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The Chemistry of Polymerized Oils. I. Characteristics of Some Pilchard Stand Oil Fractions

F. J. JOUBERT and DONALD A. SUTTON, National Chemical Research Laboratory, Pretoria, South Africa

THE work reported here is a part of a long-term research being undertaken by this Laboratory into the organic and physical chemistry of thermally polymerized oils. In order to place this and the future communications of the series into their proper perspective it is first desirable to discuss briefly some of the main aspects of present day knowledge relating to the composition of stand oils against the general background of polymer chemistry.

Current Views on Stand Oil Chemistry

The growth of polymer molecules during the thermal treatment of triglyceride oils results from the presence of olefinic double bonds which are situated near the center of the fatty acid chains in most vegetable oils but are fairly evenly distributed along the more highly unsaturated portion of most fish oil fatty acid chains. Although the structures of the thermally formed linkages between chains are not yet known with absolute certainty, two differing hypotheses have been advanced and discussed in detail. According to the first hypothesis (17, 22), which commands the support of the majority of authors in this field, Diels-Alder reaction takes place by the addition of a double bond in one chain to the ends of a conjugated diene system already present or formed by heating in another chain so that the linkage consists of a cyclohexene ring substituted in four neighboring positions. According to the second hypothesis (28) a hydrogen atom detached from a methylene group flanked on one or both sides by double bonds adds to one end of a double bond in another chain with the result that the two chains become linked by a single carbon-carbon bond. It has been pointed out (29) that it is unnecessary to assume, as most authors have, that the alternative structural hypotheses are mutually exclusive and, in fact, it is not impossible that both may occur together. It is reasonable to expect that the position of the formed linkages with respect to the length of the chains concerned will have an important influence on the viscous and other physical properties of a given stand oil and furthermore that the structure of the linkages themselves will considerably in-

fluence physical properties. In this connection one may quote the fact that comparatively minor alterations in chemical structure alter considerably the physical properties of many polymer types (5). Apart from these structural considerations it is to be expected that the molecular weight distribution of a given stand oil will largely determine its physical properties.

Molecular Weight Distribution of Stand Oils

Theoretical Considerations. The theory of molecular weight distribution in polycondensation reactions between pure monomers has been developed by Flory (19), and the degree of deviation, which exists in practice from the mathematically necessary basic assumption that no intramolecular reaction occurs, has been tested by comparing observed and calculated gel points. Thus in the cases of the glycerol/phthalic acid system and of the pentaerythritol/adipic acid system the observed extents of reaction at the gel points were found to be somewhat greater than the calculated figures, indicating a minor but definite degree of intramolecular reaction so that the number average molecular weights, weight average molecular weights, and complete molecular weight distributions calculated by using Flory's equations in conjunction with the measured extents of reaction at any given time deviate, but not considerably so, from those which actually exist in the cases studied by Flory.

The relevance of Flory's work to the case of stand oils and other surface coating materials has already been recognized (24, 32) although Bradley who early recognized (12) the importance of functionality considerations and who has published widely on the stand oil problem (12-15), differs from Flory at some points (17). Flory's theory may be very usefully applied in qualitative terms to the interpretation of several important physico-chemical aspects of stand oil formation. For example, the viscosity/time relationships observed during thermal polymerization are of the same general type as those Flory records for polyesterification reactions, which have been interpreted by him in terms of his general theory. Again, the

