Polymerization, Copolymerization, and Isomerization

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EACH of the three topics which are the title of the paper could easily require an hour's discussion. However they have a rather direct bearing on each other, and I shall discuss them primarily in relation to one another. First, it is always proper to define the terms. Polymerization reactions are intermolecular combinations which are functionally capable of proceeding indefinitely and thus may theoretically lead to molecules of unlimited size. Naturally, copolymerization is the same kind of reaction but at least two members of the same or different series of compounds are involved. Isomerization is a reaction which effects a change in physical or chemical properties without changing the molecular formula.

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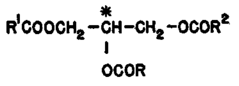
Isomerization

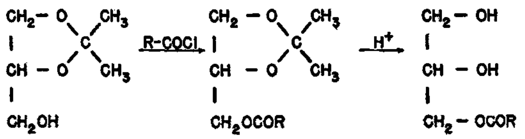
Although triglycerides of fatty acids found in natural oils are not ordinarily considered to be optically active unless they have an asymmetric carbon in the fatty acid chain, a properly substituted glyceride molecule does have an asymmetric carbon. In Formula I the asymmetric carbon of the glycerol part is marked with an asterisk.



$$\mathrm{R^1COOCH_2-\underset{\underset{\displaystyle OCOR}{|}}{\overset{*}{C}H}-CH_2-OCOR^2}$$

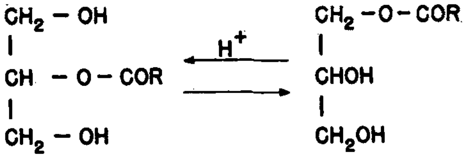
I

When R^1 and R^2 are different, the β-carbon of the glycerol becomes asymmetric. I know of no example in vegetable oils where this type of molecule has optical activity. Optically active monoglycerides can be prepared from d-acetonyl glycerol (II). Treatment of II with a fatty acid chloride, such as stearoyl chloride, and subsequent acid hydrolysis give an optically active monoglyceride. This monoglyceride on treatment with a different fatty acid chloride, such as palmitoyl chloride, gives an inactive triglyceride. Treatment of III with an aromatic acid chloride does give an optically active triglyceride (3).

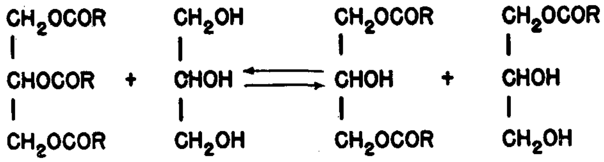


II III

For some time it has been known that dilute acid or alkali will isomerize a 2-monoglyceride to a 1-monoglyceride. However it was demonstrated recently that the 1-monoglyceride is actually in equilibrium with the 2-monoglyceride in the presence of dilute acid or alkali at room temperature. A 9 to 1 ratio in favor of the 1-monoglyceride results (17).



If the conditions are more drastic, such as an alkaline catalyst at higher temperatures, a random arrangement of the fatty acid radicals is effected, which is similar to the results of treating a triglyceride with glycerol. Thus when a mole of additional glycerol is reacted per mole of triglyceride, approximately 50% of the hydroxyl groups are esterified.



The mole percentages of the reactants at equilibrium are approximately 13 free glycerol, 37 each of mono- and diglycerides, and 13 triglycerides at the random pattern expected (13). Results obtained with four different amounts of glycerol are shown in Table I.

TABLE I

Mono- and Diglycerides from Cottonseed Oil
200°C. for 5 Hours

Hydroxyl Esterified, %	50	41	31	23
Mole %				
Free glycerol	12	22	34	46
Monoglyceride	37 (28)[a]	42 (39)[a]	42 (49)[a]	40 (62)
Diglyceride	37 (45)	27 (44)	21 (44)	13 (36)
Triglyceride	14 (27)	8 (18)	3 (7)	0.5 (2)

[a] Percent by weight of fatty material.

Now isomerization in the glyceride molecule is not limited to monoglycerides. Triglycerides can be readily isomerized from a given configuration to a random configuration. This isomerization is somewhat more complex than the isomerization of a monoglyceride, but concentration of a single pure triglyceride in the isomerization mixture can be readily calculated. For example, a fat containing 0.5 mole of linolenic acid would have 0.125 mole of trilinolenin. If the acids in a fat were only stearic and oleic acids, the amount of the different glycerides present would be represented by the expression $S^3 + 3S^2O + 3SO^2 + O^3$, where S and O are the mole fractions of stearic and oleic acids, and $3S^2O$ is the amount of the distearoglycerides present, etc. This type of isomerization is important in industrial fats. The characteristics of shortening fats can be considerably changed by treatment with an ester interchange catalyst, such as sodium methoxide. If this reacting system is fractionated without destroying the catalyst, then a comparatively pure glyceride can be separated from a fat containing a mixture of glycerides. Thus far, only necessarily slow low-temperature procedures have been perfected (12) for

