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Reactions of Unsaturated Fatty Alcohols. II. Polymerization Of Vinyl Ethers and Film Properties of Polymers[1]

W. J. SCHNEIDER, L. E. GAST, E. H. MELVIN, C. A. GLASS, and H. M. TEETER, Northern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

IN A PREVIOUS PUBLICATION (6) we have described the preparation and properties of stearyl, soybean, and linseed vinyl ethers from the corresponding alcohols, using acetylene at atmospheric pressure. Preliminary experiments on the polymerization of these vinyl ethers with ionic catalysts were described, and the drying properties of the soybean and linseed polymers were observed. This paper reports the results of a more detailed study of the factors affecting polymerization and the preparation and properties of films from soybean and linseed polymers.

Preparation and Properties of Vinyl Ether Polymers

Soybean and linseed vinyl ethers were prepared from commercial samples of the respective alcohols (Unadol 40 and 90, Archer-Daniels-Midland Co.[2]). Stearyl vinyl ether was prepared from stearyl alcohol (Eastman Kodak white label).

A typical polymerization was carried out in the following manner. Three grams of vinyl ether monomer and 9 ml. of solvent were placed in a reactor fitted with a thermometer and stirrer. The flask was cooled in an ice bath or dry ice-ethanol bath to the temperature desired for polymerization. The catalyst was then added dropwise until a rapid temperature rise was noted. In most low temperature polymerizations the reaction was usually complete in less than 10 min. The catalyst was neutralized with ammonium hydroxide. The solution was washed with water, and the polymer was isolated by removing the solvent. In a few experiments polymerization was carried out at room temperature or above. Stearyl vinyl ether polymers were white to yellow waxy solids melting at 44° to 50°C. The polymers from linseed and soybean vinyl ethers were white to light yellow viscous oils. Molecular weights of the polymers were determined cryoscopically in cyclohexane solution (2).

Table I lists factors that influence the polymerization of fatty vinyl ethers. The first set of experiments

[2] Since the Department of Agriculture does not recommend the products of one company over those of another, these names are furnished for information only.

shows the effect of solvents on the polymerization when boron trifluoride etherate was used as a catalyst at temperatures near 0°C. Methylene chloride, carbon tetrachloride, and pentane-hexane appeared to be the most useful solvents. A polymer of high molecular

TABLE I

Effect of Solvent and Catalysts on Polymerization of Stearyl Vinyl Eether

Catalyst	Temperature (°C.)	Solvent[a]	Molecular weight of polymer	Melting point
BF₃[b]	0	CH₂Cl₂	7,700	49.5
BF₃[b]	0	Pentane-hexane	6,000	49.5
BF₃[b]	0	CHCl₃	1,300	46.5-47
BF₃[b]	0	CCl₄	11,000	50-52
BF₃[b]	0	CS₂	14,000	48
Al₂(SO₄)₃ · 3H₂SO₄ · 7H₂O	40	CHCl₃	<1,000	43-46
Al₂(SO₄)₃ · 3H₂SO₄ · 7H₂O	40	CCl₄	<1,000	37-39
Al₂(SO₄)₃ · 3H₂SO₄ · 7H₂O	0	CCl₄	<1,000	—
Al₂(SO₄)₃ · 3H₂SO₄ · 7H₂O	0	Pentane-hexane	<1,000	36
FeCl₃ · 6H₂O	0	CHCl₃	1,100	41
FeCl₃ · 6H₂O	25	C₆H₆	8,600	49
None	<0	SO₂	<1,000	25

[a] 3 parts solvent to 1 part monomer.
[b] 6% by weight in dibutyl ether.

weight was obtained when carbon disufide was the solvent. Other solvents not shown in Table I were tried with boron trifluoride-etherate catalyst, e.g., ethyl ether, acetone, tetrahydrofuran, and ethyl acetate, but little or no polymerization took place. Stearyl vinyl ether was not soluble in acetone or ethyl acetate at 0°C. Boron trifluoride-etherate was the only catalyst that worked well at 0°C. or below. It was particularly effective with soybean and linseed vinyl ethers since compatibility could be maintained at −30°C. Chloroform was a poor solvent in which to carry out polymerization with any of the catalysts studied.

