

Polymerization of Drying Oils. VI. Catalytic Polymerization of Fatty Acids and Esters With Boron Trifluoride and Hydrogen Fluoride¹

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BORON trifluoride and its complexes with oxygenated organic compounds have become important catalysts for a variety of reactions. They promote polymerizations, alkylations, condensations, and rearrangements (1) often at lower temperatures and with fewer side reactions than when other catalysts are used. Numerous patents cover the polymerization of unsaturated vegetable oils in the presence of boron trifluoride, and it has been reported that the free fatty acids or their alkyl esters (2, 7) may also be used. However a detailed report of experimental conditions and their effect on the properties of the products is lacking.

Hydrogen fluoride is likewise an important catalyst for similar reactions, but its use to polymerize fatty acid material has been only briefly mentioned. Fredenhagen (3) used hydrogen fluoride to polymerize various vegetable oils in high yields in a relatively short time but gave no experimental details.

The purpose of this report is to show the effect of boron trifluoride and of hydrogen fluoride on the polymerization of soybean fatty acid materials under a wide range of experimental conditions and to give some properties of the products. Most of the work was directed towards obtaining high yields of products containing substantial amounts of trimers and higher polymers.

Raw Materials

The fatty acid methyl esters used in this investigation were prepared by methanolysis of commercial alkali-refined soybean oil, using sodium hydroxide as a catalyst. They were distilled under reduced pressure before use.

The free fatty acids were prepared by saponification of alkali-refined soybean oil. The boron trifluoride and hydrogen fluoride were the commercial products available in steel cylinders.

The methyl ether-boron trifluoride complex was prepared from methyl alcohol and boron trifluoride by the method of Kolka and Vogt (5). The ethyl ether, dioxane, and tetrahydrofuran complexes were prepared by bubbling boron trifluoride into the respective compounds.

Boron Trifluoride Polymerization of Methyl Esters of Soybean Fatty Acids

The methyl esters of soybean acids were polymerized in round-bottom, glass flasks fitted with a reflux condenser and a thermometer extending into the reaction mixture. Usually 100-200 g. of esters were weighed into the flask, and then boron trifluoride was bubbled into the esters from a storage cylinder until the desired increase in weight was realized. The flask

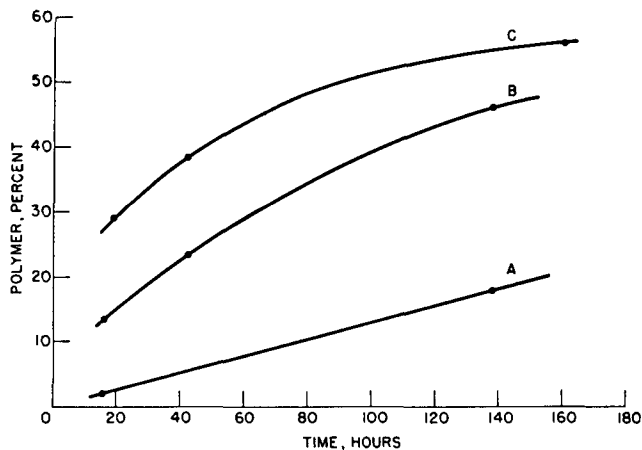


FIG. 1. Rate of polymerization of methyl esters at room temperature. Curve A, 4.0% BF₃; Curve B, 10.6% BF₃; Curve C, 14.5% BF₃.

and contents were rapidly heated to the desired reaction temperature.

To obtain the time curves of Figures 1 and 2 aliquots were removed during the polymerization. The aliquots and final products were quickly cooled, dissolved in petroleum ether, washed with water until free of acid, and dried. After removal of the solvent, the yield of polymer was arbitrarily determined as the amount not distilling at a pot temperature of 250°C. and pressure of 1 mm. by ordinary distillation.

Figures 1 and 2 show the relative rates of polymerization of the esters at various combinations of temperature and starting concentration of boron trifluoride (expressed as weight percentage of the esters). The rate was low at room temperature and increased considerably to a maximum at about 150°C. At higher

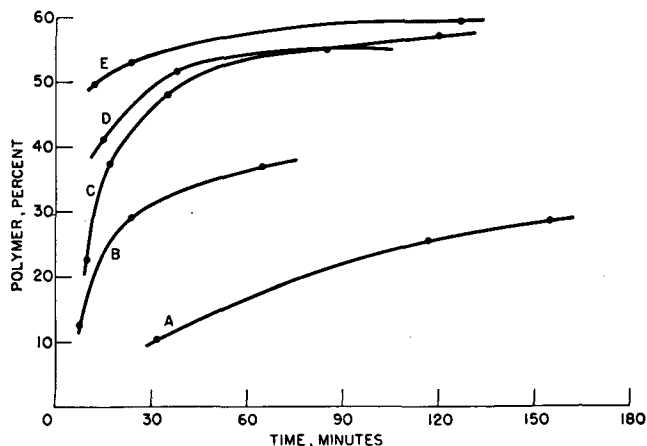


FIG. 2. Rate of polymerization of methyl esters at various temperatures and concentrations of BF₃. Curve A, 95°, 2.3%; Curve B, 95°, 4.6%; Curve C, 95°, 9.5%; Curve D, 195°, 2%; Curve E, 150°, 2.2%.

