Model Studies and the ADMET Polymerization of Soybean Oil

Qingping Tian and Richard C. Larock*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

ABSTRACT: Grubbs' ruthenium catalyst **2** has been employed in model studies of the acyclic diene metathesis (ADMET) polymerization of soybean oil. In the presence of 0.1 mol% of catalyst **2**, the ADMET polymerization of ethylene glycol dioleate afforded the isomerized (*E*)-dioleate (27%), dimer (18%), trimer (13%), tetramer (7%), pentamer (5%), hexamer (4%), heptamer (4%), and 9-octadecene (21%). Only a trace of any intramolecular cyclized product was formed. Under the same conditions, glyceryl trioleate underwent ADMET polymerization to produce dimer, trimer, tetramer, pentamer, and monocyclic oligomers, with monocyclic oligomers predominating. The high number of repeat units in the monocyclic oligomers ($n \cong 6$, 10, and 21) indicates that cross-linking occurs readily in this process. Based on our model system studies, we have examined the ADMET polymerization of soybean oil and succeeded in producing polymeric materials ranging from sticky oils to rubbers.

Paper no. J9759 in *JAOCS 79*, 479–488 (May 2002).

KEY WORDS: ADMET polymerization, Grubbs' catalyst, olefin metathesis, soybean oil.

Olefin metathesis is a reaction in which olefins are formally cleaved at the carbon-carbon double bond and new olefins result by recombination of the fragments (Eq. 1) (1,2). A wide variety of transition metal complexes have been shown to catalyze this process. Particularly important are those involving W, Mo, Re, and Ru. Until recently, the most widely used catalyst system employed WCl_6 and an alkylmetal or a Lewis acid.

$$2\ CH_3CH{=}CHC_2H_5 \xrightleftharpoons{\text{catalyst}} CH_3CH{=}CHCH_3 + C_2H_5CH{=}CHC_2H_5 \quad [1]$$
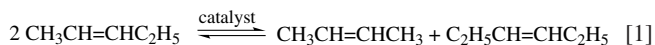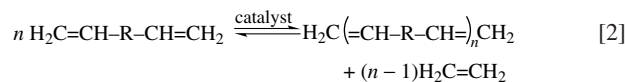
The olefin metathesis of esters of unsaturated FA has been examined. Boelhouwer and co-workers have reported the olefin metathesis of methyl oleate (3) and the more highly unsaturated esters of linoleic acid and linolenic acid (4–6) using the catalyst WCl_6/Me_4Sn (3). Using the same catalyst system, Kohashi and Foglia (7) have examined the co-metathesis of methyl oleate with other unsaturated diesters. Schuchart investigated the co-metathesis of methyl oleate and ethylene in the presence of $Re_3O_7/SiO_2 \cdot Al_2O_3/B_2O_3$ (8).

The WCl_6/Me_4Sn-catalyzed metathesis of soybean oil, which consists mostly of the TG of oleic (~23%), linoleic (~51%), and linolenic acids (~7%) has been reported to produce an improved drying oil (9). However, this inefficient and environmentally hazardous procedure, and lack of any real physical properties for the resulting oil, encouraged us recently to look at the use of a more modern olefin metathesis

*To whom correspondence should be addressed. E-mail larock@iastate.edu

catalyst, Grubbs' $(Cy_3P)_2Cl_2Ru{=}CHPh$ catalyst, for this process (10). This approach proved highly efficient for the olefin metathesis of soybean and many other natural oils and provided much more thoroughly characterized metathesized soybean drying oils. At the time, the exact nature of the metathesis process was not well understood. We now wish to report model studies on the metathesis and co-metathesis of soybean oil that fully explain the metathesis process and that have led to higher-M.W. polymeric materials with considerable industrial potential. This work nicely complements the earlier work of Finkel'shtein *et al.* (11), who have also examined the co-metathesis of synthetic and natural oils using the WCl_6/Me_4Sn catalyst.
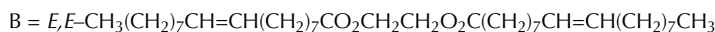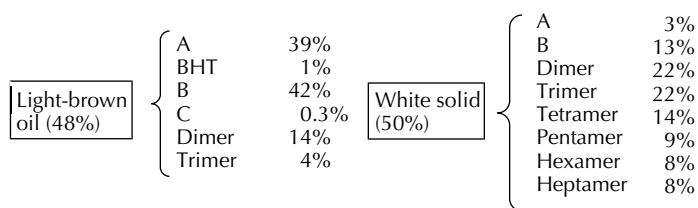
Olefin metathesis has also been employed in the synthesis of polymers, primarily through ring-opening metathesis polymerization and acyclic diene metathesis polymerization (ADMET). The latter process involving dienes allows high-M.W. polymeric products to be produced by selectively removing a volatile by-product, such as ethylene, during the reaction (Eq. 2) (12–14). The choice of catalyst has proven very important in ADMET polymerization. Thus, Schrock's well-defined tungsten and molybdenum alkylidenes, such as **1** (15–17), and more recently Grubbs' ruthenium alkylidene complex, **2** (18–20), have proven highly successful in ADMET polymerization. These Lewis acid-free catalysts show higher activities in ADMET polymerization than the classical metathesis catalysts, and the reaction can be carried out in short reaction times at room temperature while accommodating a variety of functional groups (21) (Schemes 1 and 2).

$$n\ H_2C{=}CH{-}R{-}CH{=}CH_2 \xrightleftharpoons{\text{catalyst}} H_2C\!\left(={=}CH{-}R{-}CH={\right)_n}CH_2 \quad [2]$$
$$+ (n-1)H_2C{=}CH_2$$

We envisioned that the ADMET process could be employed in the polymerization of soybean oil. Since the ADMET process proceeds as a step polymerization, the ADMET polymerization of soybean oil should be better controlled than the previously used thermal polymerization process (22,23). It was our hope that this process would convert soybean oil to useful new biodegradable materials. We now report the success of that effort.

EXPERIMENTAL PROCEDURES

General. All ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively. Gel permeation chromatography (GPC) analyses were carried out with the use of a Waters gel permeation system (410 refractive index detector; Milford,

R = CMe(CF$_3$)$_2$

1

SCHEME 1

Cy = cyclohexyl

2

SCHEME 2

MA) coupled with a Wyatt miniDawn, a laser light-scattering photometer (Wyatt Technology Corp., Santa Barbara, CA). The chromatography system was equipped with three ultra-styragel columns (Waters HR 1, 4, and 5). The M.W. were calculated by calibration with polystyrene standards. THF was utilized as the solvent, and the flow rate was 1.0 mL/min, with the system equilibrated at 40°C.

GC–MS spectrometric analyses were performed using a Finnigan Magnum Ion Trap Detector (San Jose, CA). The MS system was configured in the electron impact ionization mode with the automatic gain control feature turned on. A DB5-MS column was used in the experiments. Atmospheric pressure chemical ionization (APCI) MS experiments were performed on a Finnigan TSQ 700 mass spectrometer equipped with a Finnigan APCI ion source.

TLC was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F; Maidstone, United Kingdom), and visualization was effected with short-wavelength UV light (254 nm) or a basic KMnO$_4$ solution [3 g KMnO$_4$ + 20 g K$_2$CO$_3$ + 5 mL NaOH (5%) + 300 mL H$_2$O].

