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Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of Perfectly Alternating Copolymers from a Single Monomer

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ABSTRACT: Perfectly alternating unsaturated copolymers can be synthesized from a single monomer by being cognizant of the ADMET structure/reactivity relationships for substituted trienes. The Lewis acid free Schrock catalyst $W(CHR')(NAr)(OR)_2$ in which Ar = 2,6-C_6H_3-*i*-Pr_2, R′ = CMe_2Ph, and R = $CMe(CF_3)_2$ is employed in this research where the tungsten catalyst's inability to metathesize a trisubstituted olefin is exploited. The perfectly alternating nature of these polymers is clearly supported by ^1H and ^{13}C NMR spectroscopy as well as by UV spectroscopy for the polymer obtained from 5,6-diphenyl-1,5,9-decatriene.

Introduction

Acyclic diene metathesis (ADMET) polymerization has been well established as a method for synthesizing a variety of unsaturated polymers.[1] α,ω-Dienes containing a variety of functional groups can be condensed to linear polyalkenamers with regularly spaced olefin units using Lewis acid free Schrock alkylidenes of the type $M(CHR')(NAr)(OR)_2$ where M = W (catalyst **1**) or Mo (catalyst **2**), Ar = 2,6-C_6H_3-*i*-Pr_2, R′ = CMe_2Ph, and R = $CMe(CF_3)_2$.[2] Previously, we reported that while the molybdenum-based Schrock catalyst was active toward 1,1-disubstituted olefins, the tungsten-based catalyst proved to be inert.[3] This lack of catalytic activity exhibited by the tungsten complex has been exploited in the synthesis of a series of alternating hydrocarbon copolymers from a single triene, and the results are described herein.

Experimental Section

^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained with a Varian XL Series NMR superconducting spectrometer system. Spectra were recorded at room temperature in $CDCl_3$, and all chemical shifts reported are internally referenced to tetramethylsilane. Heteronuclear gated and decoupled quantitative ^{13}C NMR spectra were run for 10−14 h with a pulse delay of 10−20 s.[7] Carbon relaxation times (T_1) were determined by standard methods. Differential scanning calorimetry (DSC) data were collected on a DuPont DSC 2910 differential scanning calorimeter with nitrogen purge gas at a heating rate of 10 °C/min. The thermal gravimetric analysis (TGA) of the polymers was carried out on a DuPont Hi-Res TGA 2950 thermogravimetric analyzer under a flow of dry nitrogen at a heating rate of 10 °C/min. Size exclusion chromatography (SEC) was carried out with the use of Phenomenex Phenogel 5500 and 5000 Å columns coupled together, a Waters Associates differential refractometer, and a Perkin-Elmer LC-75 spectrophotometric detector on polymer samples 0.5% (w/v) in THF. The instrument was relatively calibrated with 1,4-polybutadiene standards obtained from Polysciences, Inc., ranging from M_n = 900 to M_n = 22 000. Vapor pressure osmometry (VPO) data were obtained, for polymer samples ranging from 10 to 30 g/L in toluene, on a Wescan Model 233 vapor pressure osmometer at 50 °C. Intrinsic viscosities were determined with an Oswaldt dilution viscometer at 25 °C in toluene.

Synthesis of 5-Methyl-1,5,9-decatriene (4). The procedure for the synthesis of **3** was directly analogous to that used to produce 3,6-dimethyl-2,6-octadiene.[12] Twenty milliliters of 5-hexen-2-one (Aldrich) (173 mmol) was added to an ylid prepared from 72 g (175 mmol) of 1-pentenyltriphenylphosphonium bromide and 87.5 mL of a 2.0 M solution of *n*-butyllithium in pentane. The isolated product was distilled at 78 °C at 15 mmHg.[8] Yield: 45%. ^1H NMR: 1.60 (s, 1.2H); 1.69 (s, 1.8H); 2.12 (m, 8H); 4.95 (m, 4H); 5.18 (br, 1H); 5.82 (m, 2H). ^{13}C NMR: 16.0, 23.4, 27.3, 27.4, 31.4, 32.3, 32.4, 34.0, 34.2, 39.1, 114.3, 114.5, 124.1, 124.9, 134.8, 134.9, 138.8. Anal. Calcd for $C_{11}H_{18}$: C, 88.00; H, 12.00. Found: C, 87.35; H, 12.32.