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temperatures the starting concentration of BF_3 was of minor importance because of the decreasing solubility of the catalyst which is practically insoluble and has little catalytic effect at 300° .

Practical conditions for high yields are in the neighborhood of 2% BF_3 at 150° - 200° for one hour. Five-gallon batches of methyl esters have been polymerized under such conditions in closed pilot plant equipment resulting in yields of over 60% of residual polymeric esters (2).

Properties of the Polymerized Esters

Though boron trifluoride promoted polymerization of the methyl esters of soybean oil at a much faster rate than heat alone or in conjunction with catalysts not of the Friedel-Crafts type, the products were very dark brown and had high acid numbers (25-50). Other properties varied, of course, with the amount of polymers present. The polymeric residue from regular distillation had a viscosity of P or above (Gardner) and a refractive index (30°) of 1.4810 to 1.4860. Polymers obtained in the highest yields usually had the highest viscosities and refractive indices, indicating a low ratio of dimer to higher polymers.

A batch of polymeric soy esters from boron trifluoride catalysis and one from anthraquinone catalysis was fractionated in a cyclic molecular still to obtain information on the proportion of dimers, trimers, and higher polymers. In Figure 3 the mean percentage distilled is plotted against the refractive index of each fraction (a quick, rough measure of the degree of polymerization). In contrast to nonionic catalysis, boron trifluoride catalysis resulted in a much lower ratio of dimers to higher polymers. If the higher polymers are desirable, boron trifluoride proves to be an efficient catalyst.

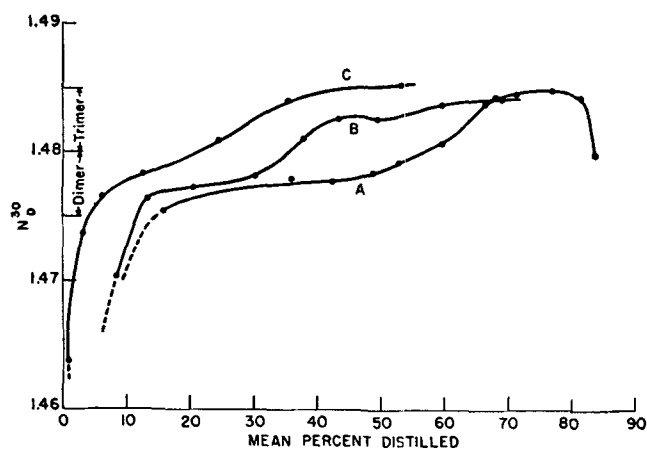


Fig. 3. Molecular distillation of polymerized esters. Curve A, anthraquinone catalyst; Curve B, HF catalyst; Curve C, BF_3 catalyst.

The residue from molecular distillation of the boron trifluoride catalyzed polymerizate amounted to about 35% of the total polymeric fractions and was a very viscous liquid of deep brown color having a refractive index of over 1.49. Its acid number and methoxyl content were 22 and 7.5%, respectively, thus accounting for about 85% of the original ester groups.

The butyl and iso-octyl esters of the residual polymeric material (from molecular distillation) have been

prepared and examined for their viscosity characteristics. Kinematic viscosities were determined with Cannon-Fenske-Ostwald viscometers and are given in Table I. The calculated viscosity indices were 130

TABLE I
Kinematic Viscosities (Centistokes)

	65°C.	80°C.	100°C.
Butyl esters.....	14.5	24.3	39.0
Iso-octyl esters.....	26.2	48.2	80.2

for the butyl esters and 118 for the iso-octyl esters. The esters became very viscous but retained flow properties when cooled to -35°C . Though probably too viscous by themselves, they may prove to be useful as thickeners or viscosity index improvers for low viscosity lubricants. In an oxidation test the esters were stable and retained their original viscosities.

Use of Boron Trifluoride—Ether Complexes

The boron trifluoride complexes with ethers were effective catalysts and, being liquid or solid at room temperature, were convenient to use. The polymerizations were conducted in glass flasks fitted with reflux condensers. Catalysts can be recovered by vacuum distillation though there is usually some decomposition.

TABLE II
Polymerization of Soybean Methyl Esters With Boron Trifluoride-Ether Complexes for Four Hours

Ether	Complex/ 150 g. ester grams	Tempera- ture °C.	Polymeric fraction		
			Yield %	Refractive Index n_D^{30}	Color (Gardner)
Me_2O	10	150-158	59	1.4809	15 Very dark
	100	120-127	74	1.4896	
Et_2O	10	139-142	50	1.4812	16 17-18
	100	136-137	73	1.4871	
Dioxane	3	150-153	44	1.4803	Very dark Very dark
	40	150-155	82	1.494	
Tetrahydro- furan	100	150-160	80	1.5208	Very dark

Experimental data and results are given in Table II. The polymerizations occurred at relatively low temperatures and resulted in high yields of polymers. A significant advantage of the use of the aliphatic ether complexes was the great improvement in color of the product. The cyclic ether complexes promoted unusually high yields of polymers having a dark color like that obtained with BF_3 alone.