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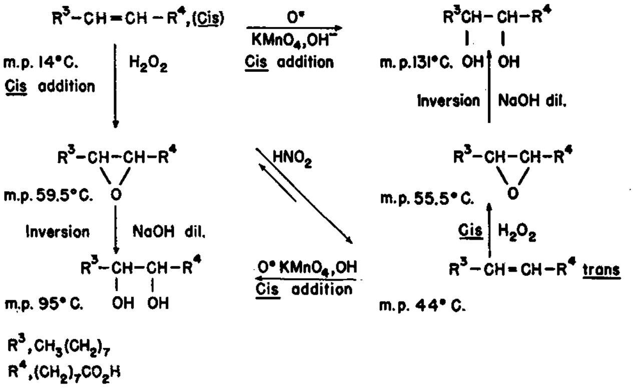
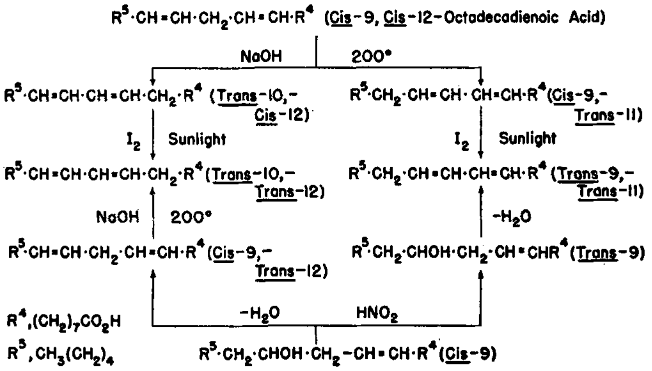
effecting fractionation of triglycerides when the interchange reaction is progressing. If a rapid economic method of segregation and exchange is found, a major step in the conversion of fats to chemical raw materials may be achieved. Uniform products are necessary for building blocks in new materials or for new chemical intermediates.

Isomerization in fatty acids is a particularly difficult subject to study experimentally. Perhaps the best illustration of that difficulty is the various inversions which occur when a simple fatty acid, such as oleic and its *trans* isomer elaidic acid, undergoes chemical oxidation. Oleic acid can be converted to elaidic acid by use of catalysts such as nitrous acid. The reactions which actually occurred during the oxidation of oleic and elaidic acids and the products formed were subjects of controversy for many years. The following equations show a few of the changes that occur and illustrate the ease with which configurations can change (21):



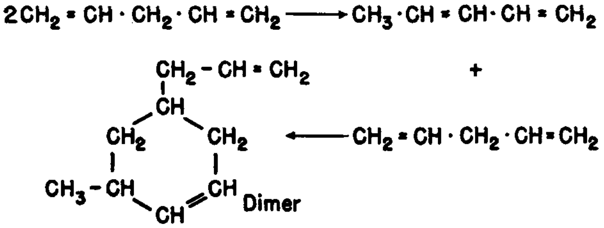
Naturally the *cis-trans* isomerization is still more complex in the octadecadienoic acids. This problem also resulted in some differences of opinion among chemists. Indeed all the experimental problems have not yet been solved. The following equations show the different isomeric, conjugated octadecadienoic acids which have been isolated and identified (18):



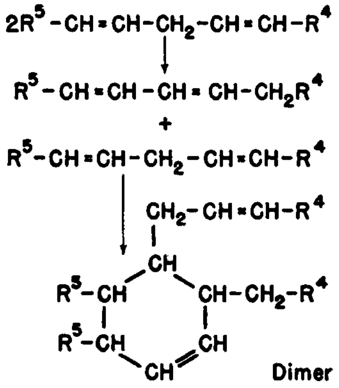
Linoleic acid is converted by alkali at 200°C. to a mixture of *cis* and *trans* isomers. The double bond which moves presumably goes predominantly to the *trans* form. Indeed, if any *cis, cis*-conjugated linoleic acid exists, it has not been isolated. The double bond which has not moved in the alkali isomerization can be converted to the *trans* form by iodine and sunlight. These same isomeric 9,11- and 10,12-*trans, trans* forms can be obtained from ricinoleic and ricinelaidic acids by isomerization and dehydration.

Polymerization

The reactions involved in heat polymerization of drying oils have for the most part been clarified. Nonconjugated linoleic and linolenic acids are isomerized at the high bodying temperatures to conjugated derivatives. These conjugated derivatives react with nonconjugated derivatives to give dimeric products. The original basis for the belief that this type of condensation occurred was the work done by Farmer (1) on the polymerization of 1,4-pentadiene. This diolefin isomerizes at relatively low temperatures to give 1,3-pentadiene. The conjugated isomer reacts as a typical diene in the Diels-Alder reaction and reacts predominantly with the double bond of the unconjugated isomer:



Similarly the accepted mechanism for the polymerization of a dimeric fat product involves a shift of double bonds and probably a *cis-trans* isomerization:



For this reaction of linoleate Wheeler (25) has summarized the evidence as follows:

1. In studies with methyl linoleate, conjugation rapidly rises during heat polymerization to a fairly low concentration, 5-7 percentage. Chances of collision of a conjugated with a nonconjugated linoleate are consequently much greater than chances of collision between two molecules of conjugated linoleate.

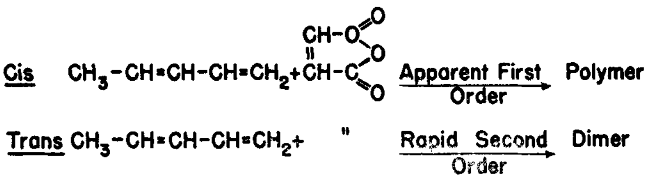
2. Rate studies on mixtures of conjugated with nonconjugated linoleate show that the two do react with one another.