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Ethylene glycol and glycerol were purchased from Fisher Scientific (Pittsburgh, PA). 1,9-Decadiene, ethyl vinyl ether, 2,6-di-*tert*-butyl-4-methylphenol (BHT), *N,N*-dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, and oleic acid were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). Catalysts **1** and **2** were provided by Professor Kenneth B. Wagener (Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL). Catalyst **2** was also purchased from Strem Chemicals, Inc. (Newburyport, MA). 5-Hexenyl 4-pentenoate and di-5-pentenyl 1,4-benzenedicarboxylate were prepared according to previous literature procedures (16).

Ethylene glycol dioleate (5). Ethylene glycol dioleate (**5**) was prepared according to a literature procedure (24). Ethylene glycol (1.097 g, 17.7 mmol) was added to a solution of oleic acid (10 g, 35.4 mmol) in 50 mL of CCl$_4$ at 0°C. This was followed by the addition of 4-(dimethylamino)pyridine (4.32 g, 35.4 mmol). Most of these components dissolved after stirring for 30 min. A solution of *N,N*-dicyclohexylcarbodiimide (7.31 g, 35.4 mmol) in dry CCl$_4$ was added to the mixture, which was then allowed to stir at room temperature for 5 h. The resulting mixture was filtered, and the precipitate was washed with CCl$_4$. Evaporation of the filtrate under reduced pressure gave the crude product, which was purified by flash chromatography (20:1 hexanes/EtOAc) to afford a colorless liquid (7.13 g, 12.1 mmol, 68%): ^{1}H NMR (CDCl$_3$) δ 0.87 (*t, J* = 6.2 Hz, 6H), 1.27 (*m*, 40H), 1.61 (*m*, 4H), 2.00 (*m*, 8H), 2.31 (*t, J* = 7.5 Hz, 4H), 4.26 (*s*, 4H), 5.24–5.36 (*m*, 4H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.9, 27.1, 27.2, 29.1, 29.13, 29.2, 29.3, 29.6, 29.7, 29.8, 31.9, 34.1, 62.0, 129.7, 130.0, 173.5 (one sp^3 carbon missing due to overlap); IR (CDCl$_3$) 3002, 2952, 1742, 1456 cm^{-1}; MS (APCI) *m/z* 591 (MH)$^+$.

Glyceryl trioleate. Glyceryl trioleate was prepared according to a literature procedure (24). Glycerol (0.429 g, 4.66 mmol) was added to a solution of oleic acid (5.0 g, 17.7 mmol) in 25 mL of CCl$_4$ at 0°C. This was followed by the addition of 4-(dimethylamino)pyridine (2.162 g, 17.7 mmol). Most of these components dissolved after stirring for 30 min. A solution of *N,N*-dicyclohexylcarbodiimide (3.652 g, 17.7 mmol) in 30 mL of dry CCl$_4$ was added to the mixture, which was then allowed to stir at room temperature for 6 h. The resulting mixture was filtered. and the precipitate was washed with CCl$_4$. Evaporation of the filtrate under reduced pressure gave the crude product, which was purified by flash chromatography (20:1 hexanes/EtOAc) to afford a colorless liquid (2.10 g, 2.37 mmol, 51%): ^{1}H NMR (CDCl$_3$) δ 0.87 (*t, J* = 6.6 Hz, 9H), 1.28 (*m*, 60H), 1.60 (*m*, 6H), 1.99 (*m*, 12H), 2.30 (*dt, J* = 1.5, 6.0 Hz, 6H), 4.13 (*dd, J* = 6.0, 12.0 Hz, 2H), 4.29 (*dd, J* = 6.0, 12 Hz, 2H), 5.24–5.39 (*m*, 7H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.1, 27.2, 29.0, 29.10, 29.13, 29.2, 29.3, 29.5, 29.7, 29.8, 31.9, 34.1, 34.2, 62.1, 68.9, 129.6, 129.7, 130.0, 172.8, 173.3 (14 sp^3 carbons missing due to overlap); IR (CDCl$_3$) 3002, 2924, 1744, 1463 cm^{-1}; MS (APCI) *m/z* 886 (MH)$^+$.

ADMET polymerization of ethylene glycol dioleate. In a nitrogen-filled dry box, catalyst **2** (2.0 mg, 2.43 µmol) was weighed into a Schlenk tube with a magnetic stir bar. After being capped with a stopcock, the flask was removed from the dry box and attached to a manifold. Another Schlenk flask loaded with ethylene glycol dioleate was also connected to the manifold. The manifold was evacuated and filled with argon three times. The two Schlenk flasks were then opened to the manifold. Under a steady flow of argon, ethylene glycol dioleate (1.5 mL, 1.39 g, 2.36 mmol) was transferred to the flask charged with catalyst **2**. The flask was then switched to the vacuum line, and the reaction mixture was slowly warmed to 55°C for 24 h while stirring. The flask was removed from the bath and allowed to cool. Then CH$_2$Cl$_2$ (10 mL), ethyl vinyl ether (0.1 mL), and BHT (15 mg) were added to the flask. Ethyl vinyl ether and BHT were used to terminate the reaction and to stabilize the polymer product, respectively. After 12 h of stirring,

FIG. 1. Composition of the two fractions.

an additional 20 mL of CH_2Cl_2 was added to the solution, and the resulting solution was poured into 200 mL of rapidly stirring methanol at 0°C. The white precipitate formed was then separated from the solvents by centrifugation, followed by decanting of the solvents, and then dried by pumping overnight. This procedure yielded a white solid (0.69 g, 50% weight recovery): m.p. 49–53°C. The solvent portions were collected, concentrated and dried by pumping overnight, affording a light-brown oil (0.66 g, 48% weight recovery). A portion of the white solid (0.2 g) was further partitioned by flash chromatography, yielding eight fractions (Fig. 1). The light-brown oil was also processed by flash chromatography, affording six fractions (Fig. 1). The following are the spectral data for these fractions:

(i) (Z)- and (E)-9-octadecene (Fig. 1, Compound A). ^{1}H NMR (CDCl$_3$) δ 0.89 (t, J = 6.9 Hz, 6H), 1.20–1.33 (m, 24H), 1.94–1.98 (m, 4H), 5.35–5.41 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.8, 27.7, 29.2, 29.4, 29.6, 29.7, 29.8, 32.0, 32.7, 129.9, 130.4; IR (CDCl$_3$) 2952, 2849, 1463 cm^{-1}; high-resolution MS (HRMS) *m/z* 252.2815 (calcd. for C$_{18}$H$_{36}$, 252.2817).

(ii) E,E-ethylene glycol dioleate (Fig. 1, Compound B). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.27 (m, 40H), 1.59–1.64 (m, 4H), 1.90–1.98 (m, 8H), 2.32 (t, J = 7.5 Hz, 4H), 4.26 (s, 4H), 5.24–5.36 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 29.1, 29.12, 29.2, 29.23, 29.3, 29.5, 29.6, 29.7, 31.9, 32.6, 34.1, 62.0, 130.1, 130.5, 173.6 (one sp^3 carbon missing due to overlap); IR (CDCl$_3$) 3002, 2845, 1734, 1462 cm^{-1}.

(iii) Compound C (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 1.20–1.40 (m, 20H), 1.59–1.64 (m, 4H), 1.90–2.10 (m, 4H), 2.32 (t, J = 7.5 Hz, 4H), 4.30 (s, 4H), 5.30–5.40 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 24.7, 27.8, 28.7, 28.8, 28.9, 31.9, 34.3, 62.0, 130.8, 173.6; MS (APCI) *m/z* 339 (MH)$^+$.

