The Chemistry of Metathesized Soybean Oil

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ABSTRACT: New materials derived from metathesized soybean oil have been prepared and characterized. Thermal polymerization of metathesized soybean oil in the presence of air results in yellow, brittle gels. These materials display a curious tendency to produce audible popping sounds when exposed to chlorinated organic solvents, such as chloroform or dichloromethane. Complete hydrogenation of metathesized soybean oil has been accomplished in excellent yields utilizing 10% palladium on carbon in dichloromethane. A new, very mild, effective epoxidation procedure for soybean oil, utilizing methyltrioxorhenium (VII) (MTO) and pyridine as the catalyst system and hydrogen peroxide as the oxidant, has been developed. This epoxidation reaction affords excellent yields of epoxidized soybean oil with some control of the degree of epoxidation at very low MTO concentrations (< 0.5 mol%). This reaction is also very effective for the epoxidation of metathesized soybean oil to higher molecular weight epoxidized soybean oil materials.

Paper no J8841 in *JAOCS 76,* 99–102 (1999).

KEY WORDS: Epoxidation, hydrogenation, infrared spectra, metathesized soybean oil, molecular weight, nuclear magnetic resonance spectra, polymerization, soybean oil.

The development of new, value-added materials from cheap, readily available, renewable natural resources remains a challenge for the scientific community. For instance, recent developments in simple heat bodying, or thermal polymerization of soybean oil, have led to the development of new ink vehicles (1–3). Major industrial modifications of soybean oil have included epoxidation (4) and hydrogenation (5). Hydrogenation and partial hydrogenation of soybean oil have been utilized to increase the melting point of the material in order to produce a large number of food products (5). The epoxidation of soybean oil has led to materials that serve as blending agents to improve the properties of a variety of polymers (4,6). More recently, Crivello and Narayan (7) have introduced technology that allows for rapid ultraviolet-induced cationic polymerization of epoxidized soybean oil to produce coatings.

Attempts to produce metathesized soybean oil have met with limited success until very recently. Erhan *et al.* (8) have prepared metathesized soybean oil by utilizing the classical tungsten-tin catalyst system. Their metathesized soybean oil, utilized as an additive at low concentrations, dramatically decreases the drying time of soybean oil. The use of Grubbs' catalyst for the preparation of metathesized soybean oil provided us with a means to produce relatively large (0.25 kg) samples of metathesized soybean oil in a relatively cost-effective and environmentally friendly manner (9).

Ready access to reasonably large, well-characterized samples of metathesized soybean oil provided the opportunity to explore the chemistry of these very interesting new oligomeric materials. Our goal in this study has been to extend the modifications that have been applied to soybean oil to metathesized soybean oil. In doing so, we hope to produce new, higher molecular weight materials with industrially useful properties that may find applications as value-added products from soybean oil. Such applications may include ink vehicles (1–3), photocurable coatings (7), and commercial polymer additives (4,6).

MATERIALS AND METHODS

Commercial vegetable oil samples were purchased from local vendors and utilized as received, unless otherwise indicated. 10% Palladium on carbon and methyltrioxorhenium (VII) (MTO) were purchased from the Aldrich Chemical Company (Milwaukee, WI) and were used as received. Metathesized soybean oil (Soy B) and metathesized, ethanol-insoluble soybean oil (Soy A) were prepared as described previously (9).

Hydrogenations. Soybean oil (40 g) or metathesized oil (110 g) was dissolved in dichloromethane (10 mL CH_2Cl_2/1 g oil) in an appropriately sized round-bottom flask with a magnetic stir bar. The catalyst, 10% palladium on carbon (5 w/w%), was added, and the solution was stirred vigorously. A hydrogen balloon fitted on a one-way flow adapter was connected to the flask *via* a ground glass joint. A positive pressure of hydrogen was maintained throughout the reaction. The reaction was monitored by periodic ^1H nuclear magnetic resonance (NMR) spectral analysis of small aliquots. The resulting suspension was filtered through celite with suction three times, followed by gravity filtration through Whatman #1 filter paper. The solvent was removed on a rotary evaporator, and the resulting white or off-white solid was evacuated for 16 h prior to spectroscopic analysis.

