Ruthenium-Catalyzed Metathesis of Vegetable Oils

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ABSTRACT: A new process for the acyclic diene metathesis of vegetable oils utilizing Grubbs' ruthenium catalyst $(Cy_3P)_2Cl_2Ru = CHPh$ has been developed. The higher molecular weight oligomers obtained can be separated from the unreacted oil and the lower molecular weight alkene by-products easily. The reaction proceeds in the absence of solvent, with very low catalyst concentrations (0.1 mole %) under moderate temperatures and low pressures. This process does not require the stringent exclusion of water and oxygen that the previous method (Me_4Sn plus WCl_6) required. Low pressures appear to favor polymerization by removing the alkene by-products. The metathesis reaction has been shown to be effective for many unsaturated vegetable oils, although some cases require oil pretreatment with silica gel. This process is effective on a 2–200 g scale. Chromatographic separation and characterization of metathesized soybean oil indicate that the process involves intermolecular and intramolecular carbon–carbon double-bond formation.

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KEY WORDS: Grubbs' catalyst, metathesis, molecular weight, oligomerization, polymerization, vegetable oil, viscosity.

The olefin metathesis of vegetable oils has received considerable attention as a means of producing materials with improved drying properties (1–3). A recent study indicates that the addition of 5 wt% metathesized soybean oil to unmodified soybean oil results in a dramatic decrease in the drying time of the soybean oil (4). These improvements in drying properties could make soybean oil, an oil native to North America, competitive with more expensive imported oils, such as linseed, tung, or dehydrated castor oils.

The standard metathesis conditions utilized in the past (Me_4Sn plus WCl_6) to form metathesized vegetable oils suffer from a number of disadvantages (3,4). The use of a chlorinated solvent, chlorobenzene, results in disposal problems. The standard conditions also require a relatively large catalyst load that also results in disposal difficulties. Finally, the catalyst system utilized is extremely sensitive to moisture and oxygen, complicating the process and hampering reproducibility.

Recent advances in the development of metathesis catalysts in the Grubbs' group spawned a family of ruthenium carbene catalysts that have significant advantages over the more traditional tungsten-based catalysts (5). Grubbs' catalysts were shown to be insensitive to the presence of oxygen,

and with modifications to the ligand system, these catalysts were actually shown to be active in water (6).

The application of Grubbs' ruthenium catalyst $(Cy_3P)_2Cl_2Ru = CHPh$ to the acyclic diene metathesis (ADMET) of vegetable oils may result in a more environmentally friendly, convenient process to produce metathesized vegetable oils. The authors' goal in this study was to develop this more favorable metathesis process and better understand the physical properties and structure of the resulting metathesized materials.

MATERIALS AND METHODS

Metathesis reactions. Commercial, food-grade vegetable oil samples from the following companies were purchased from local vendors: Wesson corn, soybean, sunflower, and canola oils (Hunt-Wesson, Inc., Fullerton, CA); Mazola corn oil (Best Foods Division, CPC International, Inc., Englewood Cliffs, NJ), Crisco soybean and canola oils (Procter & Gamble, Cincinnati, OH); New Horizon soybean oil (Rose Acre Farms, Inc., Seymour, IN), Hain safflower oil (The Hain Food Group, Inc., Uniondale, NY), Aldrich safflower seed oil (Aldrich Chemical Company, Milwaukee, WI); Loriva hi-oleic safflower, sesame, and walnut oils (Loriva Supreme Foods, Inc., Hauppavge, NY); Hy-Vee sunflower oil (Hy-Vee Food Stores, Inc., Chariton, IA); Planters peanut oil (Nabisco Foods, Inc., Planters Division, Winston-Salem, NC); and Italica olive oil (Italica Imports, Scarsdale, NY). The oil was utilized as received unless otherwise indicated. The crude soybean oil was obtained directly from solvent extraction using the Iowa State University Center for Crops Utilization Research's pilot plant-scale, batch-hexane extractor (French Oil Mill, Piqua, OH). Grubbs' catalyst was purchased from Strem Chemicals (Newbury Port, MA).