Aluminum hexahydrosulfate has been used as a polymerization catalyst at elevated temperatures (30°-120°C.) with the lower alkyl vinyl ethers (e.g., ethyl, n-butyl, isopropyl, and isobutyl) to produce polmers of high molecular weight (4). The use of this catalyst with the higher alkyl vinyl ethers at 40°C. gave polymers of low molecular weight as shown in Table I. A more suitable catalyst at room

temperature and above is ferric chloride hexahydrate. Both aluminum hexahydrosulfate and ferric chloride hexahydrate at room temperature and about gave colored products not only with stearyl vinyl ether polymer but also with soybean and linseed polymers.

Data on polymerization of soybean vinyl ether at low temperatures in methylene chloride are shown in Table II.

By varying the amount of solvent, polymers of different degrees of polymerization could be obtained. If no solvent were used, the product was a gel insoluble in common solvents. For solutions having a 3:1 ratio of methylene chloride to monomer, polymers of moderate molecular weight were obtained at

TABLE II
Effect of Monomer and Catalyst Concentration on Polymerization of Soybean Vinyl Ether

BF$_3$ in dibutyl ether, %	Solvent to[a] monomer ratio	Temperature[b] (°C.)	Molecular weight of polymer
6	3:1	−30	3,500– 5,000
6	2:1	−30	6,000– 8,000
6	1.5:1	−30	9,000–10,000
6	No solvent	25–80	Gelled
12.5	3:1	30	40,000
12.5	3:1	0	30,000
12.5	3:1	−30	100,000

[a] Solvent was CH$_2$Cl$_2$.
[b] Initial temperature.

temperatures down to 0°C. At −30°C. the degree of polymerization was significantly increased, and polymers of higher molecular weight were obtained.

Table III shows the changes in unsaturation and conjugation as soybean and linseed alcohols are converted to vinyl ethers and finally to polymers. Some reduction in diene conjugation was observed with both soybean and linseed polymers, suggesting that the unsaturated side chains of these polymers were involved to some extent in the polymerization. A reduction in iodine number also accompanied the polym-

TABLE III
Changes in Unsaturation During the Preparation and Polymerization of Soybean and Linseed Vinyl Ethers

Compound	% Conjugation Diene	% Conjugation Triene	Iodine value
Soybean alcohol	31.6	0.78	118.3
Soybean vinyl ether	44.2	0.85	—
Soybean vinyl ether polymer	37.9	0.10	97.4
Linseed alcohol	13.8	1.5	166.5
Linseed vinyl ether	30.3	0.10	—
Linseed vinyl ether polymer	24.5	0	100.1

erization. In the soybean work the conjugated diene and iodine value was reduced to 84.8% and 82.5% of their original value, respectively. With the linseed series the reduction in conjugated diene and iodine value was 80.8% and 60% of the original values, respectively. No explanation is apparent for the large reduction of iodine value during polymerization of the linseed polymer.

A number of bulk polymerizations were carried out with soybean vinyl ether, using various catalysts. The results are shown in Table IV. Although boron trifluoride and stannic chloride induced different rates of polymerization, the products were insoluble gels. A chain terminator might prevent gelation in the experiment with stannic chloride. Stannous chloride and ferric chloride polymerizations gave viscous oils

TABLE IV
Bulk Polymerization of Soybean Vinyl Ether Using Various Catalysts

Catalyst	Reaction time (min.)	Maximum temperature (°C.)	Molecular weight of polymer
BF$_3$-etherate	1	45	Insol. gel
SnCl$_4$	7	47	Insol. gel
SnCl$_2$	5	56	6,000
FeCl$_3$ · 6H$_2$O	1	65	5,500
AlCl$_3$	60	25	Monomer[a]
ZnCl$_2$	1,200	25	Monomer[a]

[a] Some polymerization near catalyst particles.

with molecular weights from 5,000–6,000. This lack of reaction with aluminum and zinc chloride appears to be caused by the insolubility of these catalysts in the monomer.