Studies with *cis-trans*-conjugated linoleates and *trans-trans*-conjugated linoleates indicate that further isomerization reactions may be involved. These studies may be summarized as follows:

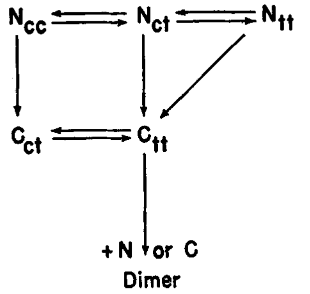
Cis-Trans-Linoleate $\xrightarrow{\Delta}$ Dimer -- First Order Reaction

Trans-Trans-Linoleate $\xrightarrow{\Delta}$ Dimer -- Second Order Reaction

Apparently *cis-trans*-conjugated linoleate isomerizes to *trans-trans*-conjugated before the diene reacts in the Diels-Alder reaction. These data are in agreement with the information available on the Diels-Alder reaction of simple conjugated olefins (10).



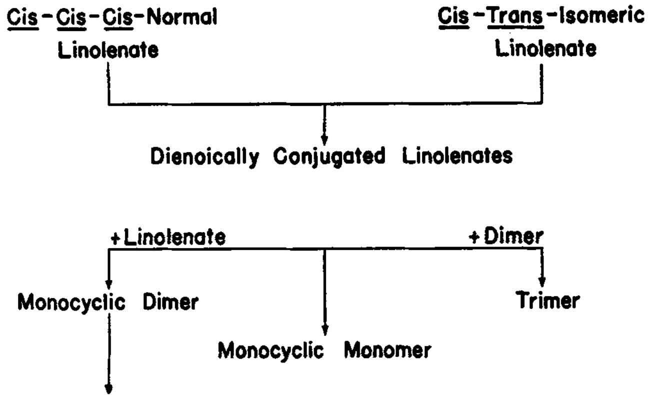
Thus the polymerization of nonconjugated linoleate may be summarized as a complex reaction involving isomerization to *cis-trans*-conjugation, to *trans-trans*-conjugation, and finally a Diels-Alder reaction primarily between the nonconjugated linoleate and the *trans-trans*-conjugated linoleate. Incidentally *trans-trans*-nonconjugated linoleate does polymerize somewhat more readily than the *cis-cis*-nonconjugated linoleate. The following schematic diagram summarizes the reactions which occur where N stands for pentadiene-nonconjugated isomers, C stands for butadiene-conjugated isomers, and small c and t denote *cis* and *trans* forms:



Although the diene part of an acyclic chain involved in a Diels-Alder reaction apparently must be a *trans-trans* form in order to react readily, the dienophile, such as maleic or fumaric acid, can have either *cis* or *trans* configuration. Consequently there is no apparent choice between the nonconjugated linoleates regarding reactivity as dienophiles. However conjugated linoleates of *cis-trans* isomerism would be much more active dienophiles than the nonconjugated forms.

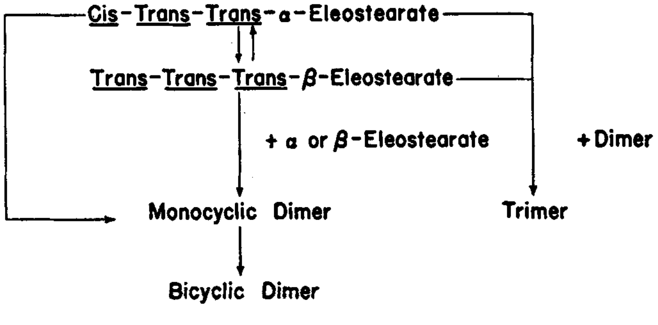
The formation of trimeric fatty acids from dimeric fatty acids most likely occurs by a reaction of the dimer with a conjugated linoleate. However the unsaturation as measured by iodine value suggests that some other mechanism may be effective. The iodine values of dimers and trimers from non-conjugated linoleates are approximately equal, indicating that the loss in unsaturation in going from dimer to trimer was not comparable to the loss of unsaturation which occurs when the dimer is formed (9).

The polymerization of trienoic acid proceeds in a manner similar to but not identical with that of the dienoic. More isomeric forms are possible and the products differ in structure, but the reactions involved, *i.e.*, isomerization to conjugation and from *cis* to *trans* forms, are undoubtedly similar in nature. The products differ in their structure because monocyclic dimers are formed from linoleates and bicyclic dimers are formed from the trienoic acids, and incidentally a monomeric cyclic derivative is obtained, or derivatives which do not hydrogenate to stearic acid (24). The polymerization reactions of the nonconjugated trienoic acid are summarized in the following schematic diagram:



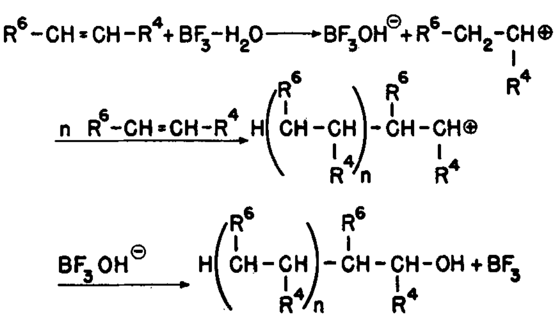
Normal linolenate when heated to high temperatures probably isomerizes to give *cis-trans*-nonconjugated linolenates and conjugated linolenates in which both 2 and 3 double bonds are conjugated. These conjugated derivatives react with nonconjugated linolenates to give a monocyclic dimer which rearranges to give a bicyclic dimer. The dimeric product reacts with the conjugated linolenate to give a trimer. Some monomeric cyclic derivative is formed from the linolenate containing either 2 or 3 double bonds in conjugation, whereas, in the polymerization of linoleates without catalyst the dimeric products predominate, trimeric products are much higher in the polymers of the linolenates if any prolonged polymerization is carried out (9, 19).