Epoxidations. Soybean oil (6 g) or metathesized oil (110 g) was dissolved in dichloromethane (1 mL CH_2Cl_2/1 g oil) in a round-bottom flask containing a stir bar. MTO and pyridine were added in the amounts indicated in Table 1. The flask was cooled in an ice bath, and 30% hydrogen peroxide (1.5 equivalents/double bond) was added dropwise with vig-

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TABLE 1
Methyltrioxorhenium(VII)-Catalyzed Epoxidation of Soybean and Metathesized Soybean Oils

Entry	Time (h)	Oil[a]	MTO (mol%)[b]	Pyridine (mol%)	Epoxidation (%)[c]	Yield (%)
1	2	Soy	0.1	1.2	24	98
2	2	Soy	0.2	2.4	55	97
3	2	Soy	0.5	6.0	97	100
4	2	Soy	1.0	12	100	100
5[d]	24	Soy	0.5	6.0	100	97
6	24	Soy A	0.05	0.6	13	96
7	24	Soy A	0.1	1.2	28	99
8	24	Soy A	0.3	3.6	82	98
9	24	Soy A	0.5	6.0	98	91
10[d]	24	Soy A	1.0	12	96	90
11	24	Soy B	0.05	0.6	15	91
12	24	Soy B	0.1	1.2	71	94
13	24	Soy B	0.3	3.6	93	95
14	24	Soy B	0.5	6.0	100	96
15[d]	24	Soy B	1.0	12	91	88

[a]Soy A, ethanol-insoluble metathesized soy oil; Soy B, metathesized soy oil, purified by filtration through silica gel.
[b]MTO, methyltrioxorhenium (VII).
[c]% Epoxidation determined by ^{1}H nuclear magnetic resonance spectral integration (disappearance of vinylic hydrogens vs. appearance of epoxide ring hydrogens).
[d]Reaction performed utilizing *ca.* 100-g sample of oil or metathesized oil.

orous stirring. The reaction was stirred and allowed to warm to room temperature for the appropriate amount of time (Table 1). The mixture was then transferred to a separatory flask and shaken with 10% sodium sulfite until the bright yellow color diminished. The methylene chloride solution was then washed with water and then brine, followed by drying over sodium sulfate. The solution was filtered and concentrated on a rotary evaporator, followed by 16 h of evacuation on a vacuum pump. The products from the large-scale reactions (Table 1, entries 5, 10, and 15) were passed through activity I basic alumina (60 g) by employing a mixture of hexanes (500 mL) and ethyl acetate (500 mL) as eluant.

Spectroscopic analysis. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity spectrometer (Palo Alto, CA) at 300 and 75.5 MHz, respectively. IR spectra were recorded on a BIORAD FTS-7 IR spectrometer (Hercules, CA).

Gel permeation chromatography. Molecular weight determinations were conducted by a combination of GPC and multiple-angle laser light scattering (MALLS) utilizing a Waters gel permeation system (Milford, MA) (410 refractive index detector) coupled with a Wyatt miniDAWN light-scattering system (Milford, MA). In those cases where MALLS was unsuccessful, the molecular weights were calculated by calibration with polystyrene standards. 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.

RESULTS AND DISCUSSION

Thermal polymerization of metathesized soybean oil (0.3–1.0 g) in air at 130°C for 24 h with occasional mixing resulted in the formation of yellow gels with brittle, crystalline surfaces. The presence of air was important, as the material quickly hardened where exposed to air, but did not appear to gel or polymerize below the surface. After cooling, exposure of the material to chloroform or methylene chloride resulted in substantial swelling and significant audible popping noises which lasted for several minutes. Exposure of the material to other solvents, such as hexanes, ethyl acetate, tetrahydrofuran, diethyl ether, benzene, or carbon tetrachloride, also produced some swelling and popping noise, but at a much lower amplitude. Material heated longer than 24 h did not have the combination of soft and brittle regions, and did not produce audible sounds to any significant extent. It may be that the popping noises were due to the chlorinated solvents quickly swelling the internal, soft regions of the polymeric materials, causing fractures in the brittle surface regions. Removal of the solvent from the swollen polymeric materials by vacuum or heating was unsuccessful in producing materials that would again produce audible sounds. Fully swollen material contained *ca.* 1 mL of solvent/1 g of material, which may allow for this material to be used as a selective absorbent for methylene chloride and chloroform, as these solvents are absorbed much more rapidly than other solvents.