(iv) Dimer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.20–1.40 (m, 56H), 1.59–1.64 (m, 8H), 1.90–1.98 (m,

12H), 2.31 (t, J = 7.5 Hz, 8H), 4.26 (s, 8H), 5.24–5.42 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 27.2, 27.3, 29.0, 29.04, 29.1, 29.17, 29.2, 29.4, 29.5, 29.6, 29.7, 29.74, 29.8, 31.9, 32.6, 34.1, 62.0, 129.7, 129.9, 130.1, 130.2, 130.3, 130.5, 173.6 (two sp^3 carbons missing due to overlap); IR (CDCl$_3$) 3052, 2952, 1739, 1461 cm^{-1}; MS (APCI) *m/z* 930 (MH)$^+$.

(v) Trimer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.20–1.40 (m, 72H), 1.56–1.64 (m, 12H), 1.90–2.01 (m, 16H), 2.31 (t, J = 7.5 Hz, 12H), 4.26 (s, 12H), 5.24–5.42 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.9, 27.1, 27.2, 27.3, 28.9, 29.0, 29.1, 29.15, 29.2, 29.3, 29.5, 29.55, 29.6, 29.72, 29.8, 31.9, 32.5, 32.6, 34.1, 62.0, 129.7, 129.8, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2920, 1739, 1462 cm^{-1}; MS (APCI) *m/z* 1268 (MH)$^+$.

(vi) Tetramer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.20–1.40 (m, 88H), 1.56–1.64 (m, 16H), 1.90–2.10 (m, 20H), 2.31 (t, J = 7.5 Hz, 16H), 4.26 (s, 16H), 5.24–5.42 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 12.4, 14.1, 22.7, 24.9, 27.1, 27.2, 27.3, 28.9, 29.0, 29.1, 29.16, 29.2, 29.3, 29.5, 29.55, 29.6, 29.72, 29.8, 31.9, 32.5, 32.6, 34.1, 62.0, 129.7, 129.8, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2920, 1738, 1461 cm^{-1}; MS (APCI) *m/z* 1605 (M)$^+$.

(vii) Pentamer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.20–1.40 (m, 104H), 1.56–1.64 (m, 20H), 1.90–2.10 (m, 24H), 2.31 (t, J = 7.5 Hz, 20H), 4.26 (s, 20H), 5.24–5.42 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 27.1, 27.2, 29.0, 29.1, 29.19, 29.2, 29.4, 29.5, 29.6, 29.7, 29.75, 29.8, 31.9, 32.6, 34.1, 62.0, 129.8, 129.9, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3051, 2921, 1738, 1462 cm^{-1}; MS (APCI) *m/z* 1946 (MH)$^+$.

(viii) Hexamer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6H), 1.20–1.40 (m, 120H), 1.56–1.64 (m, 24H), 1.90–2.10 (m, 28H), 2.31 (t, J = 7.5 Hz, 24H), 4.26 (s, 24H), 5.24–5.42

(m, 14H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.8, 24.9, 27.2, 29.1, 29.16, 29.2, 29.3, 29.39, 29.4, 29.6, 29.7, 29.8, 32.0, 32.6, 32.7, 34.2, 62.0, 129.9, 130.2, 130.3, 130.6, 173.6; IR (CDCl$_3$) 3052, 2922, 1738, 1469 cm^{-1}; MS (APCI) m/z 2282 (M)$^+$.

(ix) Heptamer (Fig. 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (*t*, *J* = 6.3 Hz, 6H), 1.20–1.40 (*m*, 136H), 1.56–1.64 (*m*, 28H), 1.90–2.10 (*m*, 32H), 2.31 (*t*, *J* = 7.5 Hz, 28H), 4.26 (*s*, 28H), 5.24–5.42 (*m*, 16H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 29.0, 29.1, 29.18, 29.2, 29.3, 29.4, 29.51, 29.6, 29.71, 29.8, 31.9, 32.6, 32.7, 34.1, 62.0, 129.9, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2921, 1737, 1461 cm^{-1}; MS (APCI) m/z 2622 (MH)$^+$.

ADMET polymerization of glyceryl trioleate or soybean oil. In a nitrogen-filled dry box, catalyst **2** (2.0 mg, 2.43 µmol) was weighed into a Schlenk tube containing a magnetic stir bar. After being capped with a stopcock, the flask was removed from the dry box and attached to a manifold. Another Schlenk flask containing glyceryl trioleate or soybean oil was also connected to the manifold, and the mixture was degassed by three freeze–thaw cycles. The manifold was evacuated and filled with argon three times. The two Schlenk flasks were then opened to the manifold. Under a steady flow of argon, glyceryl trioleate (1.90 g, 2.14 mmol) or soybean oil (2 mL,

1.89 g, 2.14 mmol, assuming that the average M.W. of soybean oil is 884) was transferred to the flask charged with catalyst **2**. The flask was then switched to the vacuum line, and the reaction mixture was slowly warmed to 55°C for the specified period of time while stirring. After that, the flask was removed from the bath and allowed to cool. If the resulting polymer was a brown oil, procedure A was used to work up the reaction mixture. Procedure B was employed when the resulting product was a rubber.

In procedure A, CH$_2$Cl$_2$ (20 mL), ethyl vinyl ether (0.2 mL), and BHT (30 mg) were added to the reactant flask. After 12 h of stirring, an additional 20 mL of CH$_2$Cl$_2$ was added to the solution, and the resulting solution was poured into 200 mL of rapidly stirring MeOH at 0°C. The stirring was continued until the product appeared free of color. Then the solvent was decanted off, and the remaining solvent was evacuated. The residual material was then collected, dried by pumping overnight, and recorded as MeOH/CH$_2$Cl$_2$-insoluble fraction B (Table 1). The MeOH solution was also concentrated, dried, and recorded as MeOH/CH$_2$Cl$_2$-soluble fraction A (Table 1).

In procedure B, the resulting rubbery material was first processed utilizing procedure A. The soluble fraction was

TABLE 1
ADMET Polymerization of Soybean Oil

Entry	Oil (mL)	Catalyst **2** (mol%)	Temp. (°C)	Vac/Ar	Time (h)	Crude product (%)	Fraction A (*r*)	Fraction B (*r*)	Fraction C
1	1	1.5	r.t.	Vac	120	85 Brown rubber			
2	1	1.4	r.t.	Vac	192	86 Brown, sticky rubber	30 (0.36)	43 (1.23)	18
3	1	1.4	r.t.	Vac	240	87 Brown rubber	24 (0.29)	45 (1.19)	15
4	1	1.4	r.t.	Ar	240	99 Dark-brown oil	40 (0.29)	58 (1.19)	—
5	1	1.4	55	Vac	15	86 Brown rubber	23 (0.31)	36 (1.19)	27
6	2	1.5	55	Ar	24	99 Deep-brown oil	37 (0.29)	66 (0.98)	—
7	2	0.2	r.t.	Vac	240	89 Light-brown oil	17 (0.21)	71 (1.0)	—
8	2	0.2	r.t.	Ar	240	100 Brown oil	38 (0.27)	62 (1.06)	—
9	2	0.2	55	Vac	63	82 Brown rubber	18 (0.30)	30 (1.10)	34
10	2	0.2	55	Ar	62	99 Brown oil	43 (0.28)	55 (1.05)	—
11	2	0.1	55	Vac	192	81 Brown rubber	24 (0.47)	31 (1.10)	26
12	2	0.1	55	Vac	24	90 Brown oil	23 (0.31)	67 (1.19)	—
13	2	0.1	55	Ar	24	98 Brown oil	41 (0.33)	57 (0.85)	—
14	2	0.01	55	Vac	168	100 Light-brown oil	100 (0.56)	—	—
15	2	0	55	Vac	212	99 Brown oil	99 (0.56)	—	—

*a*See the Experimental Procedures section for the workup procedure. r.t., room temperature; Vac, vacuum.