Synthesis of Poly(5-methyl-1,5,9-decatriene) (5). The monomer was synthesized and dried as previously described. Twenty milligrams of catalyst, $W(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$, where R = phenyl, was used for this reaction. The reaction was allowed to continue until the contents could no longer be stirred by magnetic agitation; at this time, the flask was opened to the atmosphere and the polymer was dissolved in toluene and passed through an alumina column, followed by freeze-drying from chloroform. Yield: 89. ^1H NMR: 1.60 (s, 1.2H); 1.72 (s, 1.8H); 2.05 (br, 8H); 5.13 (br, 1H); 5.42 (br, 2H). ^{13}C NMR: 16.0, 23.8, 26.0−34.0 (multiple signals); 39.8, 124.0−126.0 (multiple signals), 129−131 (multiple signals), 35.5 (multiple signals). IR (neat, cm^{-1}): 2918, 2847, 1666, 1447, 966. Anal. Calcd for C_9H_{14}: C, 88.52; H, 11.48. Found: C, 88.04; H, 11.67. GPC: M_w = 26 000 PDI = 1.98. VPO: M_n = 12 980. TGA (onset, N_2): 378.29 °C. DSC: T_g = −58.38 °C.

Synthesis of 5,6-Dimethyl-1,5,9-decatriene (6). This monomer was synthesized utilizing McMurry carbonyl coupling chemistry.[9] The $TiCl_3(DME)_{1.5}$ reagent was prepared by refluxing DME (350 mL) in the presence of $TiCl_3$ (25 g, 162 mmol) for 48 h under argon. The light blue precipitate was collected by filtration under argon followed by washing with dry pentane; the dry powder was stored in an argon atmosphere (32.0 g, 80%). The zinc−copper coupling catalyst was prepared by the addition of $CuSO_4$ (0.75 g, 4.7 mmol) to a suspension of zinc dust (9.8 g, 150 mmol) in nitrogen-purged water. This solid was washed with acetone, and ether, and subsequently dried and stored in an argon atmosphere.

The $TiCl_3(DME)_{1.5}$ (21.0 g, 86 mmol) reagent and Zn/Cu (20 g) catalyst were weighed out and mixed dry in the reaction flask under argon. DME (500 mL) was added to this mixture, followed by refluxing for 2 h. Then 2.0 mL (17.25 mmol) of 5-hexen-2-one (Aldrich) in 10 mL of DME was added dropwise and the reaction refluxed overnight. After cooling to room temperature, the reaction was diluted with 300 mL of pentane, filtered through a pad of Florisil, and concentrated via rotary evaporation to yield the crude product. This product was distilled at 80 °C at 15 mmHg. Yield: 95%. ^1H NMR: 1.65 (s, 3H); 2.13 (m, 4H); 5.02 (m, 2H); 5.85 (m, 1H). ^{13}C NMR: 18.0, 18.2, 32.4, 32.8, 33.8, 34.1, 114.1, 128.0, 128.2, 139.2.

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Anal. Calcd for $C_{12}H_{20}$: C, 87.80; H, 12.20. Found: C, 87.33; H, 12.48.

