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The Polymerization of Vinyl and Allyl Esters of Fatty Acids[1a,b]

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This work was undertaken to determine why the vinyl and allyl esters of unsaturated fatty acids polymerize slowly and incompletely. It was found that the polymerization rate decreases as the degree of unsaturation in the fatty ester increases. The esters of the dienoic fatty acids polymerize very slowly, and the degree of polymerization is low. It makes little difference in the polymerization rate whether the double bonds are conjugated or separated by a methylene group. The retardation of polymerization and low degree of polymerization are explained by the reaction of radical initiators and polymer chains with the unsaturation in the fatty acid molecule. These reactions give new radicals which react by radical combination, thereby either robbing the system of initiator radicals or terminating polymer chains.

It has been shown that vinyl and allyl esters of fatty acids polymerize and can be copolymerized with other monomers.[2a,b,3]

In attempting to polymerize the vinyl or allyl esters of the fatty acids obtained from soybean oil or cottonseed oil, however, it was found that the rate of polymerization was low and the reaction ceased when only a fraction of the esters was converted to polymer. When sufficient catalyst was added to attain high conversion, the polymer gelled.

In order to learn more about the cause of the low rate of polymerization, it was decided to study the polymerization of the vinyl and allyl esters of pure representative fatty acids occurring in these oils. The fatty acids chosen were stearic, oleic, linoleic and 10,12-octadecadienoic acids. Though the latter acid is not a component of the oils, it was included to assure a comparison of the retarding activity of conjugated double bonds and double bonds separated by a methylene group. The linoleate ester was believed to be the one responsible for the low rate of polymerization since the acid had been shown to retard peroxide catalyzed polymerizations in other systems.[4,5]

All of the data presented are obtained from mass polymerizations without agitation. The degree of conversion (Figs. 1 and 2) was determined by following the change in refractive index of the solution containing the polymer. A direct relationship between per cent. polymer and refractive index change was assumed. This was verified by making known solutions of polymer in monomer and determining the refractive index. The refractive indices of the monomers and polymers are given in Table I. A small error is introduced because of the decomposition of the catalyst, but this was assumed to be fairly constant in all the polymerizations.

The rate curves shown in Figs. 1 and 2 represent polymerizations carried out at 80° using 2% benzoyl peroxide as initiator. It is evident that the rate of polymerization drops off rapidly as unsaturation increases. Thus vinyl stearate polymerizes very rapidly under these conditions; the rate of polymerization of vinyl oleate is intermediate, whereas those of vinyl linoleate and vinyl 10,12-octadecadienoate are extremely slow. The allyl esters polymerize at rates which decrease in the same order, although the over-all rates are lower than those of the corresponding vinyl esters.

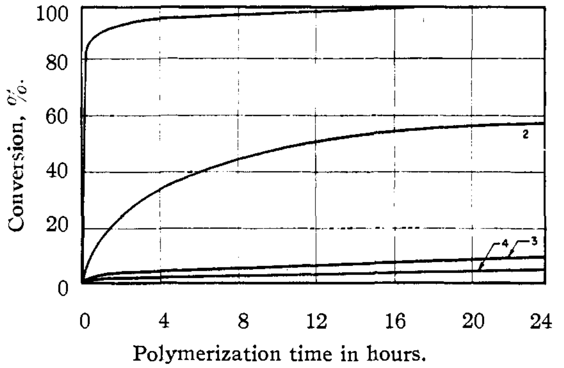

Fig. 1.—Mass polymerization rate of vinyl fatty esters at 80° using 2% benzoyl peroxide: 1, vinyl stearate; 2, vinyl oleate; 3, vinyl linoleate; 4, vinyl 10,12-octadecadienoate.

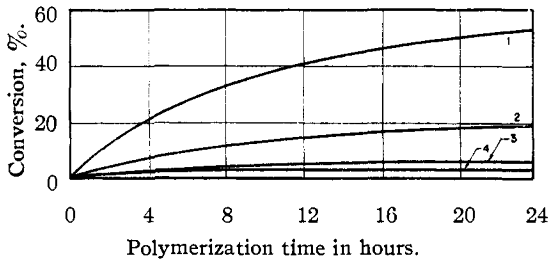

Fig. 2.—Mass polymerization rate of allyl fatty esters at 80° using 2% benzoyl peroxide: 1, allyl stearate; 2, allyl oleate; 3, allyl linoleate; 4, allyl 10,12-octadecadienoate.

