Macromolecules 1992, 25, 3862-3867

Acyclic Diene Metathesis (ADMET) Polymerization. The Synthesis of Unsaturated Polyesters

J. T. Patton, J. M. Boncella, and K. B. Wagener*

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611-2046

Received December 17, 1991; Revised Manuscript Received February 27, 1992

ABSTRACT: The first acyclic diene metathesis (ADMET) polymerization using the molybdenum catalyst $Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ (R = Me, Ph) is presented. This catalyst is much faster in the metathesis of terminal olefins than its tungsten counterpart. 1,4-Benzenedicarboxylic bis(1-hexenyl) ester, 1,4-benzenedicarboxylic bis(1-pentenyl) ester, 1,4-benzenedicarboxylic bis(1-butenyl) ester, and 1-hexenyl 1-pentenoate successfully undergo ADMET homopolymerization. These polymerizations are initiated under bulk conditions and are continued in solution to produce poly[oxy-5-decenyloxyterephthaloyl], poly[oxy-4-octenyloxyterephthaloyl], poly[oxy-3-hexenyloxyterephthaloyl], and poly(oxy-3-octenyl ester), respectively. No metathesis activity is observed for 1,4-benzenedicarboxylic bis(1-propenyl) ester or 1-hexenyl 1-butenoate due to the negative neighboring group effect. This negative neighboring group effect involves either the coordination of the carbonyl oxygen to the metal center or simply the polarization of the double bond such that the intermediates of the metathesis process are not favored. The copolymerization of 1,4-benzenedicarboxylic bis(1-pentenyl) ester and 1,9-decadiene produces a random copolymer. All polymer structures were determined by IR, ^1H NMR, and ^{13}C NMR spectroscopy, and number-average molecular weights were determined by end-group analysis and vapor-pressure osmometry. Synthesis, characterization, and the general limitations of this polymerization are discussed.

Introduction

Acyclic diene metathesis (ADMET) polymerization has been established as a viable synthetic route to high molecular weight unsaturated polymers and copolymers containing various functionalities if certain synthesis rules are obeyed.[1-6] The synthesis of polymers via ADMET chemistry was not possible until the discovery that Lewis acid free catalyst systems were required to avoid competing vinyl addition chemistry.[7-9] The polymers that result from ADMET chemistry are perfectly linear and free from branching and other defects. They are pure in that no other repeat unit is present and the end groups are well-defined.

Conventional methods of preparing unsaturated polyesters involve the polycondensation reaction at elevated temperature between glycols and dibasic acids, esters, or anhydrides (Figure 1).[10,11] The useful range of number-average molecular weights for these polymers is generally moderate (15 000–20 000), allowing for easy processibility via molding or coating. Curing of the olefin present in the repeat units is then performed via thermal or irradiation methods. These conventional methods can result in a significant loss of unsaturation and branching during the polyesterification step. Thus, ADMET polymerization to yield unsaturated polyesters may offer a better route to unsaturated polyesters.

The metathesis of carbonyl-containing compounds has received attention in the past.[12] Until the development of Lewis acid free metathesis catalyst systems, however, the metathesis of unsaturated compounds containing the carbonyl functionality had been unsuccessful due to the rapid poisoning of the catalyst system. Only low conversions were observed, and thus highly reactive classical homogeneous metathesis catalyst systems such as WCl_6–$SnMe_4$ and $WOCl_4$–$SnMe_4$ have seen only limited success in the metathesis of unsaturated esters. Heterogeneous catalyst systems based on Re_2O_7/Al_2O_3–$SnMe_4$ also have been used in the attempted metathesis of unsaturated esters; however, as is the case for previous homogeneous catalyst systems, conversions are less than the necessary >99% required for successful step polymerization chemistry.[12,13]

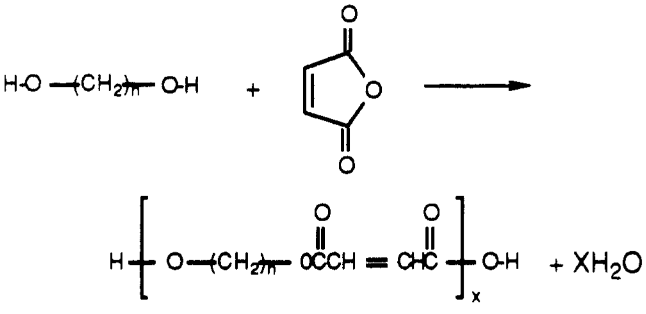
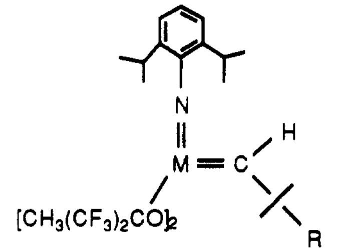


Figure 1. Conventional synthesis of unsaturated polyesters.



Catalyst	M	R
1a	Mo	Ph
1b	Mo	CH_3
2a	W	Ph
2b	W	CH_3

Figure 2. Catalyst systems that successfully promote ADMET polymerizations.