Synthesis of Poly(5,6-dimethyl-1,5,9-decatriene) (7). The monomer **5** was synthesized and dried as previously described. This reaction is analogous to the polymerization of 5-methyl-1,5,9-decatriene. Twenty milligrams of catalyst, $W(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$, where R = phenyl, was added directly to the reaction flask that contained 2.0 g of the monomer. The reaction was terminated via exposure to the atmosphere. The contents of the flask were dissolved in toluene and passed through a column of alumina, followed by freeze-drying from chloroform. Yield: 98%. ^{1}H NMR: 1.69 (m, 3H); 2.17 (br, 4H); 5.34 (0.24H); 5.42 (0.76H). ^{13}C NMR: 18.0, 18.2, 26.0, 26.5, 29.3, 29.8, 31.5, 32.0, 34.6, 35.0, 128.1, 128.4, 129.7, 130.4. Anal. Calcd for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 87.90; H, 11.32. SEC: M_w = 22 100. PDI = 1.93. VPO: M_n = 11 420. TGA (onset, N_2): 365.23 °C. DSC: $T_g = -53.74$ °C.

Synthesis of 5,6-Diphenyl-1,5,9-decatriene (8). The method used to synthesize **7** is analogous to the procedure used for 5,6-dimethyl-1,5,9-decatriene. The ketone, 1-phenyl-4-penten-1-one, used in this coupling was synthesized according to literature procedures.[10] Acetophenone *N*,*N*-dimethylhydrazone was obtained by mixing acetophenone (2 g, 200 mmol) with *N*,*N*-dimethylhydrazine (20 mL, 250 mmol) and *p*-toluenesulfonic acid (0.25 g) in 200 mL of benzene and refluxing for 2 h. with removal of water by means of a Dean–Stark trap. The solution was neutralized with dilute KOH, washed with water, and dried over $MgSO_4$. After filtration, the solvent was removed through rotary evaporation, leaving behind acetophenone *N*,*N*-dimethylhydrazone. Acetophenone *N*,*N*-dimethylhydrazone (24.0 g, 150 mmol) was dissolved in 300 mL of dry THF under argon. Lithium diisopropylamide (150 mmol) was added at −78 °C, followed by allyl bromide (21.5 mL, 250 mmol). The reaction was warmed slowly to room temperature overnight and then poured into a pentane/water mixture. The organic layer was extracted with brine and water and dried over $MgSO_4$. The solvent was removed by rotary evaporation, leaving a yellow liquid. 1-Phenyl-4-penten-1-one *N*,*N*-dimethylhydrazone was isolated after distillation at 75 °C at 0.5 mmHg. Concentrated HCl was added dropwise to a solution of 1-phenyl-4-penten-1-one *N*,*N*-dimethylhydrazone in 100 mL of pentane, and the solution was stirred for 1 h. The reaction was diluted with water, and the product was extracted with pentane, washed with water, and dried over $MgSO_4$. The crude product was isolated after filtration by removal of the pentane. 1-Phenyl-4-penten-1-one was distilled at 62 °C at 0.1 mmHg.

5,6-Diphenyl-1,5,9-decatriene was synthesized by titanium coupling of 1-phenyl-4-penten-1-one, (2.0 g), yielding 1.6 g of product after distillation at 98 °C at 10 mmHg. Yield: 89%. ^{1}H NMR: 2.12 (m, 2H); 2.71 (t, 2H); 5.17 (m, 2H); 5.92 (m, 1H); 7.18 (m, 4H); 7.37 (m, 1H). ^{13}C NMR: 32.6, 33.9, 114.8, 125.7, 127.5, 129.9, 138.1, 138.4, 143.0. IR (neat, cm^{-1}): 3073, 2923, 1945, 1876, 1822, 1750, 912. UV/vis: $\epsilon = 9700$ L mol^{-1} cm^{-1}, $\lambda_{max} = 247$ nm. Anal. Calcd for $C_{22}H_{24}$: C, 91.67; H, 8.33. Found: C, 91.12; H, 8.67. GC/MS: M$^+$, 288.1858, M (100), 205.1019.