TABLE 2
Composition of the MeOH/CH$_2$Cl$_2$-Insoluble Fraction

Entry/ component	w/w (%)	r (exp)	r^a (theory)	n	Structural assignment	Comments
1	5	0.39	0.44	1	Isomerized trioleate	Yellow oil
2	10	0.70	0.66	2	Dimer	White wax
3	6	0.85	0.80	3	Trimer	White oil
4	3	0.99	0.89	4	Tetramer	White, sticky oil
5	3	1.08	0.95	5	Pentamer	White, sticky oil
6	15	1.17	1.00	6	Monocyclic oligomer	White, very sticky oil
7	17	1.28	1.04	7	Monocyclic oligomer	Very sticky oil
8	31	1.43	1.06	8	Monocyclic oligomer	White, very sticky oil

^{a}The theoretical value of r is calculated as $4n/(3n + 6)$, where n is the number of repeating units (see Eq. 4 in text).

recorded as fraction A (Table 1), and the residual rubber was further partitioned by Soxhlet extraction using CH$_2$Cl$_2$ as the solvent. The CH$_2$Cl$_2$ solution was collected, dried, and recorded as fraction B (Table 1). The remaining rubber was recorded as fraction C (Table 1).

Fraction B, obtained from ADMET polymerization of glyceryl trioleate, was further partitioned by flash chromatography and eight components were isolated. The following are the spectral data for these components:

(i) Component 1 (Table 2, entry 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (*m*, 9H), 1.20–1.42 (*m*, 60H), 1.50–1.65 (*m*, 6H), 1.90–2.10 (*m*, 12H), 2.30 (*dt*, J = 1.5, 7.2 Hz, 6H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 2H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 2H), 5.24–5.39 (*m*, 7H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 29.0, 29.1, 29.13, 29.2, 29.25, 29.3, 29.36, 29.5, 29.6, 29.63, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR (CDCl$_3$) 3002, 2921, 1744, 1461 cm^{-1}; MS (APCI) *m/z* 886 (MH)$^+$.

(ii) Component 2 (Table 2, entry 2). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 12H), 1.20–1.42 (*m*, 96H), 1.50–1.65 (*m*, 12H), 1.90–2.10 (*m*, 20H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 12H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 4H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 4H), 5.24–5.39 (*m*, 12H). ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 29.0, 29.1, 29.12, 29.16, 29.18, 29.23, 29.3, 29.4, 29.5, 29.6, 29.62, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.6, 129.7, 129.8, 130.1, 130.2, 130.22, 130.5, 172.8, 173.3; IR (CDCl$_3$) 3001, 2922, 1744 cm^{-1}.

(iii) Component 3 (Table 2, entry 3). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 15H), 1.20–1.42 (*m*, 132H), 1.50–1.65 (*m*, 18H), 1.90–2.10 (*m*, 28H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 18H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 6H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 6H), 5.24–5.39 (*m*, 17H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.13, 29.2, 29.23, 29.3, 29.5, 29.6, 29.63, 29.66, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 129.8, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR (CDCl$_3$) 3002, 2922, 1744, 1461 cm^{-1}.

(iv) Component 4 (Table 2, entry 4). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 18H), 1.20–1.42 (*m*, 168H), 1.50–1.65 (*m*, 24H), 1.90–2.10 (*m*, 36H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 24H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 8H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 8H), 5.24–5.39 (*m*, 22H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.12, 29.2, 29.24, 29.3, 29.5, 29.6, 29.63, 29.66, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1,

34.2, 62.1, 68.9, 129.8, 130.1, 130.2, 130.22, 130.3, 130.5, 172.9, 173.3; IR (CDCl$_3$) 3002, 2922, 1744, 1447 cm^{-1}.

(v) Component 5 (Table 2, entry 5). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 21H), 1.20–1.42 (*m*, 204H), 1.50–1.65 (*m*, 30H), 1.90–2.10 (*m*, 44H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 30H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 10H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 10H), 5.24–5.39 (*m*, 27H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.17, 29.2, 29.22, 29.26, 29.4, 29.5, 29.6, 29.66, 29.7, 29.72, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.8, 130.1, 130.2, 130.4, 130.6, 172.9, 173.3; IR (CDCl$_3$) 3002, 2949, 1739 cm^{-1}.
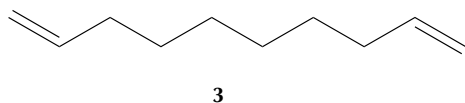
(vi) Component 6 (Table 2, entry 6). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 3H), 1.20–1.42 (*m*, 36H), 1.50–1.65 (*m*, 6H), 1.90–2.10 (*m*, 8H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 6H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 2H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 2H), 5.24–5.39 (*m*, 5H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.14, 29.2, 29.23, 29.3, 29.5, 29.6, 29.67, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 129.8, 130.1, 130.2, 130.23, 130.5, 172.9, 173.3; IR (CDCl$_3$) 2952, 1753, 1462 cm^{-1}.

(vii) Component 7 (Table 2, entry 7). ^{1}H NMR (CDCl$_3$) δ 0.80–0.90 (*m*, 3H), 1.19–1.42 (*m*, 36H), 1.50–1.65 (*m*, 6H), 1.90–2.10 (*m*, 8H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 6H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 2H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 2H), 5.22–5.39 (*m*, 5H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.2, 29.23, 29.4, 29.5, 29.6, 29.63, 29.7, 29.76, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.6, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR (CDCl$_3$) 2946, 1738, 1456 cm^{-1}.
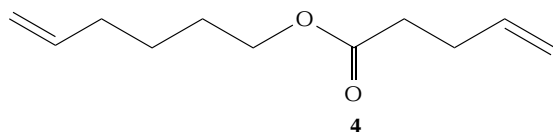
(viii) Component 8 (Table 2, entry 8). ^{1}H NMR (CDCl$_3$) δ 0.81–0.90 (*m*, 3H), 1.20–1.42 (*m*, 36H), 1.50–1.65 (*m*, 6H), 1.90–2.10 (*m*, 8H), 2.30 (*dt*, J = 1.5, 7.5 Hz, 6H), 4.13 (*dd*, J = 6.0, 12.0 Hz, 2H), 4.29 (*dd*, J = 6.0, 12.0 Hz, 2H), 5.22–5.38 (*m*, 5H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.2, 29.3, 29.5, 29.6, 29.63, 29.7, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 130.1, 130.2, 130.22, 130.5, 172.8, 173.3; IR (CDCl$_3$) 2952, 1739, 1463 cm^{-1}.

RESULTS AND DISCUSSION

Evaluation of ADMET polymerization catalysts. Since the catalyst is very important in ADMET polymerization, our ini-

3

SCHEME 3

4

SCHEME 4

$$n \begin{array}{l} CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_2 \\ | \\ CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_2 \end{array} \xrightarrow[55°C,\ vacuum,\ 24\ h]{0.1\ mol\%\ of\ catalyst\ \mathbf{2}}$$

5

$$\begin{array}{l} CH_3(CH_2)_7CH \\ | \\ CH_3(CH_2)_7CH \end{array} \Bigg[\begin{array}{l} =CH(CH_2)_7CO_2CH_2 \\ | \\ =CH(CH_2)_7CO_2CH_2 \end{array} \Bigg]_n + (n-1)\ CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$$

9-octadecene

[3]

tial work focused on an evaluation of the most widely used catalysts today, Mo-based catalyst **1** and Ru-based catalyst **2**. Two representative dienes, 1,9-decadiene (**3**) and 5-hexenyl 4-pentenoate (**4**), were chosen as model monomers for ADMET polymerization (Schemes 3 and 4). When diene **3** was allowed to react with catalyst **1**, rapid evolution of ethylene (violent bubbling) was observed. However, the polymerization did not proceed to completion even after 4 d, and a liquid was obtained. The ^{1}H NMR spectrum of the product showed two clearly separated peaks for the terminal olefinic protons ($\delta = 4.97$) and the newly formed internal olefinic protons ($\delta = 5.40$). End-group analysis (16) based on the integration of these two types of olefinic protons indicated that the number of the repeating units (X_n) in the polymer was only three and the average M.W. (M_n) was 358. On the other hand, when catalyst **2** was employed, the reaction started relatively slowly. Although only a few bubbles were observed when catalyst **2** was mixed with **3**, the reaction proceeded more completely and solidified after 4 d. End-group analysis indicated $X_n = 142$ and $M_n = 15,620$.

