The Chemistry of Polymerized Oils. VI. The Molecular Weight Distribution of Thermally Polymerized Oils

C. A. J. HOEVE and DONALD A. SUTTON, National Chemical Research Laboratory,
South African Council for Scientific and Industrial Research, Pretoria, South Africa

THE THERMAL POLYMERIZATION of drying oils is a well-known technical process. Upon heating, the viscosity rises in a characteristic manner. The increase in viscosity is due to molecular growth, but little is known about the molecular weight distributions which result. The viscosity and drying properties are doubtless related to the molecular weight distribution, and it is therefore of technical as well as of fundamental interest to investigate this property.

The direct approach of fractionating with solvents and determining the molecular weight of each fraction has been applied (2, 8, 16), but difficulties inherent in the method make it extremely laborious and of limited quantitative value. The only species which can be determined by molecular distillation are the monomeric triglycerides.

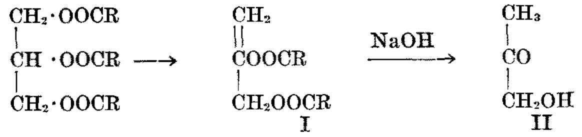
An indirect approach lies in the application of Flory's theory of polycondensation reactions (5). Adams and Powers (1) had already attempted to apply a method of this kind. The extent of reaction used in their calculations was based upon the observed iodine value decrease, and certain simplifying assumptions about the functionalities of the component acids and their distribution were made. The effects of the assumptions made are discussed by one of us elsewhere (7); the important difference between Adams and Powers' approach and ours which needs emphasis at this point is that we assess the extent of linking between acid chains by measuring the proportions of monomeric, dimeric, and trimeric acid chains experimentally. This method removes uncertainties arising from interpretation of iodine value decrease in terms of chain linking. The object of the present paper is to draw attention to the successful application (7) of Flory's theory to thermally polymerized oils made from relatively slowly polymerizing triglycerides and to discuss the practical outcome of this application.

Application of Flory's Theory to Polymerized Linseed and Sunflower Seed Oils. Flory (5) investigated polyesterification reactions and proved that, in the model systems used by him, a) each acid and alcohol group had, at any moment, the same reactivity and b) intramolecular reaction occurred to a minor extent and could be neglected as a first approximation. From a) it follows that the reaction of any given functional group with any other is purely a matter of chance. From these assumptions and the measured extents of reaction, molecular weight distributions, number average molecular weights, and weight average molecular weights were calculated. Later the treatment was generalized by Stockmayer (13).

Polymerized oils are polyesters made up from glycerol, monoacids, diacids, and triacids. The alcohol groups are esterified to completion, but some of the acid groups are uncombined. The original unpolymerized oils contain a mixture of fatty acids having different degrees of unsaturation and polymerization rates. If no ester interchange occurs during polymerization, the molecular weight distribution will be partly dependent upon the original distribution of acids in the glycerides. For example, an oil consisting only of mono-oleodilinolein will give a result different from an oil consisting of two-thirds of trilinolein and one-third of triolein. If the acids are randomly distributed in the glycerides or if the exact state of randomness is known, then Flory's theory can be applied. Opinions differ with respect to the degree of randomness existing in natural triglyceride oils, but it is certain that they are, at least, not in the most ordered state possible. In the case of linseed oil and sunflower seed oil, which may be taken as typical examples of the relatively slowly polymerizing type, a random state is produced at 300°C. by ester interchange in a time shorter than that usually employed in practice for polymerization (7). Flory's theory can thus be applied to these cases. It may not apply with precision to the very early stages of polymerization (*e.g.*, <2 hours' heating at 300°), but even here it will lead to a good approximation of the true state of affairs.

Given the knowledge that a random distribution of monoacids, diacids, and triacids occurs over the alcohol groups of the glycerol molecules, the following additional data and considerations apply to the solution of the molecular weight distribution problem. The extent of reaction of the alcohol groups is one since none are uncombined. The extent of reaction of the acid groups is one minus the weight fraction of free acids. The proportions of monoacids, diacids, and triacids can be found by molecular distillation of the corresponding methyl esters.