Preparation and Properties of Unsaturated Vinyl Ether Polymer Films

Alkali Resistance. Films of soybean and linseed vinyl ether polymers were prepared by adding 1 g. of polymer to 3 g. of toluene. Metal naphthenate driers and, in some cases, antioxidants (1% by weight of polymer) were added, and the films were cast on small Pyrex test tubes to prevent exposure of the edge of the film to solvents. The films were baked at 150°C. for one hr. and then evaluated for alkali resistance by immersing in 5% aqueous alkali. The results of this study are shown in Table V. The hardest films were

TABLE V
Alkali Resistance of Unsaturated Vinyl Ether Polymers Baked for 1 Hour at 150°C. on Pyrex Tubes

Drier	Anti-oxidant[a]	Solubility in 5% NaOH (Time in min.) Soybean	Solubility in 5% NaOH (Time in min.) Linseed	Type of film[b] Soybean	Type of film[b] Linseed
0.1% Co	—	3	20	MH	MH
0.1% Co	—	3	20	H	H
0.1% Co	HQ	3	20	VH	VH
0.1% Co	NA	20	—	H	MH
0.1% Co	PNA	20	—	H	S
0.17% Mixed[c]	—	3	—	H	H
0.17% Mixed	HQ	100	—	H	H
0.17% Mixed	NA	60	—	H	H
0.17% Mixed	PNA	100	—	H	H
0.4% Pb	—	—	—	S	S
0.4% Pb	HQ	—	—	S	S
0.4% Pb	NA	—	—	S	S
0.4% Pb	PNA	—	—	S	S
0.1% Mn	—	4	70	VH	H
0.1% Mn	HQ	5	70	VH	H
0.1% Mn	NA	5	120	VH	H
0.1% Mn	PNA	5	120	VH	H

[a] HQ = Hydroquinone, NA = β-naphthylamine, PNA = Phenyl β-naphthylamine.
[b] VH = very hard, H = hard, MH = medium hard, S = soft.
[c] Mixed drier containing 24% lead, 6% cobalt, and 6% manganese.

obtained with cobalt and manganese driers, but they had the least resistance to alkali. Under the same conditions linseed vinyl ether polymer films were more resistant to attack by alkali than the soybean films. In general, addition of aromatic amines increased resistance to alkali. Alkali resistance was significantly improved when lead naphthenate was used as a drier; however the films were softer. The best compromise for film hardness and alkali resistance on Pyrex glass was obtained by using a mixed drier containing cobalt, lead, and manganese.

If films containing cobalt drier were baked for 1 hour at 150°C. on soft glass or metal surfaces, they were unaffected by immersion for three days in 5% aqueous alkali.

Solvent Resistance. Films were cast on small test tubes as described in the previous section. Baked

soybean and linseed films containing cobalt drier were resistant to a wide variety of solvents, including 95% ethanol, n-butanol, acetone, white gasoline, kerosene, chloroform, mineral oil, and n-hexane. Benzene produced some swelling of the films. Films were immersed in these solvents for 20 hrs. Films of soybean and linseed polymers were also prepared, containing cobalt and hydroquinone, cobalt and β-naphthylamine, and cobalt and phenyl β-naphthylamine. Immersion of these films in the solvents listed previously gave the same results as films not containing antioxidants.

Soybean Polymer Emulsions. Emulsions of soybean vinyl ether polymers were prepared in a small vial fitted with a high-speed stirrer. In a typical preparation 10 g. of polymer, 0.1% cobalt as cobalt naphthenate, and 0.5 g. of the ammonium salt of conjugated soybean fatty acids were stirred at 5,000 r.p.m. while 10 ml. of distilled water were added slowly over 5 min. After stirring for another 15 min., the contents formed a creamy emulsion of considerably lower viscosity than the original soybean polymer. Films of the emulsion were cast on glass slides and baked for 1 hr. at 150°C. The resulting films appeared to be continuous and to have properties equivalent to those of films cast from toluene solution.
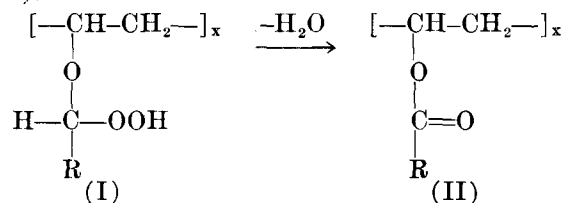
Degradation of Vinyl Ether Polymers

Alkali solubility of baked films from soybean and linseed vinyl ether polymers, containing certain metal naphthenate driers, was unexpected because the ether linkage should be resistant to alkali. To ascertain whether degradation was occurring at the ether linkage or in the side chain, infrared spectroscopic studies were made during drying of soybean polymer films containing cobalt drier.

