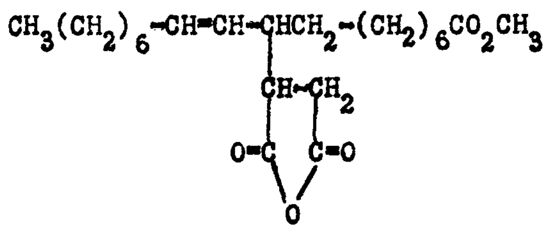
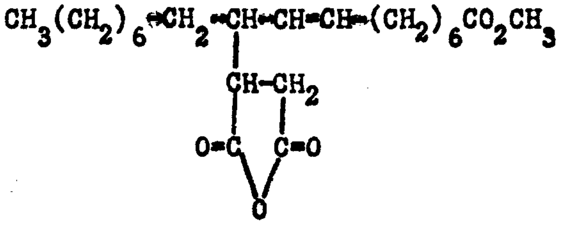
Polymerization of Drying Oils. III. Some Observations on Reaction of Maleic Anhydride With Methyl Oleate and Methyl Linoleate

H. M. TEETER, M. J. GEERTS,[1] and J. C. COWAN, Northern Regional Research Laboratory,[2]
Peoria, Illinois

IN connection with the utilization of soybean oil to produce polyamide resins such as Norelac (4) it occurred to us that the monomeric distillate derived from the preparation of polymeric fat acids could be reacted with maleic anhydride to form polybasic acids for polyamide manufacture. Clocker (3) has shown that a reaction does occur between maleic anhydride and oleic and linoleic acids. Wheeler and his coworkers (1) have shown that the molar ratios in which maleic anhydride reacts with methyl oleate, methyl linoleate, and methyl linolenate are approximately 1:1, 2:1, and 3:1, respectively. Ross, Gebhart, and Gerecht (9) have shown that methyl oleate reacts at the double bond with a shift of the double bond to the 8, 9 or 10, 11 positions and that the structures of the adducts are as follows:

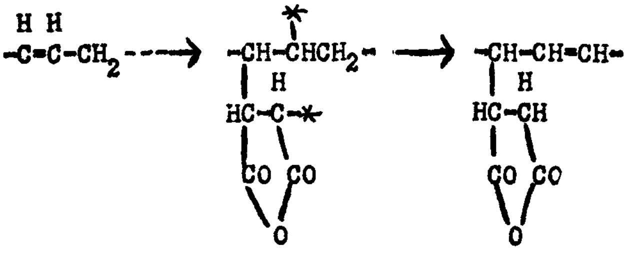


I

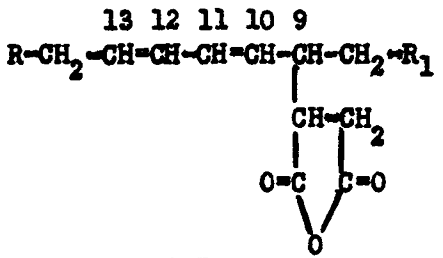


II

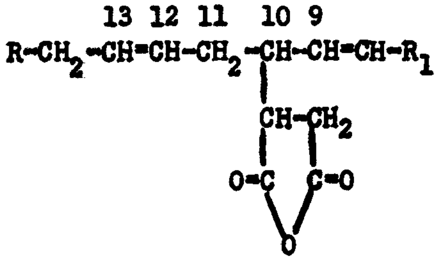
It has been suggested (5) that the mechanism involves addition of maleic anhydride to the double bond with formation of a diradical which is then stabilized by intramolecular transfer of hydrogen:



By a similar mechanism methyl linoleate may react to give four isomeric adducts containing one maleic anhydride grouping. Two of these are shown in formulas III and IV.[3] The others are similar, but are derived from reaction at the 12, 13 double bond.

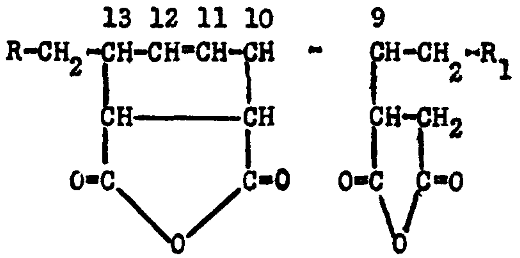


III



IV

These monoadducts would be expected to react further with maleic anhydride to form adducts containing two anhydride groupings. III should add maleic anhydride by the Diels-Alder reaction to form V while IV could react in either of two ways to yield VI and VII. A similar group of diadducts, including VII, would be expected from the other two monoadducts.



