Reactions of Unsaturated Fatty Alcohols. VII. Polymerization of Vinyl Ethers Catalyzed by Stannic and Ferric Chlorides[1]

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POLYMERS showing promise as protective coatings can be obtained by polymerization of polyunsaturated fatty vinyl ethers, such as those derived from soybean and linseed alcohols. Boron trifluoride was initially used as a catalyst for this polymerization (3, 6, 8). Use of this catalyst however required cooling of the reaction mixture to temperatures of the order of −30°C. A further disadvantage was that the strongly exothermic polymerization reaction was difficult to control at subzero temperatures, particularly in the preparation of more than a few grams of polymer.

It was found (9) that use of stannic chloride as a catalyst permitted initiation of polymerization of polyunsaturated fatty vinyl ethers at room temperature and appeared to offer a number of advantages in comparison with boron trifluoride. This paper presents the results of a detailed study of the conditions required for efficient polymerization of unsaturated fatty vinyl ethers with stannic chloride as catalyst and describes a satisfactory procedure for preparing polymers in quantities up to 1 kg. Some information is included on the use of ferric chloride hexahydrate, another catalyst reported (7) to initiate polymerization of vinyl ethers at room temperature.

Polymerization with Stannic Chloride

Starting Materials. Conjugated soybean vinyl ether (99.5%; conjugated diene, 36.0%; conjugated triene, 0.25%) and conjugated linseed vinyl ether (99.5%; conjugated diene, 31.0%; conjugated triene, 5.98%; conjugated tetraene, 0.29%) were prepared as previously described (3, 6, 8). Nonconjugated soybean vinyl ether (99.2%; conjugated diene, 0.9%) and nonconjugated linseed vinyl ether (98.9%; conjugated diene, 1.26%; conjugated triene, 0.59%) were prepared from samples of the respective nonconjugated fatty alcohols by a transvinylation technique (9, 10).

Generalized Procedure. The basis for study of reaction variables described in subsequent paragraphs was as follows. Polymerization studies were carried out in a round-bottomed flask fitted with a stirrer, thermocouple, nitrogen inlet, separatory funnel, and reflux condenser. The reactor was charged with the appropriate monomers and solvent. The flask was purged of air with nitrogen, and the stannic-chloride catalyst solution was added with rapid stirring under a continuous flow of nitrogen. After a suitable interval the mixture was quenched by adding 50% aqueous methanol. The product layer was washed three times with 50% aqueous methanol, dried over sodium sulfate, and freed of solvent by distillation. Except where otherwise indicated, molecular weights of products were determined cryoscopically in cyclohexane.

Type of Solvent. Data on polymerization of conjugated soybean vinyl ether in various solvents are shown in Table I. Comparison of polymerizations conducted in methylene chloride, chloroform, and carbon tetrachloride shows that the polymer prepared in chloroform had the lowest molecular weight. This solvent effect was also observed in polymerizations, using boron trifluoride-etherate (6) and ferric chloride hexahydrate (*v.i.*) catalysts. Because of its satisfactory performance, boiling point, and low toxicity in comparison with benzene, toluene appeared to be the more suitable solvent for routine use.

TABLE I

Polymerization[a] of Conjugated Soybean Vinyl Ether in Different Solvents

Solvent[b]	Molecular weight	Degree of polymerization	Viscosity (Gardner)	Color
Methylene chloride	3,390	11.6	X-Y	1
Chloroform	1,280	4.4	P-Q	1
Carbon tetrachloride	4,550	15.5	Z_5	1
Ethylene dichloride	2,910	10.0	Z-Z_1	3
Heptane	5,850	20.1	Z_6	5
Hexane	3,940	13.5	Z_6	3
Benzene	5,260	18.0	Z_5-Z_6	1
Toluene	4,450	15.2	Z_6	2

[a] Initiated at 25°C.; 4.8 mmoles $SnCl_4$ (added in benzene solution) per mole of monomer.
[b] 3 ml./g. monomer, except heptane, 5 ml./g. monomer.

Catalyst Concentration. Increasing the catalyst concentration increased the molecular weight of the polymer (Table II). In these experiments the catalyst was added in solution in benzene, toluene, or carbon tetrachloride without affecting the results.

Eley and Pepper (1) and Eley and Richards (2) report similar results for the polymerization of *n*-butyl and 2-ethylhexyl vinyl ether, respectively. However, when more than 4.8 mmoles of stannic chloride were used per mole of conjugated soybean vinyl ether monomer, the polymer darkened. Polymerization was substantially complete except when less than 1 mmole of catalyst was used.

