Polymerization of Styrene With Ethyl Linoleate[1]

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THERE is little published data on the interaction of styrene with drying oils or drying oil acids. Polymers have been reported, but not studied in detail, from the reaction of styrene with tung oil (1, 2, 3), dehydrated castor oil (4, 5), oiticica oil (1, 6), and linseed oil (3, 6, 7).

Hewitt and Armitage (5), who treated various drying oil polymers with styrene to prepare varnish resins, postulated that two processes might be involved: a) action of unconjugated fatty acid radicals on styrene by a chain-transfer process, and b) actual copolymerization of styrene at the double bonds of conjugated fatty acids. Recently evidence of the inhibitory effect of linoleic and linolenic acid soaps on the copolymerization of styrene and butadiene has accumulated (8).

The purpose of the present investigation was to study the nature of the products obtained, whether copolymers or modified polystyrenes, when styrene and ethyl linoleate were combined under copolymerization conditions. Aqueous soap emulsions heated at 40° with a persulfate catalyst were used for most of the work. The ethyl linoleate was a mixture of conjugated and unconjugated material; it was used both directly and after oxidation. The course of the polymerization was followed by the determination of yields, iodine values, saponification numbers, and intrinsic viscosities.

Experimental

1. *Source of Ethyl Linoleate.* The linoleic acid used was a mixture of 9,12 and conjugated isomers obtained by low temperature recrystallization (9) (to remove saturated and oleic acids) of a commercial linoleic acid, "Isoline."[3] The resulting acid was esterified with ethanol containing hydrogen chloride as catalyst. Typical constants on the distilled ester were: b.p. 178-180°C. at 3 mm., acid number zero, total iodine value by use of the Woburn (10) IBr solution 162 (calculated 165), partial iodine value by use of Wijs ICl (11) 130, per cent conjugation[4] 35. Attempts to prepare the 9,11 acid by Mangold's method (12) gave such small yields that work with the pure conjugated isomer was abandoned.

2. *Oxidation of Ethyl Linoleate.* Ethyl linoleate was oxidized by passing oxygen through it at 80°C. for several hours in an attempt to increase the amount of conjugated ester (13). The partial iodine value decreased after sufficient time as shown in Table I, but conjugation was not increased markedly, except in one case which was not duplicated.

3. *Technique of Polymerization.* The container used for Runs I-III was a 50-ml. test-tube with an elongated neck. For Runs IV-X 8-oz. beverage bottles were substituted for the tubes. Containers were cleaned before use by the Fryling technique (14).

TABLE I
Treatment of Ethyl Linoleate With Oxygen

Time of passage of oxygen, hr.	Total I.V.	Partial I.V.	% Conjugation [a]
3	146	86.3	82
3	138	110	42
3	164	129	43
8	131	109	34
5	138	111	40

[a] The per cent conjugation = 2 (total I.V. — partial I.V.) × 100/total I.V.

The reaction mixtures in the tubes contained the following quantities of ingredients: 10 g. combined monomers, 18 g. water, 4 g. sodium oleate and 0.06 g. potassium persulfate. For the bottles the amounts of combined monomers were 20 g. except for Run IV when 60 g. was used; proportions of the other ingredients were the same except for 4 g. of soap per 20 g. of monomers in Runs VIII-X. After the containers were filled, they were flushed several times with the gas being used for the reaction medium, then sealed, and placed in a large water bath kept at 40°C. (± 0.2°) and arranged for end-over-end rotation of the containers.

Styrene was separated from inhibitor by alkaline washing, drying, and distillation under reduced pressure immediately before use.

4. *Isolation and Purification of the Polymers.* At the end of the heating period 1 ml. of 1% hydroquinone solution (per 10 g. monomers) was added, and the emulsion was steam-distilled to remove unchanged styrene. It was then coagulated by stirring during slow addition of the latex to methanol containing 1 ml. of conc. hydrochloric acid per 100 ml. The product separated as crumbs, or as a gummy precipitate which became granular on removal of adhering ester by soaking in methanol.

The products were most conveniently purified by solution in dioxane and reprecipitation from methanol, as suggested by Snyder et al. (15). In some cases grinding in methanol and prolonged standing were needed to change a gummy to a powdery precipitate. After the third reprecipitation all the products were obtained in the form of fine white powders, which were dried to constant weight at 60° *in vacuo* before analysis. This procedure was adequate to remove adhering ethyl linoleate as shown by checking the constancy of the iodine values after the second and third reprecipitations on samples from two different runs.

The use of phenyl-β-naphthyl amine as an antioxidant during reprecipitations was discontinued after Run IV because it was found to have a serious effect on the iodine values. A control experiment showed this antioxidant to have an apparent iodine value of about 320. All iodine values reported in the tables were done on samples freed from antioxidant by reprecipitations.