The molybdenum analog of Schrock's catalyst (Figure 2) has been described to be more tolerant of the carbonyl functionality as demonstrated in its application in the

0024-9297/92/2225-3862$03.00/0

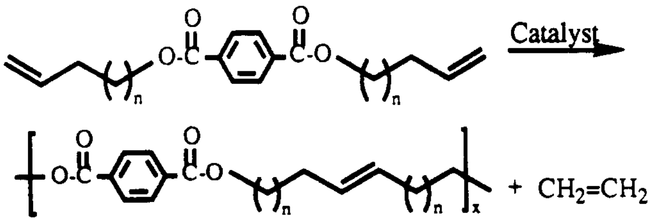


Figure 3. ADMET polymerization of an aromatic-containing ester.

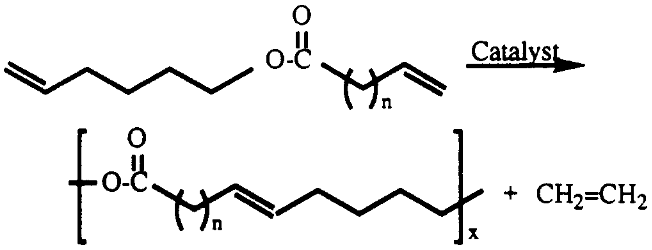


Figure 4. ADMET polymerization of alkyl ester diolefins.

ring-opening metathesis polymerization of functionalized norbornenes.[14-20] This paper reports the first successful acyclic diene metathesis (ADMET) polymerization of an ester-containing monomer using this molybdenum-based catalyst and demonstrates the successful polymerization of monomers containing a high degree of polar functionality, leading to unsaturated polymers possessing a high degree of crystallinity (Figure 3). Simple alkyl monomers were also used to define the synthesis rules of the ADMET polymerization of monomers containing the ester functionality (Figure 4).

Experimental Section

Monomer syntheses were performed under a dry-argon atmosphere using standard Schlenk techniques. Toluene and pentane were extracted with cold concentrated sulfuric acid followed by basic potassium permanganate. Tetrahydrofuran (THF), pentane, and toluene were distilled from potassium benzophenone ketyl. $M(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ (R = Me, Ph) (M = Mo, W) was prepared according to literature methods.[16,21] All other solvents and reagents were purged with argon and used without further purification.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300-MHz) or a Varian XL-200 (200-MHz) spectrometer. NMR data are listed as parts per million downfield from TMS. Obvious multiplicities and routine coupling constants are not listed. Spectra are obtained in $CDCl_3$ unless otherwise noted. IR data were recorded on a Perkin-Elmer 281 infrared spectrometer. Gel permeation chromatography (GPC) analyses were carried out with the use of Phenomenex Phenogel 5 500- and 5000-Å columns coupled, a Waters Associates differential refractometer, and a Perkin-Elmer LC-75 spectrophotometric detector on polymer samples 0.1–0.3% w/v in THF. The GPC columns were calibrated versus commercially available polystyrene samples ranging from 910 to 1.10×10^6. Vapor-pressure osmometry was carried out with the use of a Wescan 233 molecular weight apparatus at 50 °C on polymer samples ranging from 10 to 30 g/L in toluene. Differential scanning calorimetry (DSC) was carried out using a Du Pont DSC 2910 differential scanning calorimeter. Thermogravimetric analysis (TGA) was carried out using a Du Pont Hi-Res TGA 2950 thermogravimetric analyzer. Elemental analyses were by Atlantic Microlab, Inc., Atlanta, GA.

1,4-Benzenedicarboxylic Bis(1-hexenyl) Ester (3). Terephthaloyl chloride (5.0 g, 0.025 mol) was purged with argon and then dissolved in 50 mL of dry THF followed by the dropwise addition of dry pyridine (3.90 g, 0.050 mol, exothermic) via a syringe. 5-Hexen-1-ol (10.0 g, 0.10 mol) was added dropwise via a syringe, after which the mixture was heated to reflux for 3 h under argon. The THF was removed in vacuo. The residue was dissolved in 50 mL of H_2O and washed with 100 mL of diethyl ether. The ether fractions were combined, washed once with 10% aqueous HCl, and washed twice with 10% aqueous Na_2CO_3. Initial distillation via short-path distillation under full vacuum yielded the product as a colorless oil (8.79 g, 92%). Further purification for polymerization of 3 was accomplished by distillation via short-path distillation under full vacuum onto sodium and stirring overnight followed by filtration of the monomer through a Celite bed with the aid of pentane, after which the pentane was removed in vacuo. The monomer was then redistilled via short-path distillation under full vacuum into a round-bottomed storage flask equipped with a Rotaflow stopcock and molecular sieves. It had the following spectral properties: ^1H NMR ($CDCl_3$) δ 1.54 (p, 4 H), 1.79 (p, 4 H), 2.12 (q, 4 H), 4.33 (t, 4 H), 4.91–5.10 (m, 4 H), 5.69–5.92 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 138.2, 134.1, 129.1, 115.1, 65.5, 33.2, 27.8, 25.2. The IR spectrum (neat) showed a characteristic absorption at 1710 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.79; H, 7.95.

