TABLE 4.

Stability Values and Protection Factors of Stabilized Lard Obtained by Various Rapid Stability Tests.

| Antioxidants added | Stability | | | | | | Protection factors | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A.O.M. | | | O₂-Abs. (macro) 100° | O₂-Abs. (B-W) 100° | Oven test 63° | A.O.M. | | | O₂-Abs. (macro) 100° | O₂-Abs. (B-W) 100° | Oven test 63° |
| | (moist air) 98.5° | (dry air) 98.5° | (dry O₂) 98.5° | | | | (moist air) 98.5° | (dry air) 98.5° | (dry O₂) 98.5° | | | |
| *percent* | *hours* | *hours* | *hours* | *hours* | *hours* | *days* | | | | | | |
| Steam-rendered lard-D (control). | 2 | 1.8 | 1.5 | 1 | 1.2 | 1.5 | 1 | 1 | 1 | 1 | 1 | 1 |
| +.01 toc[1]+.04 lec[2]+.04 d-IP[3].. | 30 | 24 | 15 | 15 | 14 | 16 | 15 | 13 | 10 | 15 | 12 | 11 |
| +.02 NDGA[4] | 37 | 33 | 34 | 22 | .... | 49 | 19 | 18 | 23 | 22 | .... | 33 |
| Steam-rendered lard-E[5](control). | 5.5 | 5.5 | 4 | 3.3 | 2.8 | 4 | 1 | 1 | 1 | 1 | 1 | 1 |
| +.01 toc +.04 lec +.04 d-IP[6].. | 68 | 53 | 23 | 23 | 19 | 33 | 12 | 10 | 6 | 7 | 7 | 8 |
| +.01 toc +.04 lec +.04 d-IP[7].. | 84 | 66 | 30 | 29 | 28 | 44 | 15 | 12 | 8 | 9 | 10 | 11 |
| +.02 NDGA | 64 | 57 | 45 | 41 | .... | 51 | 12 | 10 | 11 | 12 | .... | 13 |

[1] A mixture of tocopherols was added as a concentrate (34% in vegetable oil).
[2] Commercial soya lecithin.
[3] d-Isoascorbyl palmitate.
[4] Nordihydroguaiaretic acid.
[5] The same lard as (D) except that about 12% of hardened lard had been added and then deodorized.
[6] After the addition of tocopherol, the lard was deodorized; then lecithin and d-isoascorbyl palmitate were added.
[7] The tocopherol, lecithin, and d-isoascorbyl palmitate were added after the lard was deodorized.

this series of tests (Table 4), the use of dry air in the active-oxygen method gave lower stability values than did the use of moist air. Differences due to dry air were most significant for preparations containing tocopherol, lecithin, and d-isoascorbyl palmitate. When dry oxygen was employed, the stability values were somewhat comparable with those obtained by the oxygen-absorption methods. In this series, owing to the relatively low stability of the control, protection factors by the different methods are exaggerated and may be subject to greater error.

## Summary

A COMPARISON was made of stability values and protection factors as determined by three widely used rapid methods—the active-oxygen, oxygen-absorption, and the oven-test methods. In most instances there was fair agreement between the results by the active-oxygen and oxygen-absorption methods, as indicated by protection factors. In general, use of dry air instead of moist air in the active-oxygen method resulted in little significant difference in the stability values although in some preparations, differences were found that may be significant. Use of dry oxygen in the active-oxygen method gave results comparable with those obtained by the oxygen-absorption method. In experiments in which an oven test was also used, the protection factors in most cases were in general agreement with those obtained by the other two methods.

The synergistic antioxidant effect of acidic compounds with phenolic antioxidants was most pronounced when lard of low stability was used. Likewise, the protection factors were disproportionately greater when antioxidants were added to lard of low stability than when added to lard of good stability. The results indicate that comparison of antioxidants by means of protection factors is valid only when the same substrate is used. Protection factors so obtained help to evaluate the order of effectiveness of various antioxidants but do not yield a strict quantitative comparison of the protective power of the antioxidants when applied to other substrates.

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# Allylic Esters of Polymeric Fat Acids

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THE CHEMISTRY of the acids obtained by polymerization of the polyunsaturated fat acid components of vegetable and cereal oils of the northern region has been studied extensively at this laboratory. Since organic compounds containing the allyl grouping have been widely investigated as sources of industrially useful polymers, it was of interest to study allylic esters of these polymeric fat acids.