5. *Analyses.* Iodine values of the polymers shown in Tables II and III were determined by the Woburn method (10) using 0.35 N iodine bromide in carbon

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tetrachloride with a chloroform solution of the polymer sample. Data in the tables are the average results of several individual analyses on each sample. The percentage of ester in the polymer was calculated from iodine values on the assumption that if ethyl linoleate copolymerized with styrene, there would be one double bond per ester unit. Hence per cent ester $=$I.V.$\times$100/82.4, where 82.4 is the theoretical iodine value for a polymer that is wholly ester.

TABLE II

Emulsion Polymerization of Styrene in the Presence of Unoxidized Ethyl Linoleate

Run No.[a]	Conj. of ester, %	Time, hr.	Atm.	Iodine value of polymer	Conversion, %[b]
I	35	12	Air	1.2[c,d]	
II	23	16	CO$_2$	2.9[c]	30
III	23	16	Air	1.9[c]	46
IV	40	15	O$_2$	4.3[c]	50
V	24	21	N$_2$	7.6	21

[a] The ester-styrene ratio in parts by weight was 50:50 for all the runs of Table II. [b] Based on total monomers. If the figures for % conversion are based on styrene, all the values should be doubled. [c] In addition to the usual constituents, 0.09 g. of potassium ferricyanide was used per 10 g. of combined monomers. [d] In some samples of Run I dodecyl mercaptan was used, both with and without the ferricyanide. In none of the products was there appreciable unsaturation.

It was found that the ester alone showed no tendency to polymerize when heated without styrene in the emulsion in the presence of oxygen. The only change, as indicated by iodine values, was a slight decrease in total unsaturation.

In the determination of saponification numbers it was necessary to use a 0.5 N solution of potassium hydroxide in 1:1 diethylene glycol-dioxane, and to reflux for five hours. Titration was done with aqueous hydrochloric acid using a pH meter.

6. *Determination of the Yield.* The percentage conversion was determined by heating to constant weight a known portion of the product after precipitation and soaking with methanol. Since it is possible that not all of the unchanged ester or other impurities were removed from the polymers after this one precipitation, the conversion values should be considered as approximate.

7. *Viscosity Determinations.* Viscosities of solutions of the polymers in dioxane, and in some cases in benzene or toluene also, were determined with an Ostwald viscometer at 25°C. ($\pm$ 0.02°). Intrinsic viscosities, [η], found by extrapolating to infinite di-

lution the straight line plot of η_{sp}/c against c, where c is expressed in grams per 100 ml. of solution, are shown in Table III.

Approximate molecular weights (given in Table IV) were calculated on the assumption that the products were entirely polystyrene, and that the equation [η] $=$ KM^a is valid. Ewart's values (17) for K and a were used for the benzene solutions (7.54 $\times$ 10^{-5} and 0.783, respectively), and the values of Goldberg, Hohenstein and Mark (18) were used for the toluene solution (3.7 $\times$ 10^{-4} and 0.62). The number of ester groups per molecule was calculated from the iodine values and the molecular weights.

TABLE IV

Viscosity Average Molecular Weights

Run No.	Ester in monomers,%	[η]	Mol. wt., approx.	Number of ester groups per molecule
VII	50	0.56	88,000	52
IX-A	25	0.92	300,000	35
IX-C	45	0.59	94,000	22

Discussion of Results

The data of Tables II and III show that the ester content of the polymer was higher in those prepared from styrene with oxidized rather than unoxidized ethyl linoleate. None of the polymers from the unoxidized ester had as high a linoleate ester content as 12% or over while four of the products from the oxidized ester did. Whether the greater polymerizing tendency of the oxidized ester is due to the catalytic effect of peroxides formed during the oxidation, or to a greater reactivity of the conjugated form, or to some other cause is not known.

The values from Runs VIII and IX show that increasing the ester content of the monomer mixture up to a certain point raised the percentage of ester in the polymer. The monomer mixture of most favorable composition, 50% ester, which represents an approximately 1:3 molar ratio of ester to styrene gave polymers having a maximum ester to styrene ratio of 1:13.

The yield of polymer was in general decreased by increasing the proportion of ester in the monomer mixture; at a concentration above 50% no solid polymer was formed. Hence the linoleate ester seems to be exerting its well-known inhibitory effect on the polymerization of vinyl compounds (8).

