C−H out-of-plane bending peak at 967 cm^{-1} in the IR spectrum show the hydrogenation of the unsaturated ester functional polymer (**14**) to be quantitative.

Unlike the EMMA model copolymer, the EMAA unsaturated model copolymer (**15**) precipitated during the course of its hydrogenation; interchain hydrogen bonding apparently leads to solubility problems that are difficult to address. A black, tacky residue was obtained that was not appreciably soluble in common organic solvents, including chloroform, toluene, ethyl acetate, methanol, ethanol, THF, and DMSO. A mixture of *p*-xylene and 1-butanol successfully dissolved most of the material at reflux, but some black particles remained insoluble. The remaining material eventually dissolved when a small amount of sodium hydroxide was added to the mixture, which would disrupt intermolecular hydrogen bonding. A grayish precipitate formed after the solution was slowly added to acidic methanol (1 M HCl) and stirred for about an hour. The precipitate became a translucent, faintly black, viscous material after drying at 70 °C under vacuum. The absence of olefinic resonances in the ^{1}H NMR spectrum and the absence of the alkene C−H out-of-plane bending peak at 968 cm^{-1} in the IR spectrum of the saturated EMAA model copolymer (**11**) indicate that the hydrogenation was successful.

NMR data were complicated by solubility issues as well. A triplet at 0.88 ppm in the ^{1}H NMR spectrum is attributed to the methyl end groups that are evident in low molecular weight oligomers. Only oligomers appear in the NMR spectra since the high molecular weight portion of the polymer sample is insoluble in deuterated chloroform. In fact, the polymer sample phase separates in the NMR tube, with the higher molecular weight portion remaining insoluble. GPC data collected in THF present an erroneously low M_n of 4100 g/mol for this reason. It is important to note that the absence of observable end groups in the ^{1}H NMR and IR spectra of the unsaturated precursor polymer (**15**) suggests the actual molecular weight of the EMAA model copolymer (**11**) is sizable; the value should be sufficiently high (M_n > 15 000 g/mol) to allow a meaningful comparison of its thermal behavior with that of commercial EMAA copolymers.

Thermal Analysis of ADMET Ethylene/Methyl Methacrylate (EMMA) Model Copolymers. Ethylene/methyl methacrylate (EMMA) copolymers are produced commercially by Sumitomo Chemical Co., Ltd., under the trade name Acryft, copolymers which are manufactured by a high-pressure radical polymerization process similar to that used to produce low-density polyethylene (LDPE).[13] This process results in both random incorporation of the acrylate copolymer and the introducion of both short- and long-chain alkyl branches via chain transfer and intramolecular “backbiting” reactions.

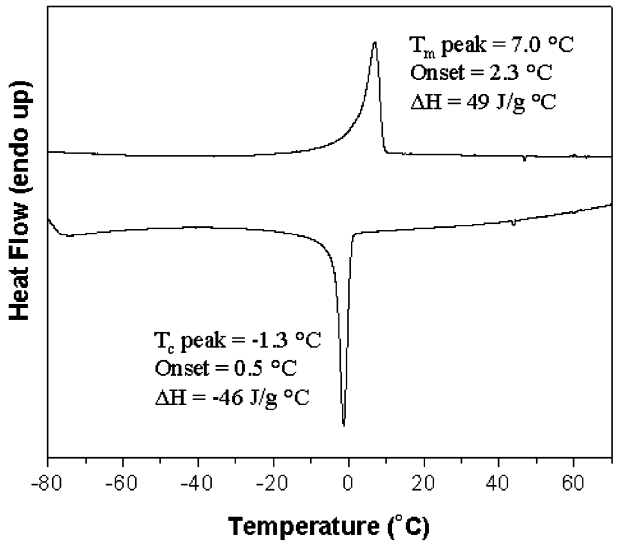


Figure 3. DSC trace for the EMMA model copolymer **10**.