Synthesis of Poly(5,6-diphenyl-1,5,9-decatriene) (9). The monomer **7** was synthesized and dried as previously described. This reaction is analogous to the polymerization of 5-methyl-1,5,9-decatriene. Twenty milligrams of catalyst, $W(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$, where R = Phenyl, was added directly to the reaction flask that contained 2.0 g of the monomer. The reaction was terminated via exposure to the atmosphere. The contents of the flask were dissolved in toluene and passed through a column of alumina, followed by freeze-drying from chloroform. Yield: 94%. ^{1}H NMR: 2.20 (br, 2H); 2.74 (br, 2H); 5.56 (br, 1H); 7.15 (br, 4H), 7.42 (br, 1H). ^{13}C NMR: 26.2, 31.8, 32.4, 34.2, 114.8, 125.8, 126.6, 130.0 (multiple signals), 138.1, 143.2, 143.4. IR (neat, cm^{-1}): 3074, 2923, 1944, 1874, 1802, 1752, 910. UV/vis: $\epsilon =$ 9700 L mol^{-1} cm^{-1}, λ_{max}= 247 nm. Anal. Calcd for $C_{20}H_{20}$: C, 82.30; H, 7.70. Found: C, 82.04; H, 7.86. SEC: M_w = 12 400. PDI = 1.86. VPO: M_n = 6360. TGA (onset, N_2): 372.74 °C. DSC: T_g = 21.46 °C

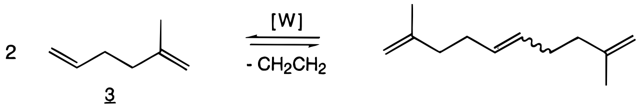

Figure 1. Metathesis of 2-methyl-1,5-hexadiene.

Results and Discussion

Alternating copolymers normally are synthesized by the chain polymerization of two monomers of different polarity. Since pure hydrocarbon monomers generally possess similar electronic properties, these monomers usually form randomly distributed copolymers and show little tendency toward alternation. Consequently, alternating copolymers of nonpolar dienes are relatively unknown. The ADMET reaction of triene monomers offers a viable route to perfectly alternating copolymers.

The application of olefin metathesis chemistry to the synthesis of alternating hydrocarbon polymers was first reported by Ofstead using ring-opening metathesis polymerization (ROMP). He described the ring-opening metathesis polymerization of a series of unequally substituted cyclooctadienes,[4] such as 1-methyl-1,4-cyclooctadiene, 1-ethyl-1,4-cyclooctadiene, 1-chloro-1,4-cyclooctadiene, and 1,2-dimethyl-1,4-cyclooctadiene, and in each case, the polymerization proceeded predominantly, but not exclusively, through the metathesis of the unsubstituted olefin in the ring. Consequently, a mostly alternating but not completely alternating copolymer structure was generated.

Forming alternating hydrocarbon copolymers via typical ADMET condensation techniques (bulk reactions at relatively low temperatures) is based on the selectivity of the tungsten catalyst **1**, an opportunity which is clearly demonstrated in the metathesis of the model compound, 2-methyl-1,5-hexadiene (**3**) (Figure 1). Catalyst **1** selectively and quantitatively metathesized the unsubstituted vinyl group of **3** while leaving the methyl-substituted alkene unreacted—i.e., polymer does not form since the compound is effectively monofunctional in olefin.[3] This is the case since trisubstituted olefins are inert to metathesis in the presence of tungsten-based Schrock catalysts.

This catalyst selectivity can be exploited in the synthesis of perfectly alternating hydrocarbon copolymers using three properly designed difunctional ADMET monomers possessing an internal, inert olefin. Step polymers with number-average molecular weights between 6000 and 12 000 are the result.

Polymerization of 5-Methyl-1,5,9-decatriene. 5-Methyl-1,5,9-decatriene (**4**) is the acyclic diene analog of 1-methyl-1,4-cyclooctadiene, and this compound **4** was used to synthesize an alternating copolymer structure containing the repeat units of isoprene and 1,3-butadiene (Figure 2).