1,4-Benzenedicarboxylic Bis(1-pentenyl) Ester (4). The preparation of 4 from terephthaloyl chloride (5.0 g, 0.025 mol), pyridine (3.90 g, 0.050 mol), and 4-penten-1-ol (4.32 g, 0.050 mol) was analogous to the procedure for 3, yielding the product as a colorless oil (6.44 g, 94%) with the following spectral properties: ^1H NMR ($CDCl_3$) δ 1.88 (p, 4 H), 2.21 (q, 4 H), 4.35 (t, 4 H), 4.95–5.14 (m, 4 H), 5.72–5.97 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 137.8, 134.1, 129.8, 115.7, 64.9, 30.0, 28.0. The IR spectrum (neat) showed a characteristic absorption at 1715 cm^{-1} (C=O). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.38; H, 7.31.

1,4-Benzenedicarboxylic Bis(1-butenyl) Ester (5). The preparation of 5 from terephthaloyl chloride (12.50 g, 0.0246 mol), pyridine (9.81 g, 0.124 mol), and 1-butenol (10.0 g, 0.139 mol) was analogous to the procedure for 3, yielding the product as a colorless oil (15.03 g, 89%) with the following spectral properties: ^1H NMR ($CDCl_3$) δ 2.50 (q, 4 H), 4.37 (t, 4 H), 5.02–5.21 (m, 4 H), 5.72–5.97 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 165.9, 134.0, 133.9, 129.9, 117.6, 64.2, 33.1. The IR spectrum (neat) showed a characteristic absorption at 1720 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.96; H, 6.65.

1,4-Benzenedicarboxylic Bis(1-propenyl) Ester (6). The preparation of 6 from terephthaloyl chloride (5.0 g, 0.025 mol), pyridine (3.9 g, 0.05 mol), and allyl alcohol (3.9 g, 0.05 mol) was analogous to the procedure for 3, yielding the product as a colorless oil (5.27 g, 87%) with the following spectral properties: ^1H NMR ($CDCl_3$) δ 4.83 (dd, 4 H), 5.24–5.48 (m, 4 H), 5.92–6.15 (m, 2 H), 8.11 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 165.7, 134.1, 132.0, 129.9, 118.9, 66.0. The IR spectrum (neat) showed a characteristic absorption at 1720 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.15; H, 5.66.

1-Hexenyl 1-Pentenoate (7). 1-Pentenoic acid (10.0 g, 0.10 mol), 5-hexen-1-ol (9.0 g, 0.090 mol), and 5 drops of concentrated H_2SO_4 were refluxed in 150 mL of benzene in a Dean–Stark apparatus for 12 h with the occasional removal of H_2O. The benzene was removed in vacuo, and the remaining oil was mixed with 50 mL of diethyl ether and washed with a 10% Na_2CO_3 solution (3 × 50 mL) followed by one wash with a NaCl solution. The ether solution was dried over $MgSO_4$ and filtered, and the ether removed in vacuo. The resulting oil was then distilled via short-path distillation under a static vacuum into a flask containing CaH_2 and stirred for 12 h. The mixture was filtered through a Celite bed with the aid of pentane, after which the pentane was removed in vacuo. The colorless oil was redistilled via short-path distillation under static vacuum into a storage flask equipped with a Rotaflow stopcock and molecular sieves (14.75 g, 81%) with the following spectral properties: ^1H NMR ($CDCl_3$) δ 1.47–1.54 (m, 2 H), 1.54–1.71 (m, 2 H), 2.07 (q, 2 H), 2.38 (s, 4 H), 4.07 (t, 2 H), 4.84–5.11 (m, 4 H), 5.67–5.92 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 173.2, 138.5, 136.9, 128.6, 115.6, 114.8, 64.2, 33.8, 33.6, 29.6, 28.3, 25.8. The IR spectrum (neat) showed a characteristic absorption at 1735 cm^{-1} (C=O). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.48; H, 9.92.

1-Hexenyl 1-Butenoate (8). The preparation of 8 from vinylacetic acid (5.0 g, 0.058 mol), 5-hexen-1-ol (5.23 g, 0.052 mol), and 5 drops of concentrated H_2SO_4 was analogous to the procedure for 7, yielding the product as a colorless oil (7.53 g, 77%) with the following spectral properties: ^1H NMR ($CDCl_3$) δ 1.37–1.52

(m, 2 H), 1.52–1.72 (m, 2 H), 1.98–2.16 (q, 2 H), 3.01–3.16 (d, 2 H), 4.00–4.19 (t, 2 H), 4.90–5.26 (m, 4 H), 5.68–6.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 171.8, 138.1, 130.9, 128.3, 118.5, 115.1, 65.0, 39.4, 33.2, 28.0, 25.2. The IR spectrum (neat) showed a characteristic absorption at 1740 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59. Found: C, 71.10; H, 9.64.