possibility, which arises directly from Flory's work, of finding a simple relationship between viscosity and molecular weight averages is very attractive and has already been recognized (8, 32). The theory provides a satisfactory explanation of the sudden and reproducible gelation which occurs, for example, when tung oil is heated, in the absence of air, under standard conditions. Unfortunately very considerable difficulties prevent the satisfactory application of the theory to the calculation of quantitative molecular weight distributions in the case of stand oils although Adams and Powers (1, 2) have carried out such calculations on the basis of assumptions which are unproven and of doubtful validity. The difficulties arise, in part, from the fact that several reactions occur during thermal treatment; thus some loss of unsaturation occurs by intramolecular cyclization in addition to that expended in molecule linking. Further, the question of the degree of randomness existing in the natural triglyceride oils before heating has not been completely settled (18), let alone the degree of randomness existing in stand oils heated at various temperatures for various times. Again, iodine values may not indicate true losses of unsaturation as some of the double bonds in stand oils may be fairly unreactive, and this uncertainty will accentuate the difficulty of correlating unsaturation loss with extent of molecule linking. A further main difficulty arises from the fact that the triglyceride oils used as starting materials are complex mixtures containing fatty acid chains with different potential functionalities so that the linked chains in typical stand oils consist mainly of two-chain units with lesser, but not inappreciable, amounts of three-chain (and higher) units. In these respects a knowledge of the proportions of one-chain units, two-chain units, three-chain units, etc., existing in saponified stand oils would enable calculation of the molecular weight distributions existing in the original materials to be made, provided that a) the assumption that the carboxyl and hydroxyl groups are esterified in stand oils so as to give the same result as that which would obtain by an equal probability of reaction is valid, as in the cases Flory studied (it may be noted that this assumption is valid for simple triglycerides prepared by heating glycerol with fatty acids [6]) and b) the experimental determinations could be made accurately enough. An experimental approach with regard to a) would be to separate the acids derived from stand oils into one-chain, two-

chain, etc., fractions, hydrogenate the fractions separately (to prevent subsequent additional chain linking), and then react the acids in the appropriate proportion with the equivalent amount of glycerol. The number average molecular weight of the resultant fully esterified mixture could be calculated by Flory's methods and compared with the experimental results for both the original stand oil and for the synthesized hydrogenated material. Such a comparison would indicate to what degree it is justifiable to apply Flory's equations to the calculation of the complete molecular weight distributions for these materials, having made assumption a).

Experimental Data. Complementary to the above considerations, experimental fractionations of stand oils should provide molecular weight distribution data, the accuracy of which will obviously depend on the precision with which fractionation into molecular weight species can be carried out. It is to be anticipated that two opposing factors will influence the ease of accomplishing perfect fractionation with these materials: a) the large difference (ca. 900) between the molecular weights of the n and $n+1$ mer will facilitate fractionation; b) the differing geometrical forms arising from differing degrees of branching, etc., in species having the same molecular weight will make fractionation more difficult than would be the case if all molecules of equal weight had the same structure.

Until fairly recently it was believed that stand oils contained monomers, dimers, trimers, and small amounts of other very low polymers, but this view can now be regarded as disproven by the work of Bernstein (7, 8, 10) and of Sutton and Sherwood (31).

Bernstein fractionated linseed and soya bean stand oils by using, as extracting solvents, a series of alcohols in the range n propyl to n dodecyl and determined the number average molecular weights of the fractions which included all polymers up to at least the heptamer; the percentages of the various molecular weight species in each fraction were calculated from the observed molecular weights and complete molecular weight distribution tables computed. Although this work was a considerable advance on any previously published, the molecular weight distribution tables cannot be highly accurate since a) the cryoscopic method as used is inaccurate in the several thousand region for which it was here employed

TABLE I
Characteristics of Non-Polymeric Fraction and Derived Methyl Esters

Fraction	$E_{1\text{cm.}}^{1\% \text{ a}}$			Conjugated ^b Diene+ Triene	C and H	I. V. ^c	Sap. Equiv.	Mol. Wt. ^d	n_D^{20}
	2,350,	2,690,	3,000- 3,200 A. U.						
Non-Polymeric Fraction.....	45	39	%	%	141	1.4771
Distillate 1.....	40	22	6	109	288	269	1.4511
Distillate 2.....	44	31	5	141	296	282	1.4589
Distillate 3.....	165	160	50	24	C, 78.3; H, 11.4	174	314	314	1.4669
Distillate 4.....	63	47	9	133	300	285	1.4590
Distillate 5.....	82	63	11	174	318	319	1.4867
Distillate 6.....	177	103	40	23	C, 79.0; H, 10.9	205	364	362	1.4897
Residue 6.....	85	64	12	12	C, 78.3; H, 10.4	181	353	460	1.5011

^a Ethyl alcohol solvent.