This paper reports the preparation and polymerization of the allyl, β-methallyl, and β-chlorallyl esters of polymeric soybean fat acids and of purified dilin-

oleic acid which is the principal constituent of these acids. Bradley and Johnston (1, 2) and Cowan (7) have described the preparation, properties, and composition of polymeric fat acids; and Bradley and Johnston (2) and Cowan and Wheeler (6) have reported the isolation of dilinoleic acid and its physical and chemical properties.

## Materials

*Polymeric fat acids* prepared from soybean oil were obtained from the Procter and Gamble Company. The acids had the following constants: acid value, 191; iodine value [3 min. Wijs (10, 11)], 76.5; saponification number (2 hours), 193; $n_D^{30}$ 1.4871.

TABLE I.

Esters of Polymeric Soybean Fat Acids

(Direct esterification with p-toluene sulfonic acid catalyst)

| No. | Alcohol /acid (equiv.) | Catalyst (per-cent) | Reflux (hours) | Product Acid value | Product Sap. No.[1] | Product $n_D^{30}$ |
|---|---|---|---|---|---|---|
| Allyl | | | | | (175.5) | |
| 1 | 2.5 | 2[2] | [3] | 1.54 | | 1.4818 |
| 2 | 10 | 4 | 4.0 | 3.80 | 174.0 | 1.4835 |
| 3 | 10 | 4 | 6.5 | 2.22 | 177.5 | 1.4838 |
| 4 | 10 | 4 | 8.0 | 2.38 | 174.2 | 1.4810 |
| 5 | 20 | 4 | 8.0 | 2.83 | | 1.4823 |
| Methallyl | | | | | (168.0) | |
| 6 | 16 | 4 | 8.0 | 32.0 | 116.8 | 1.4797 |
| 7 | 16 | | 15.0 | 125.0 | | |
| 8 | 2.5 | 2 | 3.0 | 122.0 | | |
| Chlorallyl | | | | | (158.0) | |
| 9 | 2.6 | 3 | 5.0 | 9.86 | | 1.4890 |
| 10 | 12 | 5 | 7.0 | 27.3 | [5] | 1.4946 |
| 11 | 4 | 8[2] | 10.0 | 31.8 | | 1.4932 |
| 12 | 5 | 3 | 14.0 | 4.87 | 175.0 | opaque |
| 13 | 2.5 | 1 | 20.0 | 5.0 | 175.0 | opaque |
| 14 | 10 | 2 | 25.0[4] | 23.5 | | 1.4890 |

[1]Reflux time 4 hours. Calculated value in parenthesis.
[2]H$_2$SO$_4$ catalyst.
[3]Azetropic distillation; benzene entrainer.
[4]At 100°C.
[5]Anal. calc'd: Cl. 8.6; found: Cl, 8.75.

*Methyl dilinoleate* (2, 6) was prepared from polymerized methyl esters of soybean fat acids by fractionation in a molecular still. It had the following constants: acid value, 6.98; iodine value, 75 (3 min. Wijs); saponification number (2 hours), 198; $n_D^{30}$, 1.4767.

*Allyl alcohol* and *β-methallyl alcohol* were obtained from the Eastman Kodak Company. They were dried over potassium carbonate and fractionated through a 65-cm. by 1.5-cm. column packed with glass helices. The boiling ranges at 760 mm. of the fractions retained were 94° to 95° C. and 112° to 113° C., respectively.

*β-Chlorallyl alcohol* was obtained from the Shell Development Company. It was dried over potassium carbonate and fractionated through the packed column; its boiling point was 131° to 135° C. at 760 mm.

## Methods of Preparation

*Direct Esterification of Polymeric Soybean Fat Acids.* A mixture of the acid and the allylic alcohol was refluxed in the presence of p-toluene-sulfonic acid or sulfuric acid as a catalyst. The reaction mixture was distilled until the pot temperature reached 100° C. A current of carbon dioxide was then introduced, and final traces of alcohol were removed *in vacuo.* If the allylic alcohol boiled above 100° C., its removal was conducted entirely *in vacuo.* The residue was dissolved in Skellysolve F. The solution was washed with water until neutral and concentrated by distillation of solvent; the residual solvent was removed *in vacuo.* Purification by distillation was not possible because polymerization occurred.

*Transesterification of Methyl Dilinoleate.* A mixture of methyl dilinoleate and the allylic alcohol was refluxed under anhydrous conditions in the presence of sodium hydroxide, sodium, zinc dilinoleate, or zinc oxide. The reaction mixture was then treated in the manner described for direct esterification. The acid number of esters prepared in this way was less than 2.