TABLE III

Polymerization [a] of Styrene in the Presence of Oxidized Ethyl Linoleate

Run No.	Conj. of ester, %	Ester in monomers, %	Yield [b] of polymer, %	I.V. of polymer	Composition of polymers % Ester From % Ester	Composition of polymers % Ester From sap. No.	Mols. styrene per 1 mol. ester	Intrinsic viscosity at 25°C.
VI	82	50	....	15	19	18	13	0.19[c]
VII	82	50	....	15	19	....	13	0.47[c], 0.56[d]
VIII								
A	42	25	59	1.9	2.3	....	125	....
B	42	50	20	9.8	12	18	22	....
C	42	60	0[f]	....	....	....	....	....
D	42	75	0[f]	....	....	....	....	....
IX								
A	34	25	63	3.0	3.6	....	78	0.84[c], 0.92[e]
B	34	35	....	6.1	7.4	....	37	0.35[c]
C	34	45	70	6.2	7.5	....	36	0.54[c], 0.59[d]
D	34	50	30	9.5	12	12	23	0.30[c]
X	40	50	36	6.4	7.8	....	35	....

[a] Emulsion polymerization at 40°C. for 18-20 hours except Run VII which was a bulk polymerization heated at 80°C. for 42 hours. An atmosphere of oxygen was used in all runs except VII, done under air and X under nitrogen. [b] Based on total monomers. [c] In dioxane. [d] In benzene. [e] In toluene. [f] No solid product was obtained.

The data of Table III seem to indicate that the ethyl linoleate was acting like a chain transfer agent since the higher the proportion of it in the monomer mixture, the lower the intrinsic viscosity of the polymer formed. This general trend is shown by Run IX even though the 45% mixture is out of order.

Although the ester appears to limit chain length, its action is not solely that of a chain transfer agent. Table IV shows that there are many more ester groups per molecule than to be expected if the linoleate ester functioned as a modifier of the mercaptan type studied by Snyder et al. (15) and by Wall and co-workers (16). These investigators found an average of one modifier group per chain. It is probable that the ester both copolymerizes with the styrene in the normay way and also exerts some modifying action, as suggested by Hewitt and Armitage (5). The tendency to copolymerization is most marked in the case of the bulk polymerization (VII) since the product in this case had a high ester content without a correspondingly low molecular weight.

Summary

The emulsion polymerization at 40°C. of mixtures of oxidized ethyl linoleate and styrene with potassium persulfate as catalyst yielded copolymers containing a maximum of one mole of ester per thirteen moles of styrene. A product of similar composition was obtained by bulk polymerization at 80°C.

When the amount of ester in the monomer mixture was increased to 50 per cent in the emulsion polymerization, the ester content of the polymer was increased and the molecular weight and yield were decreased.

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Studies on Candelilla Wax. II. Its n-Paraffins

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THE traditional methods of isolating wax paraffins, described by Chibnall et al. (1) and Leys (5), are laborious and time-consuming. Both methods require an initial saponification of the wax, which often is very difficult. Moreover, the resulting paraffin fractions are impure and require further purification. For the purpose of isolating the hydrocarbons of candelilla wax required for this investigation, there was developed a simple, rapid chromatographic procedure which eliminates involved treatment of the saponified wax. The method described is suitable for large-scale work and reduces the time required for the isolation of the paraffins to a matter of a few hours.

Isolation Procedure. A column, 14 inches long and two inches in diameter, was packed with activated alumina (Grade F-20, Aluminum Ore Co.). The candelilla wax was dissolved in dry petroleum ether, heating being necessary to dissolve the wax. The cooled wax solution was then drawn rapidly through the column by gentle suction, a yellow band making itself evident. On cooling, the wax solution gelatinized somewhat; this however presented no particular difficulty. After the washing of the column with petroleum ether, the solvent was evaporated from the colorless percolate. A white residue of paraffins was obtained. These, redissolved in petroleum ether, were passed through a fresh column of alumina, after which the recovered paraffins were heated with concentrated sulfuric acid. The fact that very little blackening of the paraffins occurred when isolated by this procedure attested to their purity. After removal of the sulfuric acid by washing with water the dried paraffins were crystallized from petroleum ether whereupon beautiful white crystals were obtained.

The same procedure was used for the quantitative determination of paraffins in this wax. Approximately 50-gram samples were used, the wax solution being passed through only one column of alumina. The paraffins were heated with sulfuric acid although this treatment may be omitted if candelilla samples are to be analyzed as a routine operation. After filtration and washing, the paraffins were brought to constant weight. Excellent checks were obtained; the hydrocarbon content averaged 52.2%.

Separation of Hydrocarbon Fractions. Numerous workers (6, 8) have used adsorption techniques to separate paraffin mixtures. In 1947 Hirschler and Amon (4) found that even geometric isomers of