Similar results were observed for the reactions of diene **4**. In the presence of catalyst **1**, a sticky oil was obtained. According to end-group analysis, X_n was 20 and M_n was 2,840. When catalyst **2** was used, the reaction afforded a very sticky oil, which had substantially higher X_n (100) and M_n (14,200) values.

These results indicate that catalyst **1** is more reactive than catalyst **2**, but catalyst **2** affords polymers of higher M.W. This can be explained by the high reactivity of catalyst **1** toward moisture and oxygen and the fact that trace impurities in the monomer will destroy the catalyst (16). On the other hand, catalyst **2** is only mildly sensitive to oxygen and very stable to water, alcohols, and most organic solvents (25). Thus, catalyst **2** survives longer and affords polymers with higher X_n and M_n. Catalyst **2** appears to be the better catalyst for our ADMET polymerizations and was thus employed in all subsequent work.

Polymerization of ethylene glycol dioleate. After the successful ADMET polymerization of terminal dienes **3** and **4**, our attention turned toward the ADMET polymerization of the internal diene ethylene glycol dioleate (**5**), easily prepared in 68% yield from oleic acid and ethylene glycol. The ADMET polymerization of dioleate **5** was conducted using 0.1 mol% catalyst **2** at 55°C under a vacuum for 24 h (Eq. 3).
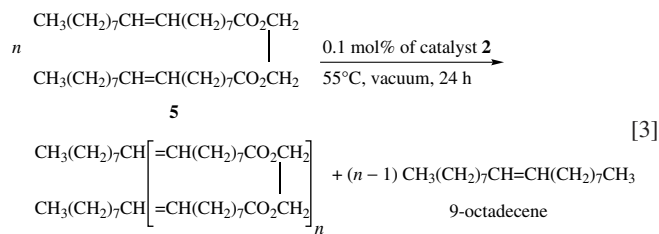
After workup, two fractions, a light-brown oil (48%, w/w) and a white, waxy solid (50%, w/w), were obtained. Each fraction was then further partitioned by flash chromatography. The composition of each fraction is shown in Figure 1.

The major components of the first fraction (a light-brown oil) are compound A, 9-octadecene (39%, w/w), which is the product expected to accompany formation of the polymer, and compound B, the *E,E*-isomer of the starting dioleate (42%, w/w). Only a trace amount of the intramolecular cyclization product, compound C (0.3%, w/w), was isolated from this fraction. This indicates that the reaction does not proceed to a significant extent by intramolecular cyclization, but does follow the anticipated ADMET process to produce oligomers. On the other hand, the second fraction (the white, waxy solid) was mainly composed of the dimer (22%, w/w), trimer (22%, w/w), and tetramer (14%, w/w). It is very interesting that even pure pentamer, hexamer, and heptamer were isolated from this fraction.

The overall product composition from the ADMET polymerization of the dioleate **5** was determined by combining the isolated masses of each component from both fractions. These combined masses were used to calculate an overall isolated percent yield for each component. Thus, 27% of the starting dioleate **5** was converted to the *E,E*-isomer B. The remaining dioleate (73%) underwent ADMET polymerization to afford the following components: dimer (18%), trimer (13%), tetramer (7%), pentamer (5%), hexamer (4%), heptamer (4%), and 9-octadecene (21%).

All of these isolated compounds have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, APCI MS, and GPC. The ^{1}H NMR spectra match the molecular structures of the assigned compounds. For example, the dimer was calculated to possess the protons CH=CH, O$_2$CCH$_2$, CH$_2$–CH=, O$_2$CCH$_2$CH$_2$, other CH$_2$, and CH$_3$ in the ratios 1.00:1.00:1.50:1.00:7.00:0.75. The actual observed integration ratios were 1.00:1.01:1.52:0.98:7.03:0.69, respectively. Thus, the experimental values were consistent with the theoretical ones.

The *Z/E*-configuration of these components can be determined by ^{13}C NMR spectral analysis. The olefinic carbons of the starting dioleate **5** (*Z,Z*-configuration) appear at 129.7 and 130.0 ppm. Component B shows two olefinic carbon peaks at 130.1 and 130.5 ppm. Considering that *trans* olefinic carbons generally have higher chemical shifts than the corresponding *cis* olefinic carbons, we have tentatively assigned compound B the *E,E*-configuration. It has also been observed that the ^{13}C NMR spectra of all of the oligomers formed in the reaction show both *cis* ($\delta < 130.0$ ppm) and *trans* ($\delta > 130.0$ ppm)

TABLE 3
Results from MS Atmospheric Pressure Chemical Ionization (APCI) and Gas Permeation Chromatography (GPC)[a]

Oligomer	FW	MS (APCI)	GPC (M_n)	M_n/FW
Dioleate	590	591 (MH)$^+$	1289	2.18
Dimer	929	930 (MH)$^+$	1796	1.93
Trimer	1267	1268 (MH)$^+$	2385	1.88
Tetramer	1604	1605 (MH)$^+$	2996	1.86
Pentamer	1945	1946 (MH)$^+$	3542	1.82
Hexamer	2282	2282 (M)$^+$	4443	1.95
Heptamer	2621	2622 (MH)$^+$	6551	2.50

[a]M_n, number average M.W.; FW, formula weight.

TABLE 4
Optimization of the Acyclic Diene Metathesis (ADMET) Polymerization of Dioleate 5

Entry	Catalyst (mol%)	Vac/Ar[a]	Time (h)	Light-brown oil(w/w%)	White, waxy solid (w/w%)
1	0.1	Vac	24	48	50
2	0.1	Vac	48	47	49
3	0.1	Ar	24	64	37
4	0.05	Vac	28	59	40
5	0.2	Vac	24	62	38
6	0.5	Vac	24	63	43
7	1.0	Vac	43	57	44

[a]For abbreviation see Table 1.

olefinic carbon peaks, where the latter peaks are much more intense than the former ones. This indicates that the carbon-carbon double bonds in these oligomers have both *Z*- and *E*-configurations, with the *E*-configuration predominating.

As shown in Table 3, the results from MS (APCI) match the corresponding formula weights (FW). However, there are differences between the GPC results and the FW. Presumably, this is due to the difference in the hydrodynamic volume of the polyester samples and the polystyrene standard utilized (16). Similar discrepancies were observed in all of the GPC experiments, including the oligomers prepared from glyceryl trioleate and soybean oil to be discussed later. As shown in Table 3, entry 1, the M_n/FW ratio for the dioleate is 2.18, and the other ratios are similar to this value. This suggests that the M_n is approximately linear with FW and M_n can be corrected by dividing by a factor of approximately 2.