The catalyst (0.1 mole %) was placed in a 25- or 50-mL Schlenk flask under nitrogen in a glove box. The flask was then connected to a standard dual line Schlenk system with vacuum and argon capabilities. Small-scale optimization experiments involved the addition of vegetable oil (2.0 mL) to the catalyst under argon *via* a gas tight syringe. Larger scale reactions (100–200 g) involved the transfer of oil from a 250-mL Schlenk flask to the catalyst flask *via* cannula. The catalyst flask was then stirred vigorously until the catalyst was completely dissolved and the oil/catalyst mixture was then returned to the original flask. This process was repeated three times to ensure complete transfer of the catalyst. The reaction flask was then subjected to the temperature and atmospheric conditions indicated for the desired reaction time.

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Small-scale reactions were quenched with ethyl vinyl ether (0.2 mL) and BHT (30 mg) with stirring in dichloromethane (20 mL) for 12 h, followed by stirring in methanol (400 mL) to remove unreacted oil and low molecular weight by-products. The methanol-insoluble material was then collected, evacuated to remove volatile contaminents, and analyzed (workup A).

Larger-scale reactions were quenched with ethyl vinyl ether (2.0 mL) in the absence of solvent. The resulting material was stirred in ethanol (1 L ethanol/30 g material) to dissolve unreacted oil and low molecular weight materials. The resulting ethanol-insoluble material was collected, evacuated for at least 12 h and analyzed (workup B). Alternatively, the material was dissolved in 50:50 hexane/ethyl acetate and passed through 60 g silica gel in an attempt to remove the catalyst. The resulting solution was concentrated and evacuated to yield material that still contained unreacted oil and low molecular weight by-products (workup C).

Spectroscopic analysis. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in CDCl$_3$ on a Varian Unity (Palo Alto, CA) spectrometer at 300 MHz and 75.5 MHz, respectively. Infrared (IR) spectra were recorded on a BIORAD (Cambridge, MA) FTS-7 Infrared Spectrometer.

Gel permeation chromatography. Molecular weight determinations were conducted by a combination of gel permeation chromatography (7), and multiple-angle laser light scattering (MALLS) utilizing a Waters Corp. (Milford, MA) gel permeation system (410 refractive index detector) coupled with a Wyatt (Santa Barbara, CA) miniDAWN. In those cases where MALLS was unsuccessful, the molecular weights were calculated using a Waters gel permeation chromatograph calibrated with polystyrene standards (1.2×10^2–1.1×10^5) obtained from Waters Corp. The chromatography system was equipped with three ultrastyragel columns (Waters HR 1, 4, and 5).

Tetrahydrofuran was utilized as the solvent, and the flow rate was 1.0 mL/min, with the system equilibrated at 40°C.

Rheological analysis. Viscosity measurements were performed on a double-gap cylinder rheometer (Haake Corp., Karlsruhe, Germany; Rheostress RS75; cylinder DIN 54453) utilizing 65-mL samples at room temperature. The samples were subjected to increasing shear-rate sweeps from 0–500 s^{-1}.

RESULTS AND DISCUSSION

Initial studies focused on the effect of temperature, reaction time, and atmosphere on the production of metathesized oil from corn and soybean oils (Tables 1 and 2). In order to evaluate the degree of metathesis, some quick, inexpensive assay was desirable. It was decided that the ratio *r* of the peak integrations in the ^{1}H NMR spectrum of the glycerin methylene protons (H$_a$, Fig. 1, 4.11–4.32 ppm) to the terminal methyl protons of the fatty acid chain (H$_b$, Fig. 1, 0.83–0.91 ppm) should provide a means of evaluating the degree of oligomerization. The theoretical value of *r* for an oligomer comprised of *n* triglycerides with *c* intramolecular macrocycles could be calculated by utilizing the formula $r = 4n/((3n + 6) - 6c)$. If there were no macrocycles in the structure ($c = 0$), *r* could be expected to range from 0.67 ($n = 2$, dimer) to 1.33 ($n = \infty$). As more triglyceride molecules became linked, the ratio of H$_a$ to H$_b$ increased since H$_a$ increased by 4, while H$_b$ increased by 3. However, if there was at least one macrocycle ($c \geq 1$) in the structure, *r* could be expected to be at least 1.33. Experimental *r* values were an average of *r* values for all of the oligomeric structures present in the material being analyzed. However, an increase in *r* was indicative of either an increase in molecular weight of the material and/or the formation of macrocycles.