As mentioned earlier, Brookhart and Grubbs recently have directed research toward producing ethylene/polar monomer copolymers using transition-metal-based catalysis.[2,3,14] Brookhart’s palladium-based catalysts have been used in the copolymerization of ethylene with acrylates and other polar monomers, and while high molecular weights and variable degrees of comonomer incorporation were obtained, these copolymers were amorphous, highly branched materials. Further, most of the ester groups were located at the ends of the branches rather than directly pendant to the polyethylene backbone.[2,14] The copolymerization of ethylene with acrylates using Grubbs’ nickel-based catalysts has yet to be demonstrated; however, these catalysts do tolerate the presence of ethyl acetate and other functional additives during ethylene homopolymerization.[3]

It is difficult to establish the true relationship between the comonomer content and thermal behavior in these chain polymers due to the random distribution of pendant functional groups and variable degrees of alkyl branching present. Studies of this nature have been reported both for commercially available and specially designed, periodic (regioregular) copolymers. Matsuo and co-workers studied three commercially available random EMMA copolymers with 3, 6.5, and 14.6 mol % methyl methacrylate (MMA) and found that melting points decreased with increasing MMA content (T_m = 100, 85, and 64 °C, respectively).[13] Yokota and coworkers prepared two periodic EMMA copolymers: one an alternating copolymer and the other an ethylene−ethylene−(MMA) copolymer, using unsaturated precursor polymers made from methyl 2-methyl-2,4-pentadienoate and 1,3-butadiene/MMA, respectively.[15] The unsaturated precursor polymers were quantitatively hydrogenated with platinum black, palladium on activated carbon, or *p*-toluenesulfonylhydrazide. While the alternating EMMA copolymer was completely amorphous in the absence of annealing, the ethylene−ethylene−(MMA) copolymer was semicrystalline and had a surprisingly high melting temperature (90 °C). Both of these periodic EMMA copolymers were reported to be atactic.

The ADMET EMMA copolymer **(10)**, which has 48 pendant groups per 1000 carbon atoms (equivalent MMA content is 9.5 mol %), is semicrystalline (Figure 3), exhibiting a melting point at 7 °C. While the melting endotherm is fairly sharp, it exhibits a long gradual premelting, a phenomenon that is mirrored in the recrystallization curve on the cooling scan. Further, the

Table 1. Melting Transitions of the ADMET EMMA Model Copolymer (10), Yakota's Periodic EMMA Copolymers, and Matsuo's and Macknight's Random EMMA Copolymers

EMMA copolymer type	% MMA	T_m (°C)
periodic copolymers		
Yakota[15]	50	amorphous
Yakota[15]	33.3	90
ADMET model (**10**)	9.5	7
random copolymers		
Matsuo[13]	14.6	64
Matsuo[13]	6.5	85
Macknight[16]	3.5	94
Matsuo[13]	3.0	100

absence of significant supercooling and the near equivalence of the enthalpies of melting and crystallization suggest that this EMMA model copolymer crystallizes fairly rapidly.

Table 1 compares all the EMMA copolymers that are mentioned above; melting points are listed as a function of MMA content for Yakota's periodic EMMA copolymers, Matsuo's and Macknight's random EMMA copolymers, and the ADMET-made EMMA model copolymer (**10**). Two striking observations can be made from a comparison of these data. First, the ADMET model polymer melts at a significantly lower temperature than the random EMMA copolymers with similar "MMA" contents, an observation that is consistent with previous findings. Such behavior has been observed for all of the ADMET ethylene-based model copolymers studied to date. Second is the observation of the anomalously high melting point of Yakota's ethylene−ethylene−MMA periodic copolymer (90 °C). It is surprising that this polymer crystallizes at all, and even more so that its melting point is so high, when the alternating EMMA is amorphous and the ADMET model copolymer exhibits a low melting point. Further, Yakota's alternating EMMA and ethylene−ethylene−MMA copolymers exhibit glass transition temperatures at 5 and −6 °C, respectively, while a glass transition was not observed for the ADMET EMMA model copolymer (**10**) in the temperature range studied (−80 to 100 °C), even when the sample was quenched rapidly from the melt into liquid nitrogen prior to scanning.