V

Since methyl oleate adds only one molecule of maleic anhydride, diadducts of types VI and VII would not be expected to react further with maleic anhydride.

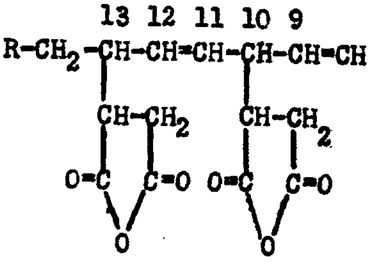
All of these structures (I-VII) are essentially monomeric rather than polymeric and none of them represent monomers of high functionality when considered for the preparation of polyamides. I would be expected to react with ethylene diamine to give an imide polymer as follows:

---

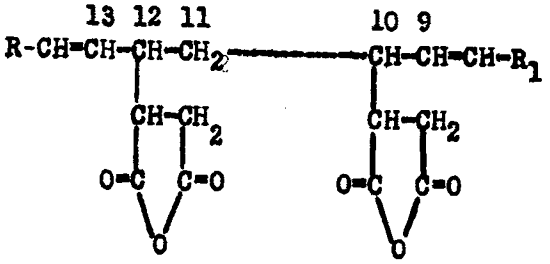
[1] Present address: Pure Oil Company, Box 266, Winnetka, Illinois.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[3] In these and subsequent formulas $R = CH_3(CH_2)_3$ and $R_1 = -(CH_2)_6CO_2CH_3$.



VI



VII

This polymer should be soluble and flexible. In accordance with Flory's predictions and experimental data (6) it should not readily crosslink unless the unsaturation is reactive or amide formation rather than imide formation occurs. Similarly, the adducts from linoleic acid should behave like trimeric fat acids in the preparation of polyamide resins (4), or like tricarballyic acid in the preparation of polyesters (6).

In view of these considerations the maleic anhydride reaction product with monomeric distillate, which would be expected to contain approximately 68% of the oleic acid adduct and 17% of the linoleic acid adduct, was reacted with ethylene diamine. Contrary to the expectation that the reaction would proceed smoothly to a branched polyamide resin at an extent of reaction of 0.7 to 0.8, gelation occurred at low reaction temperatures and apparently long before any appreciable extent of reaction had occurred.

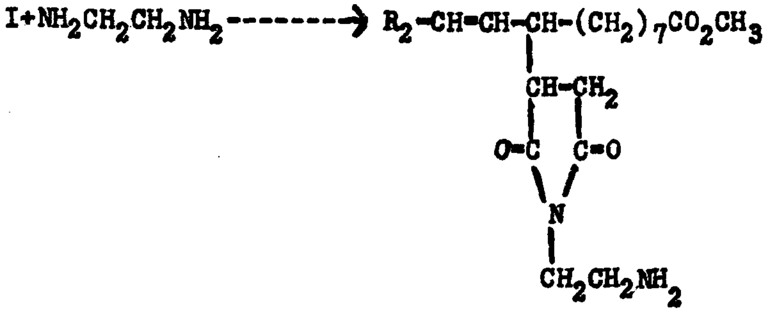
To determine the cause of this gelation, the methyl oleate adduct was prepared in a purified form and reacted with ethylene diamine to give a linear flexible polymer. This behavior indicated that the crosslinking factor present in the maleic anhydride reaction product with monomeric distillate probably came from the linoleic acid.

Pure methyl linoleate obtained by the debromination procedure (7) was reacted with approximately two moles of maleic anhydride and the unreacted maleic anhydride removed. When the linoleic acid adduct was reacted with ethylene diamine, gelation again occurred at low reaction temperature and presumably at a low extent of reaction.