TABLE I

Monomer	Refractive index, n^{30}_D Monomer	Polymer	Conversion, %	Intrinsic viscosity, [η]
Vinyl stearate	1.4368[a]	1.4580[a]	85	0.166
Vinyl oleate	1.4539	1.4749	57	.119
Vinyl linoleate	1.4632	1.4877	9	.033
Vinyl 10,12-octadecadienoate	1.4750	1.4897	4	.019
Allyl stearate	1.4367[a]	1.4602[a]	52	.063
Allyl oleate	1.4536	1.4791	19	.058
Allyl linoleate	1.4626	1.4882	5	.041
Allyl 10,12-octadecadienoate	1.4731	1.4888	3	.040

[a] Index taken at 55°.

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[1] (a) Paper No. 102, Journal Series, Research Laboratories, General Mills, Inc. (b) Presented before the High Polymer Forum at the 116th Meeting of the American Chemical Society in Atlantic City, N. J.

[2] (a) Swern, Billen and Knight, THIS JOURNAL, **69**, 2439 (1947); (b) Swern and Jordan, *ibid.*, **70**, 2334 (1948).

[3] Powers, *Ind. Eng. Chem.*, **38**, 837 (1946).

[4] Frank, Adams, Blegen, Deanin and Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).

[5] Wilson and Pfau, *ibid.*, **40**, 530 (1948).

The intrinsic viscosities of the polymers drop in the same order as the rates of polymerization (Table I). That this decrease in molecular weight is not correlated with the extent of conversion is proved (Table II) by the fact that intrinsic viscosities of polyvinyl and polyallyl stearates remained relatively constant, despite the extent to which the polymerization was carried. The low conversions were obtained by interrupting the polymerizations by cooling and shortstopping with hydroquinone.

TABLE II

Stearate	Conversion, %	Intrinsic viscosity, [n]
Polyvinyl	15	0.14
Polyvinyl	27	.160
Polyvinyl	47	.161
Polyallyl	18	.045
Polyallyl	24	.049
Polyallyl	34	.049
Polyallyl	53	.049

Polymerization of Esters of Linoleic Acid.—Previous reports[4,5] describing the retardation of polymerization by linoleic acid have offered no detailed explanation for this phenomenon. Retardation of polymerization leading to lower molecular weight polymers is generally ascribed to the presence of molecules which terminate polymerization by losing labile univalent atoms such as hydrogen or chlorine to the polymer chain, but which at the same time fail to initiate new chains.[6,7]

According to this mechanism, the hydrogens on the active methylene of C_{11} of linoleate would be most readily lost to form a linoleate free radical. This free radical would resonate to the more stable 10,12- and 9,11-forms. These would presumably disproportionate to form conjugated diene and conjugated triene, which would be largely monomeric. The polymeric material would be largely polyvinyl (or polyallyl) linoleate.

Accordingly, polymerizations were made with di-*t*-butyl peroxide (to avoid spectral interference by aromatic structure), and the monomers and polymers were examined by ultraviolet spectroscopy to estimate the amount of normal and conjugated polyene esters.[8]

The polymers were isolated by stripping the monomers *in vacuo* (0.1 mm.) at a maximum temperature of 200°, and extracting the residue repeatedly with methanol. Data on the polymerizations are given in Table III.

TABLE III

POLYMERIZATION OF LINOLEIC ESTERS

Linoleate	% DTBP[9]	Polym. temp., °C.	Polym. time, hr.	Conversn.,[10] %	Intrinsic visc. [n][11]	Methanol sol.[12]
Vinyl	3	130	24	20.5	0.034	70.0
Allyl	3	130	24	21.0	.043	62.0

The spectral analyses of the extracted polymers and of the methanol extract of the stripped polymers are given in Table IV.

TABLE IV

SPECTRAL ANALYSIS OF LINOLEIC POLYMERS

Material	Specific α at 234 mμ Before isom.	Specific α at 234 mμ After isom.	Norm. ester, %[13]	Conjugated ester,[13] %	Remainder, %
1 Polyvinyl linoleate	15.3	48.3	41.2	19.2	39.6
2 Methanol extract of 1	32.2	51.6	22.3	37.0	40.7
3 Polyallyl linoleate	17.5	32.2	19.3	23.0	57.7
4 Methanol extract of 3	29.9	45.0	17.4	34.3	48.3

Spectral analyses of the recovered monomers from the vinyl and allyl ester polymerizations showed that there were no appreciable amounts of conjugated esters in them. The recovered monomers were essentially the same as the original ones.