TABLE 1
Acrylic Diene Metathesis (ADMET) Polymerization of Corn Oil Samples

Entry	Oil brand	Time (h)	Temperature (°C)	Vacuum[a]	Workup[b]	Alcohol-insoluble (% recovery, *r*[c])	Alcohol-soluble (% recovery, *r*[c])
1	Wesson corn	24	23	yes	A	37, 0.79	62, 0.40
2	Wesson corn	24	23	no	A	35, 0.76	68, 0.43
3	Wesson corn	24	55	yes	A	58, 1.01	40, 0.41
4	Wesson corn	24	55	no	A	48, 0.86	53, 0.36
5	Wesson corn	120	55	no	A	53, 0.94	46, 0.28
6	Wesson corn	120	55	yes	A	52, 0.88	42, 0.38
7	Wesson corn	3	55	yes	A	51, 0.84	50, 0.34
8	Wesson corn	6	55	yes	A	45, 0.92	50, 0.41
9	Wesson corn	3	95	yes	A	34, 0.94	59, 0.48
10	Wesson corn	72	23	yes	A	46, 0.91	49, 0.35
11	Wesson corn	72	23	yes	B	52, 0.84	43, 0.29
12	Wesson corn	120	23	yes	A	41, 0.93	57, 0.42
13	Wesson corn	120	23	no	A	49, 0.85	53, 0.35
14	Wesson corn	24	55	yes	A	56, 0.94	35, 0.38
15	Wesson corn	24	55	no	A	60, 0.86	38, 0.24

[a]Reactions were run at pressures of less than 50 mTorr if vacuum is indicated. If vacuum is not indicated, the reactions were conducted under a positive pressure.
[b]As described in the Materials and Methods section, workup A involved precipitation of material from methanol, while workup B involved precipitation of material from ethanol.
[c]See the explanation of *r* values in the text. Wesson corn oil, Hunt-Wesson, Inc., Fullerton, CA.

TABLE 2
ADMET Polymerization of Soybean Oil Samples

Entry	Oil brand	Time (h)	Temperature (°C)	Vacuum[a]	Degas[b]	Workup[c]	Alcohol insoluble (% recovery, r^d)	Alcohol soluble (% recovery, r^d)
1	Wesson	24	55	yes	yes	B	61, 1.05	29, 0.34
2	Wesson	24	23	no	yes	B	48, 0.86	47, 0.33
3	Wesson	24	55	yes	no	A	48, 0.89	48, 0.36
4	Wesson	24	55	no	no	A	39, 0.90	61, 0.40
5	Wesson	24	55	yes	no	B	62, 1.12	34, 0.30
6	Wesson	24	55	no	no	B	54, 0.97	47, 0.26
7	Wesson	24	23	yes	yes	B	37, 0.84	59, 0.41
8	Wesson	24	23	no	yes	B	37, 0.82	63, 0.39
9	Wesson[e]	24	55	yes	yes	A	57, 1.06	31, 0.37
10	Wesson[e]	24	55	no	yes	A	36, 0.94	58, 0.39
11	Crisco	24	55	yes	no	A	59, 1.10	30, 0.38
12	Crisco	24	55	no	no	A	37, 0.88	58, 0.36
13	New Horizon	24	55	yes	yes	A	64, 1.01	32, 0.35
14	New Horizon	24	55	no	yes	A	52, 0.85	47, 0.38
15	Crude	24	55	yes	yes	B	22, 0.79	72, 0.49
16	Crude	24	55	no	yes	B	15, 0.68	82, 0.44
17	Crude	24	23	yes	yes	B	2, 0.60	96, 0.46
18	Crude	24	23	no	yes	B	5, 0.67	94, 0.50
19	Crude	72	55	yes	yes	A	46, 0.69	47, 0.45
20	Crude[e]	24	55	yes	yes	A	65, 0.98	25, 0.29
21	Crude[e]	24	55	no	yes	A	54, 0.88	38, 0.26