The eleostearates, or conjugated trienoic acids, behave somewhat similarly to the nonconjugated trienoic, but the reaction is much faster. The reactions which occur in heat polymerization can be summarized as follows:



Incidentally recent work has confirmed the 9,11,13-*cis-trans-trans*-configuration for α-eleostearic acid and 9,11,13-*trans-trans-trans*-configuration for β-eleostearic acid (6). Also a monocyclic dimer containing conjugated *trans-trans* bonds (8) and a monocyclic monomer (24) have been found.

Ionic Polymerization. Boron trifluoride, hydrogen fluoride, and other catalysts will polymerize unsaturated fatty acids or esters to dimer, trimer, and probably higher polymeric products. Ionic catalysts would be expected to give different products from thermal polymerization which involves a Diehl-Alder addition reaction. However little information is available on mechanism of fatty acid or ester polymerization with these ionic catalysts. The properties of the products and theoretical considerations suggest the following reactions (11):



$$R^6\text{-}CH{=}CH\text{-}R^4 + BF_3\text{-}H_2O \longrightarrow BF_3OH^{\ominus} + R^6\text{-}CH_2\text{-}\underset{\substack{|\\ R^4}}{CH}{}^{\oplus}$$

$$\xrightarrow{n\ R^6\text{-}CH=CH\text{-}R^4} H\left(\overset{\substack{R^6\\ |}}{CH}\text{-}\underset{\substack{|\\ R^4}}{CH}\right)_n\text{-}\overset{\substack{R^6\\ |}}{CH}\text{-}\underset{\substack{|\\ R^4}}{CH}{}^{\oplus}$$

$$\xrightarrow{BF_3OH^{\ominus}} H\left(\overset{\substack{R^6\\ |}}{CH}\text{-}\underset{\substack{|\\ R^4}}{CH}\right)_n\text{-}\overset{\substack{R^6\\ |}}{CH}\text{-}\underset{\substack{|\\ R^4}}{CH}\text{-}OH + BF_3$$

$n = 1$ to 5

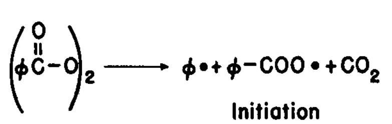
$R^6 = CH_3(CH_2)_4\text{-}CH = CH\text{-}CH_2\text{-}$

Ionic catalysts have not been used much in either polymerization or copolymerization of drying oils because dark brown products are obtained. Consequently they are not of general interest to the protective coating industry.[2]

Copolymerization

Copolymerization of fatty molecules with a variety of materials has attracted a lot of interest commercially during the past 20 years. This interest has been primarily directed toward the preparation of new materials suitable for protective coatings. One of the most controversial subjects in copolymerization is the reaction of styrene with fatty products. Before proceeding to discuss this subject, I believe it would help to briefly review the polymerization of styrene (2).

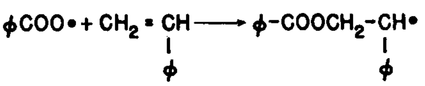
Styrene undergoes additional polymerization by a free radical or ionic mechanism. Let us direct our attention to the free radical mechanism because it is more important industrially and is directly related to our subject. A typical initiator of polymerization is benzoyl peroxide which dissociates to form benzoyl and phenyl free radicals.



$$\left(\phi\overset{\substack{O\\ \|}}{C}\text{-}O\right)_2 \longrightarrow \phi\bullet + \phi\text{-}COO\bullet + CO_2$$

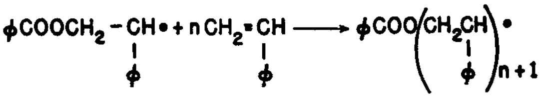
Initiation

These free radicals react with styrene molecules to give an adduct.



$$\phi COO\bullet + CH_2 = \underset{\substack{|\\ \phi}}{CH} \longrightarrow \phi\text{-}COOCH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\bullet$$

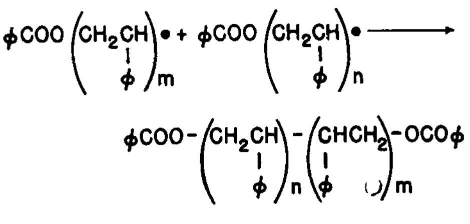
This adduct is a free radical and reacts rapidly with many styrene molecules to form a long chain.



$$\phi COOCH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\bullet + nCH_2{=}\underset{\substack{|\\ \phi}}{CH} \longrightarrow \phi COO\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_{n+1}\bullet$$