^b Assuming $E_{1\text{cm.}}^{1\%} = 1,000$ for diene (23) and $E_{1\text{cm.}}^{1\%} = 2,060$ for triene (26).

^c Wijs one hour.

^d Method of Menzies and Wright (25).

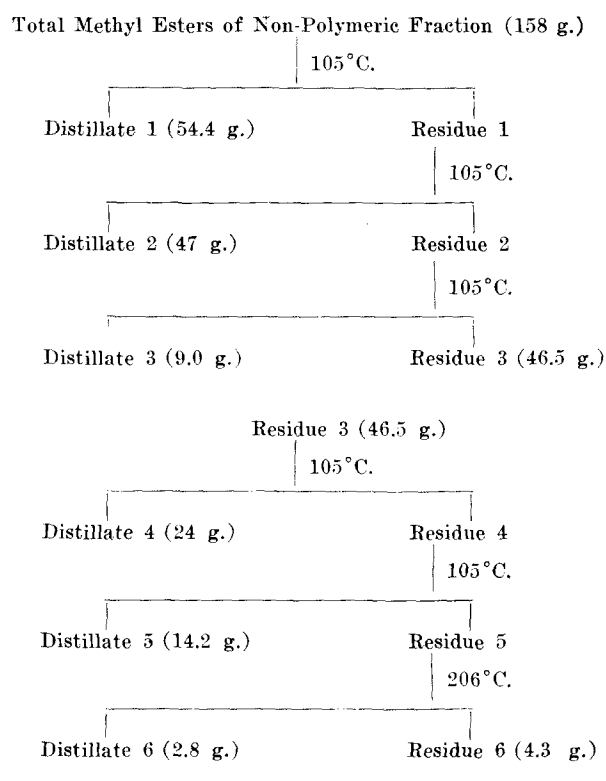
and b) calculation of the composition of each fraction was necessarily based on the assumption that only two molecular weight species were present.

Sutton and Sherwood fractionated linseed stand oils and also the total polymeric portions of stand oils by extracting with acetone continuously in a liquid/liquid extractor; they measured the number average molecular weights, using the Signer isothermal distillation equilibrium method as modified by Gee (20). In contrast to Bernstein's statements (9) that acetone is of little value for these fractionations it was found that the procedure enabled the rapid preparation of the highly viscous, least soluble components in appreciable percentages by weight although it was not considered that the fractionation achieved was very precise. These highly viscous fractions had number average molecular weights higher than the highest figures recorded by Bernstein, and the results showed a marked dependence of apparent molecular weight on concentration so that extrapolation to infinite dilution was necessary. This concentration dependence makes it clear that the cryoscopic method is unlikely to be of value with these materials. No attempt was made to establish molecular weight distributions since it was considered that these would be misleading unless solvent fractionation was carried to the stage where further fractionation of a reputed *n* mer fraction gave sub-fractions which consisted entirely or almost entirely of *n* mers.

New Work on Pilchard Stand Oil

Separation into Non-Polymeric and Polymeric Fractions. A light viscosity stand oil prepared in a commercial vacuum plant from refrigerated South African pilchard oil was used. The stand oil had been made by heating the oil to a top temperature of 273°C., holding it at this temperature 15 minutes and allowing to cool; the total time for which the temperature was in excess of 150°C. was 5½ hours. The stand oil had the following properties: iodine value (Wijs, one hour) = 144; saponification value = 185; unsaponifiable matter = 1.5%; viscosity = 1.2 poises/29.5°C. In order to remove nearly completely the non-polymers the oil was submitted to distillation in a Hickman five-inch rotating disc molecular still at 250°C., the non-distilled portion being recycled at temperatures up to 280°C. until the rate of distillation was negligible at 280°C. The total heating time on the rotating disc was probably less than one second. In duplicate runs the distillates represented 65% and 66.5% respectively of the weight of the stand oil, indicating the presence of approximately 35% of total polymers. The small differences between results of duplicate runs is attributed to the fairly large hold-up of the still and to the difficulty of distilling the last traces of non-polymer.