In a freshly prepared polymer film a rather simple spectrum was obtained with strong bands at 2,860, 1,460, 1,370, 1,100, 1,000, 940, and 720 cm.$^{-1}$. After the film had dried 4 hrs. at room temperature, it was essentially tack-free. There were changes in the spectrum as shown in Table VI, and their probable interpretation is as follows. The appearance of hydroxyl absorption near 3,330 cm.$^{-1}$ and of a carbonyl absorption at 1,720 cm.$^{-1}$, and the disappearance of *cis, trans* and *trans, trans* conjugated diene with bands at 1,000 and 940 cm.$^{-1}$ accompanied by appearance of *trans* isolated bonds with a band absorbing at 970 cm.$^{-1}$. After drying 2 days the hydroxyl and carbonyl bands were stronger. A new band appeared at 1,180 cm.$^{-1}$, and the *trans* isolated absorption became weaker. At 10 days the hydroxyl band became very broad, the carbonyl adsorption was stronger, the new band at 1,180 cm.$^{-1}$ was very strong, and the C-O-C ether band at 1,100 cm.$^{-1}$ became weaker. Soybean films that had been baked on Pyrex tubes for 1 hr. at 150°C. and were completely soluble in alkali had spectra similar to air-dried films except that the

band at 1,180 cm.$^{-1}$ was dominant in the 1,000-1,600 cm.$^{-1}$ region and the C-O-C band at 1,100 cm.$^{-1}$ appeared as a shoulder on this stronger band.

Films containing cobalt that were baked on soft glass, metal plates, and Pyrex showed essentially the same absorption bands in the infrared. However, in the spectra of films cast on soft glass and metal, the band at 1,180 cm.$^{-1}$ was weaker than in spectra from films cast on Pyrex and was about equal in strength to the band at 1,100 cm.$^{-1}$.

Pertinent bands in the infrared spectrum of polyvinyl palmitate are shown in the last line of Table VI. An expected strong band at 1,180 cm.$^{-1}$, ascribed to the C-O linkage of esters, appears in the spectrum both of this material and of higher fatty acid esters in general (1). The appearance of a band at 1,180 cm.$^{-1}$ in the vinyl ether polymer films suggests that a similar linkage is formed during their oxidative degradation. The alkali solubility of baked films on Pyrex lends support to this idea since an ester linkage is known to be attacked by alkali. Formation of an ester linkage is compatible with current ideas on ether oxidation (3). The first step involves attack at the α-carbon atom to produce a hydroperoxide (1) followed by elimination of water to produce an ester (II).

$$[\text{—CH—CH}_2\text{—}]_x \quad \xrightarrow{\text{—H}_2\text{O}} \quad [\text{—CH—CH}_2\text{—}]_x$$

$$\begin{array}{ccc} \text{O} & & \text{O} \\ | & & | \\ \text{H—C—OOH} & & \text{C}=\text{O} \\ | & & | \\ \text{R} & & \text{R} \\ \text{(I)} & & \text{(II)} \end{array}$$

This mechanism requires formation of a C_{18} fatty acid and polyvinyl alcohol as degradation products by hydrolysis or saponification of (II).

In order to obtain chemical data on the degradation products, the alkali-soluble products from an oxidized film were isolated. The acidic portion appeared to be a C_{18} fatty acid and had a neutral equivalent of 282. No information could be obtained on other degradation fragments. Larger amounts of degradation products could not be obtained conveniently by oxidation of bulk samples of soybean vinyl ether polymer because gelation occurred rapidly, thus preventing further effective oxidation.

Since oxidation of stearyl vinyl ether polymer would not be complicated by the presence of double bonds in the side chain, this polymer was selected for further study. A film of stearyl vinyl ether polymer containing cobalt naphthenate was baked for 1 hr. at 150°C. The oxidized film had an infrared spectrum similar to that obtained from baked soybean films and was soluble in alkali. These results indicated that oxidative degradation of stearyl vinyl ether

TABLE VI

Changes in the Infrared Spectrum of Polyvinyl Soybean Ether Films During Aging

Compound	Air-drying time (hours)	Pertinent bands in cm.$^{-1}$						
		3,330	1,720	1,180	1,100	1,000	970	940
Soybean polymer	0.5	—	—	—	S^a	S	—	M^a
Soybean polymer	4	M	M	—	S	—	S	—
Soybean polymer	48	M	S	M	S	—	M	—
Soybean polymer	240	S (Broad)	VS^a	VS^a	S	M	—	—
Polyvinyl palmitate	—		S	S	S	—	—	—

^{a} VS = very strong; S = strong; M = medium.

polymer followed the same course as that of the soybean polymer.