Propagation

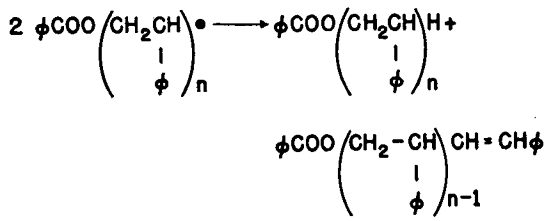
Now this reaction, or propagation, is functionally capable of proceeding indefinitely as necessary by definition. However other reactions occur which cause cessation of this propagation reaction. Cessation or termination reactions in the polymerization of vinyl compounds can occur in a number of ways. For example, coupling or disproportionation may occur.



$$\phi COO\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_m\bullet + \phi COO\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_n\bullet \longrightarrow$$

$$\phi COO\text{-}\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_n\text{-}\left(\underset{\substack{|\\ \phi}}{CH}CH_2\right)_m\text{-}OCO\phi$$

Coupling

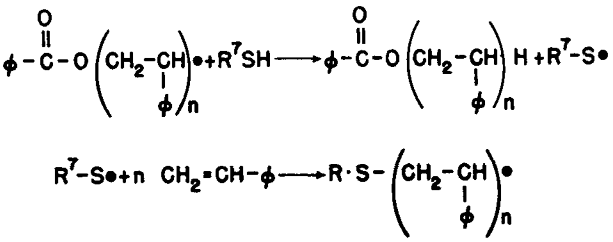


$$2\ \phi COO\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_n\bullet \longrightarrow \phi COO\left(CH_2\underset{\substack{|\\ \phi}}{CH}\right)_n H +$$

$$\phi COO\left(CH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\right)_{n-1}CH = CH\phi$$

Disproportionation

Now cessation or terminating reactions can and do occur readily with molecules other than the propagating chains. Solvent molecules, such as benzene or toluene, or modifiers deliberately added to reduce molecular weight such as dodecyl mercaptan, and molecules such as methyl linolenate can react to terminate these growing chains. One major difference between dodecyl mercaptan and methyl linolenate is that the mercaptan acts primarily as a chain transfer agent and the linolenate does not.



$$\phi\text{-}\overset{\substack{O\\ \|}}{C}\text{-}O\left(CH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\right)_n\bullet + R^7SH \longrightarrow \phi\text{-}\overset{\substack{O\\ \|}}{C}\text{-}O\left(CH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\right)_n H + R^7\text{-}S\bullet$$

$$R^7\text{-}S\bullet + n\ CH_2{=}CH\text{-}\phi \longrightarrow R\cdot S\text{-}\left(CH_2\text{-}\underset{\substack{|\\ \phi}}{CH}\right)_n\bullet$$

$R^7 = C_{12}H_{25}\cdot$

Butadiene and other conjugated dienes polymerize readily with conjugated monomers such as styrene and acrylonitrile. Incidentally nonconjugated vinyl monomers also readily copolymerize with one another but do not copolymerize readily with conjugated monomers (2).

Now let us consider what is known about the copolymerization of styrene with fatty esters. Harrison and Tolberg (15) recently reported on the polymerization of styrene with pure fatty derivatives and have clarified most of the so-called mysteries of styrene copolymerization with fatty molecules. Styrene polymerization was initiated by benzoyl peroxide with a number of pure fatty esters under comparable and controlled conditions. Results are summarized in Table II. Methyl stearate and oleate behave as solvents for the polymerization reaction with some transfer reactions occurring which reduced slightly the molecular weight. Slightly more methyl oleate was combined in the polymer than methyl stearate, indicating some difference in reactivity of the two esters toward

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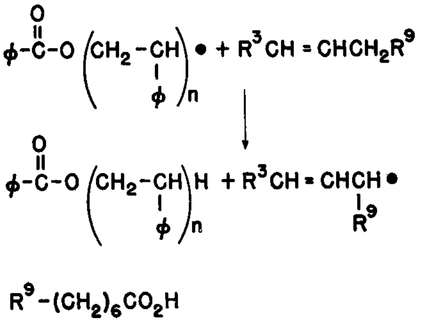
[2] At the Short Course it was disclosed that bodied oils of good color obtained by polymerization with ionic catalysts are available commercially.

TABLE II

Copolymerization of Styrene

Solvent	Molecular weight	No. of fatty esters per molecule
Methyl stearate	39,000	0.64
Methyl oleate	39,000	1.7
Methyl linoleate	19,000	3.0
Methyl tt 10,12-octadecadienoate	40,000	14.5
Methyl linolenate	13,000	1.1
Methyl alkali conjugated linoleate	33,000	12.1
Bulk	49,000	....
Benzene	28,000	....

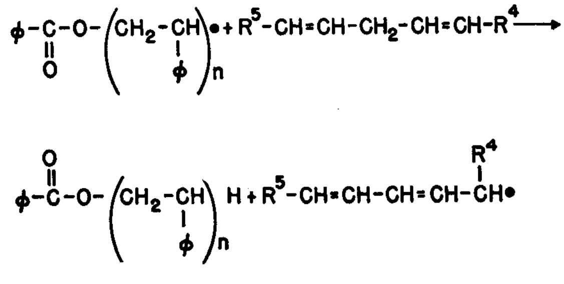
free radicals. However methyl oleate appeared to act as a chain transfer agent.



