Peroxide Catalyzed Polymerization of Styrene in Pure Fatty Methyl Esters[1,2]

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IN 1946 Hewitt and Armitage (11) described a process for reacting styrene with drying oils (largely dehydrated castor oil or linseed oil) to produce superior surface coating materials. Based upon their examination or analysis of the reaction products and in analogy with the copolymerization of styrene with butadiene, they proposed a course for this complex process. They emphasized three important points in regard to the process. a) Styrene copolymerizes with the fatty esters containing conjugated unsaturation in the same manner as it does with butadiene (i.e.) by proceeding largely by 1,4 addition across the conjugated double bonds. b) Styrene is also bound to the non-conjugated unsaturated esters. The union occurs through "chain-transfer." The growing chain is terminated by annexing an hydrogen atom from the fatty ester. This hydrogen atom presumably comes from a position α to a carbon-carbon double bond, and its removal leaves a new free radical capable of initiating another chain. c) The molecular weight of polymer or copolymer is lower than that of regular polystyrene because of the modifying action of the fatty esters (1).

Since 1946, many other investigators have published results of studies of this reaction. There is considerable disagreement regarding whether or not the fatty esters are chemically bound to the polystyrene. The entire picture has been made more complex by the variety of conditions under which the reaction has been carried out. Brunner and Tucker (3, 4) heated styrene with tung oil and with dehydrated castor oil in xylol solution at reflux temperatures without catalyst. They separated the polymeric material and examined it by infrared analysis and also by other analytical methods. From the tung oil they obtained a mixture of a) a copolymer comprising about eight styrene molecules for each eleostearate unit and b) a low molecular weight product having a one to one mole ratio of styrene to ester. The latter was believed to result from a Diels-Alder addition of styrene and eleostearate. With the dehydrated castor oil they found no evidence of a combination of polystyrene and fatty ester. Kappelmeier (13) saponified styrenated oils and alkyds, then separated the acidified products by extraction with alcohols of increasing molecular weight. He determined the acid values of the different fractions and concluded that all of the polystyrene was combined with fatty acids. Petit and Fournier (15) studied the products of the styrenation of linseed oil, using benzoyl peroxide as catalyst. They saponified the reaction products and separated the acids from polystyrene. They concluded that there was no combination of polystyrene and oil. Dyer and Maxwell (5) studied the reaction of styrene with the ethyl esters of the acids obtained from dehydrated castor oil. With one exception they carried out the reactions in emulsion, using potassium persulfate as the initiator. On the basis of iodine values of the isolated polymers they concluded that the ethyl esters of dehydrated castor oil acids copolymerized with styrene.

Bezman and Browning (2) studied the reaction of a number of oils with styrene. They also used the emulsion polymerization technique. On the basis of infrared studies of carefully extracted products, they concluded that the presence of conjugated unsaturation in the fatty ester did not assure its copolymerization with styrene. They found that the amount of fatty ester chemically bound to styrene could be increased markedly by thermally polymerizing the oils and blowing them prior to the reaction with styrene. Contrary to the results of Petit and Fournier (15), Schroeder and Terrill (17) found that both raw and blown linseed oil combined with styrene under polymerization conditions. Falkenburg, Hill, and Wolff (7, 8) studied the reaction of styrene with oils as well as with methyl esters of most of the common fatty acids. They concluded that styrene did not copolymerize with the esters and that homogeneity of the product was no criterion of copolymerization.

The work herein described was carried out to determine the effect of each of several different fatty esters on the polymerization of styrene. Equal weights of styrene and fatty ester were mixed and polymerized using benzoyl peroxide as the initiator. By determining the polymerization rate, molecular weight, and composition of polymer, data were gathered which indicate the role of each ester.

Experimental

Materials. Each methyl ester was made by refluxing the fatty acid for 4 hours in 10 times its weight of absolute methanol containing 1% of concentrated sulfuric acid (based on fatty acid) as the catalyst.

Methyl stearate had a saponification value of 188.6 and a capillary m.p. of 39-39.5°C.