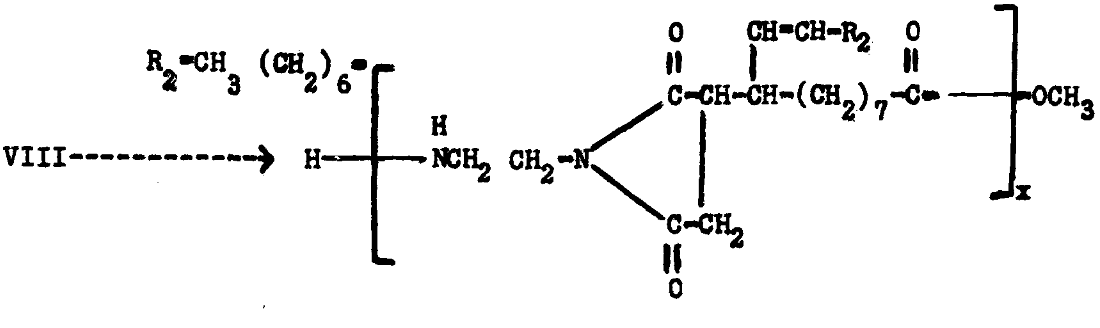
A second preparation of the linoleate adduct was passed through a molecular still and separated into two components, one volatile and the other non-volatile in the still.

In general, the properties of the volatile component corresponded to those of an adduct of one molecule of maleic anhydride with one of methyl linoleate, and the properties of the non-volatile component corresponded to those of an adduct of three molecules of maleic anhydride with two of methyl linoleate. While the volatile adduct should be similar to the oleate adduct in its reaction with ethylene diamine, the non-volatile adduct would be pentafunctional with respect to imide polymer formation with ethylene diamine and would therefore greatly facilitate gelation of the imide polymer at a low degree of reaction. We suggest that the presence of this non-volatile adduct in the reaction products of maleic anhydride and methyl linoleate or monomeric distillate is responsible for our failure to obtain satisfactory polyamides in these cases.

The compositions indicated for the volatile and non-volatile adducts are based principally upon the



VIII

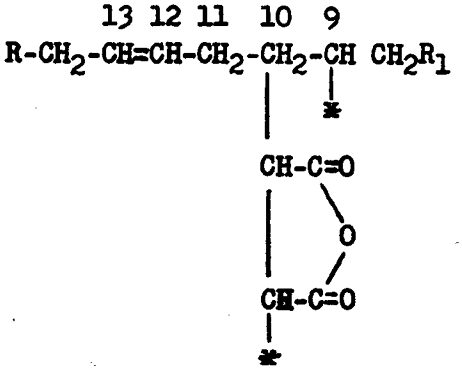


observed values of the neutralization and saponification equivalents for these materials. A comparison of the values of these quantities to be expected for adducts containing various molecular proportions of methyl linoleate and maleic anhydride indicates that neutralization and saponification equivalents should be more satisfactory criteria of structure than elementary analysis.

Since the non-volatile product was not subjected to purification beyond the removal of a certain amount of volatile material, the possibility existed that the non-volatile product might be a complex mixture of several substances of high molecular weight. The good agreement between calculated and observed values for molecular weight, neutralization equivalent, and saponification equivalent appear to indicate that the non-volatile product does consist primarily of the adduct involving three molecules of maleic anhydride and two of methyl linoleate.

The formation of the non-volatile polymer-like adduct appears to indicate that the mechanism of the reaction involves free radicals. If free radicals are involved, these are probably first formed from maleic anhydride, and they may then attack methyl linoleate either at a double bond or at a methylene group adjacent to the unsaturation. Our data appear to indicate that under the reaction conditions employed, attack by free radicals occurred at a double bond in methyl linoleate rather than at a methylene group. The most important fact supporting this view is that the products isolated are substantially less unsaturated than would be predicted for structures formed by mechanisms involving attack at a methylene group.

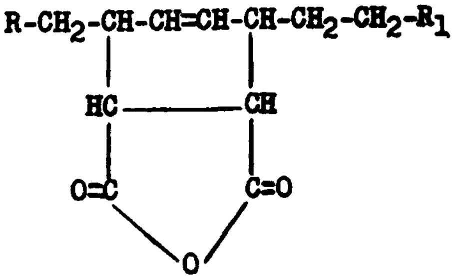
Upon the basis of attack by a free radical at the double bond, the first intermediate would be a diradical having a structure similar to IX. Comparable radicals would also be formed by attack at carbons 9, 12, and 13.