Rates of polymerization and maximum temperatures of the reaction mixture increase with increasing catalyst concentration (Figure 1). At low concentrations

TABLE II

Effect of Catalyst Concentration on Polymerization of Conjugated Soybean Vinyl Ether

$SnCl_4$[a]	Solvent	Molecular weight of polymer	Unreacted monomer
Mmole			%
0.48	Benzene[b]	370	65.8
0.96	Benzene	2,730	6.1
1.92	Benzene	3,175	0.5
4.8	Benzene	5,260	3.0
9.6	Benzene	5,400	0.0
2.4	Heptane[c]	4,920	3.7
4.8	Heptane	5,850	1.6
9.6	Heptane	7,750	1.3

[a] Per mole of monomer. Reaction initiated at 25°C.
[b] Anhydrous; 3 ml./g. monomer.
[c] 5 ml./g. monomer.

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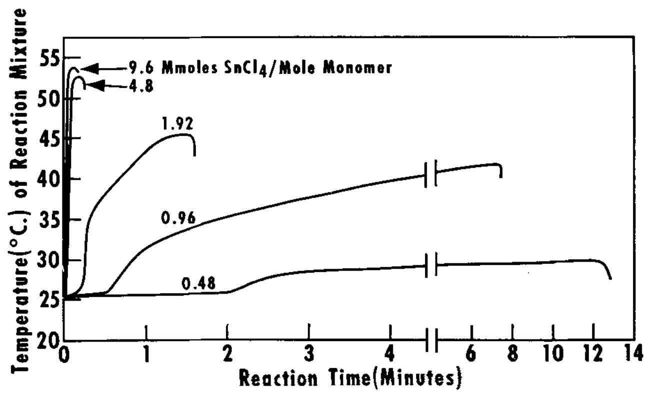

FIG. 1. Effect of catalyst concentration on rate of polymerization of conjugated soybean vinyl ether, basis of 3 ml. benzene/g. monomer and with reaction initiated at 25°C.

an induction period was observed. The sudden decrease in temperature at the end of each reaction results from addition of the quenching agent.

Quenching Time. Two polymerizations were conducted which differed only in that one was quenched when the reaction mixture reached its maximum temperature and the other was quenched 4 min. later. The molecular weights of the respective polymers were 5,260 and 4,820, and their Gardner colors were 1 and 6. Because no other differences in properties were observed, it was concluded that for optimum results polymerization should be quenched at the maximum temperature obtained by the reaction mixture.

Water. A series of polymerizations of conjugated soybean vinyl ether was carried out in benzene containing varying amounts of water. The results, shown in Table III, demonstrate that as the amount of moisture in the solvent was increased, the molecular weight of the polymer decreased.

TABLE III

Effect of Water Content on Polymerization[a] of Conjugated Soybean Vinyl Ether in Benzene[b] Solution

Water	Molecular weight of polymer
%	
0.003	5,000
0.011	3,440
0.023	2,600
0.053	2,360
0.077[c]	2,060

[a] Initiated at 25°C.; 4.8 mmoles $SnCl_4$/mole monomer.
[b] 3 ml./g. monomer.
[c] Benzene saturated with water at 25°C.

Solvent Ratio. According to data in Table IV, increasing the volume of solvent used per gram of monomer increased the time of reaction, decreased the maximum temperature attained by the reaction mixture, and decreased the molecular weight of the polymer. As the molecular weight decreased, the viscosity of the polymers also decreased from over Z_6 to Z_1.

TABLE IV

Polymerization[a] of Conjugated Soybean Vinyl Ether in Benzene Solutions of Varying Concentration

Solvent ratio	Reaction time	Max. reaction temp.	Molecular weight of polymer
Ml./g. monomer	*Sec.*	*°C.*	
1	5	71	10,000
2	12	57	7,200
3	18	53	5,400
4	25	47	4,750
5	45	41	3,520
6	60	36	3,900
7	90	36	3,080
8	160	34	3,290
9	180	33	2,700
10	210	32	2,200

[a] Initiated at 25°C.; 4.8 mmoles $SnCl_4$/mole monomer.