*Polymerization.* Small amounts of the esters were catalytically polymerized in test tubes placed in a heated, thermostatically controlled block. Stirring was accomplished by introducing a current of carbon dioxide. Large amounts were polymerized under carbon dioxide in tubes equipped with stirrers and

heated in an oil bath. The progress of polymerization was followed by noting the change in refractive index. Polymerization by heat alone was accomplished by heating the esters at 300° C. under a pressure of 0.1 mm.

## Results and Discussion

*Esterification.* The results of typical preparations of the allyl, methallyl, and chlorallyl esters of polymeric fat acids and of dilinoleic acid are summarized in Tables I and II. The esters of polymeric fat acids were obtained by direct esterification while those of dilinoleic acid were prepared by transesterification of methyl dilinoleate. Since the esters could not be purified by distillation, saponification numbers and acid values were used in estimating the extent of esterification. Esters with allyl alcohol were readily obtained by both procedures. Saponification numbers were found which differed only slightly from the calculated value for allyl dilinoleate, 175.5, and acid numbers below 4 were easily achieved.

TABLE II.

Esters of Dilinoleic Acid

(Transesterification)

| No. | Alcohol /ester (equiv.) | Catalyst (percent) | Reflux (hours) | Product Sap. No.[1] | Product $n_D^{30}$ |
|---|---|---|---|---|---|
| Allyl | | | | (175.5) | |
| 1 | 10 | 4 NaOH | 10 | 180.6 | 1.4793 |
| 2 | 10 | 2 ZnD[2] | 10 | 175.4 | |
| 3 | 10 | 1.5 Na | 10 | 177.3 | 1.4790 |
| Methallyl | | | | (168.0) | |
| 4 | 8 | 0.6 NaOH | 10 | 193.5 | 1.4777 |
| 5 | 5 | 1.0 Na | 4.5 | 179.5 | 1.4808 |
| 6 | 10 | 1.0 Na | 4.5 | 173.5 | 1.4808 |
| 7 | 15 | 1.0 Na | 4.5 | 181.0 | 1.4811 |
| Chlorallyl | | | | (158.0) | |
| 8 | 10 | 2 CH$_2$ONa | 4 | 221.0 | 1.4779 |
| 9 | 10 | 2 Na | 6 | 190.6 | 1.4804 |
| 10 | 4 | 0.6 ZnO+ 0.6 ZnD[2] | 5 | 170.6 | 1.4846 |

[1]Reflux time, 4 hours. Calculated value in parentheses.
[2]ZnD: Zinc dilinoleate.

With β-methallyl alcohol, direct esterification with acid catalysts was unsatisfactory because the acid catalyzed the isomerization of methallyl alcohol to isobutyraldehyde (9, 16). In the absence of a catalyst, little esterification occurred. Groll and Hearne (8) have reported good esterification of β-methallyl alcohol with lower fatty acids by distillation of the alcohol with a slight excess of the acid. Ryan and Shaw (14) preferred to react the acid anhydride with the alcohol, stating that little esterification occurs by heating acid and alcohol. The methods of these workers were not applicable to polymeric fat acids as their success depends upon the volatility of the acid and the ester.

Transesterification of methyl dilinoleate with β-methallyl alcohol was almost complete. The lowest saponification number found for the resulting esters was 173.5 (calculated 168) as compared with a saponification number of 191 for methyl dilinoleate.

With β-chlorallyl alcohol, direct esterification in the presence of p-toluene sulfonic acid or sulfuric acid resulted in products having acid values varying from about 10 to 32. Acid values below 10 were obtained by prolonged refluxing of the reaction mixture, but the esters were very dark-colored and opaque. Direct esterification procedures have been recommended by Coleman and Hadler (4, 5) and by Taylor (17), but these investigators were able to purify their chlorallyl esters by distillation or crystallization.
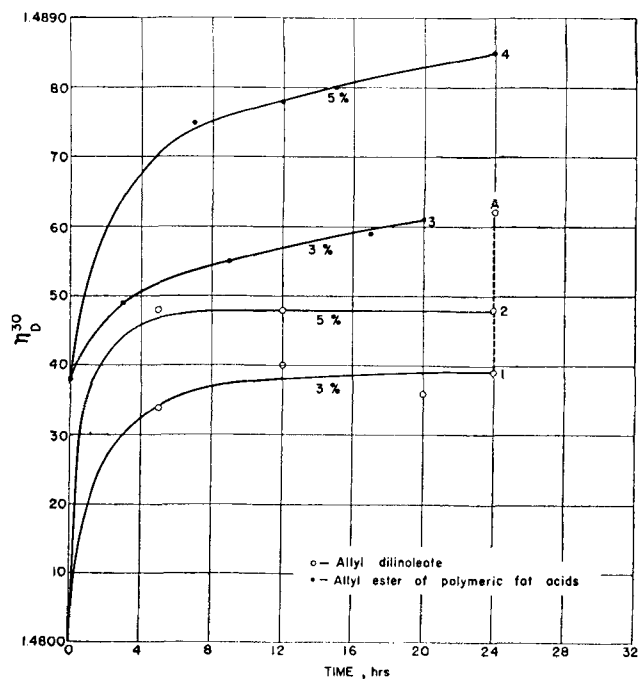
Fig. 1. Polymerization of allyl esters at 160°C. with aluminum chloride catalyst.