Complete hydrogenation of soybean oil was readily accomplished utilizing 10% palladium on carbon in methylene chloride under a slight positive pressure of hydrogen (Table 2, entry 1). Some material was lost in the filtration processes, as the hydrogenated soybean oil had a tendency to crystallize from the dichloromethane. Attempts to redissolve this material utilizing hot dichloromethane and hot chloroform were unsuccessful. This material melted at 69–70°C. Metathesized soybean oil samples were also readily hydrogenated utilizing the catalytic 10% palladium on carbon system. Table 2 (entries 2 and 3) indicates that there was essentially no loss of material in the hydrogenation of the metathesized oils. The resulting solids were white or very pale cream-colored crystalline materials. The melting point of the hydrogenated, metathesized soy oil samples is 10–16°C lower than the melting point of hydrogenated soybean oil. Hydrogenated soybean oil is essentially one pure compound, while the metathesized samples consist of a mixture of oligomers. These mixtures were thus expected to have a lower melting point and a wider range than the corresponding pure material, and they do.

Our initial attempts at epoxidation of soybean oil and the metathesized materials focused on the use of stoichiometric amounts of *m*-chloroperbenzoic acid (10,11). While this approach was satisfactory for simple soybean oil, the metathe-

TABLE 2
Hydrogenation of Soybean and Modified Soybean Oils

Entry	Oil[a]	10% Pd/C (w/w%)	Time (h)	Yield (%)	Melting point (°C)
1	Soy	5	32	88	69–70
2	Soy A	5	24	99	58–60
3	Soy B	5	48	99	53–55

[a]See Table 1 for abbreviations.

sized oils did not respond well to peracid oxidation. Attempts to extract out the *m*-chlorobenzoic acid from the reaction suspension utilizing aqueous sodium carbonate or sodium bicarbonate resulted in tedious emulsions. Furthermore, the material isolated from this process tended to polymerize in a few hours, indicating an undesirable short shelf life. This polymerization was probably due to incomplete removal of *m*-chlorobenzoic acid from the product. The trace amount of acid present is presumably initiating acid-catalyzed epoxide ring-opening polymerization of the epoxidized materials.

Ideal conditions to produce epoxidized material with a prolonged shelf life would involve an epoxidation that could be conducted at neutral or slightly basic pH. Such a reaction has been developed recently by Sharpless and co-workers (12) for the epoxidation of small molecule olefins. The Sharpless conditions utilize a catalytic amount of MTO, pyridine as a co-catalyst, and an excess of hydrogen peroxide as the oxidant. Although MTO is relatively expensive, its use is required in such small quantities as to make the cost comparable to oxidations employing *m*-chloroperbenzoic acid.

Epoxidations of soybean oil using hydrogen peroxide catalyzed by MTO are outlined in Table 1, entries 1–5. Essentially complete epoxidation of soybean oil occurs at 0.5 mol % MTO or greater, based on the number of moles of double bonds in soybean oil (an average of 4.6 double bonds/triglyceride). The reaction and work-up are conducted in a minimal amount of solvent (1 mL CH_2Cl_2/1 g oil) at room temperature. The reactions produce epoxidized soybean oil essentially quantitatively. The use of decreased amounts of catalyst results in material that contains both epoxide functionality and unreacted double bonds (Table 1, entries 1 and 2). Partial epoxidation may be of interest for producing materials similar to vernonia oil, which behaves both as an unsaturated oil and an epoxidized oil. By controlling the amount of catalyst utilized in the reaction, one can prepare materials with a predictable degree of unsaturation and epoxidation.

The MTO-catalyzed epoxidation of metathesized soybean oil samples resulted in the isolation of the first examples of epoxidized, metathesized soybean oil. As with the soybean oil reactions, the use of 0.5 mol% MTO or higher resulted in essentially complete epoxidation of the metathesized oil. Use of less than 0.5 mol% MTO resulted in partially epoxidized material. In each case, the recovery of epoxidized or partially epoxidized material was very high, ranging from 88 to 99%. In entries 10 and 15 (Table 1), the reaction was conducted on approximately a 100-g scale to determine how easily the reaction scale could be increased. Once again, there was excellent recovery of highly epoxidized materials. The degree of epoxidation was slightly lower than in the corresponding small-scale reactions, possibly due to the increased difficulty of promoting efficient mixing in the biphasic reaction mixture.