IX

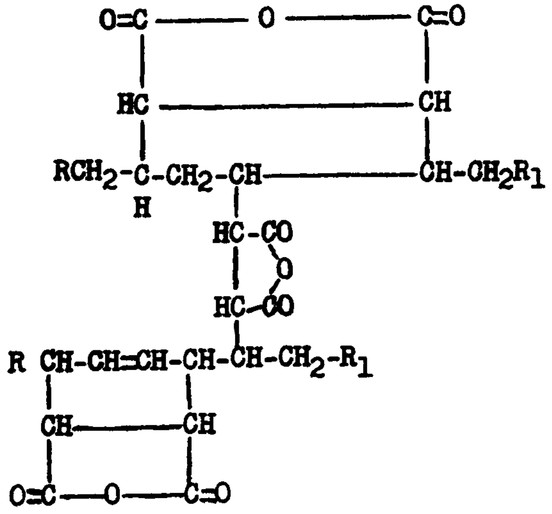
Stabilization of this radical by transfer of hydrogen from carbon 8 would yield a product having the structure IV. However, consideration of spatial relationships indicates that IX could be readily stabilized by ring closure to carbon 13 and transfer of hydrogen from carbon 11 to carbon 9; the product would have the structure X. The presence of structures similar to X would account both for the reduced unsaturation and the small amount of conjugation found in the volatile mono-adduct.

The formation of the polymeric adduct is readily accounted for by combination of two radicals such as IX. Stabilization appears to occur by combination with an additional molecule of maleic anhydride followed by transfer of hydrogen. The low iodine number of the polymeric adduct indicates that ring closure of the type indicated in X may be occurring during stabilization. The combination with an additional molecule of maleic anhydride appears to be reasonable because the initial ratio of reactants was two molecules of maleic anhydride to one of methyl linoleate. Since a substantial amount of a mono-adduct was formed, there would be available an excess of maleic anhydride over the amount required for a polymer obtained by simple combination of radicals like IX.



X

No experimental data are available to permit assignment of a definite structure to the polymeric adduct. One possible structure, which is illustrative of the type of polymer formed by the suggested mechanism and which would have the properties shown by the polymeric adduct isolated, is shown in XI.



XI

One unexpected property of maleic anhydride adducts of fat acids is the difficulty with which they may be saponified. Both Morrell (8) and Wheeler (1) have commented upon their inability to obtain correct saponification values for maleic anhydride adducts. In our work this difficulty was noted with the oleate adduct and with the mono-adduct of methyl linoleate, while with the polymeric adduct the difficulty was greatly intensified. Thus, correct saponification values for the two mono-adducts were obtained by extending the usual reflux with alco-

TABLE 1

Polyamides From Ethylene Diamine and Adducts of Maleic Anhydride With Methyl Oleate, Methyl Linoleate, and Monomeric Distillate

Type of adduct	Reactants			Properties of product		
	Amount of adduct	Ethylene diamine 95%	Reaction conditions	Neutral equivalent	CH_3O	Solubility
	Moles	*Moles*			*Per cent*	
Oleate	0.0193	0.0193	17 hrs.; 156°-166°	5864 (acid)	....	Sol. isopropyl and butyl alcohols
Oleate	0.0196	0.0196	16.5 hrs.; 204°-222°	2175 (base)[2] 5740 (acid)	1.18 1.23 2.62	Sol. isopropyl and butyl alcohols
Linoleate	0.0122	0.0122	6 min.; 170°-210°	....	....	Insol. chloroform
Linoleate	0.0122	0.0244	14 min.; 160°-165°	....	....	Insol. chloroform
Monomeric distillate	0.018 [1]	0.025	Heated to 175°C. during 42 minutes	....	....	Insol. butyl alcohol and chloroform

[1] Calculated from composition of monomeric distillate.

[2] M.W. [Signer's Method (2)], 2600.

holic potassium hydroxide to 3 hours, while with the polymeric adduct such an extension of time or alternatively heating the sample for 8 minutes at 135°C. with a normal solution of potassium hydroxide in diethylene glycol resulted in saponification of only one ester group in addition to the anhydride groups. To saponify the second ester group, it was necessary to heat the polymeric adduct for 8 hours at 135°-140° with the diethylene glycol solution. These results suggest that the difficulties of saponification are due to decreased reactivity of the ester groups rather than of the anhydride groups as observed by Morrell (8) in the case of adducts of eleostearic acid.