Thermal Analysis of ADMET Ethylene/Methacrylic Acid (EMAA) Model Copolymers. Rees and co-workers first synthesized ethylene/methacrylic acid (EMAA) copolymers in 1964 and thereby introduced the world to ionic polymers (ionomers).[17] Currently, EMAA copolymers are produced commercially by DuPont under the trade name Surlyn, and they have a variety of uses in commerce. Similar to the EMMA copolymers discussed in the previous section, these copolymers are produced by high-pressure radical polymerization processes. The MAA comonomer is randomly distributed throughout the polymer backbone, and variable degrees of alkyl branching are present as a result of chain transfer and "backbiting" reactions. Additionally, a small quanitity of ester groups are incorporated into commercial EMAA copolymers during their polymerization. These factors make precise structure−property relationship studies difficult.

Several studies conducted with both carboxylic acid and partially neutralized (ionomer) forms of commercial EMAA copolymers show a nearly linear dependence of percent crystallinity on MAA content and a decrease in the melting temperature with increasing MAA content.[16,18−20] Random copolymers having greater than 13.3 mol % MAA are completely amorphous.[18] Also, Yakota and co-workers have prepared two periodic EMAA copolymers with acid groups on every 4th and 6th carbon atom of the polyethylene backbone, respectively, by hydrolyzing their periodic EMMA copolymers.[21] Both of these periodic EMAA polymers have high T_g's (132 and 99 °C, respectively) and are completely amorphous.[22]

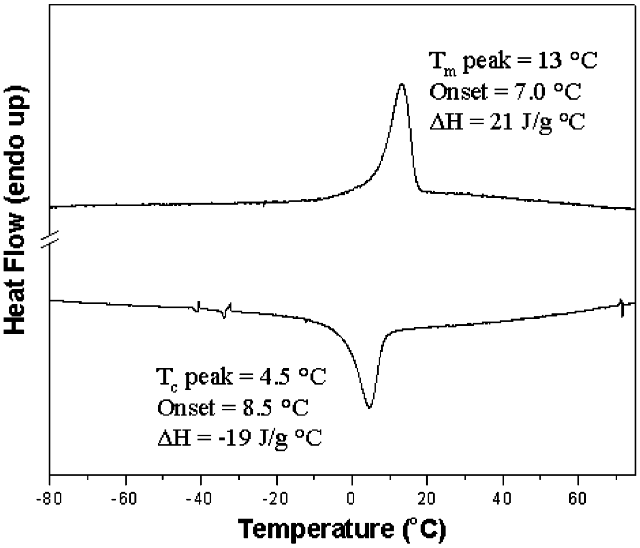


Figure 4. DSC trace for the EMAA model copolymer **11**.

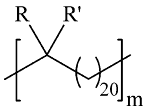
Table 2. Thermal Transitions of the ADMET EMAA Model Copolymer (11), Yakota's Periodic EMAA Copolymers, and Coleman's and Macknight's Random EMAA Copolymers

EMAA copolymer type	% MAA	T_m (°C)	T_g (°C)
periodic copolymers			
Yakota[22]	50	amorphous	132
Yakota[22]	33.3	amorphous	99
ADMET model (**11**)	9.5	13	NA
random copolymers			
Coleman[20]	28.5	amorphous	25−32
Coleman[20]	20.4	amorphous	25−32
Coleman[20]	13.3	53	
Coleman[20]	6.5	87	
Macknight[16,19]	3.5	95	25

By comparison, the ADMET EMAA copolymer (**11**), which has 48 pendant groups per 1000 carbons (equivalent MAA content is 9.5 mol %), melts at 13 °C (Figure 4). It recrystallizes at 4.5 °C in the cooling scan, and the enthalpy associated with this transition closely matches that of the enthalpy of melting (20.7 and 21.6 J/g, respectively). Like its ester analogue polymer (**10**), the DSC trace of this carboxylic acid-functionalized polyethylene (**11**) lacks significant supercooling, and the enthalpies of melting and crystallization are nearly equivalent. These results suggest fast crystallization in a manner similar to the EMMA model copolymer.