Poly(oxy-5-decenyloxyterephthaloyl) (9). In a nitrogen-filled drybox, **1a** (0.01 g, 1.54 × 10^{-5} mol) was weighed into a Schlenk tube equipped with a stopcock and two addition arms with break-seals for additional catalyst additions. Each of the break-seal containers was charged with **1a** (0.005 g, 7.67 × 10^{-6} mol) dissolved in 1.5 mL of toluene. Compound **3** (2.0 g, 6.05 × 10^{-3} mol) was then added to the catalyst in the Schlenk tube and the mixture stirred. Rapid evolution of ethylene was observed and the reaction mixture became solid within 5 min. Toluene (20 mL) was then added to the mixture, which was then sealed, removed from the drybox, and attached to a vacuum line where the system was exposed to a slight vacuum to aid in the removal of ethylene. The reaction mixture was then slowly warmed to 45 °C and allowed to stir under a static vacuum. At 3-h intervals, each of the two break-seals was broken. The initial catalyst to monomer ratio was 400:1. Three hours after the second catalyst addition, compound **9** was purified by dissolution in warm toluene followed by dropwise addition of the polymer solution into rapidly stirring methanol at 0 °C. The white precipitate was then separated from the solvents by centrifugation followed by decanting of the solvents, yielding **9** as a white powder (1.66 g, 92%) with the following spectral properties: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.54 (p, 4 H), 1.79 (p, 4 H), 2.12 (q, 4 H), 4.33 (t, 4 H), 4.91–5.10 (m, 4 H), 5.38–5.49 (br, 2 H), 5.69–5.92 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.0, 134.3, 130.4, 129.8, 129.7, 65.5, 32.0, 28.1, 25.9. The IR spectrum (film) showed a characteristic absorption at 1705 cm^{-1} (C=O). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 68.79; H, 7.41.

Room-Temperature Synthesis of 9. In a drybox equipped with a nitrogen atmosphere **1a** (0.01 g, 1.53 × 10^{-5} mol) was weighed into a Schlenk tube equipped with a stopcock followed by **3** (2.0 g, 6.05 × 10^{-3} mol). Rapid evolution of ethylene was observed, and the reaction mixture became solid within 5 min. The solid was then dissolved in 20 mL of toluene and allowed to stir for an additional 8 h in a closed reaction vessel. The oligomers were purified as in the 45 °C case (1.74 g, 95%).

Poly(oxy-4-octenyloxyterephthaloyl) (10). The preparation of **10** from **1a** (0.011 g, 1.65 × 10^{-5} mol) in the Schlenk tube and **1a** (0.005 g, 7.67 × 10^{-6} mol) in each of the two break-seals was analogous to the procedure for **9** (45 °C case) with **4** (2.0 g, 0.006 61 mol) to yield **10** as a white powder (1.53 g, 94%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.88 (p, 4 H), 2.21 (br, 4 H), 4.35 (t, 4 H), 4.95–5.14 (m, 4 H), 5.45–5.57 (br, 2 H), 5.72–5.97 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 134.2, 130.0, 129.8, 65.0, 28.9, 28.5. The IR spectrum (film) showed a characteristic absorption at 1710 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 68.40; H, 6.70.

Poly(oxy-3-hexenyloxyterephthaloyl) (11). The preparation of **11** from **1a** (0.012 g, 1.82 × 10^{-5} mol) in the Schlenk tube and **1a** (0.005 g, 7.67 × 10^{-6} mol) in each of the two break-seals was analogous to the procedure for **9** with **5** (2.0 g, 0.007 29 mol) to yield poly(oxy-3-hexenyloxyterephthaloyl) as a white powder (1.62 g, 90%) with the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 2.50 (br, 4 H), 4.37 (t, 4 H), 4.95–5.14 (m, 1 H), 5.57–5.73 (br, 2 H), 5.72–5.97 (m, 2 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 165.9, 134.1, 129.8, 128.7, 126.9, 64.6, 32.1. The IR spectrum (film) showed a characteristic absorption at 1705 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 66.23; H, 5.73.

Poly(oxy-3-octenyl ester) (12). In a drybox equipped with a nitrogen atmosphere **1a** (0.018 g, 2.74 × 10^{-5} mol) was weighed into a Schlenk tube equipped with a stopcock followed by **7** (2.0 g, 0.011 mol). Rapid evolution of ethylene was evident, and the reaction was allowed to stir until the reaction mixture became too thick to stir after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 h (1.68 g, 99%). It had the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.37–1.52 (m, 2 H), 1.52–1.72 (m, 2 H), 1.92–2.16 (br, 2 H), 2.16–2.50 (br, 2 H), 3.93–4.20 (t, 2 H), 5.27–5.60 (br, 2 H); ^{13}C NMR ($CDCl_3$) δ 173.4, 131.2, 130.4, 129.6, 128.8, 64.4, 34.3, 34.2, 32.2, 28.1, 28.0, 26.0, 25.9. The IR spectrum (film) showed a characteristic absorption at 1735 cm^{-1} (C=O). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.18; H, 9.18.

Attempted Polymerization of 8. **1a** (0.019 g, 2.97 × 10^{-5} mol) and **8** (2.0 g, 0.012 mol) were reacted in an analogous procedure for the synthesis of **12**. Upon addition of the monomer to the catalyst there was no apparent evolution of ethylene, and after 3 h ^{1}H NMR revealed only unreacted starting material.