Methyl oleate had a saponification value of 191.7 and an iodine value of 84.1 (Wijs).

Linoleic acid was prepared by debromination of 9, 10,12,13 tetrabromo octadecanoic acid. The methyl ester had a saponification value of 194 and an iodine value of 172.5 (Wijs).

t,t 10,12 Octadecadienoic acid was prepared from dehydrated castor oil acids according to the procedure of von Mikusch (14). The methyl ester had a specific α 230 mμ value of 109.1 (theory for 100% conjugation = 109.52).

Methyl ester of alkali conjugated linoleic acid was conjugated by heating it in diethylene glycol with an excess (10% molar) of NaOH over that required for neutralization. The temperature was held at 200° C. for 20 minutes. The methyl ester of the conjugated acids had a specific α value at 234 mμ of 82.3 [theory for 100% conjugation of cis,trans ester==93.04 (12)].

Pure methyl linolenate was obtained from the Hormel Foundation.

The styrene was Dow commercial grade. It was redistilled under vacuum before use.

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Pure benzoyl peroxide was prepared by precipitating it from a chloroform solution by the addition of methanol.

Polymerization. The styrene and esters were polymerized in 1-oz. small-mouth, screw-cap bottles. The bottle caps were equipped with oil resistant sealing gaskets so that a hypodermic needle could be inserted. Periodically a small sample was withdrawn from each bottle through the needle, and the refractive index of the solution was determined. The degree of polymerization was calculated from the change in refractive index. A linear relation between change in index and degree of polymerization was assumed. The bottles were charged with 10 g. of styrene, 10 g. of methyl ester, and 0.2 g. of benzoyl peroxide. One bulk polymerization of 20 g. styrene with 0.4 g. of benzoyl peroxide and one solution polymerization of 8 g. of styrene with 0.16 g. of benzoyl peroxide in 12 g. of benzene were run as controls. The bottles were heated in an oil bath held at 70 ± 0.5°C. No agitation was used because the mixtures were homogeneous.

Separation of Polystyrene. The polymer was separated from unpolymerized materials by two methods. a) The low molecular weight materials were removed by distillation under reduced pressure. b) The polymer was removed by successively precipitating it by pouring its benzene solution into methanol. The first procedure was carried out as follows. The product was placed in a 100-cc. round bottom flask. For stripping an alembic head was attached to the flask, and the system was evacuated to 0.1 mm. with a mechanical pump through a dry ice trap, placed to catch the styrene. The flask was heated in a wax bath, which was raised to 205°C. When the bath temperature reached 205°C., the flask was removed and cooled in air under vacuum.

Each stripped polymer was dissolved in 50 cc. of benzene and the solution was poured into 150 cc. of absolute methanol. The mixture was refluxed for 10 minutes, then left to stand for 16 hours before filtering. The polystyrene was then removed, dried, ground in a mortar, and extracted with 75 cc. of absolute methanol. After separating and drying it was ready for analysis.

The second procedure was as follows. Each polymeric product was diluted with 30 cc. of A. R. benzene. This gave a viscous solution, which was poured into 150 cc. of absolute methanol. The mixture was warmed to reflux for 5 minutes, cooled, and the polymer removed. It was redissolved in 50 cc. of benzene and the precipitation repeated. The polymer was refluxed with 150 cc. of methanol, cooled, separated, and dissolved in 50 cc. of A. R. benzene. The precipitation was repeated as described. The polymer was again dissolved in 50 cc. of benzene and poured into 50 cc. of absolute methanol while shaking the mixture. The polymer separated as a liquid lower layer. This was precipitated by pouring it into methanol. The polymer was dried, ground in a mortar, and extracted at room temperature with 75 cc. of absolute methanol. After separation and drying it was ready for analysis. Analysis showed that there was no significant difference in the composition of the products isolated by the two procedures.