Table 2 lists thermal transitions as a function of MAA content for Yakota's periodic EMAA copolymers, McKnight's and Coleman's random EMAA copolymers, and the ADMET EMAA model copolymer (**11**). Again, it is immediately apparent that the ADMET polymer has a significantly lower melting point (>40 °C) than the random EMAA copolymers containing similar "MAA" content. A possible explanation for this phenomenon is that the pendant groups in ADMET ethylene-based copolymers are included in the polyethylene crystal phase, while the pendant groups are largely excluded

Table 3. Peak Melting Temperatures for an Analogous Series of ADMET Ethylene-Based Model Copolymers



ADMET polymer	R	R′	T_m (°C)
1[5]	H	H	134
2d[6]	CH_3	H	62
9c[11,12]	CH_3	CH_3	45
4b[8]	$OC(O)CH_3$	H	35
11	CO_2H	CH_3	13
10	CO_2CH_3	CH_3	7

in many random copolymers. In fact, X-ray scattering studies conducted on methyl branched ADMET polyethylenes have revealed that the methyl groups are included in the crystal phase,[23] while DSC and X-ray studies conducted on random EMAA copolymers by MacKnight support the view that the methacrylic acid side groups are largely excluded.[19] The inclusion of more "defects" in the crystal phase can be expected to lower the melting point significantly, whereas the exclusion of many of the "defects" in random copolymers should bring the melting point closer to that of the parent polyethylene homopolymer.

A comparison of the melting points between a random EMMA copolymer and an analogous random EMAA copolymer with those of the ADMET versions further illustrates this point. MacKnight found that the random copolymers (each with 3.5 mol % comonomer) melted at the same temperature,[16] despite the difference in the relative size of the ester and carboxylic acid pendant groups. The fact that the difference in size of these pendant groups has no effect on the melting temperature supports the exclusion model for these two random copolymers. The ADMET-made model EMMA and EMAA copolymers (each with 9.5 mol % "comonomer") have melting points that differ slightly (by 6 °C), which supports the inclusion model for these periodic copolymers. However, these models are not mutually exclusive, since other random copolymers with similar comonomer contents have somewhat different melting temperatures. It is likely that, in random copolymers, some pendant groups are included in the crystal phase, while the majority are excluded. Also, hydrogen bonding and other interactions among polar pendant groups can influence the crystallinity and melting point of a polymer, making the strict comparison of copolymers with diverse functional groups more complicated.

Table 2 also lists the glass transition temperatures for a number of the EMAA copolymers. While the random copolymers all exhibit glass transitions between 25 and 32 °C, those of Yokota's periodic EMAA copolymers are much higher (99 and 132 °C for 33.3 and 50 mol % MAA, respectively). The Yokota periodic copolymers both have a relatively high MAA content, so their glass transition temperatures more closely resembles that of poly(methacrylic acid) ($T_g = 228$ °C).[22] By comparison, and like the EMMA model copolymer (**10**), the EMAA model copolymer (**11**) does not exhibit a glass transition temperature in the temperature range studied (−80 to 100 °C).

Melting Point Comparisons for ADMET Ethylene-Based Model Copolymers. The peak melting temperatures of an analogous series of ADMET ethylene-based model copolymers are listed in Table 3, where the polymers are listed in order of increasing steric bulk of their pendant groups. The significant effect of varying the identity of the pendant group can immediately be seen from the breadth of the range of melting points, which spans nearly 130 °C from ADMET linear polyethylene to the ADMET EMMA model copolymer. In accord with previous findings,[9] the melting points of these polymers decrease with increasing steric bulk of their pendant groups.