Since free acids are formed at 300°C. from neutral glycerides, it follows that in some molecules the glycerol moieties must have undergone change. Paschke and Wheeler (10) recognized this problem and drew attention to the work of Skraup and Hedler (12), who put forward the following scheme for breakdown at 200°C.:



$$\begin{array}{ccccc} CH_2\cdot OOCR & & CH_2 & & CH_3 \\ | & & \| & & | \\ CH\cdot OOCR & \longrightarrow & COOCR & \xrightarrow{NaOH} & CO \\ | & & | & & | \\ CH_2\cdot OOCR & & CH_2OOCR & & CH_2OH \\ & & \text{I} & & \text{II} \end{array}$$

It is essential to know whether diesters of type I are present because the difunctionality of this postulated component would bring about some modification of the calculated molecular weight distributions. Although we have been unable to elucidate the exact mode of glycerol moiety breakdown, the evidence given below shows that combined glycerol is the only source of —OH groups in polymerized linseed and sunflower oils. The results calculated from the considerations mentioned in the preceding paragraph are therefore unaffected by the fact that breakdown of glycerol moieties occurs. The evidence is as follows:

a) No 2 keto 1 hydroxy propane (II above) could be detected in the saponification product from a linseed oil (alkali refined, iodine value 180) which had been polymerized at 300° C. for 8 hrs.

b) Heating of tristearin for long periods at 300°C. caused no material increase in its iodine value.
c) When tributyrin was heated for long periods (*ca.* 10 hrs.) at 300°C., distillation yielded no fraction of boiling point between that of butyric acid and tributyrin.
d) After heat treatment of sunflower seed oil (Solexol refined, iodine value 136) for 8 hrs. at 300°C. the product was analyzed for acids and glycerol. The glycerol analysis was carried out by the specific potassium periodate method (3) and showed that 86.7% of the original glycerol survived in the polymerized oil. 94.6% of the combined carboxyl groups in the original oil survived in the polymerized oil; of these 8.2% were free and 86.4% were combined. It is therefore clear that the only esters present are glycerides.

As has already been mentioned, the number and weight average of molecular weights can also be derived from the data used in calculating the molecular weight distributions. The weight average molecular weight is of particular importance with respect to viscosity. A few light scattering experiments have been carried out on polymerized linseed oils (15), and it was found that the viscosities were roughly proportional to the weight average molecular weights; these results need confirmation and repetition on a larger variety of specimens. With linear polyesters the square root of the weight average molecular weight is proportional to the logarithm of the viscosity (4), and with some degree of branching this relationship still holds (11). For blends of polymerized and monomeric linseed oil the following equation was approximately followed (6, 9): $\log \eta = (1 - x) \log \eta_1 + x \log \eta_2$ where $(1 - x)$ and x were the weight fractions and η_1 and η_2 the viscosities of the components. This equation implies that the weight average molecular weights of such blends are proportional to the logarithm of the viscosities (14); in such blends a random state is not attained, and the result shows that, in addition to the weight average molecular weight, the molecular weight distribution is also a factor in determining viscosity. As a practical illustration of these factors it has been found (7) that heating of such blends to create a random state by ester interchange results in a marked drop in viscosity.

Comparison Between Theoretical and Experimental Results. Paschke and Wheeler (10) determined the amounts of monomeric triglycerides in certain polymerized linseed oils. The amounts of free acids and the total amounts of monoacids, diacids, and triacids were determined in the same oils. From the latter analyses the amount of monomeric triglycerides can be calculated, using Stockmayer's equation (13). The same result can also be obtained in a much simpler way. If a random state exists, the probability that a glycerol molecule is esterified with three monoacids is M^3, where M is the amount of acid groups on a number basis residing on monomeric acids. M is equal to the weight fraction of monomeric acids. The total weight of the oil is somewhat more than the amount of glycerol molecules would indicate since free acids are present. If this is taken into account, the weight fraction of monomeric triglycerides is $P_B M^3$, where P_B is given by one minus the weight fraction of free acids. When measured and calculated results are compared, it should be noted that free acids are also present in the crude distilled monomeric triglyceride fraction and a correction must be applied to the measured values. The results calculated from Paschke and Wheeler's data (10) are given in Table I.