Copolymerization of 4 and 1,9-Decadiene (13). **4** (0.50 g, 0.0017 mol) and 1,9-decadiene (0.22 g, 0.001 65 mol) were mixed together and then added to a Schlenk tube preloaded with **1a** (0.005 g, 8.27 × 10^{-6} mol). Rapid evolution of ethylene was observed. Within 15 min the reaction mixture went solid, after which 20 mL of toluene was added for an additional 8 h. The reaction flask was then removed from the drybox and the polymer purified as described for the aromatic homopolymers. It had the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.18–1.45 (s, 8 H), 1.72–2.08 (m, 4 H), 4.23–4.41 (t, 4 H), 5.27–5.56 (m, 4 H), 8.02–8.17 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 134.2, 131.9, 130.2, 130.0, 129.6, 129.2, 128.7, 128.3, 128.0, 125.5, 64.5, 32.6, 29.8, 29.7, 29.0, 28.9, 28.4, 28.3. The IR spectrum (film) showed a characteristic absorption at 1720 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{33}O_4$: C, 74.77; H, 8.63. Found: C, 73.80; H, 8.44.

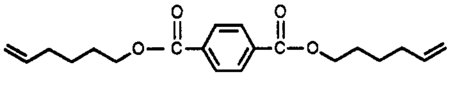
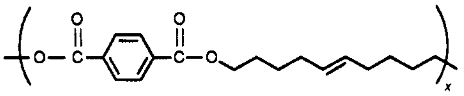
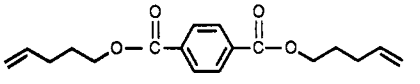
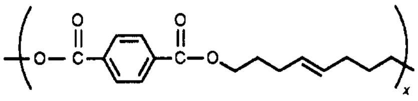
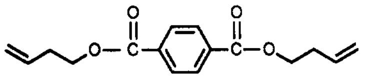
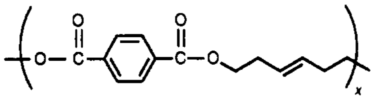
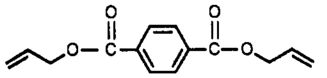
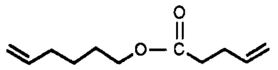
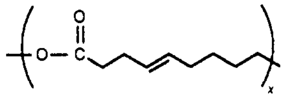
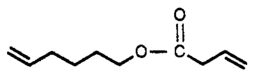
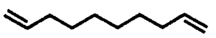
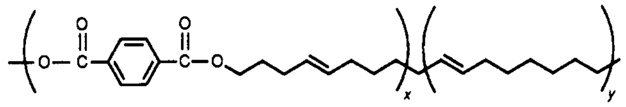
Results and Discussion

The first example of the ADMET polymerization of esters was performed using the tungsten catalyst, **2b** (Figure 2), and a monomer possessing eight methylene spacers between the ester functionality and the olefin.[22] While this demonstrated the viability of the ADMET polymerization of ester-containing olefins, it did not address the limitations of these polymerizations. In order to establish the synthesis rules and conditions for the polymerization of these ester monomers, a study was undertaken to determine the number of methylene spacers between the olefin and the ester group required to allow a successful ADMET polymerization. A summary of the monomers studied and the polymers formed is found in Table I. We have also examined, to a limited extent, the reactions that may involve the deactivation of the catalyst.

ADMET Chemistry and the Negative Neighboring Group Effect. Table I lists the unsaturated ester monomers with various numbers of methylene spacers between the ester group and the olefin used in this research. The polymerization of the linear alkyl ester, **7**, demonstrates that monomers with as few as two methylene spacers from the carbonyl side of the ester polymerize successfully using the molybdenum catalyst, **1**. The polymerization proceeds rapidly at room temperature and exhibits no evidence of chain transfer or branching in either the ^{1}H or ^{13}C NMR data as well as the optimal MWD (molecular weight distribution) of 2.0. This polymerization demonstrates the ability to rapidly synthesize high molecular weight unsaturated polyesters using the molybdenum catalyst, **1**, at room temperature. By comparison, the analogous alkyl ester, **8**, in which only one methylene spacer is present, shows no evidence of metathesis.

The number of methylene spacers between the ester functionality and the olefin is a factor in these polymerizations. This observation agrees with a similar study of monomers containing the ether functionality.[6] The minimum number of methylene spacers between the olefin and the ester from the oxygen side is also two for successful metathesis to occur, as demonstrated with the aromatic esters **3–6**. In some classical catalyst systems, reactivity has been observed in systems with only one methylene spacer present.[13]

Table I
Polymerization of Acyclic Unsaturated Esters

monomer		polymer	
	(3)		(9)
	(4)		(10)
	(5)		(11)
	(6)	no reaction	
	(7)		(12)
	(8)	no reaction	
4 + 			(13)

There are two possible reasons for this lack of reactivity when less than two methylene spacers are present, and we term this phenomenon a negative neighboring group effect. First, the ester may polarize the olefin such that the successful formation and decomposition of the metallocycles in the catalytic cycle are hindered. Second, the carbonyl might coordinate with the metal center. This coordination would result in the formation of five- or six-membered rings in the case of monomers 8 and 6, respectively (Figure 5). The coordination of the carbonyl back into the metal center of a metallacyclobutane resulting in four-membered rings has been observed in similar systems.[23] When a reaction of a 2:1 ratio of monomer 6 and molybdenum catalyst, 1a, was performed, the alkylidene signal disappeared immediately with no evidence of productive metathesis. Varying the number of methylene spacers from two to four had no obvious effect on the rate of polymerization. Regardless of the explanation, it is clear that having less than two methylene spacers between the olefin and the ester functionality prevents polymerization. We plan to elucidate this phenomenon with further reactions.