Initiation Temperature. Polymerizations initiated at several temperatures ranging from 25° down to −25° gave polymers with molecular weights shown in Table V. Molecular weights above 10,000 were obtained by viscosity measurements at 25°C. on benzene solutions at three concentrations. Extrapolation to zero concentration gave the intrinsic viscosity. Molecular weights were then evaluated from a plot of intrinsic viscosity *vs.* molecular weight (number average). This plot was based on cryoscopic determination of molecular weight for a series of polymers that were prepared at 25°C. with stannic chloride as catalyst and had varying molecular weights below 10,000. It was assumed that this plot of intrinsic viscosity *vs.* molecular weight could be linearly extrapolated with validity beyond molecular weights of 10,000 (4). Pepper has shown (5) that a plot of intrinsic viscosity *vs.* molecular weight for low molecular-weight polystyrene continues to be linear for high molecular-weight polymers. Viscosities and intrinsic viscosities of the vinyl ether polymers are also listed in Table V.

TABLE V

Polymerizations[a] of Conjugated Soybean Vinyl Ether Initiated at Different Temperatures

Initiation temperature	Properties of polymer		
	Molecular weight	Intrinsic viscosity	Viscosity
°C.			*Sec.*[b]
25	4,700	0.126	68
10	9,600	0.250	345
0	17,000	0.305	410
−10	20,000	0.335	486
−25	24,500	0.386	650

[a] 4 ml. toluene/g. monomer; 4.8 mmoles $SnCl_4$/mole monomer.
[b] Time in seconds for the bubble to rise 7.5 cm. in a Gardner-Holt viscosity tube at 25°C. (Z_6 is 195 sec.).

Monomer Purity. Because the principal impurity likely to be found in vinyl ethers is fatty alcohol, various amounts of nonconjugated soybean alcohol were added to nonconjugated soybean vinyl ethers before polymerization. Results of these experiments are itemized in Table VI. As the alcohol content of the monomer increased, the molecular weight of the polymers decreased.

TABLE VI

Polymerization[a] of Mixtures of Nonconjugated Soybean Alcohol and Vinyl Ether

Vinyl ether in mixture	Molecular weight of polymer	Degree of polymerization
%		
99.4	5,500	18.8
94.2	2,790	9.6
88.3	1,490	5.1
84.4	1,090	3.7
80.9	980	3.4

[a] 3 ml. benzene/g. monomer; 4.8 mmoles $SnCl_4$/mole monomer.

Infrared spectra of the polymers showed that this reduction in molecular weight was not caused by the presence of residual fatty alcohol.

Similar results were obtained with conjugated monomer and alcohol. For satisfactory results in polymerization, fatty alcohol content of polyunsaturated fatty vinyl ethers should be less than 2%.

Comparison of Conjugated and Nonconjugated Monomers

Polymers prepared from nonconjugated soybean vinyl ether had slightly higher molecular weights and considerably lower viscosities than did polymers prepared under identical conditions from conjugated monomer (Table VII). This difference in viscosity suggests that the conjugated system participates in polymerization to a greater extent than the 1,5-pentadiene system of the nonconjugated monomer.

TABLE VII

Polymerization [a] of Conjugated and Nonconjugated Soybean Vinyl Ether

	Conjugated		Nonconjugated	
Solvent ratio, ml./g. monomer	3	5	3	5
Molecular weight	5,130	3,390	5,500	3,690
Viscosity (Gardner)	Z_5-Z_6	Z_3-Z_4	Y	X-Y

[a] Benzene solution; initiated at 25°C.; 4.8 mmoles $SnCl_4$/mole monomer.

Recommended Procedure for Polymerization

On the basis of investigation of the variables affecting polymerization of soybean vinyl ether with stannic chloride, the following procedure is recommended for laboratory polymerization up to 1 kg. of soybean vinyl ether. Polymers prepared by this procedure will normally have molecular weights of 4,000–6,000. This molecular-weight range appears to be satisfactory for studies of the film-forming properties of the polymers. This procedure may also be used for preparing copolymers if pilot experiments show that the exothermic heat of reaction from polymerization of the desired mixture of monomers will not raise the reaction temperature to the boiling point of toluene.

A 12-liter, 3-necked, Morton type of flask is equipped with a stainless-steel stirrer, a condenser, and a straight tube 45 cm. in length. An inlet tube for nitrogen and an iron-constantan thermocouple are inserted through the condenser to a point just above the stirrer. The straight tube is used for rapid addition of catalyst and quenching agent. Temperature of the reaction mixture is followed by an automatic recorder to which the thermocouple is attached.