In the styrene polymer from methyl oleate approximately 1.7 molecules of methyl oleate were present at a molecular weight of 40,000. Consequently some chains must have been terminated by a transfer reaction shown in the above equations and other chains initiated by a free radical formed from methyl oleate.

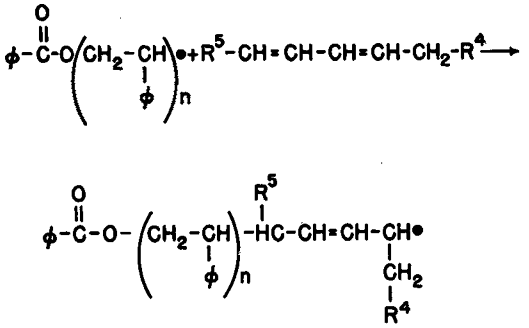
In the presence of methyl linoleate and linolenate the rate of polymerization of the styrene is drastically reduced and the molecular weights achieved were substantially lower.

Styrene in methyl linoleate and methyl linolenate attained molecular weights of 19,000 and 13,000, respectively. These are approximately one-half and one-third that attained in methyl stearate and oleate. Consequently these two polyunsaturated esters are effective chain terminating agents. The mechanism of the termination is not known, but it may occur as follows:



We have formed here a conjugated diene which is a free radical; it can couple readily to terminate another chain; it can react with peroxide-derived free radicals to reduce initiation and rate of polymerization. It might react to abstract a hydrogen from another molecule to form a conjugated diene. This last reaction may occur to a minor extent because some methyl linoleate is apparently incorporated in the chain; *i.e.*, 3 molecules of methyl linoleate per polymer chain. However only 1 molecule of methyl linolenate was found per polymer chain, indicating that termination is the primary reaction and probably the only reaction with a growing chain.

With pure esters of *trans-trans-* and *cis-trans-*octadecadienoic acids, copolymerization of the styrene with the conjugated ester resulted with molecular weights comparable to styrene polymerization in a solvent medium. Twelve to 14 ester groups were combined in the chains of styrene. The conjugated esters reacted at the rate of about 1 mole for every 15 moles of styrene. This behavior could be represented as follows where n=15:



Naturally this new free radical could continue to react with both styrene and conjugated fatty esters until transfer or termination of the free radical occurs.

This information helps to explain the results of copolymerization with fatty esters. Little or no polymerization occurs in unmodified drying oils because free radicals are destroyed by linoleic and linolenic esters. A polymerization of styrene can be initiated in an unmodified vegetable oil provided enough catalyst is used and a relatively low molecular weight is desired.

Oxidized or blown oils show a much greater tendency to copolymerize because the linoleate and linolenate contents are reduced, some of the double bonds have been shifted to conjugation, and a high percentage of hydroperoxides are found in the blown oil. This greater potential supply of free radicals naturally might reduce molecular weight but would increase the amount of total polymer formed. Bodied oils from nonconjugated oils probably would copolymerize to a limited extent because these bodied oils have some conjugated esters, reduced linolenic and linoleic content, and substantially more polymeric esters. The latter would behave more like methyl oleate

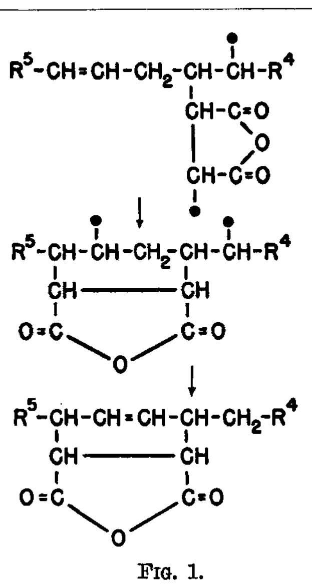
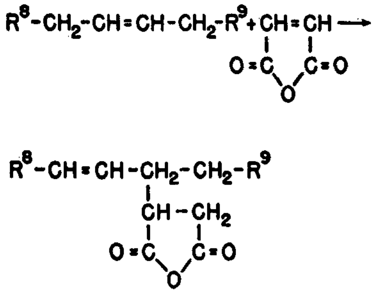


FIG. 1.

and stearate and enter into the polymerization to a limited extent.

This copolymerization of styrene with conjugated esters as first demonstrated and visualized by Hewitt and Armitage (16) was expected because both are conjugated monomers. Vinyl acetate and similar nonconjugated monomers do not readily copolymerize with conjugated monomers, and vinyl esters would not be expected to copolymerize with conjugated esters.

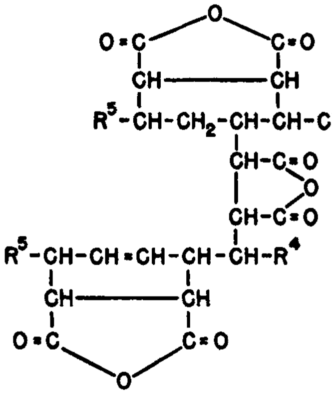
Maleic Anhydride. Drying oils modified with maleic anhydride have enhanced drying properties and are used extensively. Like many reactions with fatty esters, the reaction is not simple and straightforward. Oleic acid will react with maleic anhydride to introduce a group at the 8, 9, 10, and 11 positions. The maleic anhydride group in each of the four derivatives is attached to a carbon atom which is not part of a double bond (7).