A comparison of the entire series of ADMET ethylene-based model copolymers produced to date can be made with a few logical assumptions. By assuming that the melting point of an ADMET ethylene/methyl acrylate (EMA) model copolymer (**5**) with 20 methylene "spacers" between pendant groups lies between the melting points of the analogous EMA model copolymers with 18 and 22 methylene "spacers" (**5a** and **5b** with $T_m = 14$ and 37 °C, respectively), it is apparent that the EMAA (**11**) and EMMA (**10**) model copolymers melt at lower temperatures than their EMA analogue. Since the ADMET ethylene/ethyl acrylate (EEA) model copolymer (**6**) melts only 1 °C lower than the analogous EMA model copolymer (**5a**), the EMAA (**11**) and EMMA (**10**) model copolymers should melt at lower temperatures than the EEA analogue as well. Last, by assuming that the melting point of an ADMET ethylene/styrene model copolymer with 20 methylene "spacers" is not more than 19 °C higher than its analogue (**7**) with 18 methylene "spacers" ($T_m = -12$ °C), we can conclude that the EMAA (**11**) and EMMA (**10**) model copolymers melt at higher temperatures than the ethylene/styrene analogue. This seems reasonable because none of the other model copolymers with 20 "spacers" melt more than 12 °C higher than their 18 "spacer" analogues.

Using these arguments and the data from Table 3, the following list of comonomers is arranged in order of increasing steric bulk of the pendant group and decreasing melting point of the corresponding ADMET ethylene-based model copolymer: carbon monoxide, vinyl chloride, propylene, isobutylene, vinyl acetate, methyl acrylate, ethyl acrylate, methacrylic acid, methyl methacrylate, and styrene.

Conclusions

The synthesis, characterization, and thermal behavior have been described for ADMET-made models of ethylene/methyl methacrylate (EMMA) (**10**) and ethylene/methacrylic acid (EMAA) (**11**) copolymers possessing sequence ordered pendant groups. These ADMET model copolymers exhibit sharper melting transitions at lower melting points relative to their random copolymer counterparts. These observations could be a manifestation of the pendant groups (defects) included in the crystalline regions of the ADMET model copolymers, defects which are largely excluded from the crystalline regions of the random copolymers. A comparison of these EMMA and EMAA model copolymers with other ADMET ethylene-based model copolymers[9] suggests that the melting point of these polymers decreases with increasing steric bulk of the pendant group.

Experimental Section

1. Instrumentation and Analysis. The ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Associates Gemini 300 or VXR-300 superconducting spectrometer system. Chemical shifts for ^1H NMR were referenced to TMS, and those for ^{13}C NMR were referenced to residual signals from $CDCl_3$ solvent. Reaction conversions and purity of products were monitored by chromatography. Gas chromatography was performed on a Shimadzu GC-17A gas chromatograph equipped with a Hewlett-Packard HP-5 cross-linked 5% phenylmethylsiloxane column (length = 25 m, film thickness = 0.33 μm, i.d. = 0.2 mm) and a flame ionization detector. The GC injector temperature was 250 °C, and the column temperature program consisted of holding at 50 °C for 1 min, increasing at a rate of 10 °C/min for 20 min, and holding at 250 °C for 10 min. The column pressure was set to 115 kPa, and the flow was set to 250 mL/min with helium as the carrier gas. Thin-layer chromatography (TLC) was performed on Whatman aluminum backed, 250 μm silica gel-coated plates, using mixtures of hexanes and ethyl acetate as the mobile phase. TLC plates were stained with phosphomolybdic acid (10%) in ethanol to see UV-inactive products and impurities. High-resolution mass spectra (HRMS) were obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the electron ionization (EI) mode. GPC data were obtained using a Waters Associates 6000A liquid chromatograph apparatus equipped with a HP refractive index detector (Agilant 1047A at 254 nm). HPLC grade THF was used as the mobile phase, and a column bank consisting of two PLgel 5 μm MIXED-C columns (300 mm length each) was used as the stationary phase (molecular weight range of 200−2 000 000 g/mol). Polymer samples were prepared in HPLC grade THF (~5% w/w) and passed through a 45 μm syringe filter prior to injection. A constant flow rate of 1.0 mL/min at 35 °C was maintained, and the instrument was calibrated using polystyrene standards from Polymer Laboratories. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