The Non-Polymeric Fraction. The non-polymeric material was a mobile light colored oil which solidified partially at 5°C. It had the following properties: iodine value (Wijs, one hour) = 141; saponification value = 187; unsaponifiable matter = 1.7%; viscosity = 0.5 poises/29.5°C. In order to test experimentally Powers' assertion (1, 2, 27) that the monomeric triglycerides of low viscosity stand oils contain appreciable amounts of linked chains, the non-polymeric fraction was saponified and the corresponding methyl esters were distilled in a three-stage falling film molecular still (30) according to the following scheme:



It will be seen from Table I that the saponification equivalents of all six distillates correspond within experimental error with the molecular weights, thus indicating the absence of linked chain material. Only in Residue 6 is the molecular weight higher than the saponification equivalent. If it is assumed that Residue 6 consists of monomeric and dimeric methyl esters only, then somewhat less than one-half of this material is dimeric so that the percentage of linked chains in the total non-polymeric fraction is less than 1.5. This behavior parallels the case of linseed stand oil non-polymer, which was similarly examined (31). The examination of isolated non-polymer and polymer for the purpose of detecting linkages between chains is to be preferred to the examination of total low viscosity stand oils as recently reported by Barker, Crawford, and Hilditch (3), who hold views similar to those of Powers.

The presence, to a minor extent, of links between chains not contributing to molecular weight increase is to be anticipated in the polymeric fraction in accordance with Flory's general thesis. It would however be surprising if large numbers of linked chains were formed in the non-polymer since such a reaction involves the unlikely formation of large ring systems (including the ester groups) whereas reaction between chains not in the same triglyceride molecules involves no such large ring formation and would therefore be the preferred mode of linkage.

The six distillates and final residue were examined for specific ultra violet absorption bands. All fractions had maxima characteristic of conjugated dienes (near 2,350 A.U.) and conjugated trienes (near 2,690 A.U.) and, in addition, Distillate 3, Distillate 6, and Residue 6 had maxima of low intensity near 3,200 A.U., possibly due to minor amounts of tetraene conjugation. The percentages of conjugated diene plus conjugated triene calculated in Table I make no allowance for irrelevant background absorption and will

therefore be slightly in excess of the true figures. The presence of conjugated unsaturation is in accord with the report by Bradley and Richardson (15) that conjugated diene is formed during the polymerization of linseed oil; the greater conjugation on heating, here reported, is in accord with the more highly unsaturated nature of the starting material (11). The percentage of conjugated diene exceeds that of conjugated triene in all fractions. This is to be expected since the formation of conjugated triene necessitates a greater degree of double bond shift and by further polymerization conjugated triene gives rise to conjugated diene in the dimer (4), contrary to literature reports (14, 15) and in contrast to the formation of conjugated diene in the non-polymers formed by the action of hot alkali (16).

The Polymeric Fraction. The total polymeric fraction was darker in color than the non-polymeric fraction; the observed viscosity varied somewhat from one preparation to another, probably due to the difficulty of removing every trace of non-polymer. Such viscosity variations probably represent minor differences in non-polymer content since a linear relationship is reported to exist between the logarithm of the viscosity and the composition of the stand oil mixtures (21, 33). A typical sample had the following properties: iodine value (Wijs, one hour) = 146; saponification value = 180; unsaponifiable matter = 1.4%; viscosity = 31 poises/29.5°C.