[a]Reactions were run at pressures of less than 50 mTorr if vacuum is indicated. If vacuum is not indicated, the reactions were conducted under a positive pressure.
[b]Oil was freeze-pump-thaw degassed three times prior to reaction if degas is indicated. If degas is not indicated, the oil was used directly as received.
[c]As described in the Materials and Methods section, workup A involved precipitation of material from methanol, while workup B involved precipitation of material from ethanol.
[d]See the explanation of r values in the text.
[e]Oil sample purified by passage through flash-grade silica gel prior to reaction. Crisco, Procter & Gamble, Cincinnnati, OH; New Horizon, Rose Acre Farms Inc., Seymour, IN; Crude, Iowa State University Center for Crops Utilization Research, Ames, IA. See Table 1 for abbreviation and other company source.

Analysis of the data in Table 1 indicated that an optimal yield of oligomeric alcohol-insoluble material was produced in reactions that proceed for 24 h at 55°C (Table 1; entries 3, 4, 14, and 15). Decreasing the temperature to room temperature required an increase in reaction time to 120 h to obtain similar results (entries 12 and 13). Increasing the reaction temperature beyond 55°C results in a decrease in yield (compare entries 7 and 9), possibly due to accelerated decomposition of the catalyst.

Similar observations have been made for the ADMET polymerization of various soybean oil samples (Table 2). A comparison of entries 1 and 2 with entries 5 and 6 indicates that degassing of the oil sample prior to the reaction is not necessary. This is an indication of the decreased sensitivity of the catalyst

to oxygen or water as compared to standard Me_4Sn/WCl_6 conditions (4). The unprocessed soybean oil behaved poorly under the optimized conditions. However, silica gel pretreatment resulted in acceptable yields and r values. This was an indication that soybean oil processing removes some compounds that presumably serve to poison the catalyst. In those cases in which the oil behaved well without the silica gel pretreatment, prior oil treatment did not result in improved metathesized oil yields (compare entries 1 and 2 to entries 9 and 10). Generally, all processed soybean oil samples behaved similarly in the metathesis reaction. Thus, this process was insensitive to the source of the soybean oil and was reproducible.

In most cases in which the reaction was run under vacuum, compared to an inert atmosphere, the low-pressure reactions resulted in a higher yield and a higher r value. This may be due to the removal of lower molecular weight alkenes from the system, resulting in a shift in equilibria that favors oligomerization or intramolecular cyclization. Consistent with this theory is the observation of colorless oils in the liquid nitrogen trap following reaction completion.

A comparison of entries 1, 5, 9, 11, and 13 in Table 2 indicates that under the optimized conditions of low pressure and a 24-h reaction time at 55°C, an r value of 1.0 to 1.12 is obtained. If there are no intramolecular cyclizations, then this
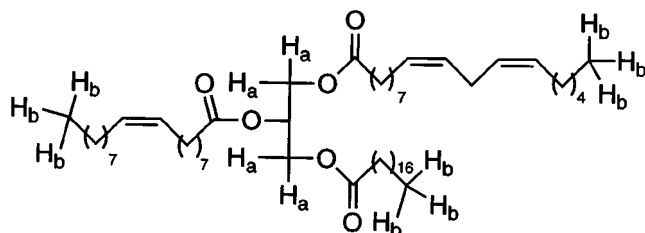
FIG. 1. Vegetable oil model.

indicates that on average between 6 and 10 triglycerides have been linked together to form the oligomeric oil.