To show that mixtures of polystyrene and fatty esters are actually separable, the following experiment was carried out. Each of the fatty esters was mixed with 1% benzoyl peroxide and heated for 24 hours at 70°C. Each product was mixed with an equal weight of polystyrene dissolved in benzene. The resultant solution was precipitated and extracted in the same manner as described above. Analysis of each of the extracted polystyrenes by infrared analysis showed the presence of no fatty ester in any of the samples.

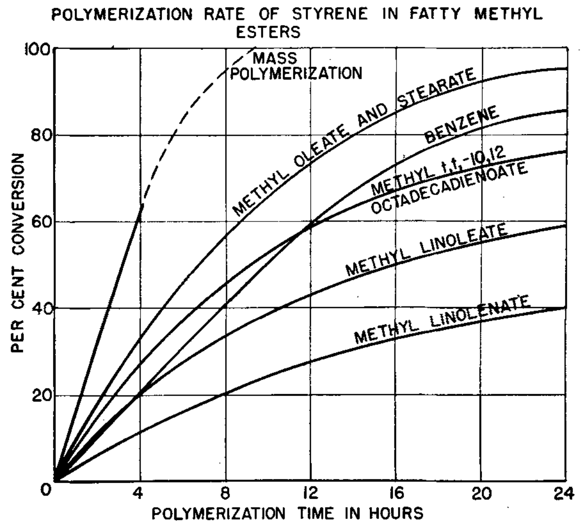

FIG. 1

Molecular Weight of Polystyrenes. About 0.75 to 1% solutions of polymer in A. R. benzene were prepared and filtered through a medium pore size, sintered glass filter. The viscosities were determined, using an Ostwald viscosimeter. The intrinsic viscosities were calculated from the relative vicosities by the method of Tingey (9) and the molecular weight according to the relationship of Ewart (9).

Infrared Analysis of Polymers. The infrared spectra of the styrene polymers were recorded from 2 to 8 μ on a Beckman IR-2 Spectrophotometer equipped with a slit drive (18). The lower frequency band (1725 cm^{-1}) was assigned to the benzoate ester formed from the benzoyl peroxide initiator. The 1740 cm^{-1} band was assigned to the fatty methyl esters. For analytical purposes the polymers were considered to be three component systems consisting of two esters and the polymer.

For the purpose of determining quantitatively the amounts of fatty methyl esters, it was necessary to determine the contribution of the benzoate ester as well as that of the polymer at each frequency. Three compounds were used for this purpose: methyl stearate, methyl benzoate, and polystyrene free of benzoate and fatty ester. The null potentiometer circuit of the IR-2 was used to measure the optical density. The measurements were made only at the two carbonyl frequencies since the contribution of polystyrene was small and constant for samples of the same concentration.

Each sample was dissolved in chloroform and placed in a sealed cell of 1 mm. thickness. The instrument was set precisely at the maximum of the carbonyl band of one of the reference esters. The optical densities of all of the samples were measured at this setting. The instrument was then reset at the absorption maximum of the carbonyl band of the other reference ester, and the densities again measured. The concentration of fatty ester and benzoate present were calculated from two simultaneous equations, involving optical densities, extinction coefficients, and concentration of ester and benzoate.

Results and Discussion

In this work styrene was polymerized in solution in the methyl esters of pure fatty acids. The following three things were determined: a) the polymerization rate of styrene in the different esters, b) the molecular weight, and c) the composition of the polymeric material.

Polymerization Rate. Examination of the curves shown in Figure 1 shows that styrene polymerizes more slowly in the presence of fatty esters than it does in bulk. In the case of methyl stearate and methyl oleate the reduction in rate is about what one would expect as the result of dilution by a solvent. For the polymerization in methyl t,t 10,12 octadecadienoate the rate again is somewhat slower but apparently in the same class as the first two esters. In the case of the polymerization of styrene in methyl linoleate and methyl linolenate it is obvious that these esters are acting in some capacity in addition to that of solvent. The pronounced reduction in rate indicates that one or both of two things are happening. a) Fewer polymer chains are being initiated than in the other faster polymerizations. b) The polymer chains are being terminated at low molecular weight without appreciable chain transfer occurring. If the first process were occurring, the molecular weight of the polymer would be about the same as it was in the other esters. This, of course, is not true if the second process is occurring. It is apparent that knowledge of the molecular weight and composition of the polymer will help in explaining the role these esters play in the polymerization.