TABLE I

Amounts of Monomeric Triglycerides in Polymerized Linseed Oil

Duration of polymerization at 300°C. in hours	Amount of monomeric triglycerides in weight percentage	
	Measured[a]	Calculated
1.5	57.1	56.2
3	35.3	34.9
6	22.1	20.3

[a] From Paschke and Wheeler (10) with correction for free acid content.

The agreement between calculated and measured values is surprisingly good. Unfortunately the amounts of other molecular weight species cannot be measured. They can however be calculated by using Stockmayer's equations (13). As an illustration some results are given in Table II.

TABLE II

Calculation of Molecular Weight Fractions of Polymerized Linseed Oil in Weight Percentage[a]

Triglyceride species	Oil Polymerized at 300°C. for		
	1.5 hrs.	3 hrs.	6 hrs.
Monomer	56.2	34.9	20.3
Dimer	19.3	16.0	9.3
Trimer	8.8	9.4	5.7
Tetramer	4.3	6.0	3.7
Pentamer	2.2	4.1	2.6

[a] Using percentages of acids species given by Paschke and Wheeler (10).

It is seen that the amount of higher polymers is quite appreciable in the oil which was polymerized for 6 hrs. since less than 50% of the total weight consists of molecules smaller than hexamer. It is now obvious why the direct method of solvent fractionation has given so little information of quantitative value. The relatively small amounts of different higher molecular weight species are difficult to determine experimentally by solvent fractionation techniques.

No corrections for intramolecular reactions are applied in Tables I and II.

Another way of checking the theory is to compare calculated and measured weight average molecular weights. The number average molecular weight can be used to indicate the amount of intramolecular reaction when it is taken together with the known extent of reaction, but the number average is independent of the distribution of acids over the glycerol molecules and is consequently not a wholly satisfactory criterion for the validity of Flory's theory. The weight average molecular weight can be measured by light scattering

TABLE III

Comparison Between Theoretical and Experimental Weight Average Molecular Weights

Sample	M_w by light scattering[a]	Calculated[b] M_w (assuming no association)	Calculated[b] M_w (maximum correction for association)
Polymerized sunflower seed oil[c]	3,550	3,350	3,490
Polymerized linseed oil[d]	64,100	26,200	191,000

[a] Hexane solution, using 4358 Å and 5461 Å lines, Brice-Phoenix photometer.

[b] Using experimentally determined percentages of acid species.

[c] Original Oil, I.V. = 136, heated 8 hrs. at 300°; when I.V. = 98, free fatty acids = 5.8%. Corresponding acids consisted of 65.8% monomer, 26.6% dimer, and 7.6% trimer by weight; ratios of acid groups present were 67.1, 26.1, and 6.9, respectively, after correcting for found equivalent weights.

[d] Original Oil, I.V. = 180, heated 8 hrs. at 300°; when I.V. = 94, free fatty acids = 8.0%. Corresponding acids consisted of 53.7% monomer, 29.4% dimer, and 16.9% trimer by weight; ratios of acid groups present were 55.0, 29.3, and 15.8, respectively, after correcting for found equivalent weights.

experiments. Only two experiments have been carried out, and the results are given in Table III.

In the case of polymerized sunflower seed oil the agreement is satisfactory. The linseed oil was highly polymerized, and the calculations become inaccurate because of the unknown magnitude of association in solution caused by free acid groups present in large molecules. This effect can be very great if the weight average molecular weight is high, and an attempt has been made to correct for it by using equations which have been solved (15). The calculated values given have also been corrected for intramolecular reaction by assuming the same amount of intramolecular reaction as in the case of an esterification reaction between glycerol and dimeric acids (7).

Conclusion

In the case of slowly polymerizing oils it should now be possible to follow the changes in molecular weight distribution as polymerization proceeds and to study the relationship between this distribution and the viscosity.

Whether or not Flory's theory can be applied to rapidly polymerizing oils depends largely upon the fatty acid distribution over the glycerol molecules in any particular oil. It is probable that an approximation to a random state exists so that the polycondensation theory will be approximately followed.

The application of the theory is not limited to the thermal polymerization of oils. Provided that a random state exists, the theory can also be applied to the drying of oil films which is a catalytic polymerization. It would appear to be very attractive to investigate film properties as a function of the molecular weight distribution.