Polymerization occurs exclusively through the metathesis of the unsubstituted vinyl groups, yielding the perfectly alternating copolymer **5**. Any deviation in the alternating sequence of this polymer would require the formation of a tetrasubstituted alkene where two of the four substituents would be the polymer backbone. The tungsten catalyst **1** cannot produce such an olefin, and monitoring the stereochemistry of the isoprene unit confirmed the alternating structure of polymer **5**. The methyl protons of the isoprene structure, both in the monomer and in the polymer, produce a proton signal at 1.7 ppm for the *Z* isomer and at 1.6 ppm for the *E* isomer (Figure 3).[5] The stereochemistry of the isoprene unit in polymer **5** remained unchanged from the mono-

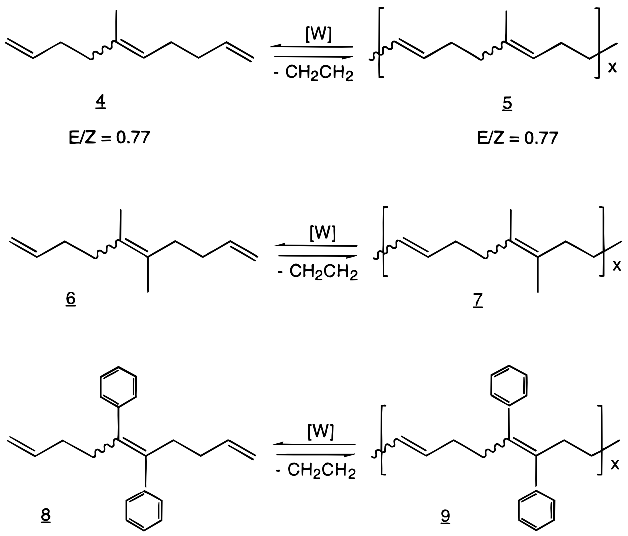

Figure 2. Alternating copolymer syntheses.

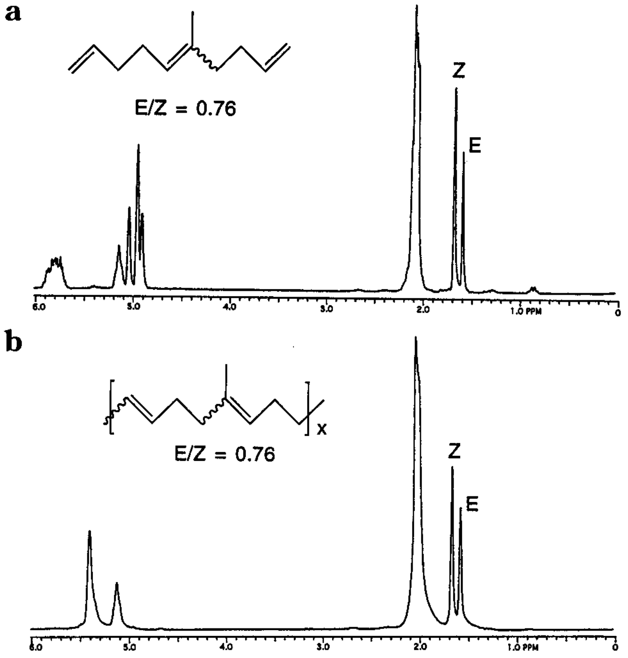

Figure 3. ^{1}H NMR spectral analysis of 5-methyl-1,5,9-decatriene (**4**) polymerization: (a) ^{1}H NMR spectrum of 5-methyl-1,5,9-decatriene (**4**); (b) ^{1}H NMR spectrum of poly(butadiene-*alt*-isoprene) (**5**).