The polymerization reaction has also been run under a variety of reaction conditions in an effort to improve the yield of solid product and minimize the amount of catalyst **2** used (Table 4). It has been shown that the presence of a vacuum is necessary for the reaction to produce good yields of solid product (compare entries 1 and 3). The smallest amount of catalyst used in the reaction was 0.05 mol% (entry 4), and the reaction still afforded a fair yield of solid product (40%). However, when more catalyst was employed, the yields of solid product did not increase accordingly (entries 5–7). The best yield was obtained when 0.1 mol% of catalyst **2** was used (entry 1).

Polymerization of glyceryl trioleate and glyceryl trilinoleate. Glyceryl trioleate was readily prepared in 51% yield from oleic acid and glycerol. Polymerization of the trioleate was examined by employing the best conditions developed for the polymerization of the dioleate **5** (Eq. 4). The resulting crude product (a very sticky oil) was dissolved in CH_2Cl_2 and then poured into an excess of MeOH (workup procedure A). Two fractions, a MeOH/CH_2Cl_2-soluble fraction (32%, w/w) and a MeOH/CH_2Cl_2-insoluble fraction (67%, w/w), were isolated. The MeOH/CH_2Cl_2-insoluble

fraction was further partitioned by flash chromatography, and eight components were isolated (Table 2).

The structural assignments for these components (Table 2, entries 1–8) are based on ^{1}H NMR spectral data. The ^{1}H NMR spectra of these components are similar to the starting trioleate, differing only in the peak integrations. Analysis of the peak integration data provides information about the structure of these components. Our attention was focused on the ratio of the ^{1}H NMR spectral peaks corresponding to OCH_2CHCH_2O to the terminal CH_3 protons. This ratio is defined as *r*. If the trioleates link only with each other in a straight chain with no intramolecular cyclization, the value of *x* in Equation 4 should be equal to $(n-1)$. Then the ratio *r* can be described as $4n/[9n - 6(n-1)]$, i.e., $4n/(3n + 6)$. According to this equation, the theoretical values of *r* for the acyclic oligomers, from monomer to octamer, are recorded in column 4 of Table 2 (entries 1–8, *n* = 1–8). A comparison of the experimental values of *r* (Table 2, column 3) and the theoretical ones (Table 2, column 4) suggests that components 1 to 5 can be tentatively assigned as isomerized trioleate, dimer, trimer, tetramer, and pentamer, respectively. The ^{13}C NMR spectrum of component 1 shows new peaks for the olefinic carbons (δ = 130.2, 130.5 ppm), which presumably correspond to the *E*-isomer, suggesting that component 1 is simply the isomerized *E,E,E*-trioleate. The olefinic carbons in compounds 2–8 show intense peaks at δ = 130.2–130.6 ppm. This indicates that the carbon-carbon double bonds in these compounds are predominantly of the *E*-configuration. This phenomenon is consistent with observations made during our study of the oligomers formed in the ADMET polymerization of the ethylene glycol dioleate **5**.

Note that there is a significant discrepancy between the experimental and theoretical values of *r* for components 6–8 (Table 2, compare columns 3 and 4 of entries 6–8). This suggests the possibility of intramolecular cyclization. If only one intramolecular cyclic ring is formed in the oligomer, the value
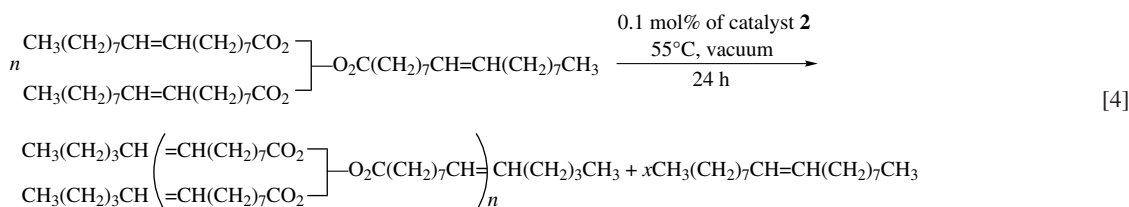
$$
n\begin{array}{l} CH_3(CH_2)_7CH=CH(CH_2)_7CO_2 \\ \\ CH_3(CH_2)_7CH=CH(CH_2)_7CO_2 \end{array}\Big] O_2C(CH_2)_7CH=CH(CH_2)_7CH_3 \xrightarrow[\substack{55°C, vacuum \\ 24\ h}]{0.1\ mol\%\ of\ catalyst\ \mathbf{2}}
$$

$$
\begin{array}{l} CH_3(CH_2)_3CH \\ \\ CH_3(CH_2)_3CH \end{array}\Big(\begin{array}{l} =CH(CH_2)_7CO_2 \\ \\ =CH(CH_2)_7CO_2 \end{array}\Big] O_2C(CH_2)_7CH\Big)_n = CH(CH_2)_3CH_3 + x CH_3(CH_2)_7CH=CH(CH_2)_7CH_3
$$

[4]

TABLE 5
GPC Results for the Monocyclic Oligomers and the Approximate Number of Repeating Units[a]

Entry	Component	M_n	M_w	PDI	n
1	Trioleate	1172	1518	1.29	1
2	6	5375	7448	1.38	6
3	7	8182	11478	1.40	10
4	8	17459	27963	1.60	21

[a]The value of n is calculated as $n = M_n/(1.32 \times 632)$. M_w, weight average M.W.; PDI, polydispersity. For other abbreviation see Table 3.

of x in Equation 4 is expected to be n; thus, r can be calculated as $4n/(9n − 6n)$, i.e., 1.33. This indicates that all monocyclic oligomers have the same value of r, regardless of the number of repeating units (n) in the polymer or the size of the cyclic ring. Since the experimental values of r (Table 2, entries 6–8) are close to 1.33, we have tentatively assigned components 6–8 as monocyclic oligomers. For component 8, the experimental value of r is 1.43. This is even higher than 1.33 and indicates the possibility of bicyclic oligomers in component 8, since the r value of the bicyclic oligomers can be calculated as $4n/(3n − 6)$, which is larger than 1.33.

The GPC results from analysis of the starting trioleate and the presumed monocyclic components 6–8 are summarized in Table 5. A discrepancy between the FW of the trioleate (884) and its M_n (1172) is observed (entry 1) and the ratio of M_n over the calculated FW is 1.32. In analogy to our previous results from the polymerization of the dioleate 5, which suggested that M_n is approximately linear with FW, we have assumed that this linear relationship also exists for the trioleate system. Thus, M_n in Table 5 is corrected by a factor of 1.32. The corresponding numbers of repeating units can be approximately calculated from these corrected M_n. According to Equation 4, the M.W. of the monocyclic oligomers should be the mass of the reactant ($884 \times n$) minus the mass of 9-octadecene ($252 \times n$); so the number average M.W. is $632 \times n$. Then $n = M_n/(1.32 \times 632)$. The results are summarized in Table 5. The average number of repeating units of component 6 is thus calculated as 6. This appears to be reasonable, since the previous component (component 5) was assigned as a pentamer ($n = 5$). As expected, the average number of repeating units of component 7 is even higher than that of component 6 ($n \cong 10$, Table 5, entry 3). It is very interesting that component 8, which is the major oligomer formed in the reaction, has a high average repeating unit number. The significantly higher degree of polymerization of the trioleate ($n \cong 6, 10, 21$) than that of the dioleate 5 ($n = 2–4$) suggests that there has been additional polymerization by cross-linking. This is to be expected, since the trioleate, which has three double bonds, may behave as a trifunctional monomer to produce dendrimers. In the ideal dendrimer case, after m generations, n can be calculated as $n = 1 + 3^m$. Thus, a second-generation dendrimer affords $n = 10$, and the third-generation dendrimer will yield $n = 28$.