In a typical polymerization 1 kg. of conjugated soybean vinyl ether and 3 liters of anhydrous toluene are charged into the flask. With rapid stirring and nitrogen bubbling in below the liquid surface, 60-65 ml. of 8% (w/w) anhydrous stannic chloride in toluene are added rapidly. At the maximum temperature, as indicated by the recorder, the reaction is quenched with 500 ml. of 50% aqueous methanol. While still warm, the reaction mixture is washed three times with 250 ml. of 50% aqueous methanol and dried with sodium sulfate. Filtration and removal of the solvent under reduced pressure in a rotary evaporator give 900–950 g. of polymer.

Polymerization with Ferric Chloride Hexahydrate

Procedure. Polymerizations with ferric chloride hexahydrate (7) were carried out according to the following general procedure.

Ten grams of conjugated soybean vinyl ether and 30 ml. of solvent were placed in a 125-ml. Erlenmeyer flask and stirred rapidly with a magnetic stirrer. The temperature was automatically recorded by using an iron-constantan thermocouple. A gas inlet-tube was employed to maintain an inert atmosphere of nitrogen over the polymerization mixture. Ten drops of a 5% solution of ferric chloride hexahydrate in *n*-butanol were added. The exothermic reaction that ensued was complete in 2 min. When the maximum temperature was reached, the catalyst was quenched with 1 ml. of concentrated ammonium hydroxide; the solution was washed with water until neutral to litmus, dried with anhydrous sodium sulfate, and filtered; and the solvent was removed at a pressure of 1 mm.

Table VIII shows the results of polymerizations carried out in a variety of solvents. All polymers were much darker in color than those prepared with stannic chloride as catalyst (compare Table I) with the exception of the polymer prepared in chloroform solution. At least some of the color was caused by the presence of unremoved iron compounds since an improved color could be obtained by precipitation of iron as the sulfide.

TABLE VIII

Polymerization of Soybean Vinyl Ether with Ferric Chloride Hexahydrate [a] as Catalyst at 25°C.

Solvent	Solvent ratio	Molecular weight	Viscosity	Residual vinyl ether	Color
	Ml./g. monomer		*(Gardner)*	%	*(Gardner)*
None	None	2,000	Z_5-Z_6	0.4	12
Benzene	3	1,270	Y-Z	2.9	9
Hexane	3	780	W	14.8	11
Hexane	1	1,540	Z_1-Z_2	2.4	11
Methylene chloride	3	1,400	W	3.7	10
Chloroform	3	970	L	4.4	2
Carbon tetrachloride	3	2,100	Y	8.6	11

[a] 5% solution in *n*-butanol.

Although polymerization was readily initiated at 25°, ferric chloride hexahydrate appeared to be a relatively inefficient catalyst since molecular weights of the polymers were all comparatively low (2,100 or less) and since, in the majority of the experiments, the polymer contained over 3% of residual vinyl ether.

Summary

Variables affecting the use of stannic chloride as a catalyst for initiating polymerization of conjugated and nonconjugated soybean vinyl ether were studied. Molecular weight of the polymers increased with an increase in catalyst and a decrease in initiation temperature, and it decreased when the amount of moisture in the solvent, the amount of free fatty alcohol in the monomer, or the ratio of solvent to monomer was increased. Aromatic and aliphatic hydrocarbon solvents were superior to halogenated solvents for conducting polymerizations. Similar results were obtained with nonconjugated monomers except that viscosities of the polymers were considerably lower than those of polymers of the same molecular weight obtained from conjugated monomer.

To obtain polymers suitable for film-forming studies (4,000–6,000 molecular weight) polymerization is initiated preferably at 25°C. with 3 ml. of anhydrous toluene used per gram of monomer and 4.8 mmoles of stannic chloride per mole of monomer. Monomer purity should be at least 98%.

Ferric chloride hexahydrate initiated polymerization at 25°, but polymerization was incomplete, and the polymers had relatively low molecular weights.

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REFERENCES

1. Eley, D. D., and Pepper, D. C., Trans. Faraday Soc., *43*, 112 (1947).
2. Eley, D. D., and Richards, A. W., Trans. Faraday Soc., *45*, 425 (1949).
3. Gast, L. E., Schneider, Wilma J., O'Donnell, J. L., Cowan, J. C., and Teeter, H. M., J. Am. Oil Chemists' Soc., *35*, 347 (1958).
4. Gast, L. E., Schneider, Wilma J., and Teeter, H. M., J. Am. Oil Chemists' Soc., *34*, 307 (1957).
5. Pepper, D. C., Sci. Proc. Roy. Dublin Soc., *25*, No. 19, 239 (1951).
6. Schneider, Wilma J., Gast, L. E., Melvin, E. H., Glass, C. A., and Teeter, H. M., J. Am. Oil Chemists' Soc., *34*, 244 (1957).
7. Shostakavskii, M. F., Mikhantie, B. I., and Ovchinnikova, N. N., Inst. Org. Chem., Acad. Sci. USSR, Moscow, 1056 (1953), C. A. *49*, 2299 (1955).
8. Teeter, H. M., Dufek, E. J., Coleman, C. B., Glass, C. A., Melvin, E. H., and Cowan, J. C., J. Am. Oil Chemists' Soc., *33*, 399 (1956).
9. Teeter, H. M., Gast, L. E., and Cowan, J. C., Ind. Eng. Chem., *50*, 1703–04 (1958).
10. Watanabe, W. H., and Conlon, L. E., U. S. Patent 2,760,990 (August 28, 1956).