Molecular Weight of Polymeric Material. The molecular weight of the polymers obtained in the different esters are given in Table I. These are based on viscosity measurements of benzene solutions of the polymers.

TABLE I

Molecular Weight of Polymers

Polymerization Medium	Molecular Weight
Methyl stearate	39,000
Methyl oleate	39,000
Methyl linoleate	19,000
Methyl linolenate	13,400
Methyl t,t 10,12 octadecadienoate	40,000
Methyl alkali conjugated linoleate	33,000
Benzene	28,000
Bulk	49,000

A comparison of the molecular weight of the polymers prepared in different esters shows that methyl linoleate and methyl linolenate act largely as chain terminators and to only a small extent as chain transfer agents. The molecular weight of the polystyrene obtained in methyl linoleate is roughly one-half that obtained in methyl stearate or oleate. Coincidentally, the polymerization rate in methyl linoleate is slightly greater than one-half that in methyl stearate. Similarly the rate of polymerization and molecular weight of polymer obtained in methyl linolenate is roughly one-third that obtained in methyl oleate or stearate.

The behavior of the methyl esters of the conjugated diene acids was contrary to that which would be expected on the basis of the polymerization of their vinyl and allyl esters (10). The vinyl or allyl t,t 10,12 octadecadienoate ester polymerized slowly to give low molecular weight polymers as did the corresponding esters of linoleic acid. Also 10% of methyl linoleate or methyl t,t 10,12 octadecadienoate added to vinyl stearate retarded its polymerization and reduced the molecular weight of polyvinyl stearate formed about the same amount. Toward styrene the methyl esters of the two acids behave quite differently. The methyl t,t, 10,12 octadecadienoate retards the polymerization only slightly and apparently does not reduce the molecular weight appreciably. The molecular weight in this case may be in error since the constants used in calculating the molecular weight from viscosity measurements are those for polystyrene. As will be seen, this is a copolymer of styrene and methyl t,t 10,12 octadecadienoate.

Analysis of Polymers. Brunner and Tucker (3) used infrared analysis to determine qualitatively the presence of oils combined with polystyrene. Recently Bezman and Browning (2) used this method to determine quantitatively the percentage of oil in polystyrene obtained when styrene and oils were emulsion polymerized.

The results of infrared analysis on samples of polystyrene obtained by polymerizing styrene in the different methyl esters are given in Table II.

TABLE II

Composition of Polymers

Polymerization Medium	Percentage Methyl Ester In Polymer	Percentage Benzoate In Polymer	Number of Fatty Esters Per Polymer Mol.	Number of Benzoate Groups Per Polymer Mol.
Methyl stearate	0.49	.57	.64	1.8
Methyl oleate	1.28	.53	1.7	1.7
Methyl linoleate	4.7	.70	3.0	1.1
Methyl t,t 10,12 octadecadienoate	10.7	.75	14.5	2.5
Methyl linolenate	2.4	.83	1.1	.9
Methyl alkali conj. linoleate	10.8	.38	12.1	1.0
Bulk	....	.64	....	2.6

In considering the analytical results, a question arises about the state of the fatty ester found in the polymer. Is it chemically bound to the polymer, or there as an impurity which was not removed in separating polymer from unpolymerized material? The evidence shows that the methyl ester found in the polymer after the isolation steps is chemically bound to the polymer. Polystyrene which is isolated by the same procedure from mixtures of polystyrene and fatty esters shows no fatty ester on infrared analysis.