Further evidence that decreased reactivity of the ester groups of the polymeric adduct was responsible for the difficulty in saponification is found in the following facts: 1. No difficulty was encountered in the determination of the neutral equivalent by titration in aqueous pyridine. 2. If the crude linoleate adduct was washed with water considerable material was obtained which was insoluble in benzene. Such insolubility indicates at least partial hydrolysis of the anhydride groups. 3. Methoxyl groups were shown to be present in the product obtained by heating the polymeric adduct for 8 minutes at 135° with potassium hydroxide in diethylene glycol. 4. The per cent of methoxyl present in the polymeric adduct before and after partial saponification, when determined by the standard procedure using phenol and hydriodic acid, was low and satisfactory check determinations were difficult or impossible to obtain.

Experimental

Adduct of methyl oleate. The procedure of Ross, Gebhart, and Gerecht (9) was modified as follows: methyl oleate (0.444 mole) and maleic anhydride (0.888 mole) were heated in an atmosphere of nitrogen for 5 hours at 194°-202° and then for 45 minutes at 225°-230°. The reaction mixture, after cooling under nitrogen, was diluted with benzene and analyzed for unreacted maleic anhydride (1). It was found that 0.354 mole (80% of theoretical) of maleic anhydride had reacted. The solution was then washed 10 times with 100-ml. portions of water, and the solvent was removed by distillation at reduced pressure. The residue, weighing 160.6 g., contained 0.90% of maleic anhydride.

Isolation of pure oleate adduct. A composite sample of various preparations of the crude adduct was employed. The sample (124.2 g.) was passed six times through a falling-film molecular still. The first three passes (temperatures up to 136°C. and pressures of 3.0 microns or less) yielded 56.1 g. of a fore-run. The last three passes (temperatures between 126°-138° and pressures of 0.1 to 0.8 micron) yielded a non-volatile residue weighing 8.7 g. and volatile fractions weighing 58.0 g. having the following analysis:

Anal. Calcd. for Formulas I and II: Sap. equiv., 131.5; Neutral equiv. (in aqueous pyridine), 197.3; I.V., 64.3. Found: Sap. equiv. (after 3 hr. reflux with alcoholic potassium hydroxide), 132.7; Neutral equiv., 195.7; I.V., 60.5.

Adduct of methyl linoleate. Methyl linoleate (0.17 mole), prepared by debromination (8), and maleic anhydride (0.32 mole) were heated for seven hours at approximately 200°C. in an atmosphere of carbon dioxide. Analysis of the reaction mixture showed that 90% of the anhydride had reacted. Removal of unreacted maleic anhydride by washing the benzene solution with water was not satisfactory because partial hydrolysis appeared to occur with formation of considerable material which was insoluble in benzene. A sample (61.2 g.) of the reaction mixture was therefore passed through a molecular still at 0.4-0.8 micron pressure and 107°-124° in order to remove unreacted material. A volatile fraction weighing 2.7 g. was obtained. The non-volatile residue of crude linoleate adduct weighed 47.2 g.

Fractionation of linoleate adduct. A sample (42.8 g.) of the crude adduct was passed twice through a falling-film molecular still at 0.4-0.7 micron and 157°-162°C. Because of the high viscosity of the adduct it was necessary to apply heat to the inlet and outlet tubes of the still in order to promote flow. A volatile fraction weighing 12.9 g. and a non-volatile fraction weighing 26.0 g. were obtained. The volatile fraction was further purified by one passage through the still at 0.7-1.0 micron and 152°-163°, a center cut weighing 6.7 g. being retained for analysis. This fraction contained 12% of diene conjugation.

Analysis of volatile fraction. Calcd. for Formulas III, IV, and X: Sap. equiv., 130.9; Neutral equiv. (in aqueous pyridine), 196.3; I.V. (for IV) 129.4; I.V. (for X) 64.6; C, 70.4; H, 9.17. Found: Sap. equiv. (3 hr. reflux with alcoholic potassium hydroxide), 129.1; Neutral equiv. 196.5; I.V. 96.4; C, 68.0; H, 8.80.

Analysis of non-volatile fraction or polymeric adduct. Calcd. for Formula XI: M.W., 883.3; I.V., 28.7; Neutral equiv. (in aqueous pyridine) 147.1; Sap. equiv. (one ester group saponified) 126.1; Sap.

equiv. (two ester groups saponified) 110.4; OCH_3, 7.04; C. 68.0; H, 8.39. Found: M.W. [Signer's method (2)] 950; I.V., 29.1; Neutral equiv. 147.9; Sap. equiv. (after 8 min. at 135°C. with 1.0 N potassium hydroxide in diethylene glycol) 125; Sap. equiv. (after 8 hrs. at 140°) 113; OCH_3, 6.00, 6.16, 6.25, Av. 6.14; C, 66.9; H, 8.41.