Polymer Characterization and Molecular Weight Analysis. Table II compiles the reaction temperature and the molecular weight data for polymers 9–13. In all cases, the oligomers were found to be perfectly linear and pure as demonstrated by the ^{13}C NMR spectra for polymer 9 in Figure 6. The trans/cis ratio found in all of the polymers was similar to that observed in other ADMET systems where the polymers were found to be 80–90% trans.[7] All aromatic ester polymerizations were limited by the solubility of the growing oligomer since these polymerizations ceased when the oligomers precipitated from solution at both 25 and 45 °C. The polymerizations of the aromatic ester monomers 3–5 were carried out at 45 °C, a temperature at which the catalyst's reactive intermediates begin to decompose. Consequently, multiple catalyst additions produced higher molecular weight oligomers; however, the active catalyst decomposed before a true equilibrium could be established, leading to nonequilibrium molecular weight distributions. The molecular weight distributions shown in Table II are reflective of a step polymerization process.

Table II
Molecular Weight Data for Unsaturated Polyesters

polymer	T (°C)	$\bar{X}_n$	$\bar{M}_n$[a]	PDI
9	45	39	11700	3.5
9	25	20	9500 (9200)	2.3
10	45	45	12300	2.7
11	45	22	5200	2.5
12	25	101	(18400)	1.9
13	25	22	4100	2.1

[a] $\bar{M}_n$ in parentheses were determined by VPO; all others were determined by end-group analysis from ^{1}H NMR.

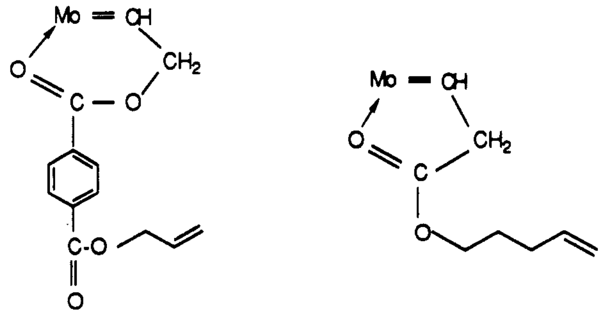


Figure 5. Negative neighboring group effect. The potential coordination of monomers 8 and 6 leading to coordinatively saturated metal centers and, hence, the lack of reactivity.

In order to demonstrate the viability of copolymerizing the aromatic esters with more flexible monomers, a copolymerization was carried out with a 1:1 mixture of 1,9-decadiene and monomer 4 and was compared with homopolymerization of monomer 4. The homopolymerization of monomer 4 produced an average degree of polymerization of 11, limited by the solubility of the growing oligomers. An identical room-temperature copolymerization resulted in an average degree of polymerization of 22. The significant increase in molecular weight at room temperature is attributed to the introduction of a flexible

Table III
Thermogravimetric Analysis Data for Unsaturated Polyesters[a]

	onset (°C)		90% wt loss (°C)	
polymer	air	nitrogen	air	nitrogen
9	251	326	487	410
10	245	335	495	418
11	291	323	500	422
12	199	257	463	480
13	278	283	489	446

[a] All values were obtained at a 5 °C/min ramp rate.

Table IV
Differential Scanning Calorimetry Data for Unsaturated Polyesters[e,f]

polymer	T_m (°C)	T_c (°C)	T_g (°C)
9	101.5[a,c]	80.7[a]	
10	39.8[b]		-50.1[b]
11	162.8[a,c]	156.9[a,c]	
12	-8.3[c]	-27.8[c]	-70.3[d]
13	39.8[b]		-46.8[b]

[a] Values obtained at 20, 10, and 5 °C/min and then extrapolated back to 0 °C/min. [b] Values determined from 5 °C/min·cycle. [c] Values determined from 4 °C/min·cycle. [d] Values determined from 9 °C/min·heating cycle. [e] Bimodal with values corresponding to the inflection point of the initial peak. [f] Peak possesses shoulder.

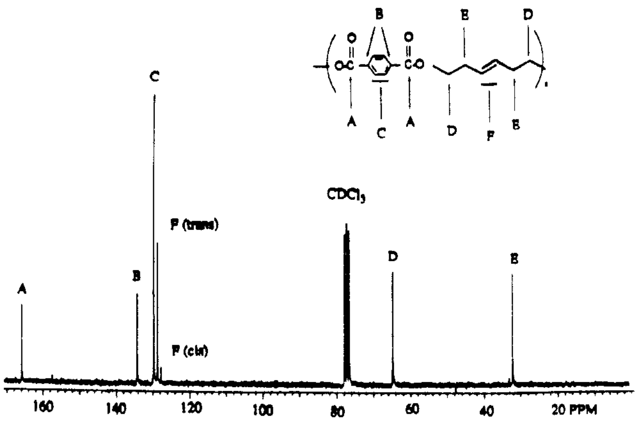


Figure 6. 50-MHz ^{13}C NMR spectra of polymer 9.