It is obvious from an examination of the analytical data that the conjugated fatty esters do not behave in the same manner as the other fatty esters. The percentage of methyl fatty ester found in the polymers polymerized in the conjugated esters is more than twice that of the next highest value. The number of fatty ester molecules per polymer molecule averages 14.5 in the case of the 10,12 methyl ester and 12.1 in the alkali conjugated methyl ester. The best explanation for this is that copolymerization occurred between styrene and the conjugated ester. This copolymerization very likely occurred largely as Hewitt and Armitage visualized it (11), through 1,4 addition to the conjugated double bonds. This is also in partial agreement with the conclusions of Dyer and Maxwell (5) who polymerized styrene with the ethyl esters of dehydrated castor acids in emulsion. In their case it appears questionable that the degree of conjugation is as high as they report for many of the blown esters. In view of the work of Bezman and Browning upon emulsion polymerization (2) it appears that the peroxide formation during blowing was more important in increasing the amount of ester combined in the polymer than was the conjugated unsaturation.

Recently Falkenburg, Hill, and Wolff (8) polymerized styrene in the presence of methyl esters of different fatty acids, including t,t 10,12 octadecadienoic. They concluded that there was no copolymerization between the esters and styrene. Their conclusion was based largely on saponification values of the polymers. We find that saponification values are not satisfactory for determining the proportion of methyl ester present in a polymer of this type. The action of potassium hydroxide in a 90-10-5 benzyl alcohol, methanol, water mixture (9) at reflux for 5 hours results in only partial saponification of the copolymer of styrene and methyl t,t 10,12 octadecadienoate. Infrared analysis showed that 71% of the methyl ester remained unsaponified.

The benzoate groups in the polymer are completely saponified by this treatment. Since this is true, polymers made with high proportions of benzoyl peroxide would be expected to show higher saponification values. In general, this was what was observed by Falkenburg *et al.* (7, 8).

The other unsaturated esters, though not present in a large proportion, are present on the average of one or more fatty ester molecules per polymer chain. In the case of styrene polymerized in the presence of methyl linolenate there are roughly one ester and one benzoate group per polymer molecule. Presence of a benzoate group can be explained on the basis that the benzoate radical initiated the chain by adding to styrene; presence of the linolenate ester can be explained as the result of chain termination by addition of a linolenate radical. The linolenate radical could be formed by loss of a hydrogen atom to a peroxide radical or to a growing polymer chain. The low proportion of linolenate combined with the polystyrene is in agreement with the results of Petit and Fournier (15) but opposed to those of Schroeder and Terrill (17).

The results show that when styrene is polymerized in the presence of methyl oleate and methyl linoleate, about two and three fatty ester groups, respectively, are included in the polymer chain. Though some of these may be combined as the result of the polymer chain involving a double bond in the fatty ester, this does not occur often enough to consider it to be true copolymerization.

On the basis of these results it is difficult to understand the results obtained by Powers (16), who apparently obtained relatively large proportions of oleic and linolenic acids combined with polystyrene by heating mixtures of styrene and the respective fatty acids without catalyst at temperatures ranging from 160 to 275°C. Either the use of fatty acids or high temperatures has a pronounced effect on the course of the reaction. Presumably the high temperatures would be more likely to affect the course of the reaction. This can only be determined by carrying out reactions of styrene with the fatty acids and with the corresponding methyl esters at various temperatures.

According to the results obtained in the polymerization of styrene in the presence of the fatty esters the following conclusions can be reached. a) Styrene does copolymerize with fatty esters which have conjugated unsaturation as Hewitt and Armitage claimed. The proportion of fatty ester copolymerizing is small compared with the proportions in the monomer charge, *i.e.*, a 50-50 weight mixture of styrene and conjugated fatty ester gives roughly a 90-10 ratio of styrene to ester in copolymer. b) The non-conjugated polyene fatty esters behave chiefly as chain modifiers and reduce the molecular weight of the polymer. They do not do this through chain transfer, as Hewitt and Armitage suggested, but largely by a chain termination process. Small proportions of ester are found in the final product. c) The saturated and mono-unsaturated esters behave in a neutral fashion, serving as solvents for the monomer and polymer. Small amounts of the ester are included in the polymer.

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