Other experiments also confirm the existence of cross-linking polymerization. The polymerization of the trioleate has been examined in the presence of 1.6 mol% of catalyst 2

for 24 h. A brown rubber was obtained in 87% yield. This rubbery material did not dissolve in organic solvents, such as CH_2Cl_2, chloroform, toluene, or benzene. Under the same conditions, the polymerization of glyceryl trilinoleate also produced a brown rubber, which was insoluble in organic solvents. We suspect that these rubbery materials are highly cross-linked polymers.

In summary, our model system studies suggest that polymerization of the dioleate and trioleate follow the expected ADMET mechanism. Since dioleate 5 or its oligomer is a linear molecule with a long chain, the intermolecular ADMET reaction is more favorable than the intramolecular cyclization. Thus, the polymerization of dioleate 5 affords a series of oligomers, from dimer to heptamer, with the dimer and trimer predominating. On the other hand, the trioleate and its oligomer possess structures like a dendrimer. This allows an olefinic group in an appropriate position of the same molecule to cyclize through the ADMET process. The polymerization of the trioleate produced monocyclic oligomers with much higher M.W. owing to possible cross-linking polymerization.

Polymerization of soybean oil. Encouraged by the success of our model system studies, the ADMET polymerization of soybean oil was examined. New Horizons soybean oil produced by Pioneer Hi-Bred, Inc. (Des Moines, IA) was employed in the following reactions. The results are summarized in Table 1. Depending on the reaction conditions, two types of products, a sticky oil and a rubbery material, have been observed. Accordingly, two efficient workup procedures, procedures A and B, have been developed for these two types of materials. In procedure A, which is applicable to the sticky oil, the crude product is dissolved in CH_2Cl_2 and then poured into an excess of MeOH. The MeOH solution and the residual material are collected as fraction A and fraction B, respectively. If the crude product is a rubbery material, procedure B is utilized for the workup. In procedure B, the crude product is first worked up utilizing procedure A. The MeOH/CH_2Cl_2-soluble fraction is recorded as fraction A and the residual rubbery material is further partitioned by Soxhlet extraction. The CH_2Cl_2 solution is collected as fraction B, and the remaining rubbery material is collected as fraction C. A "blank" workup experiment in which soybean oil was processed using procedure A has shown that soybean oil is recovered quantitatively in fraction A.

As proven in our model system studies, ^{1}H NMR spectroscopy can provide valuable information about the structural makeup of the oligomers. Again, r, the ratio of the OCH_2CHCH_2O protons over the terminal CH_3 protons, has served as an important parameter in our understanding of the structure of the oligomers. The ^{1}H NMR spectra of soybean oil and the fractions A and B obtained from the polymerization of soybean oil all have the same peaks, but the integrations differ. For soybean oil itself, r is equal to 0.56. This is measured from the ^{1}H NMR spectrum of the soybean oil. The value of r for fraction A ranged from 0.21 to 0.47 depending on the reaction conditions. This is lower than that of soybean oil and consistent with our expectation that fraction A contains unreacted or isomerized soybean oil and long-chain alkene by-product.

[5]
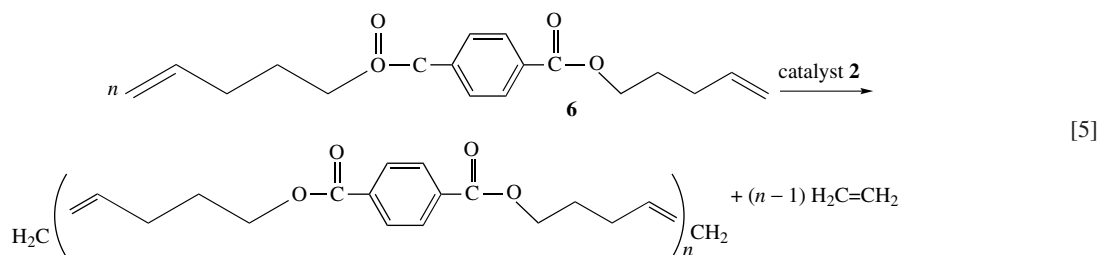
In fact, the GC–MS results obtained from the analysis of fraction A in Table 1, entry 4, showed peaks with masses of 102, 168, 208, 220, 250, 290, and 330. All of these masses can be assigned to the alkenes expected from the ADMET reaction of the TG in soybean oil. For example, mass 208 presumably comes from the alkene $CH_3(CH_2)_7CH=CH–CH_2CH=CHCH_2CH_3$. The mass of $CH_3CH_2CH=CH–CH_2CH=CHCH_2CH=CHCH_2CH=CHOCH_2CH_3$ is 220. This product is expected to be formed by metathesis of the soybean oil and the ethyl vinyl ether used to quench the reaction. The mass 250 can be assigned as $CH_3(CH_2)_7CH=CH–CH_2CH=CH(CH_2)_4CH_3$.

GC–MS analysis of fraction A from Table 1, entry 11, showed only three peaks with masses of 220, 250, and 290. The other low M.W. alkenes expected to be formed may have been removed by vacuum. The value of r for fraction B was found to be higher than that of soybean oil. This indicates the formation of oligomers. The rubbery materials of fraction C are presumably highly cross-linked polymers.

In the early stages of our investigation, a relatively high amount of catalyst **2** (1.5%) was employed and the reaction afforded a brown rubber, which did not dissolve in any common organic solvent (Table 1, entry 1). Soybean oil purified by pretreatment with CaH_2, $MgSO_4$, or Ac_2O gave the same result as the original soybean oil. Thus, soybean oil taken directly from the bottle was used in the following reactions without any further purification.

The ADMET polymerization reactions proceeded very slowly at room temperature, and long reaction times (5–10 d) were required (Table 1, entries 1–4). The reaction time can be reduced substantially by increasing the temperature to 55°C (entry 5). The effect of vacuum was also examined. Under vacuum, the reaction afforded an insoluble rubber (entries 1–3 and 5), but no rubbery material was obtained under Ar (entry 4).

Less catalyst also was employed. When 0.2 mol% of catalyst **2** was employed, the reaction at room temperature afforded a brown oil after 240 h either under vacuum or Ar (entries 7 and 8). When the reaction was run with 0.2 mol% catalyst **2** at 55°C, a rubbery material was obtained under vacuum (entry 9), but a brown oil was obtained under Ar (entry 10). A comparison of entries 3 and 7 indicates that higher amounts of catalyst favor the formation of rubbery materials.

In the presence of 0.1 mol% of catalyst **2** under vacuum, a rubbery material was obtained after 192 h (entry 11). However, if the reaction was stopped earlier (24 h), a brown oil was obtained in 90% yield (entry 12). The analogous reaction under Ar afforded a similar oily product (entry 13), but the yield of fraction B was not as good as that obtained when the reaction was run under vacuum (entry 12).

The reaction with 0.01 mol% of catalyst **2** failed (entry 14). In entry 15, without any catalyst, soybean oil was quantitatively recovered in fraction A after the reaction was run under vacuum at 55°C for 212 h. This indicates that no thermal polymerization occurred at 55°C and no oil was lost due to the vacuum.

In summary, as observed in the ADMET polymerization of the dioleate **5**, 0.1 mol% of catalyst **2** appears to give the best results. Under these conditions, the reaction affords either a rubbery material at long reaction times (entry 11) or a sticky oil at short reaction times (entry 12).

Copolymerization of soybean oil. Di-(4-pentenyl)1,4-benzenedicarboxylate (**6**) was prepared according to a literature procedure (16). The ADMET polymerization of **6** was achieved using 0.5 mol% of catalyst **2**. End-group analysis indicated that $M_n = 3718$ and $X_n = 13$ (Eq. 5).