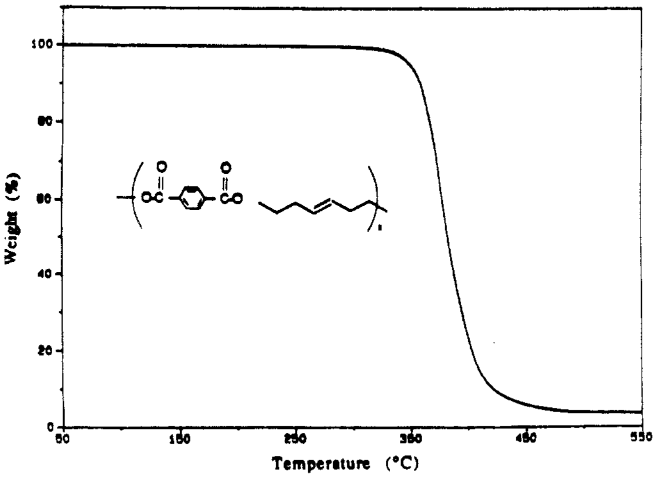


Figure 7. Thermogravimetric analysis of polymer 11 in nitrogen, with a scan rate of 5 °C/min.

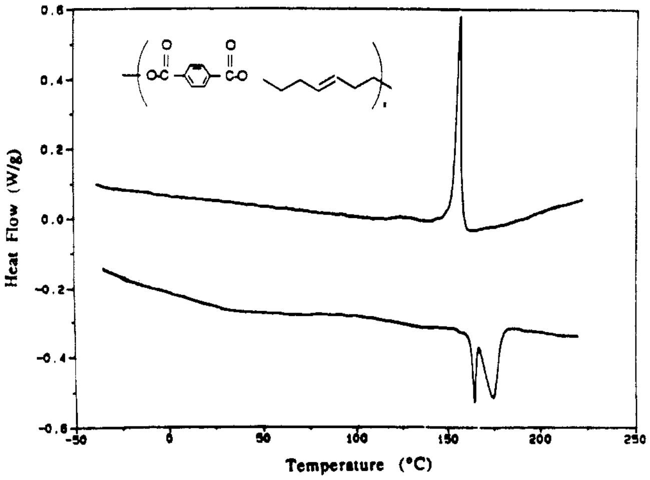
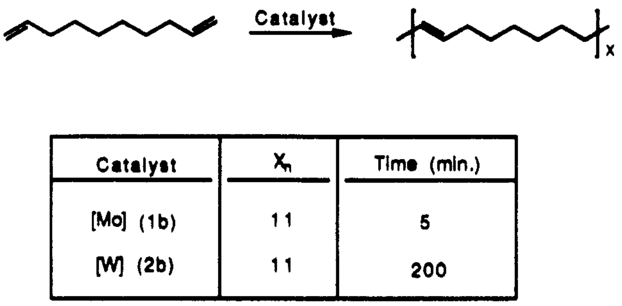


Figure 8. Differential scanning calorimetry of polymer 11, with a scan rate of 5 °C/min.



Catalyst	X_n	Time (min.)
[Mo] (1b)	11	5
[W] (2b)	11	200

Figure 9. Comparison of the use of molybdenum- and tungsten-based catalyst systems in ADMET polymerizations.

unit. The copolymer is random in nature.

Thermal Analysis of the Unsaturated Polyesters. The thermogravimetric analysis (TGA) data in Table III show that the unsaturated polyesters display a high degree of thermal stability. In all cases, the polymers exhibited total weight loss in a single step as displayed in Figure 7, which is the thermogram for polymer 11 and is representative of all the curves regardless of nitrogen or air purge.

The differential scanning calorimetry (DSC) results are depicted in Table IV. No T_g is observed for polymers 9 and 11 above -50 °C even at ramp rates of 20 °C/min. This observation as well as the sharpness of the transition peaks implies a high degree of crystallinity for polymers 9 and 11. A typical DSC curve for the above-mentioned polymers is displayed in Figure 8. Polymer 12 at slow ramp rates of 4 °C/min shows very strong recrystallization and melting peaks with no clear T_g. At 9 °C/min, however, the crystallization peak decreases significantly, reappearing in the heating cycle overlapping with the melting peak. At this rate a clear T_g is observed. Polymers 10 and 13, which contain three methylene spacers between the olefin and the aromatic peak, exhibited very slow rates of crystallization; therefore, extrapolated thermal data were difficult to obtain. A typical thermogram of these two polymers consists of a weak melting transition upon initial heating and the absence of other transitions in the remainder of the three cycles.