These facts are contrary to those expected according to the previous discussion of chain termination by hydrogen from C_{11} methylene group. These facts and others to follow are more reasonably explained by assuming reactions of the double bonds of linoleate during the polymerization. These are the reactions which involve the double bonds in the linoleic ester molecule. For example, 40% of the vinyl and 50% of the allyl linoleate polymer do not have either the normal double bonds (separated by a methylene group) or conjugated double bonds. It appears unlikely that the linoleic ester has isomerized under the conditions of polymerization to give an isomer with double bonds separated by two or more methylene groups which would not be detected by spectral analysis. A more reasonable explanation would be that the double bonds in the linoleic esters have taken part in the polymerizations. They could do this by adding to and/or by being added to by other double bonds. If, for example, a copolymerization took place between the vinyl or allyl group of one molecule and the 9,10- or 12,13-unsaturation of another, the copolymer formed would have esterified β-hydroxyethyl groups on one of the carbons 9, 10, 12 or 13 of the copolymerized linoleate. Hydrolysis of such a copolymer would give acids or polyacids with free hydroxyl groups, whereas a straight vinyl or allyl polymer would give the linoleic acid plus polyvinyl or polyallyl alcohol.

To determine whether copolymerization of the above type occurred, samples of the extracted polymers were hydrolyzed and the acids were carefully washed with water to remove any polyvinyl or polyallyl alcohols. The resulting acids were re-esterified with methanol and the hydroxyl content was determined. The results are shown in Table V.

TABLE V

HYDROXYL CONTENT OF HYDROLYZED POLYMERS

Polymer	Hydroxyl number	Ester molecules per hydroxyl group
Vinyl linoleate	56	3
Allyl linoleate	56	3

These results definitely show the presence of hydroxyl groups in the hydrolyzed polymer. These

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(6) Mayo, THIS JOURNAL, **65**, 2324 (1943).

(7) Cuthbertson, Gee and Rideal, *Proc. Roy. Soc.* (*London*), **A170**, 300 (1939).

(8) Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.*, **15**, 1 (1943).

(9) DTBP = di-*t*-butyl peroxide.

(10) Based on stripped polymer.

(11) Intrinsic viscosity of extracted polymer.

(12) Per cent. of stripped polymer soluble in methanol.

(13) These calculations are made on the basis of a specific α value of 87.1 for isomerized pure linoleic acid.

could have occurred only as a result of copolymerization of the vinyl or allyl groups with the unsaturation in the acid.

Consideration of the apparent low molecular weight of the polymer, the presence of hydroxyl groups in the oil-soluble portion of the hydrolyzed polymer, the disappearance of normal double bond configuration in the linoleic ester during the polymerization led to the proposal of the following reactions to account for these phenomena.

The free radicals formed by the decomposition of the peroxide initiator can react with the ester in a number of ways. Different peroxides will not necessarily undergo all of the reactions or any of the reactions to the same degree. There are three places in the monomer where the initiator radical can add. These positions are the 9 and 12 double bonds of the linoleate and the vinyl or allyl groups. If the new radicals formed by these additions all added readily to other double bonds, there would be no effect on polymerization rate or molecular weight of polymer. Of these radicals only the one formed by addition to the allyl or vinyl group adds readily to another double bond to propagate the chain. The radicals formed by addition to the 9 and 12 double bonds are not active in this manner. Instead, they react largely by combination with other radicals and in doing so terminate two potential polymer chains. Similarly to the initiator free radical, a free radical from a growing allyl or vinyl chain may react with the 9 or 12 double bond, resulting in ultimate chain termination.

Initiator free radicals can also remove a hydrogen from the 11 carbon atom of some linoleate molecules. The radical formed by the removal would have the 9,11- and 10,12-conjugated radicals as limiting resonance structures. These radicals do not disproportionate but couple to give dimers or combine with other radicals to terminate polymer chains. They are responsible for the conjugated material found in the polymer and especially in the methanol extract (Table IV). The net effect of these reactions is to decrease the number of polymer chains initiated and to terminate those that do start at relatively low degrees of polymerization.