The rate of polymerization of the esters in the presence of the higher concentration of the ethyl ether complex at 135°C . was studied. A yield of 57% polymers was obtained in one hour, and a maximum yield of 73% was reached in 4 hours.

Hydrogen Fluoride Polymerization of Soy Methyl Esters

The polymerizations using hydrogen fluoride as catalyst were carried out at atmospheric pressure in copper flasks or at higher pressures (above 20°C .) in sealed steel hydrogenation bombs. The reaction vessels were first charged with the cooled methyl esters, and then the weighed quantity of liquid hydrogen

fluoride was added. A mechanical stirrer was used in the copper flasks whereas the steel bomb was mechanically shaken during the reaction. At the end of the reaction the products were cooled to below 20°C. and worked up the same as the BF₃ catalyzed products.

The conditions of each experiment and data on the resulting polymeric fractions are given in Table III.

TABLE III
Polymerization of Soybean Methyl Esters
With Hydrogen Fluoride

HF concentration	Temperature	Time	Polymeric fraction		
			Yield	Refractive index	Color
%	°C.	hrs.	%	n _D ²⁰	Gardner No.
2	0-18	4	3
20	0-12	4	24	1.4732
35	0-17	4	49	1.4796	13
65	0-20	4	70	1.4833	18
12	80-88	1	18	1.4787	14
22	84-100	2	73	1.4807	14
35	80-90	1	70	1.4825	14
Saturation ^a	204	2	3	1.4618

^a HF bubbled through esters in open flask for entire reaction time.

It is evident that more than catalytic amounts of hydrogen fluoride must be used for good yields, as has been reported by Simons, *et al.* (6) for condensation reactions involving oxygenated compounds. In fact, the mole ratio of hydrogen fluoride to ester was about 3 to 1 (about 20% HF by weight) before yields were comparable to those obtained using boron trifluoride. Under optimum conditions, however, yields of 70% were readily obtained. Reactions in closed systems above 100°C. were not tried because of the corrosiveness of the catalyst.

In addition to its effectiveness at low temperatures, hydrogen fluoride has the advantage of inducing the formation of polymers having improved acidity and color. The acid numbers were less than 7, and the colors were between 13 and 18 (Gardner). The ratio of dimer to higher polymers found by molecular distillation was, as for the boron trifluoride products, relatively low (Fig. 3).

Polymerization of Free Fatty Acids

Mixed free fatty acids (acid no. = 190), prepared from soybean oil, and commercial acidified soybean oil foots (acid no. 121) have been polymerized with catalysts by procedures already described for the methyl esters. The experimental conditions and results are given in Table IV.

At the higher temperatures the free fatty acids polymerized readily and gave high yields of polymers which had relatively high acid numbers, indicating only a moderate disappearance of the acid groups. Polymerization of the acids by boron trifluoride at 30° occurred to a much greater extent than did that of the esters under similar conditions, but the low acid number indicated considerable disappearance of the acid groups. All of the polymeric

TABLE IV
Polymerization of Free Fatty Acids

Catalyst	Temperature	Time	Polymeric fraction		
			Yield	Refractive Index	Acid no.
	°C.	hrs.	%	n _D ²⁰	
4% BF ₃	30	5	39	1.4742	96
4% BF ₃	155-165	2	71	1.493	149
5% Et ₂ O·BF ₃	140	5	66	1.4855
35% HF	80-90	1	72	1.495	169
4% BF ₃ ^a	170-180	2	73	1.492

^a Soybean oil foots.

acids had a deep brown color and were even more viscous than the polymeric esters. The foots underwent considerable polymerization and may be an inexpensive source of polymeric acids.

A different batch of soybean fatty acids having an acid number of 156 was polymerized in the presence of the ethyl ether-boron trifluoride complex. A 70% yield of polymers having an acid number of 42 and a saponification number of 138 was obtained. Apparently the ether complex also functioned as an ethylating agent on the carboxyl group as reported by Hennion *et al.* (4). This alkylating power may be an explanation for the marked improvement in color when aliphatic ether-boron trifluoride complexes are used instead of cyclic ether complexes or boron trifluoride alone as catalysts for polymerization of methyl esters. Other evidence points to a relationship between the color and acidity of the products.

Summary

At relatively low temperatures boron trifluoride and hydrogen fluoride gave high yields of polymers from soybean fatty acids and methyl esters.

The use of 2% boron trifluoride as catalyst at 150° to 200° resulted in the polymerization of 50-60% of the methyl esters within one hour. The viscous polymeric fraction usually had a dark color, a high acid number, and a low ratio of dimer to higher polymer.

The boron trifluoride-ether complexes were equally effective catalysts and more convenient to handle. Use of the aliphatic ether complexes resulted in products having lighter colors.

It was necessary to use large amounts of hydrogen fluoride to produce comparable yields at less than 100°, but 70% yields of polymers having light colors and low acid numbers were obtained.

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