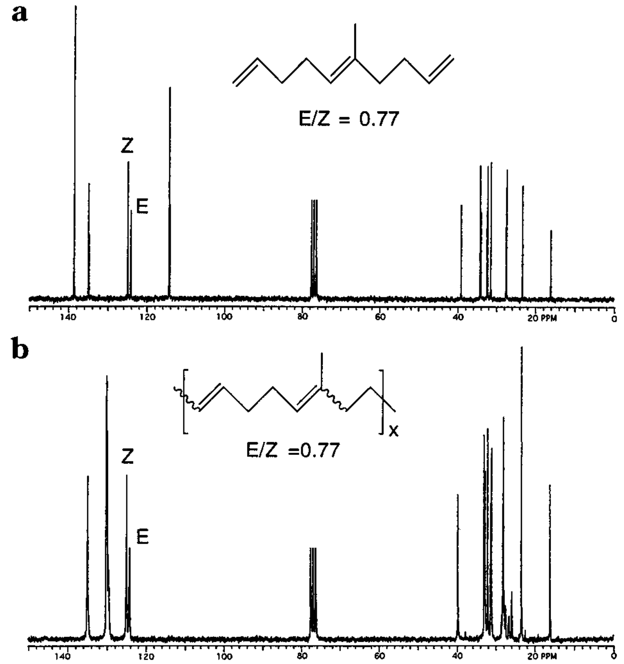

Figure 4. Quantitative ^{13}C NMR analysis of the polymerization of 5-methyl-1,5,9-decatriene (**4**), where *E*/*Z* refers to the stereochemical isomer ratio of the isoprene unit: (a) quantitative ^{13}C NMR spectrum of 5-methyl-1,5,9-decatriene (**4**); (b) Quantitative ^{13}C NMR spectrum of poly(5-methyl-1,5,9-decatriene) (**5**).

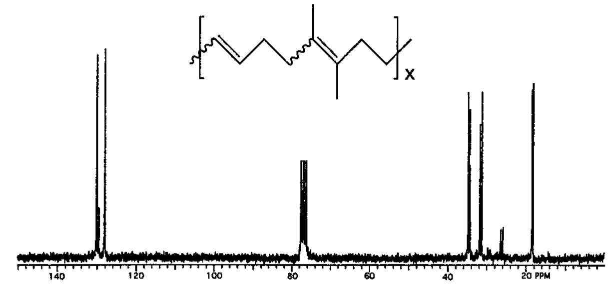

Figure 5. Quantitative ^{13}C NMR spectrum of poly(5,6-dimethyl-1,5,9-decatriene) (**7**).

mer with an *E*/*Z* isomer ratio of 0.76, which implies that this bond did not participate in the olefin metathesis reaction.

Quantitative ^{13}C NMR also confirmed that the stereochemistry of the isoprene unit remained constant after ADMET polymerization (Figure 4). The methine carbon of the isoprene unit produces two distinct carbon signals for each isomer, *Z* at 124.9 ppm and *E* at 124.1 ppm.[6] The *E*/*Z* ratio determined was 0.77 for both the monomer and the polymer. Retention of stereochemistry about the substituted olefin indicates that this bond did not participate in the olefin metathesis reaction and that the polymer structure **5** is a perfectly alternating copolymer of isoprene and 1,3-butadiene.

Polymerization of 5,6-Dimethyl-1,5,9-decatriene. The ADMET polymerization of 5,6-dimethyl-1,5,9-decatriene (**6**), shown in Figure 2, also produces an alternating copolymer with catalyst **1**, and the polymer that is formed, **7**, is analogous to that produced from the ROMP of 1,2-dimethyl-1,4-cyclooctadiene. Any participation of the tetrasubstituted olefin in the transmetathesis reaction would have resulted in the formation of isoprene units, which are known to possess methine carbons with chemical shifts at 124.9 and 124.1 ppm.[6] The quantitative ^{13}C NMR (Figure 5) of polymer **7** produced from the ADMET polymerization of 5,6-dimethyl-1,5,9-decatriene exhibits no carbon resonances in this area of the spectrum, which indicates that the tetrasubstituted olefin did not participate in the metathesis reaction, and shows that this polymer also possesses a perfectly alternating structure.