The copolymerization of soybean oil and diester **6** was investigated. In the presence of 0.5 mol% of catalyst **2**, a 50:50 (w/w) mixture of soybean oil and diester **6** produced a copolymer with 41% weight recovery. ^{1}H NMR spectral data indicated that the molar ratio of diester **6** to soybean oil in the copolymer was 4.37, which was slightly higher than that in the reactant mixture (3.09). This difference is presumably due to a difference in the relative reactivities of diester **6** and soybean oil. As a terminal diene, diester **6** should be more reactive in ADMET polymerization than soybean oil, which contains only internal carbon-carbon double bonds. Similar results have also been observed in the copolymerization of soybean oil and norbornene. This latter reaction is currently being studied further since it produces interesting coatings.

In conclusion, our studies of the ADMET polymerization of 1,9-decadiene and 5-hexenyl 4-pentenoate have suggested that Grubbs' ruthenium catalyst **2** is more efficient than Schrock's molybdenum catalyst **1**. In the presence of 0.1 mol% of catalyst **2**, the ADMET polymerization of ethylene glycol dioleate afforded isomerized *E,E*-dioleate and a series of oligomers ranging from dimer to heptamer. To our knowledge this is the first example of an internal diene participating efficiently in ADMET polymerization. Under the same conditions, glyceryl trioleate underwent ADMET polymerization to produce dimer, trimer, tetramer, pentamer, and monocyclic oligomers, with high-M.W. monocyclic oligomers predominating. We also succeeded in the ADMET polymerization of soybean oil. A variety of materials, from sticky oils to rubbers, were prepared from soybean oil. These materials hold industrial promise and may well be biodegradable.

ACKNOWLEDGMENTS

REFERENCES

1. Ivin, K.J., *Olefin Metathesis,* Academic Press, London, 1983.
2. Amass, A.J., Metathesis Polymerization: Chemistry, *Compr. Polym. Sci. 4*:109–134 (1989).
3. Van Dam, P.B., M.C. Mittelmeijer, and C. Boelhouwer, Metathesis of Unsaturated Fatty Acid Esters by a Homogeneous Tungsten Hexachloride–Tetramethyltin Catalyst, *J. Chem. Soc., Chem. Commun.*:1221–1222 (1972).
4. Van Dam, P.B., M.C. Mittelmeijer, and C. Boelhouwer, Homogeneous Catalytic Metathesis of Unsaturated Fatty Esters: New Synthetic Method for Preparation of Unsaturated Mono- and Dicarboxylic Acids, *J. Am. Oil Chem. Soc. 51*:389–392 (1974).
5. Boelhouwer, C., and J.C. Mol, Metathesis Reactions of Fatty Acid Esters, *Prog. Lipid Res. 24*:243–267 (1985).
6. Verkujilen, E., and C. Boelhouwer, Formation of Cyclohexa-1,4-diene by Metathesis of Linoleic and Linolenic Esters, *J. Chem. Soc., Chem. Commun.*:793–794 (1974).
7. Kohashi, H., and T.A. Foglia, Metathesis of Methyl Oleate with a Homogeneous and a Heterogeneous Catalyst, *J. Am. Oil Chem. Soc. 62*:549–554 (1985).
8. Mandelli, D., M.J.D.M. Jannini, R. Buffon, and U. Schuchardt, Ethenolysis of Esters of Vegetable Oils: Effect of B_2O_3 Addition to $Re_2O_7/SiO_2 \cdot Al_2O_3$-$SnBu_4$ and $CH_3ReO_3/SiO_2 \cdot Al_2O_3$ Metathesis Catalysts, *J. Am. Oil Chem. Soc. 73*:229–232 (1996).
9. Erhan, S.Z., M.O. Bagby, and T.C. Nelsen, Drying Properties of Metathesized Soybean Oil, *J. Am. Oil Chem. Soc. 74*:703–706 (1997).
10. Refvik, M.D., R.C. Larock, and Q. Tian, Ruthenium-Catalyzed Metathesis of Vegetable Oils, *J. Am. Oil Chem. Soc. 76*:93–98 (1999).
11. Finkel'shtein, E.S., V.I. Bykov, and E.B. Portnykh, The Olefin Metathesis Reaction—A Versatile Tool for Fine Organic Synthesis, *J. Mol. Catal. 76*:33–52 (1992).
12. Nel, J.G., K.B. Wagener, J.M. Boncella, and R.P. Duttweiler, Acyclic Metathesis Polymerization. The Synthesis of Highly *trans* Polyoctenamer, *Polym. Prepr. 30*:283–284 (1989).
13. Wagener, K.B., J.G. Nel, J. Konzelman, and J.M. Boncella, Acyclic Diene Methathesis Copolymerization of 1,5-Hexadiene and 1,9-Decadiene, *Macromolecules 23*:5155–5157 (1990).
14. Wagener, K.B., J.M. Boncella, and J.G. Nel, Acyclic Diene Methathesis (ADMET) Polymerization, *Macromolecules 24*:2649–2657 (1991).
15. Bauch, C.G., K.B. Wagener, and J.M. Boncella, Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of an Unsaturated Polyester, *Makromol. Chem., Rapid Commun. 12*:413–417 (1991).
16. Paton, J.T., J.M. Boncella, and K.B. Wagener, Acyclic Diene Methathesis (ADMET) Polymerization. The Synthesis of Unsaturated Polymers, *Macromolecules 25*:3862–3867 (1992).
17. Davidson, T.A., K.B. Wagener, and D.B. Priddy, Polymerization of Dicyclopentadiene: A Tale of Two Mechanisms, *Macromolecules 29*:786–788 (1996).
18. Wolfe, P.S., and K.B. Wagener, Acyclic Diene Metathesis (ADMET) Polymerization: The Investigation of Dienes Containing the Boronate Functionality, *Polym. Prepr. 37*:439–440 (1996).
19. Walba, D.M., P. Keller, R. Shao, N.A. Clark, M. Hillmyer, and R.H. Grubbs, Main-Chain Ferroelectric Liquid Crystal Oligomers by Acyclic Diene Metathesis Polymerization, *J. Am. Chem. Soc. 118*:2740–2741 (1996).
20. Schwab, P.R., H. Grubbs, and J.W. Ziller, Synthesis and Applications of $RuCl_2(=CHR')(PR_3)_2$: The Influence of the Alkylidene Moiety on Metathesis Activity, *J. Am. Chem. Soc. 118*:100–110 (1996).
21. Wolfe, P.S., F.J. Gómez, and K.B. Wagener, Metal-Containing Polymers Synthesized *via* Acyclic Diene Metathesis: Polycarbostannanes, *Macromolecules 30*:714–717 (1997).
22. Erhan, S.Z., and M.O. Bagby, Polymerization of Vegetable Oils and Their Uses in Printing Inks, *J. Am. Oil Chem. Soc. 71*:1223–1226 (1994).
23. Johnson, L.A., and D.T. Myers, Industrial Uses for Soybeans, *Practical Handbook of Soybean Processing and Utilization*, edited by D.R. Erickson, AOCS Press, Champaign, 1995, p. 380.
24. Duralski, A.A., P.R. Spooner, and A. Watts, Synthesis of Optically Active Polyunsaturated Diacylglycerols, *Tetrahedron Lett. 30*:3585–3588 (1989).
25. Nguyen, S.T., and R.H. Grubbs, Syntheses and Activities of New Single-Component Ruthenium-Based Olefin Metathesis Catalysts, *J. Am. Chem. Soc. 115*:9858–9859 (1993).