Molecular weight analysis of the hydrogenated and epoxidized materials was conducted by GPC, coupled with MALLS measurements for those samples with sufficient molecular weight and low polydispersity. Examination of soybean oil and its derivatives (Table 3, entries 1–3) illustrates that there is a significant degree of error in simple polystyrene calibration of the gel permeation chromatography trace. Soybean oil has an approximate molecular weight of 882 g/mol. Hydrogenated soybean oil should be 892 g/mol, and epoxidized soybean oil should be 956 g/mol. The experimentally-determined values are approximately twice the true value, indicating a poor correlation between the polystyrene calibration curve and the triglycerides. However, the experimentally-determined values do have a reasonable degree of precision, and the polydispersities are about 1.1, which is reasonable for these materials. Examination of the molecular weight profiles of Soy A (ethanol-washed, metathesized soy oil) illustrates that these materials are of a sufficiently high molecular weight to allow for light-scattering analysis. The light-scattering data for entries 4–6 in Table 3 illustrate that the actual molecular weights are, once again, significantly lower than the molecular weights determined by polystyrene calibration. There is a larger increase in molecular weights determined by light scattering than is war-

TABLE 3
Gel Permeation Chromatography Data for Soy and Modified Soy Oil Samples

Entry	Oil[a]	GPC–PS[b] $<M_w>$[f]	GPC–PS[b] $<M_n>$[g]	PDI–PS[c]	GPC–LS[d] $<M_w>$[f]	GPC–LS[d] $<M_n>$[g]	PDI–LS[e]
1	Soy	1972	1750	1.127	—	—	—
2	Hydrogenated soy	1990	1806	1.102	—	—	—
3	Epoxidized soy	1877	1698	1.106	—	—	—
4	Soy A	8886	5324	1.670	4085	2560	1.595
5	Hydrogenated soy A	9932	5843	1.700	5929	3754	1.579
6	Epoxidized soy A	8660	5283	1.639	5980	4188	1.428
7	Soy B	6918	5389	1.284	4101	2566	1.598
8	Hydrogenated soy B	7300	3256	2.242	—	—	—
9	Epoxidized soy B	8115	6063	1.338	4191	3016	1.389

[a]See Table 1 for abbreviations.
[b]GPC–PS: gel permeation chromatography, polystyrene calibration.
[c]PDI–PS: polydispersity index–polystyrene calibration.
[d]GPC–LS: gel permeation chromatography, multiple-angle laser light-scattering molecular weight determination.
[e]PDI–LS: polydispersity index, multiple-angle laser light-scattering molecular weight determination.
[f]M_w: weight-average molecular weight.
[g]M_n: number average molecular weight.

ranted by the increase in molecular weight due to hydrogenation or epoxidation. This is an indication that even the light scattering, which is significantly more accurate than polystyrene calibration, suffers from a fairly high degree of inaccuracy in this molecular weight range. The GPC data for the derivatives of Soy B (unseparated, metathesized soy oil) are unreliable, as each GPC trace contained at least four discernible peaks ranging from *ca.* 10000 to 2000 g/mol. This is not unexpected, as the unseparated, metathesized soybean oil should still contain unreacted soybean oil and some lower molecular weight olefins produced in the metathesis reaction, as well as the higher molecular weight metathesized materials.

Traditional spectroscopic methods were extremely useful in the analysis of the products of the above reactions. The disappearance of the vinylic hydrogen stretch (3007 cm^{-1}) in the infrared spectrum of the epoxidized and hydrogenated materials is a strong indication that the epoxidation or hydrogenation reactions have been successful. Also, the absence of any significant OH stretch in the epoxidized materials examined is a good indication that the epoxidation is proceeding without any of the acid-catalyzed ring-opening reactions that are common in acidic epoxidation reactions. The disappearance of vinylic hydrogen resonances in the ^1H NMR spectrum of the materials produced allowed for evaluation of the degree of epoxidation or hydrogenation through simple integration. In the case of epoxidation, the appearance of the epoxide ring hydrogens at δ 2.6–3.2 ppm correlated with the disappearance of the vinylic hydrogens at δ 5.2–5.4 ppm. This is consistent with observations made by Crivello and Narayan (7) about the partial epoxidation of soybean oil. ^{13}C NMR spectral analysis also provided significant evidence for the success of these reactions. In the epoxidation reaction, the sp^2 carbons at δ 127–134 ppm disappeared, and a corresponding set of peaks consistent with epoxide ring-carbons appeared at δ 53–59 ppm. In the case of hydrogenation, the loss of sp^2 carbon peaks was accompanied by a similar increase in the number and height of saturated carbon peaks at δ 25–35 ppm.

ACKNOWLEDGMENTS

This research was supported by the Iowa Soybean Promotion Board. We thank Professor Valerie Sheares (Department of Chemistry, Iowa State University) for valuable discussions and assistance with the gel permeation chromatography.

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[Received April 6, 1998; accepted September 8, 1998]