A larger amount of degraded stearyl vinyl ether polymer was prepared by passing oxygen through the polymer at 150°C. for 6 hrs. in the presence of 0.1% of cobalt naphthenate. The resulting product contained 31.4% acid calculated as stearic acid. A white crystalline acid was isolated from this mixture and chromatographed on a silicic acid column according to the procedure of Nijkamp (5). The single band obtained was eluted from the column. Material recovered from this band was placed on a second column with pure stearic acid. One band was obtained, thus confirming the identity of the acid from the degradation. A small amount of a water-soluble red oil was obtained from the degradation mixture which appeared to be a ketovinyl alcohol on the basis of infrared spectra and solubility.

The isolation of a C_{18} fatty acid and a material that appears to be a partially oxidized polyvinyl alcohol from oxidized soybean and stearyl polyvinyl ethers furnishes chemical evidence to support the proposed mechanism outlined by structures (1) and (II).

Summary

Vinyl ethers of stearyl, soybean, and linseed fatty alcohols have been prepared and polymerized in solution in hydrocarbon or chlorinated solvents at temperatures down to —30°C. with several Lewis-acid-type catalysts. Stearyl polyvinyl ether was a white, waxy solid melting at 44°–50°C. while soybean and linseed polyvinyl ethers were colorless, viscous liquids. Molecular weights of these polymers range from 1,500 to 15,000 and higher, depending on the conditions of polymerization.

Films of soybean and linseed polyvinyl ethers containing driers were cast from toluene solution. Hard films were obtained with cobalt drier by baking at 150°C. while softer films were obtained under these conditions when lead driers were used.

Soybean films containing cobalt drier and baked on Pyrex glass dissolved completely in 5% aqueous alkali. A fatty acid coresponding to the fatty alcohol side chain was isolated from this solution along with a material that appeared to be partially oxidized polyvinyl alcohol. Baked films of soybean polyvinyl ether with lead drier did not dissolve in alkali. Some improvement of alkali resistance was obtained with cobalt films by adding aromatic amines as antioxidants. Soybean polymer films containing cobalt and baked on soft glass or metal surfaces were resistant to 5% aqueous alkali for at least three days.

Soybean polyvinyl ether was emulsified with an equal weight of water, using ammonium salts of fatty acids as emulsifiers. Films were prepared from this emulsion that appeared to be continuous.

Acknowledgment

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Note on Acetone-Soluble Material in Cottonseed Meals

W. H. KING, VERNON L. FRAMPTON, and A. M. ALTSCHUL, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

FOR A NUMBER OF YEARS there has been research on inactivation of the toxic and growth-inhibiting material in cottonseed in order to extend the availability of commercial cottonseed meal for use in poultry and swine rations. The responsible substance has generally been considered to be the "free" or "unbound" gossypol remaining after processing of the seed and extraction of the oil from the meal. The considered opinion of most workers in poultry and swine nutrition is that reduction of "free" gossypol to 0.04% is sufficient to provide a meal which does not exhibit toxic or growth-inhibiting effects because of this substance when the meal is incorporated in poultry rations (10). A number of commercial and laboratory processes yield meals of 0.02 to 0.04% of "free" gossypol (9, 4), and some of these meals have been used in commercial broiler rations.

The problem of discoloration of eggs, when stored, from hens fed rations containing cottonseed meal is still unsolved. It is known that gossypol, incorporated in the diets of laying hens, causes development of an olive color in the yolks when the eggs are stored under commercial conditions (11, 12). The consensus of workers in this field is that meals containing 0.01% or more of "free" gossypol will cause the egg discoloration when used in unlimited amounts in poultry feed (3).

Efforts to eliminate completely the "free" gossypol by applying drastic mechanical action to break the pigment glands, followed by cooking to bind the liberated gossypol, have failed to produce meals containing less than the 0.02 to 0.04% of "free" gossypol (7). Reduction to values of 0.005 to 0.015% has been achieved in the laboratory by extraction with polar solvents (2, 5). None of these procedures has acquired commercial status up to the present time. Extraction with polar solvents, such as aqueous acetone or butanone, not only reduces the "free" gossypol to low values but also removes the materials responsible for egg discoloration This has been demonstrated in some physiological tests. The nature of this material therefore becomes a key to the development of methods of eliminating egg yolk discoloration.

"Free" gossypol is determined by extraction with