Differential scanning calorimetry (DSC) analyses were performed using a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min. Thermal calibrations were made using indium and *n*-octane as the standards. All samples were prepared in hermetically sealed pans. Sample sizes were typically 2−4 mg for melting transition measurements and 12−15 mg for glass transition measurements, though some of the samples were used to obtain both of these measurements. The T_m was determined as the maximum of the endotherm peak, and the T_g was determined as the temperature at which the curve passes through the half-height of the difference between the baselines before and after the temperature transition. The samples were analyzed from −100 to 100 °C, and multiple heating and cooling cycles were obtained for each to verify the results.

2. Materials. The olefin metathesis catalyst **16** was synthesized following literature procedures.[24,25] The synthesis of the carboxylic acid monomer (**13**) is reported elsewhere.[11,12] All other reagents were used as received.

3. Ester Monomer Synthesis. Synthesis of 12-Methyl-1,22-trieicosadiene-12-methyl Ester (12). A 1.20 g sample (3.18 mmol) of carboxylic acid **13** was dissolved in 25 mL of acetone in a 100 mL round-bottom flask equipped with a stir bar. A 1.16 g sample (8.39 mmol) of K_2CO_3 was added, and the mixture was stirred for 10 min. A 1.6 mL sample (26 mmol) of CH_3I was added via syringe. A preassembled simple distillation apparatus was attached to the reaction flask, and the mixture was stirred for 6 h. After distilling off the CH_3I and most of the acetone, the crude product was concentrated on a rotory evaporator. The product was dissolved in pentane, and washed twice with 3 M HCl, and twice with distilled water. The pentane layer was dried over magnesium sulfate, gravity filtered, and evaporated under reduced pressure. The ester monomer (**12**) was >99% pure by GC, and the isolated yield was 97%. Prior to polymerization, **12** was dried over CaH_2 at 0.02 mmHg for12 h and filtered through a 0.2 μm syringe filter into a Schlenk flask in an argon atmosphere drybox.

The following spectral properties were observed: ^1H NMR ($CDCl_3$): δ 1.11 (s, 3H, methyl), 1.25−1.41 (m, 30H, methylenes and 2 pro-chiral methylene protons), 1.55−1.63 (dt, 2H, pro-chiral methylene protons), 2.03 (q, 4H, allylic methylenes), 3.64 (s, 3H, methoxy), 4.91−5.02 (m, 4H, olefin), 5.74−5.87 (m, 2H, olefin). ^{13}C NMR ($CDCl_3$): δ 21.14 (methyl), 24.51, 28.91, 29.10, 29.44, 29.51, 30.09, 33.78, 39.44 (methylenes), 45.94 (tertiary carbon), 51.38 (methoxy), 114.07 (olefin CH_2), 139.15 (olefin CH), 178.12 (carbonyl). EI/HRMS: $[M]^+$ calcd for $C_{26}H_{48}O_2$: 392.3654. Found: 392.3648. Elemental analysis calcd for $C_{26}H_{48}O_2$: 79.52 C, 12.33 H. Found: 79.30 C, 12.45 H.