Kinetic Advantage of the Molybdenum-Based Catalyst versus That of Tungsten. We have observed that the molybdenum catalyst, 1, offers a kinetic advantage over the tungsten catalyst, 2, in this chemistry. When 1,9-decadiene was exposed to the tungsten catalyst, **2b**, in a 400:1 ratio, an oligomer of $X_n = 11$ was produced within 3 h, whereas, the molybdenum catalyst, **1b**, generated this oligomer in less than 5 min (Figure 9). This dramatic increase in the reaction rate is significant, and this phenomenon has been observed in similar systems.[16,24] This means that solution polymerization becomes a reality since the polymerization can proceed at a reasonable rate even when a growing polymer chain is diluted in solution. Thus, the low-temperature polymerization of stiffer and less soluble polymers becomes viable.

Conclusions

Acyclic diene metathesis (ADMET) polymerization offers a viable route for the synthesis of pure unsaturated polyesters. The use of the highly active, Mo-based, Lewis acid-free alkylidene catalyst provides a clean route to unsaturated polyesters with known vinyl end groups. The polymerizability of a monomer is limited by the number of methylene spacers between the ester functionality and the olefin, a phenomenon which we term the negative neighboring group effect. The observation that molybdenum catalyst 1 successfully polymerizes acyclic dienes is significant since it is more tolerant to polar functionalities and reacts at a significantly faster rate than tungsten catalyst 2 for some terminal olefins. Further investigation into the difference between molybdenum- and tungsten-based catalysts in acyclic diene metathesis polymerizations, as well as the polymerization of other carbonyl-containing monomers, is currently being pursued.

Acknowledgment. We thank the National Science Foundation (Grant DMR-8912026) and the University Research Initiative Program (Grant No. N00014-86-G-0224) as conducted by DARPA and the Naval Research Office for their support of this work. We also are very thankful to A. S. Gamble, C. G. Bauch, and K. Brzezinska for helpful discussions.

References and Notes

(1) Nel, J. G. *Acyclic Diene Metathesis Polymerization*. Ph.D. Dissertation, University of Florida, 1990.
(2) Nel, J. G.; Wagener, K. B.; Boncella, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 130.
(3) Nel, J. G.; Konzelman, J.; Wagener, K. B.; Boncella, J. M. *Macromolecules* **1990**, *23*, 5155.
(4) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649–2657.
(5) Nel, J. G.; Duttweiler, R. P.; Hillmeyer, M. A.; Boncella, J. M.; Konzelman, J.; Smith, D. W., Jr.; Puts, R.; Willoughby, L. *Rubber Chem. Technol.* **1991**, *64*, (1), 83.
(6) (a) Wagener, K. B.; Brzezinska, K. *Macromolecules* **1991**, *24*, 5273–5277. (b) Wagener, K. B.; Brzezinska, K. *Makromol. Chem.*, in press.
(7) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649–2657.
(8) Lindmark-Hamberg, M.; Wagener, K. B. *Macromolecules* **1987**, *20*, 2949.
(9) Wagener, K. B.; Boncella, J. M.; Nel, J. G.; Duttweiler, R. P.; Hillmeyer, M. *Makromol. Chem.* **1990**, *191*, 365.
(10) Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley-Interscience: New York, 1970.
(11) Parker, E. E.; Peffer, J. R. Unsaturated Polyester Resins. In *Polymerization Processes*; Schildknecht, C. E., Skeist, I., Eds.; Wiley-Interscience: New York, 1977; Chapter 3.
(12) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1982.
(13) Mol, J. C. *J. Mol. Catal.* **1991**, *65*, 145–162.
(14) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640–2642.
(15) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M.; *J. Am. Chem. Soc.* **1991**, *112*, 8378–8387.
(16) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.
(17) Bazan, G. C.; Oskam, J. H.; Cho, H.-N. Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899–6907.
(18) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.
(19) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384.
(20) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902–2907.
(21) Depue, R. T.; Schrock, R. R.; Feldman, J.; Yap, K.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.
(22) Bauch, C. G.; Wagener, K. B.; Boncella, J. M. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 413–417.
(23) Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260–2265.
(24) Kroll, W. R.; Doyl, G. *Chem. Commun.* **1971**, 839.

Registry No. **1a**, 139220-25-0; **1b**, 108945-98-8; **3**, 141221-24-1; **3** (homopolymer), 141221-32-1; **4**, 141221-25-2; **4** (homopolymer), 141221-33-2; (**4**)($H_2C{=}CH(CH_2)_6CH{=}CH_2$) (copolymer), 141247-84-9; **5**, 62680-75-5; **5** (homopolymer), 141221-34-3; **6**, 1026-92-2; **7**, 141221-26-3; **7** (homopolymer), 141221-31-0; **8**, 141221-27-4; **9**, 141221-28-5; **10**, 141221-29-6; **11**, 141221-30-9; terephthaloyl chloride, 100-20-9; 5-hexen-1-ol, 821-41-0; 4-penten-1-ol, 821-09-0; 3-buten-1-ol, 627-27-0; allyl alcohol, 107-18-6; 1-pentenoic acid, 591-80-0; vinylacetic acid, 625-38-7.