The optimized conditions determined in the initial study were applied to the metathesis of a variety of other oils. The results of this study are summarized in Table 3. Initially, it was assumed that highly unsaturated oils, such as safflower or sunflower oil, would perform better than oils with much lower degrees of unsaturation, such as canola or olive oil. Instead, analysis of Table 3 indicates that there is no correlation between the number of double bonds in the triglycerides and the yield or *r* value of the oils studied. All oil samples, once processed (either at the source, or by silica gel pretreatment), resulted in satisfactory yields in the range 40–60% and decent *r* values.

The need for larger quantities of metathesized oils for rheological studies, testing of drying properties, and other applications required the authors to increase the scale of this process from 2 to 200 g. In order to determine whether this scale-up was feasible without affecting the efficacy of the metathesis process, several experiments were conducted. The results of these experiments are summarized in Table 4.

A comparison of entries 1, 3, 5, 7, 9, and 11 of Table 4 to the small-scale reactions presented in Tables 1–3 indicates that there is a slight decrease in the yield and the *r* value of the material for larger-scale reactions. This may be due to a drop in the efficiency of the vacuum system and its associated benefits. The decrease in the observed *r* values indicates either a de-

TABLE 3
ADMET Polymerization of Various Oil Samples at 55°C for 24 h

Entry	Oil brand	Vacuum[a]	Degas[b]	Workup[c]	Alcohol-insoluble (% recovery, r^c)	Alcohol-soluble (% recovery, r^c)
1	Hain safflower	yes	no	A	35, 0.93	61, 0.42
2	Hain safflower	no	no	A	32, 0.86	67, 0.36
3	Hain safflower[e]	yes	yes	A	54, 1.16	33, 0.46
4	Hain safflower[e]	no	yes	A	48, 1.01	45, 0.30
5	Aldrich safflower	yes	no	A	15, 0.97	80, 0.56
6	Aldrich	no	no	A	13, 0.85	87, 0.46
7	Loriva safflower (hi-oleic)	yes	no	A	37, 0.66	63, 0.39
8	Loriva safflower (hi-oleic)	no	no	A	33, 0.64	64, 0.38
9	Wesson sunflower	yes	no	B	17, 0.64	85, 0.47
10	Wesson sunflower	no	no	B	8, 0.62	91, 0.44
11	Wesson sunflower	yes	yes	B	26, 0.80	73, 0.39
12	Wesson sunflower	no	yes	B	23, 0.78	76, 0.42
13	Wesson sunflower[e]	yes	yes	A	59, 1.03	30, 0.32
14	Wesson sunflower[e]	no	yes	A	34, 0.91	61, 0.36
15	Hy-Vee sunflower	yes	yes	A	54, 0.97	40, 0.36
16	Hy-Vee sunflower	no	yes	A	40, 0.90	59, 0.34
17	Crisco canola	yes	yes	A	63, 1.09	32, 0.28
18	Crisco canola	no	yes	A	45, 0.96	54, 0.33
19	Crisco canola	yes	no	A	59, 0.98	38, 0.30
20	Crisco canola	no	no	A	50, 0.94	49, 0.31
21	Wesson canola	yes	no	A	44, 1.00	53, 0.41
22	Wesson canola	no	no	A	51, 0.94	49, 0.30
23	Planters peanut	yes	no	A	42, 0.89	54, 0.39
24	Planters peanut	no	no	A	49, 0.76	51, 0.32
25	Loriva sesame	yes	no	A	53, 0.79	44, 0.33
26	Loriva sesame	no	no	A	49, 0.78	49, 0.28
27	Loriva walnut	yes	no	A	15, 0.99	78, 0.59
28	Loriva walnut	no	no	A	24, 0.87	73, 0.43
29	Loriva walnut[e]	yes	yes	A	62, 1.21	27, 0.32
30	Loriva walnut[e]	no	yes	A	57, 1.00	39, 0.27
31	Italica olive	yes	yes	A	36, 0.75	64, 0.39
32	Italica olive	no	yes	A	34, 0.70	67, 0.39
33	Italica olive	yes	no	A	27, 0.66	74, 0.45
34	Italica olive	no	no	A	29, 0.67	73, 0.45
35	Italica olive[e]	yes	yes	A	58, 0.87	41, 0.24
36	Italica olive[e]	no	yes	A	53, 0.90	46, 0.23