Transesterification of methyl dilinoleate with β-chlorallyl alcohol using a strong alkaline catalyst was not satisfactory since the alcohol (or an impurity) reacted with the catalyst and destroyed its activity before transesterification was complete. For the same reason saponification numbers of the chlorallyl esters were found to vary greatly with the concentration of alkali and the duration of saponification, and consequently they were not entirely acceptable as a measure of transesterification. The most complete transesterification (60% of the theoretical) was obtained with a catalyst composed of zinc oxide and zinc dilinoleate which retained its activity longer than the more strongly basic sodium or sodium methoxide.

*Polymerization.* The following discussion applies to the allyl, β-methallyl, and the β-chlorallyl esters, as no significant differences in polymeric behavior were noted among the three types.

Benzoyl peroxide, *t*-butyl peroxide, and metallic halides such as aluminum, stannic, and antimony chlorides, were effective catalysts in concentrations of 2 to 5%. Aluminum chloride was superior to the other metallic halides as it did not cause charring even on prolonged contact. Temperatures in the range of 150°-160° C. were required, and optimum results were obtained by polymerizing at about 160° C. for 18 to 24 hours. Typical polymerization curves are shown in Figures 1 and 2. Heat alone was effective only when the polymerization was conducted at reduced pressure. Gelation was obtained by heating the esters for 4 hours at 300° C. and 0.1 mm. pressure.

Viscous oils or soft gels were obtained by catalytic polymerization while elastic, sticky gels were obtained by the action of heat at reduced pressure. Extraction of the oils or gels with alcohols removed unpolymerized monomers and left a fusible polymeric residue which could be converted to a soft, transparent yellow, infusible polymer by the action of heat and catalysts. The extracted monomers were capable of more rapid polymerization than the original monomers. For example, a sample of recovered monomer gelled after

heating at 160° C. for 12 hours with 5% of aluminum chloride whereas the original monomers did not gel after 24 hours' heating under the same conditions. This effect is probably due to removal of small amounts of inhibitors because both original and extracted monomers had the same refractive index.

The yield of polymeric product, as indicated by the rise in refractive index, was greater when larger amounts of catalyst were used (Figure 1). When an ester had been polymerized for a number of hours with a given amount of catalyst, addition of more catalyst produced a final yield of polymer which was greater than that obtained when the total amount of catalyst was added at one time. In Figure 1, Point A, connected by a dotted line with curve 2, indicates the final refractive index obtained by increasing the concentration of catalyst from 5 to 8% and continuing the polymerization for an additional 12 hours.
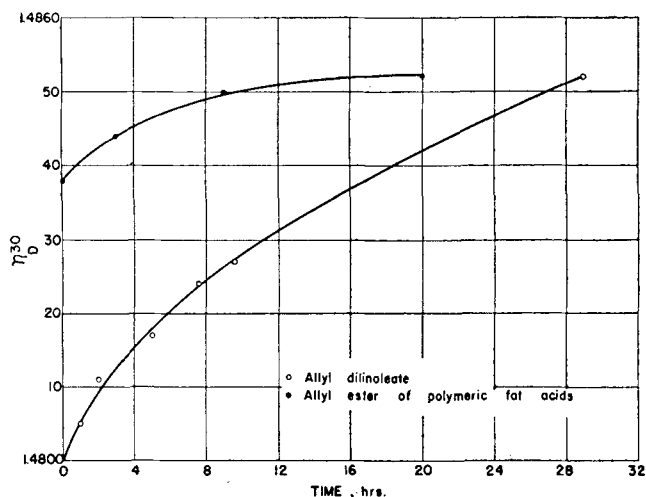


Fig. 2. Polymerization of allyl esters at 160°C. with 3% *t*-butyl peroxide catalyst.