R^8, CH_3-$(CH_2)_6$.

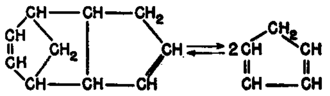
Linoleic acid however does not behave in a similar manner. Apparently, under the conditions of the polymerization, some isomerization of the linoleic acid or its adduct occurs so that a typical Diels-Alder product is obtained. (See Figure 1.)

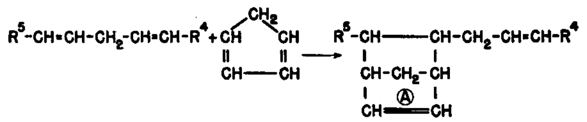
The major product of the reaction is not a monomeric adduct but is a polymeric adduct involving at least 3 moles of maleic anhydride and 2 molecules of linoleic acid. The unsaturation as measured by iodine value dropped from approximately 170 to 28, and most of the data on chemical properties of the nonvolatile adduct agree with the following structure:



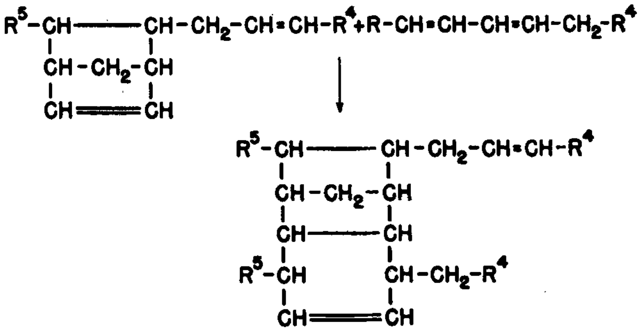
Thus maleic anhydride can react to combine two glyceride molecules, containing linoleic radicals, and act as a bodying or thickening agent (22).

Cyclopentadiene. Cyclopentadiene is another material used to improve the properties of drying oils. As normally used, dicyclopentadiene is mixed thoroughly with the oil and heated to about 250°-270°C. The dicyclopentadiene decomposes at about 170°C. to give cyclopentadiene which then reacts with unsaturated fatty acids to give a modified fatty acid derivative.





This monomeric adduct could readily react with another molecule of cyclopentadiene at the double bond in the 5-membered ring A. Because the resulting adduct would have no double bond in the 5-membered ring A, it would probably be comparatively stable and not readily decompose to give cyclopentadiene even after 2 cyclopentadiene molecules have added on to the fatty acid. Similarly, the third and fourth molecules of cyclopentadiene, which add to the double bond in the ring previously formed, give a stabilized molecule because the ring is saturated. At 250°-270°C. where most commercial copolymers are formed, the conjugated fatty acid derivatives would undoubtedly react with the adduct, as shown in the following equation:



The average number of cyclopentadiene groups connecting the fatty acid molecules in a copolymerized oil would be determined by the amounts of cyclopentadiene which was combined with the oil. In commercial practice brittle films are obtained if too great an amount of cyclopentadiene is used (14, 23).

Glyceride Polymerization. Polymerization of a drying oil by heat or catalytic means proceeds primarily through the formation of dimeric and trimeric fatty acids by intra- and intermolecular condensations of the fatty acid radicals. These condensations form dimeric, trimeric, and higher combinations of glyceride molecules. Undoubtedly side chains grow during the polymerization which, if carried out long enough, results in a three-dimensional gel containing some linear or branch molecules of lower molecular weight (4). With oils containing reactive conjugated acids in high percentages, such as tung oil, viscosity increases rapildy at bodying temperatures, and gelation occurs in a short period—12 minutes. With oils containing less reactive nonconjugated fatty acids but in high percentages, such as linseed oil, the viscosity increases somewhat more slowly at bodying temperature, but viscosity does increase rapidly just before gelation which may occur in 6-12 hr. With oils containing lower percentages of these less reactive nonconjugated fatty acids, such as cottonseed oil, the viscosity increases slowly, and gelation without autoxidation is difficult to achieve. When an additional molecule enters into the polymerization, such as maleic anhydride, the polyunsaturated acid radicals are combined with maleic anhydride to form di-, tri-, and polyglycerides. In general, the addition of maleic anhydride and cyclopentadiene speeds the reaction so that viscosity changes occur more rapidly.

Another factor, which is of some theoretical importance in the polymerization of drying oils, is the formation of intrapolymers or dimer acids in the same glyceride molecule. The interesterification reactions which occur at high temperatures of bodying apparently reduce substantially any effect which these intrapolymers may have on the properties of the products (5). The interesterification leaves only a very small percentage of intrapolymers in the bodied oil (20).