[a]Reactions were run at pressures of less than 50 mTorr if vacuum is indicated. If vacuum is not indicated, the reactions were conducted under a positive pressure of argon.
[b]Oil was freeze-pump-thaw degassed three times prior to reaction if degas is indicated. If degas is not indicated, the oil was used directly as received.
[c]As described in the Materials and Methods section, workup A involved precipitation of material from methanol, while workup B involved precipitation of material from ethanol.
[d]See the explanation of *r* values in the text.
[e]Oil sample purified by passage through flash grade silica gel prior to reaction as described in the Materials and Methods section. Hain, The Hain Food Group Inc., Uniondale, NY; Aldrich, Aldrich Chemical Company, Milwaukee, WI; Loriva, Loriva Supreme Foods, Inc., Hauppavge, NY; Hy-Vee, Hy-Vee Food Stores, Inc., Chariton, IA; Planters, Nabisco Foods, Inc., Winston-Salem, NC; Italica, Italica Imports, Scarsdale, NY. See Table 1 for abbreviation and another company source. See Table 2 for another source.

TABLE 4
Larger-Scale ADMET Polymerization of Various Oil Samples at 55°C for 24 h Under Vacuum

Entry	Oil brand	Workup[b]	%Yield, r[c]	GPC-PS[d] Mw[f]	GPC-PS[d] Mn[g]	GPC-LS[e] Mw[f]	GPC-LS[e] Mn[g]	Viscosity mPa · s
1	Hain safflower[a]	B	57, 0.87	9060	4689	6564	4534	2370 ± 2.0%
2	Hain safflower[a]	C	95, 0.46	7637	2505	—	—	500 ± 1.9%
3	Wesson corn[a]	B	53, 0.81	6738	3683	5548	4059	1280 ± 3.5%
4	Wesson corn[a]	C	96, 0.51	5274	2579	—	—	293 ± 2.0%
5	Crisco canola[a]	B	57, 0.93	8094	4417	7752	5255	1760 ± 2.7%
6	Crisco canola[a]	C	95, 0.52	8470	3225	—	—	464 ± 0.2%
7	Wesson soybean	B	51, 0.89	7324	4149	4840	3358	1200 ± 0.3%
8	Wesson soybean	C	96, 0.48	5548	2563	—	—	252 ± 4.4%
9	Crisco soybean	B	55, 0.96	6998	3494	7538	4949	1495 ± 3.4%
10	Crisco soybean	C	97, 0.49	5030	2431	—	—	261 ± 4.2%
11	New Horizon's soybean	B	49, 0.92	6008	3767	5583	3883	1228 ± 1.2%
12	New Horizon's soybean	C	95, 0.51	5345	2473	—	—	344 ± 1.2%
13	Crude soybean[a]	B	49, 0.84	5499	3524	2621	1739	717 ± 4.8%
14	Crude soybean[a]	C	96, 0.56	3787	2364	3303	2171	176 ± 1.7%

[a]Oil was purified by passage through silica gel (2 × 60 g) with hexane prior to reaction.
[b]As described in the Materials and Methods section, workup B involved precipitation of the material from ethanol, while workup C involved passage of the material through silica gel utilizing hexane/ethyl acetate.
[c]See the explanation of r values in the text.
[d]GPC-PS: gel permeation chromatography, polystyrene calibration.
[e]GPC-LS: gel permeation chromatography, multiple-angle laser light-scattering molecular weight determination.
[f]Mw: weight average molecular weight.
[g]Mn: number average molecular weight. See Table 1 for abbreviations.

crease in the average molecular weight or a decreased tendency to form cyclic structures. A comparison of the r values and the gel permeation chromatography multiple-angle laser-light-scattering molecular weight determination data for these entries indicates that there is not a good correlation between r and the number average molecular weight. This suggests that macrocycle formation occurred to some extent in these reactions.