4.1. Synthesis of the Unsaturated Ester-Functionalized Polymer (14). In an argon atmosphere drybox, 570 mg (1.45 mmol) of the dry, degassed monomer **12** was placed in a 50 mL round-bottom flask equipped with a Teflon magnetic stir bar. A 6.1 mg sample (0.0074 mmol, 200:1 monomer-to-catalyst ratio) of Grubbs' catalyst (**16**) was added, and an adapter with a Teflon vacuum valve was attached to the flask. The mixture began to bubble slightly, so the reaction vessel was quickly removed from the glovebox and attached to a vacuum line. The vessel was warmed in a 35 °C oil bath, and intermittent vacuum (open valve for ~1 s periodically) was applied until the mixture became viscous enough to leave open to vacuum ($<10^{-2}$ mmHg) after about 1 h. The mixture became more viscous and turned from purple to reddish-orange after 1 day. On the second day the temperature was increased to 45 °C, and on the sixth day it was increased to 60 °C. The reaction was removed from the vacuum line on the seventh day. The product was obtained in 98% yield. Very faint traces of terminal olefin were detected by NMR and IR spectroscopy.

The following spectral properties were observed: ^1H NMR ($CDCl_3$): δ 1.10 (s, 3H, methyl), 1.24−1.41 (m, 30H, methylenes and 2 pro-chiral methylene protons), 1.59 (dt, 2H, pro-chiral methylene protons), 1.96 (t, 4H, allylic methylenes), 3.64 (s, 3H, methoxy), and 5.29−5.44 (m, 2H, olefin). ^{13}C NMR ($CDCl_3$): δ 21.14 (methyl), 24.56, 27.21 (cis), 29.18, 29.32 (cis), 29.50 (broad peak, 2 methylenes), 29.54 (cis), 29.58, 29.66, 29.77 (cis), 30.14, 32.61, 39.52 (methylenes), 45.97 (tertiary carbon), 51.42 (methoxy), 129.86 (cis alkene), 130.32 (trans alkene), and 178.18 (carbonyl). Elemental analysis calculated for the repeat unit ($C_{24}H_{44}O_2$): 79.05 C, 12.17 H. Found: 78.71 C, 12.22 H. GPC data: $M_n = 26\,100$; PDI (M_w/M_n) = 1.9.

4.2. Synthesis of the Saturated Ester-Functionalized Polymer (10). A solution of 453 mg (1.24 mmol of olefins in the repeat units of the polymer) of unsaturated polymer (**14**) in 125 mL of toluene and ethyl acetate (75:25 v/v) was added to a Parr Instruments high-pressure stainless steel reactor equipped with a magnetic stir bar. A 50 mg sample (0.11 mmol) of Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) was added, and the reactor was sealed. The reactor was purged with hydrogen and then charged to 900 psi with hydrogen and heated to 90 °C. After 3 days the reactor was allowed to cool, the pressure was released, and inside walls of the reactor were rinsed with toluene and ethyl acetate solution (75:25 v/v). The reactor was then recharged with hydrogen to 900 psi and heated to 90 °C, and the reaction was continued for an additional 2 days. The crude product **10** was columned once through silica gel 60 with toluene and ethyl acetate (75:25 v/v) as the solvent system, precipitated in cold methanol, and then columned again. After concentrating the product on a rotory evaporator, it was dried at 60 °C under vacuum for 5 days. The isolated product was obtained in 93% yield. The product (**10**) was a clear, colorless, viscous liquid. No residual olefin was detected by NMR and IR spectroscopy.

The following spectral properties were observed: ^1H NMR ($CDCl_3$): δ 1.10 (s, 3H, methyl), 1.24−1.31 (m, 36H, methylenes), 1.37 (dt, 2H, pro-chiral methylene protons), 1.59 (dt, 2H, pro-chiral methylene protons), 3.64 (s, 3H, methoxy). ^{13}C NMR ($CDCl_3$): δ 21.14 (methyl), 24.55, 29.51, 29.61, 29.66, 29.68, 29.71 (broad peak, 3 methylenes), 30.13, 39.48 (methylenes), 45.97 (tertiary carbon), 51.40 (methoxy), and 178.18 (carbonyl). Elemental analysis calculated for the repeat unit ($C_{24}H_{46}O_2$): 78.61 C, 12.65 H. Found: 78.53 C, 12.77 H. GPC data: $M_n = 27\,200$; PDI (M_w/M_n) = 2.0.