Polymerization of Esters of 10,12-Octadecadienoic Acid.—The curves in Figs. 1 and 2 show that the corresponding esters of linoleic acid and 10,12-octadecadienoic acid polymerize at similar rates. Viscosity measurements (Table I) show that the molecular weights of the polymers are of the same order. This would lead one to believe that the two types of esters behave in much the same way on polymerization.

To determine whether or not this is true, the vinyl and allyl esters of 10,12-octadecadienoic acid were polymerized and the polymers were isolated and examined in the same way the linoleic esters were. The data for the polymerizations are given in Table VI, and the results of spectral analysis of the polymers are given in Table VII. The spectral analysis on the recovered monomers showed them to be unchanged.

TABLE VI

POLYMERIZATION OF 10,12-OCTADECADIENOATE ESTERS

Monomer	% DTBP[9]	Polym. temp., °C.	Polym. time, hr.	Conversn.,[10] %	Methanol[12] %	Intrin.[11] visc., [n]
Vinyl 10,12-octadecadienoate	6	130	45	47.4	30	0.085
Allyl 10,12-octadecadienoate	6	130	45	49.3	29	.060

TABLE VII

SPECTRAL ANALYSIS OF 10,12-OCTADECADIENOATE ESTER POLYMERS

10,12-Octadecadienoic ester	Specific α at 231 mμ	Conjugated,[14] %
1 Vinyl	28.9	29.2
2 Allyl	28.3	29.9

The data show that vinyl or allyl 10,12-octadecadienoate polymers retain only about one-third of the original conjugation. Thus, on the average, about two-thirds of the molecules in the polymers are combined through the conjugated double bonds of the esters.

A check on the hydroxyl content of the hydrolyzed, washed and re-esterified polymers showed about the same hydroxyl content as found in the linoleate polymers treated in the same manner. Compare results in Tables V and VIII.

TABLE VIII

HYDROXYL CONTENT OF HYDROLYZED POLYMERS

10,12-Octadecadienoate	Hydroxyl no.	Ester molecules per hydroxyl
Vinyl	47.6	4
Allyl	53.5	3+

All the data show a parallelism between the polymerization of the linoleic esters and the 10,12-octadecadienoic esters. Therefore, the reactions involved under polymerization conditions must be similar. The following outlined reactions are given with this point of view in mind. The initiator radical may add 1,4 or 1,2 to the conjugated double bonds. It may also add to the vinyl or allyl group. The new radicals formed by these additions behave in the same manner as described for the linoleic esters with the exception that there is a little more polymerization through the conjugated unsaturation than there is through the unconjugated unsaturation.

The initator free radicals can also remove a hydrogen from either the 9 or 14 carbon to give free radicals of conjugated and non-conjugated resonance hybrids. These radicals behave as described for the similar radicals formed from the normal linoleic esters.

Polymerization of the Esters of Oleic Acid.—The products of polymerization of the vinyl and allyl esters of oleic acid were not studied as fully as those of the dienoic acids. Since both the rate of polymerization and molecular weight of the polymer of the oleic esters is lower than those of the corresponding stearic esters, it follows that the former behave, under polymerization conditions, in a manner similar to the esters of the dienoic acids but to a much smaller degree. Thus, oleic ester can add peroxide radical or chain polymer

(14) Calculated on the basis of specific alpha values of 99 for 1, and 95 for 2.

radical at the 9,10-position. The radical formed by this addition does not add readily to the 9,10-position in another oleic ester; however, it will add to another vinyl or allyl group. This latter addition is slow enough so that it must compete with the combination of the radicals, which results in chain termination and products of lower molecular weight. Therefore, the oleic ester acts as a weak modifier in the mass polymerization system. It is a much weaker modifier than the linoleic or 10,12-octadecadienoic esters. The modifying action of the oleic ester would explain the rather anomalous observation of Swern, Billen and Knight[2a] who obtained soluble vinyl or allyl-vinyl acetate copolymers when large proportions of the higher molecular weight monomer was used and insoluble copolymers when small proportions were used.

Experimental[15]

Fatty Acids.—Eastman Kodak Co. white label stearic acid was used without further purification.

Pure oleic acid was prepared from the Mallinckrodt U.S.P. product. The methyl esters were fractionated in a Podbielniak column. The C_{18} fatty ester cut was hydrolyzed and the free acids were recrystallized twice from acetone at −40 to −45° using a 12/1 ratio of solvent to fatty acids.