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A Review of Some Physiological Effects of Gossypol and Cottonseed Pigment Glands[1]

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The earliest recorded statement on the harmful effect of cottonseed is attributed to Voelker in England in 1859 (1). Since that time many materials have been blamed for the adverse physiological effects noted after feeding cottonseed. In 1886 Longmore (2) isolated a crude pigment from cottonseed oil "foots," and Marchlewski (3) in 1899 extracted, purified, and gave the name "gossypol" to a yellow pigment which he had obtained from cottonseed "foots." These latter two investigators were interested in the pigmented material as a dye and made no mention of physiological activity. The preliminary note by Withers and Carruth (4) in 1915 entitled, "Gossypol, a Toxic Substance in Cottonseed," was their first report of separation from cottonseed kernels of a substance which appeared to be identical with the material separated from crude cottonseed oil and named by Marchlewski in 1899. Withers and Carruth found their material to be toxic to rabbits and published three additional papers (5–7), all bearing titles similar to the first one. These publications and subsequent work primarily by Schwartze (8–10), who made a positive correlation between the toxicity of raw cottonseed and gossypol content, led to the general belief that the toxicity of cottonseed can be attributed solely to its gossypol content.

With the availability of cottonseed pigment glands, separated from cottonseed kernels by a flotation process (11, 12), and of pure gossypol (13, 14) it became possible to evaluate their toxicity by determining the oral median lethal dose, *i.e.*, the oral LD_{50} value. It was found that three different samples of untreated cottonseed pigment glands containing 40.0, 37.6, and 33.7% gossypol, respectively, were more toxic to the rat than pure gossypol itself. These early findings were reported for us by Boatner in 1947 (15). From that time to the present, studies have been made on a large series of samples of gossypol and of untreated, fractionated, treated, stored, and detoxified cottonseed pigment glands (16–22).

In Table I are shown a series of 11 different samples of untreated cottonseed pigment glands, varying in acute oral toxicity in the rat (LD_{50} value) from 925 to 2170 mg./kg. body weight. It should be recognized that, while cottonseed pigment glands are toxic, they show a rather wide range of toxicity not referable to their analyzed gossypol content.

TABLE I
Toxicity and Gossypol Content of Untreated Cottonseed Pigment Glands[a]

Pigment glands	Acute oral LD_{50} in the rat	Gossypol content[b]
	mg./kg.	%
1	925	(40.0)
2	1060	(36.9^4)
3	1140	37.8^2
4	1345	34.3^2
5	1350	(33.5^3)
6	1430	32.5
7	1635	30.3^3
8	1775	(33.0)
9	1845	34.1^3
10	2000	33.2
11	2170	28.6^2

[a] Eagle *et al.* (1948, 1950, 1952).
[b] The figures in parentheses denote analytical results by the antimony chloride method of Boatner *et al.* (1947, 1948); all other analyses by method of Pons and Guthrie (1949); the exponent denotes the number of analyses averaged.

Table II shows a series of 10 different samples of gossypol, the LD_{50} values of which in the rat were determined when administered in water or in oil or in each. It may be seen that gossypol is less toxic, whether administered in oil or in water, than even the least toxic of the 11 samples of untreated cottonseed pigment glands tested.

In 1947 several papers (23, 24) were presented in which it was stated that gossypol was an appetite depressant, that intestinal irritation and other toxic manifestations previously ascribed to gossypol are not found with a pure preparation of gossypol in reasonable doses, and that purified gossypol has no generally toxic properties. The widespread publicity relative to the possible use of gossypol in the treatment of obesity in man necessitated that we determine the effect of small daily doses on the body weight and food consumption of the dog.

Four litter-mate dogs were given 19 doses of 0, 50, 100, and 200 mg. of gossypol per kg. of body weight

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