From these facts it is evident that the esters when prepared according to the methods described do not possess very great capacities for polymerization. In this respect they may be compared with esters prepared by Bradley (3) and by Muskat (12). Bradley found that allyl esters of fumaric, sebacic, phthalic, and similar dibasic acids are polymerized in the presence of benzoyl peroxide to the infusible, insoluble state in 15 to 30 minutes at 115° to 125° C. On the other hand, the allyl and methallyl esters of oxalic acid were found by Muskat to polymerize in 35 to 48 hours at 150° to 165° in the presence of 2-5% of benzoyl peroxide; however, only viscous liquids were formed from which a fusible polymer was isolated by precipitation with methanol. Allylic esters of monobasic acids polymerize slowly, as has been observed by Staudinger and Fleitmann (15), by Ryan and Shaw (14), and by Pollak (13).

It is apparent that the polymerization of allylic esters of dilinoleic acid and polymeric fat acids is similar to that of allyl and methallyl oxalate. However, a comparison of curve 1 with 3 and of 2 with 4 in Figure 1, and of the curves in Figure 2, shows that the rate of polymerization of allyl dilinoleate is from 1.6 to 2.7 times as rapid as that of the polymeric fat acid ester. This difference may be attributed in part to the presence of impurities in the polymeric fat acids since they contain some monomeric acids and substantial amounts of unidentified substances in ad-

dition to dilinoleic and trilinoleic acids. Furthermore, the polymeric fat acid esters had acid numbers ranging from 2 to 32, and the free fatty acids would be expected to deactivate the catalysts used.

The esters of dilinoleic acid, except for the β-chlorallyl ester, were relatively pure substances, as shown by their saponification numbers and negligible acid values (below 2). Nevertheless, it is probable that, since purification was not accomplished, their rate of polymerization was decreased by the presence of unidentified impurities. In their study of the polymerization of styrene, Thompson and Burk (18) showed that even as little as 0.2% of an added substance produced a marked inhibiting effect.

It is probable that substantial improvement in the properties of both esters and polymers could be achieved if satisfactory methods of purification were found. Solvent extraction is being considered for this purpose.

Another factor which was believed to be partly responsible for the failure of the esters to polymerize readily is that the fat acid portions of the esters also contain unsaturation. If it participates in the polymerization, this unsaturation might interfere with smooth polymerization through the allyl groups. As a check on this, allyl ester of tetrahydrodilinoleic acid (5) was prepared, but it failed to show any superiority or inferiority in polymerization.

*Utilization Studies.* When the fusible polymers isolated by extraction were converted to the infusible form, the products appeared too weak to be of value as plastics, films, etc. However, if the fusible form was mixed with a catalyst and a filler, such as "Kalvan," and molded under heat and pressure, discs that were quite hard and strong could be obtained. Inspection of broken specimens showed a laminar structure, which caused the discs to fracture at right angles to the direction of the molding pressure. It is believed that a suitable choice of filler, catalyst, and molding conditions would produce a more nearly isotropic molded product. These factors were not investigated.

## Suggested Uses for Polymers

The properties of these polymers suggest possible uses as modifiers and softening agents in the production of various other polymers, as tackifiers and softening agents for elastomers, and as components of surface coatings for special purposes. None of these possibilities were investigated.

## Summary

1. Allyl, β-methallyl, and β-chlorallyl esters have been prepared from polymeric soybean fat acids by direct esterification and from dilinoleic acid by transesterification of methyl dilinoleate.

2. The method of polymerizing the esters and the properties of the polymers are described.

## Acknowledgment

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# Spectrophotometric Analysis of Alkali - Isomerized Synthetic Glycerides[1]

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THE application of the spectrophotometric method for the quantitative determination of linoleic and linolenic acids in fats and oils has been suggested by several investigators. Burr and Miller (1) found Moore's (2) reaction could be made reproducible with oils and thus an empirical quantitative measure of linoleic and linolenic acids could be obtained. These investigators subjected cottonseed, corn, almond, peanut, sunflower, castor, and olive oil to alkali isomerization and on the data obtained from spectral curves calculated the linoleic content of each oil. Similar analyses by Bradley and Richardson (3), Mitchell, Kraybill, and Zscheile (4), and Barnes, Rusoff, Miller, and Burr

(5) have yielded data to support the fact that the quantitative estimation of the linoleic acid and linolenic acid content of fats can be placed on a satisfactory basis by spectrophotometric methods. Mitchell, Kraybill, and Zscheile (4) particularly, have shown that the percentages of linoleic and linolenic acids in soybean and linseed oils, calculated from spectral curves of the isomerized oils, were in good agreement with the percentages as obtained by the Kaufmann method on the mixed acids. This agreement between spectrophotometric and the Kaufmann methods is obtained only if empirical thiocyanogen values are used. Mitchell, *et al.* (4) have indicated that the amounts of linoleic, linolenic, oleic, and saturated acids may be determined in an oil simply and accurately when the iodine value of the oil is known, par-