Saponification of non-volatile component of linoleate adduct. A 0.1 g. sample of the adduct was heated for 8 minutes at 135°C. as nearly as possible under the conditions used for the determination of the saponification equivalent. The mixture was then diluted with water, acidified with dilute sulfuric acid, and the product, which was insoluble in benzene and ether, was extracted with isopropyl acetate. The extract was dried and evaporated.

Analysis calculated for Formula XIV with one ester group saponified: OCH_3, 3.36. Found: 1.57, 2.31, 3.01, 1.53, 2.05, 1.90, 2.82, 1.83. Av. 2.13.

Adduct of monomeric distillate. A sample of monomeric distillate was obtained from General Mills, Inc. Spectrophotometric analysis showed that it contained 11.6% of methyl esters of saturated fat acids, 71.5% of methyl oleate and 16.8% of methyl linoleate. It was distilled at reduced pressure to remove cracked materials of low molecular weight and any polymerized esters which might be present. A fraction reserved for reaction had the following composition: Methyl esters of saturated acids, 15.0%; methyl oleate, 68.2%; methyl linoleate, 16.8%.

An adduct was prepared from 100 g. of the distilled fraction and 70.1 g. (0.71 mole) of maleic anhydride by heating for 5 hours at 200°C. in an atmosphere of nitrogen. It was found that 0.42 mole of maleic anhydride had reacted. Unreacted materials were removed from the crude adduct by distillation at 0.3-0.5 mm. pressure to a pot temperature of 191°. The final product contained 2.55% of maleic anhydride.

Preparation of polyamides. Polyamides were prepared by mixing the adduct with a slight excess of freshly distilled ethylene diamine. A noticeable exothermic effect was observed. The salt formed was then heated for an extended period with ebullition of inert gas to produce agitation and to maintain an inert atmosphere. Data and results are given in Table I. The salt of ethylene diamine and methyl oleate adduct softened at 90°-100°C. to a mobile liquid and offered no difficulty during the heating. The salt from ethylene diamine and the methyl linoleate adduct formed readily, but it did not liquefy during the heating period. Although small samples were used, it is probable that heating was not efficient. The salt from the adduct with monomeric distillate liquefied at 90°-110°, but gelation occurred almost immediately upon reaching a temperature of 170°.

Acknowledgment

We wish to acknowledge our indebtedness to C. H. Van Etten of the Analytical and Physical Chemistry Division of this Laboratory for making the methoxyl and molecular weight determinations and for assistance in obtaining several of the saponification equivalents. We wish to further acknowledge our indebtedness to E. H. Melvin for the various spectrophotometric analyses. We are also grateful to A. C. Hovey, General Mills, Inc., for supplying the specimen of monomeric distillate.

Summary

Adducts of maleic anhydride with methyl oleate, methyl linoleate, and monomeric distillate have been prepared. Reaction of the adducts with ethylene diamine gave a linear, soluble polyamide in the case of the oleate adduct, but gelation occurred at a low degree of reaction with other adducts. The linoleate adduct was separated into monomeric and polymeric components. It is suggested that this polymeric component is responsible for the rapid gelation of polyamides from the adducts of methyl linoleate and monomeric distillate.

REFERENCES

1. Bickford, W. G., Krauczunas, P., and Wheeler, D. H. Oil & Soap *19*, 23-27 (1942).
2. Clark, E. P., "Semimicro Quantitative Organic Analysis," p. 78, New York, Academic Press (1943).
3. Clocker, E. T., U. S. Patent 2,188,882 (1940).
4. Falkenburg, L. B., Teeter, H. M., Skell, P. S., and Cowan, J. C. Oil & Soap, *22*, 143-48 (1945).
5. Farmer, E. H., J. Soc. Chem. Ind. *66*, 86-93 (1947).
6. Flory, P. J., J. Am. Chem. Soc. *63*, 3083-3100 (1941).
7. Kimura, W., Fettchem. Umschau *4*, 78 (1935).
8. Morrell, R. S., and Samuels, H. J., J. Chem. Soc. *1932*, 2251-4.
9. Ross, J., Gebhart, A. I., and Gerecht, J. F., J. Am. Chem. Soc. *68*, 1373-6 (1946).