Polymerization of 5,6-Diphenyl-1,5,9-decatriene. The ADMET polymerization of 5,6-diphenyl-1,5,9-decatriene (**8**) provided a synthetic route to a previously unknown perfectly alternating copolymer and also presented an opportunity to verify the alternating nature of this polymerization through the use of ultraviolet spectroscopy. Like stilbene, monomer **8** possesses a large molar extinction coefficient (9700 L mol^{-1} cm^{-1}) at 247 nm) that can be used to monitor the participation of this substituted olefin in the olefin metathesis reaction. A hypsochromic shift in the UV spectrum would accompany any transmetathesis of the tetrasubstituted olefin, as the conjugation of the stilbene-like structure would be replaced with a styrene-like olefin. Figure 6

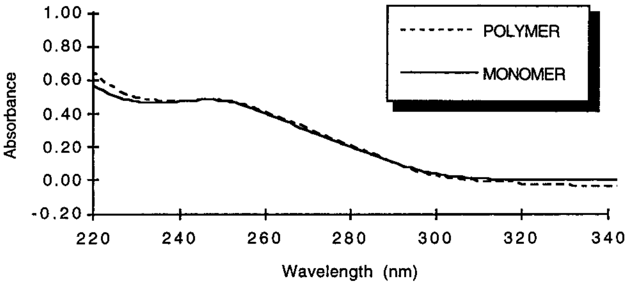

Figure 6. UV spectra for 5,6-diphenyl-1,5,9-decatriene (**8**) and the corresponding alternating copolymer **9**. Solutions are of equal concentration (polymer concentration based upon repeat unit) in pentane.

Table 1. Characterization Data of Alternating Copolymers Synthesized via ADMET Polymerization

polymer	M_n(SEC) ($\times 10^3$)	M_n (VPO) ($\times 10^3$)	PDI	T_g (°C)	TGA (°C)
5	13	13	2.0	−58	378
7	11	11	1.9	−54	365
9	6.6	6.3	1.9	21	373

[a] SEC = size exclusion chromatography, relative to polybutadiene standards, (g/mol); VPO = vapor pressure osmometry, calibrated with sucrose octaacetate (g/mol); PDI = polydispersity index = M_w/M_n; T_g = glass transition temperature measured by differential scanning calorimetry at a heating rate of 10 °C/min; TGA = thermogravimetric analysis, onset °C under nitrogen flow, heating rate = 10 °C/min.

shows the UV spectrum of the two equal concentration solutions of both the monomer **8** and the polymer **9**, where the concentration of the polymer was based upon the molecular weight of the repeat unit. The fact that these spectra are essentially identical is the strongest evidence for the perfectly alternating structure of polymer **9**.

The spectral analysis of polymers **5**, **7**, and **9**, coupled with the reactivity rules developed in the model compound study, strongly support the "perfectly alternating" nature of these polymers. These alternating polymer syntheses are examples of how understanding the synthetic rules for ADMET polymerizations leads to broadening of the application of this step condensation polymerization. Molecular weight and thermal characterization data for all these polymers are given in Table 1, illustrating that the behavior of such perfectly alternating copolymers can be varied at will. Any number of alternating copolymers are possible from this reaction scheme; one needs only design monomers with the reactivity of the olefin in mind.

Conclusions

ADMET chemistry using the tungsten analog of Schrock's catalyst provides a direct route to alternating copolymers of hydrocarbon monomers which cannot be prepared by traditional polymerization methods. This approach is not limited to hydrocarbon monomers alone, for alternating copolymers of various functionalities could be attainable through the proper design of the monomers. In the latter case, monomer design must preclude intramolecular poisoning of the catalyst by coordination of various functional groups to the metal center.[11−14]

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