An examination of the viscosity and the molecular weights for the samples described in entries 13 and 14 of Table 4 indicates that the unprocessed soybean oil behaves rather poorly under these conditions. This is probably due to incomplete purification of the soybean oil during silica gel pretreatment. Presumably, further purification of the unprocessed soybean oil would result in material that behaves similarly to the industrially processed soybean oils.

Gel permeation chromatographic analysis of the polymeric materials indicates that the ethanol-insoluble metathesized oils generally have number average molecular weights ranging from 3600 to 5300, and the polydispersities, weight average molecular weight (Mw)/number average molecular weight (Mn), are approximately 1.5 (Table 4). The application of light-scattering technology to these measurements allows for a more accurate determination of the molecular weight profile than earlier studies (4), that employed only polystyrene standards to determine apparent molecular weights. The samples that have not been precipitated from ethanol have a similar molecular weight profile, but much higher polydispersities. This is consistent with the presence of unreacted oil and lower molecular weight by-products in the material. The light-scattering technique employed in this study allows for a greater degree of confidence in the values obtained compared to studies in which polystyrene standards alone were utilized (7).

Rheological analysis of the metathesized oils indicates that these materials behave as Newtonian fluids. The viscosity of the ethanol-insoluble oils (Table 4; entries 1, 3, 5, 7, 9, and 11) is dramatically increased compared to the starting oils (*ca.* 60–80 mPa·s). The unseparated metathesized oils (entries 2, 4, 6, 8, 10, and 12) have viscosities that are higher than the starting oils, but much less than the separated materials. This is again consistent with the presence of unreacted oil and hydrocarbon side products in the metathesized material. There is no readily apparent correlation between material viscosity and the degree of unsaturation of the starting oil.

A comparison of the ^{13}C NMR and infrared spectra of the separated and unseparated metathesized oils to unmodified soybean oil did not lend any new insights into the structure of the materials. The spectra obtained from these materials were essentially identical, even in the olefinic and ester regions.

In order to develop a better understanding of the structure of the material, a sample of separated, metathesized Wesson soybean oil (Table 2, entry 9) was fractionated by chromatography on silica gel (150 g) using 9:1 hexane/ethyl acetate. Utilizing this technique, the authors were able to isolate and further characterize five fractions from the complex mixture. The characteristics and structural identification for these fractions are summarized in Table 5.

Immediately apparent is the large percentage of cyclic material in the mixture (Table 5, entry 5). A comparison of the experimental r value (1.28) with the r value calculated for material with at least one macrocycle (1.33) allows for a reasonable degree of confidence in the assignment. The apparent molecular weights determined for this sample are much higher than the apparent molecular weights for the other isolated materials (entries 2–4). It appears that following several

TABLE 5
Chromatographic Separation of Methanol-Insoluble Metathesized Wesson Soybean Oil (Table 2, Entry 9)

Entry	R_f	% Weight recovery	r	Calculated r^a	Assignment	GPC-PS Mw	GPC-PS Mn
1	0.56	3	0.44	0.44	Monomer	—	—
2	0.40	11	0.70	0.67	Dimer	3181	2584
3	0.20	10	0.80	0.80	Trimer	4497	3782
4	0.10	9	0.86	0.89	Tetramer	5599	4693
5	0.05	67	1.28	1.33	Cyclic	12830	9825

[a]Value of *r* calculated by $4n/((3n + 6) - 6c)$, where *n* is the number of triglyceride molecules, and *c* is the number of cycles in the structure.

metathesis linkages, the entropic barrier to cyclization becomes low enough that intramolecular cyclization becomes favorable. This seems reasonable considering that the greater the number of triglyceride molecules linked together, the higher the probability of intramolecular cyclization.

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