Summary

Flory's polymerization theory can be applied to polymerized oils, provided that the different acids are randomly esterified with the alcohol groups of glycerol. This state is attained when the oils are heated at 300°C. for long periods. The calculated amounts of monomeric triglycerides in polymerized linseed oils are compared with experimental results, and calculated and measured weight average molecular weights are also compared.

Acknowledgment

This paper is published by permission of the South African Council for Scientific and Industrial Research.

REFERENCES

1. Adams, H. E., and Powers, P. O., J. Applied Phys., *17*, 325 (1946).
2. Bernstein, T. M., J. Phys. and Colloid Chem., *52*, 613 (1948).
3. Colson, R., Oléagineux, *5*, 701 (1950).
4. Flory, P. J., J. Am. Chem. Soc., *62*, 1057 (1940).
5. Flory, P. J., Chem. Revs., *39*, 137 (1946).
6. Gussmann, L., p. 189, of the "Technical Proceedings of the Federation of Paint and Varnish Production Clubs," Chicago, October 25–27 (1939).
7. Hoeve, C. A. J., J. Polymer Sci., in press.
8. Joubert, F. J., and Sutton, D. A., J. Am. Oil Chemists' Soc., *29*, 287 (1952).
9. von Mikusch, J. D., Ind. Eng. Chem., *32*, 1061 (1940).
10. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *31*, 208 (1954).
11. Schaefgen, J. R., and Flory, P. J., J. Am. Chem. Soc., *70*, 2709 (1948).
12. Skraup, S., and Hedler, L., Chem. Ber., *85*, 1161 (1952).
13. Stockmayer, W. H., J. Polymer Sci., *9*, 69 (1951); *11*, 424 (1953).
14. Sutton, D. A., and Alexander, D. J., Technical Paper No. 163 of the Research Association of British Paint, Colour, and Varnish Manufacturers (1949).
15. Hoeve, C. A. J., "Some Physical Chemical Aspects of the Molecular Weight Distribution of Thermally Polymerized Oils," thesis, University of Pretoria, December, 1954.
16. Walker F. T., Mackay, T., and Taylor, K. B., J. Oil and Colour Chemists' Assoc., *36*, 667 (1953) .

[Received August 24, 1955]

A Rapid Dielectric Method for Determining the Oil Content of Safflower and Sunflower Seed[1]

ROBERT M. JOHNSON, W. HAWARD HUNT, M. H. NEUSTADT, and LAWRENCE ZELENY,
Grain Division, Agricultural Marketing Service, United States Department of Agriculture, Washington, D. C.

THE ECONOMIC IMPORTANCE of safflower seed in this country has increased in recent years, especially in the Pacific Northwest, Northern Great Plains area, and in certain sections of the Far Western and Southwestern States where the crop has possibilities as an irrigated or as a dryland winter crop. The most important characteristic of safflower seed oil is that it is the most economical source of linoleic acid available commercially. This factor makes the oil highly desirable for the manufacture of oil-modified alkyd resins and similar products (3). Sunflower seed in this country is primarily grown in the North Central States. In Canada sunflower seed production has been encouraged by the introduction of improved varieties, especially in the province of Manitoba. The most important characteristics of sunflower seed oil are its mild taste, pleasant odor, and resistance to the development of rancidity. In the United States both safflower and sunflower are grown primarily for the oil contained in the seed. The commercial products obtained from safflower and sunflower seeds are oil and oilseed or meal. Safflower seed contains from 26% to 40% oil; sunflower seed from 22% to 36%. Oil quantity therefore is an important factor governing the intrinsic commercial value of these oil-bearing seeds.

Two previous papers (1, 2) covered in detail the theory and procedure for determining rapidly the oil content of both soybeans and flaxseed by the dielectric method. The primary purpose of the work described in this paper was to modify the procedure previously adopted, to adapt the dielectric method to the determination of oil content in safflower and sunflower seeds, and to develop conversion charts for these oilseeds.

Since there are no well-established methods for determining either the oil content or moisture content in safflower and sunflower seeds, it became necessary to develop a standard procedure for determining these

---

[1] The study on which these findings are based was made under authority of the Agricultural Marketing Act of 1946 (RMA, Title II).
Presented at fall meeting, American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.