REFERENCES

1. Ahmad, A., and Farmer, E. H., J. Chem. Soc., 1176-1178 (1940).
2. Alfrey, T. Jr., Bohrer, J. J., and Mark, H., "Copolymerization," High Polymers, Vol. 8, New York, Interscience Publishers Inc., 269 pp. (1952).
3. Baer, E., and Fischer, H. O. L., J. Biol. Chem., *128*, 475-489 (1939).
4. Bernstein, I. M., J. Oil and Colour Chemists' Assoc., *32*, 447-460 (1949).
5. Barker, C., Crawford, R. V., and Hilditch, T. P., J. Chem. Soc., 1194-1200 (1951).
6. Bickford, W. G., DuPré, E. F., Mack, C. H., and O'Connor, R. T., J. Am. Oil Chemists' Soc., *30*, 376-381 (1953).
7. Bickford, W. G., Fisher, G. S., Kyame, L., and Swift, C. E., J. Am. Oil Chemists' Soc., *25*, 254-257 (1948).
8. Clingman, A. L., Rivett, D. E. A., and Sutton, D. A., J. Chem. Soc., 1088-1090 (1954).
9. Cowan, J. C., *et al.*, Ind. Eng. Chem., *41*, 1647-1653 (1949).
10. Craig, D., J. Am. Chem. Soc., *65*, 1006-1013 (1943).
11. Croston, C. B., Tubb, I. L., Cowan, J. C., and Teeter, H. M., J. Am. Oil Chemists' Soc., *29*, 331-333 (1952).
12. Eckey, E. W., Ind. Eng. Chem., *40*, 1183-1190 (1948).
13. Feuge, R. O., and Bailey, A. E., Oil and Soap, *23*, 259-264 (1946).
14. Gerhart, H. L., U. S. 2,387,895 (1945).
15. Harrison, S. A., and Tolberg, W. E., J. Am. Oil Chemists' Soc., *30*, 114-117 (1953).
16. Hewitt, D. H., and Armitage, F., J. Oil and Colour Chemists' Assoc., *29*, 109-128 (1946).
17. Martin, J. B., Abstracts of Papers 124th Meeting, Am. Chem. Soc., Chicago, Ill., Sept. 6-11 (1953) p. 90-0.
18. Nichols, P. L. Jr., Herb, S. F., and Riemenschneider, R. W., J. Am. Chem. Soc., *73*, 247-252 (1951).
19. Paschke, R. F., Kerns, J. R., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *31*, 5-7 (1954).
20. Paschke, R. F., and Wheeler, D. H., Abstracts, Am. Oil Chemists' Soc. Meeting, Chicago, Ill., Nov. 2-5 (1953) no. 23.
21. Swern, D. J., J. Am. Chem. Soc., *70*, 1235-1240 (1948).
22. Teeter, H. M., Geerts, M. J., and Cowan, J. C., J. Am. Oil Chemists' Soc., *25*, 158-162 (1948).
23. Terrill, R. L., Offic. Dig. Federation Paint and Varnish Production Clubs, no. 344, 536-554 (1953).
24. Waterman, H. I., Cordia, J. P., and Pennekamp, B., Research (London), *2*, 483-485 (1949).
25. Wheeler, D. H., Offic. Dig. Federation Paint and Varnish Production Clubs, no. 322, 661-668 (1951).

Utilization of Inedible Animal Fats

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IT is a remarkable fact that for centuries only two major uses for animal fats were discovered. Edible fats were used as food, and those deemed inedible were consigned to the soap kettle. It is even more remarkable though, just how vitally important the small percentage of the total production of animal fats that found its way into industrial usage was to the rise of industrial civilization.

Dale V. Stingley

Prior to the development of the petroleum industry, animal fats were almost without exception the sole source of lubricants for motive power and machinery, including metal working oils. Animal fats also, including whale oil, were depended upon as the main source of illumination, and today, as in the past, most of these uses, plus the many additional applications of more recent development, give animal fats a top priority rating as essential raw materials.

Sources and raw materials for inedible animal fats have been discussed in a previous lecture, but, to avoid all possibility of misunderstanding, the term "inedible animal fats" refers to fats and oils that are not suitable for human consumption. They are derived principally from cattle and swine. In this country this is a legal rather than a technical definition since the U. S. Department of Agriculture is the deciding authority and, except for a small production of animal fats produced and consumed locally within the various states, all edible animal fats are processed in government-inspected plants.

In general, inedible animal fats are referred to in the trade as "tallows" (predominately beef fats) or "greases" (predominately hog fat), with recognized grade names based on titer, free fatty acid content, M.I.U., and color standards.

A listing of the accepted grade names and specifications commonly employed is given in Table II of the paper by Kraybill in this supplement.

In our modern industrial system the key to our enormous productivity has been standardization. Natural fats and oils vary somewhat in quality and composition so the above standards were set up many years ago to establish a uniform trading basis. Unfortunately these standards, as originally established, were based on the requirements of the soap industry and are now in many cases too broad and indefinite to meet the needs of the modern industrial user. As a result, individual companies have in many cases set up their own purchase specifications in an attempt to obtain materials suitable for their needs or, in other cases, depend upon standardized products such as fatty acids, hydrogenated oils, lard oils, and other refined materials to guarantee the uniformity they require.

The need for standardized products and for fat products with modified chemical or physical properties is the reason for the existence of a sizeable industry which takes crude inedible animal fats, further processes them, and, in turn, supplies these materials to industrial users. In general, these secondary processors employ commercial grades of tallows and greases, but in many cases their needs are best served by more stringent specifications, with the result that they must be selective in their sources of raw materials.

CURRENTLY our annual production of inedible animal fats is very close to 2,700,000,000 lbs., and it is to be expected that this figure will continue upward since, as our population increases, there will be a greater need for meat with a consequent rise in the