5.1. Synthesis of the Unsaturated Carboxylic Acid-Functionalized Polymer (15). A 408 mg (1.08 mmol) sample of monomer **13** was placed in a nitrogen-purged, flame-dried 50 mL three-neck, round-bottom flask equipped with a Teflon magnetic stir bar and a valve adapter. The monomer (**13**) was dried under vacuum, with stirring, at 55 °C for 18 h. A 2.0 mg sample (0.0024 mmol, 440:1 monomer-to-catalyst ratio) of Grubbs' catalyst (**16**) was added under a nitrogen purge. The catalyst did not completely dissolve immediately. The vessel was warmed in a 55 °C oil bath, and intermittent vacuum (open valve for ∼1 s periodically) was applied until the mixture became viscous enough to leave open to vacuum ($<10^{-2}$ mmHg) after about 1 h. The catalyst dissolved completely within 30 min. The mixture became more viscous and turned from pink to orange after 1 day. On the second day the temperature was increased to 60 °C, and 2.0 mg of **16** was added. On the fourth day the temperature was increased to 65 °C, and 1.0 mg of **16** was added. On the sixth day 1.0 mg of **16** was added (for a total monomer-to-catalyst ratio of 150:1), and the mixture bubbled only slightly. The reaction was removed from the vacuum line on the seventh day. The product was obtained in 95% yield. No terminal olefin was detected by NMR and IR spectroscopy.

The following spectral properties were observed: ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 3H, methyl), 1.24−1.45 (m, 30H, methylenes and 2 pro-chiral methylene protons), 1.59−1.64 (m, 2H, pro-chiral methylene protons), 1.96−2.07 (m, 4H, allylic methylenes), 5.24−5.45 (m, 2H, olefin), and 11.68 (s, broad, 1H, acidic proton). Elemental analysis calculated for the repeat unit ($C_{23}H_{42}O_2$): 78.79 C, 12.08 H. Found: 78.49 C, 12.17 H. GPC data: $M_n = 4100$; PDI (M_w/M_n) = 1.7. (Note: the high molecular weight fraction was likely filtered from the GPC sample due to insolubility; see Discussion section.)

5.2. Synthesis of the Saturated Carboxylic Acid-Functionalized Polymer (11). Synthesized as above for **10**, with the following exceptions: a 302 mg sample (0.863 mmol of olefins in the repeat units of the polymer) of unsaturated polymer (**15**) and 20 mg (0.043 mmol) of Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) were used. The crude product (**11**) precipitated from the reaction mixture as a black residue. The polymer (**11**) was insoluble in chloroform, toluene, ethyl acetate, methanol, ethanol, THF, and DMSO. Most of the polymer dissolved in a refluxing mixture of *p*-xylene and 1-butanol (75:25 v/v), but some black particles remained insoluble. The remaining material eventually dissolved when 0.3 g of sodium hydroxide was added to the mixture. A grayish precipitate formed after the solution was slowly added to acidic methanol (1 M of HCl) and stirred for 1 h. The product (**11**) was a translucent, slightly black, viscous liquid after drying at 70 °C under vacuum for 5 days. Because of the removal of many small samples for solubility tests, an isolated yield was not calculated for this polymer. No residual olefin was detected by ^{1}H NMR and IR spectroscopy.

The following spectral properties were observed: ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 3H, methyl), 1.19−1.37 (m, 36H, methylenes), 1.42 (t, 2H, pro-chiral methylene protons), 1.62 (t, 2H, pro-chiral methylene protons), 11.62 (s, broad, 1H, acidic proton). GPC data: $M_n = 4100$; PDI (M_w/M_n) = 1.8. (Note: the high molecular weight fraction was likely filtered from the GPC sample due to insolubility; see Discussion section.)

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