Anal. Calcd. for $C_{18}H_{34}O_2$: acid number, 198.7; iodine number, 89.91; linoleic acid, 0%. Found: acid number, 200,[16] 198.4[17]; iodine number, 88.4,[16] 88.7[17]; linoleic acid, 1.0%,[16] 0.4%.[17]

Linoleic acid was made by the bromination of cottonseed fatty acids, separation and purification of the alpha-tetrabromide which was debrominated in absolute ether by the method of Frankel and Brown.[18]

Anal. Calcd. for $C_{18}H_{32}O_2$: acid number, 200.1; iodine number, 181.1. Found: acid number, 201.5; iodine number, 180.9; $n^{30}\mathrm{D}$ 1.4656.

trans-trans-10,12-Octadecadienoic acid-1 was prepared from dehydrated castor oil acids according to the method of Von Mikusch.[19] An acid melting at 56–57° was obtained which had a specific alpha value of 111 at 231 mμ.

Vinyl Esters.—The vinyl esters were made by the method of Toussaint and MacDowell.[20]

Vinyl stearate possessed constants in agreement with those reported by Swern and Jordan[3]: m.p. 36.5–37°; iodine number, 79.3.

Vinyl oleate boiled at 147–148° at 4 mμ; $n^{30}\mathrm{D}$ 1.4539; iodine number, 160.5, in agreement with the product of Swern, Billen and Knight.[2]

Vinyl linoleate had the constants: boiling range 148–150° at 0.75 mm., $n^{30}\mathrm{D}$ 1.4632.

Anal. Calcd. for $C_{20}H_{34}O_2$: iodine number, 248.6; C, 78.43, H, 11.19. Found: iodine number, 249.3; C, 78.20; H, 11.49.

Vinyl 10,12-octadecadienoate had the constants: boiling range 145–149° at 0.4 mm.; $n^{30}\mathrm{D}$ 1.4750; spα_{231} 98.5.

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.43: H, 11.19. Found: C, 78.55; H. 11.06.

Allyl Esters.—The allyl esters were prepared by the azeotropic method[2] from allyl alcohol and the fatty acids.

Allyl stearate had constants similar to the one reported by Swern and Jordan[2b]: $n^{30}\mathrm{D}$ 1.4457; saponification number 173.1; iodine number, 78.4.

Allyl oleate had properties which agreed with those reported by Swern, *et al.*,[2] $n^{30}\mathrm{D}$ 1.4536; saponification number, 177.2; iodine number, 155.0.

Allyl linoleate boiled at 148–150° at 0.1 mm.; saponification number, 181.1; iodine number, 234.5; $n^{30}\mathrm{D}$ 1.4626.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.31. Found: C, 78.64; H, 11.57.

Allyl 10,12-octadecadienoate boiled at 154° at 0.08 mm.; $n^{30}\mathrm{D}$ 1.4731; saponification number, 176.1; specific α_{232}, 95.2.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.31. Found: C, 78.63; H, 11.23.

The polymerizations were carried out in one-ounce screw-cap bottles equipped with oil resistant gaskets and perforated caps so that small samples could be removed with a hypodermic syringe without opening the bottles. The bottles were heated by suspending them in an oil-bath maintained at the desired temperature ±0.50°.

Viscosity measurements were made on solutions of about 0.6 to 1.0% concentration using Ostwald viscosimeters. The polymers were dissolved in benzene and 10 cc. of solution was used in each determination. The viscosities were determined at 30 ± 0.02°. The intrinsic viscosities $[n]$ were calculated from the expression

$$n = \ln (t/t_0)/C$$

where t = flow time of polymer solution; t_0 = flow time of benzene; C = concentration in grams of polymer per 100 cc. of solution.

Spectral Analyses.—The spectral analyses were done using a Beckmann Photoelectric Quartz Spectrophotometer, Model DU.

Acknowledgment.—We wish to express our appreciation to Dr. J. W. Opie, who did the initial work on this problem, and to Mr. H. M. Boyd for carrying out the spectral analyses.

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[15] All melting points are uncorrected; microanalyses by James Kerns.

[16] Used in the preparation of vinyl ester.

[17] Used in the preparation of allyl ester.

[18] Frankel and Brown, THIS JOURNAL, **65**, 415 (1943).

[19] Von Mikusch, *ibid.*, **64**, 1580 (1942)

[20] Toussaint and MacDowell, U. S. Patent 2,299,862.