By continuous extraction with acetone in a liquid/liquid extractor the polymeric fraction was split into three portions of increasing viscosity and diminishing acetone-solubility, namely A, 66%, viscosity 7.3 poises/29.5°C.; B, 12%, viscosity 13.6 poises/29.5°C.; and C, 20%, 102 poises/29.5°C. The number average molecular weights of A, B, and C were determined at a number of concentrations in benzene solution, using the isothermal distillation rate method due to Signer and modified by Gee (20). The results are given in Table II, from which it will be seen that the marked concentration dependence appears in the case of C but not in that of A or B.

The three results obtained for C show a decided increase as the concentration of solution decreases. Another sample (D) of viscosity 22 poises/29.5°C. was prepared from the same stand oil by similar technique. It was found that plotting the reciprocal of the observed molecular weights against concentration (Figure 1) gave a straight line so that extrapolation

TABLE II
Number Average Molecular Weights of Polymeric Fractions

Fraction	Solvent	Concentration (g./100 g. solvent)	Observed Molecular Weight
A	Benzene	1.463	2,200
	Benzene	2.334	2,300
	Benzene	3.491	2,000
	Benzene	5.869	2,200
B	Benzene	1.627	3,000
	Benzene	2.753	3,300
	Benzene	4.986	2,900
	Benzene	6.632	2,600
C	Benzene	1.401	8,600
	Benzene	1.473	7,600
	Benzene	3.544	5,800
D	Benzene	2.329	5,900
	Benzene	4.815	4,500
	Benzene	6.182	3,800
	Benzene	9.219	3,000
	Benzene	11.460	2,600
	Cyclohexane	4.849	5,000

to infinite dilution could be made. The final result so obtained for D is 8,800, representing approximately nonameric complexity. The number average molecular weight of D was determined at one concentration in cyclohexane solution to give a result of 5,000, whereas the same concentration in benzene would have given 4,400 (from Figure 1); from this it appears that cyclohexane offers no great advantage over benzene as molecular weight solvent for these materials.

It is certain that A, B, and C are complex mixtures, and attempts are at present being made to fractionate pilchard stand oils more accurately.

Fraction A was examined further by conversion to the methyl esters followed by molecular distillation

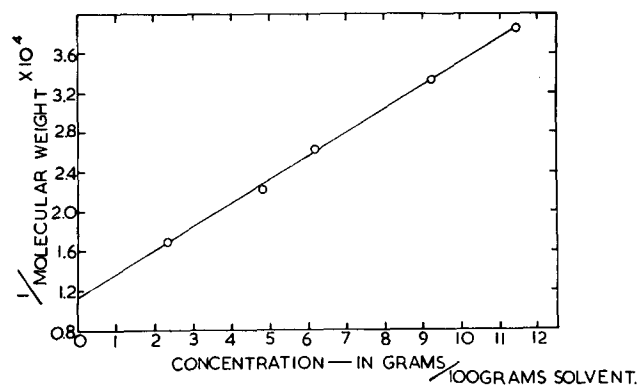


FIG. 1. Molecular weight of Fraction D in benzene solution.

TABLE III
Characteristics of Polymeric Fraction A and Derived Methyl Esters

Fraction	$E_{1\text{cm.}}^{1\%}$ ^a		Conjugated ^b Diene+ Triene	C and H	I. V. ^c	Sap. Equiv.	Mol. Wt. ^d	n_D^{20}
	2,350,	2,690 A. U.						
Total methyl esters.....	108	38	12	%
Distillate 1.....	43	18	5	C, 76.2; H, 11.8	82	286	287	1.4480
Distillate 2.....	57	22	7	C, 76.0; H, 11.7	104	300	300	1.4521
Distillate 3.....	68	38	9	167	305	1.4650
Distillate 4.....	143	88	18	C, 78.9; H, 10.2	194	314	323	1.4779
Distillate 5.....	187	99	23	179	317	435	1.4923
Distillate 6.....	200	20	1.5050
Residue 6.....	190	19	C, 77.0; H, 12.0	168	341	554	1.5172

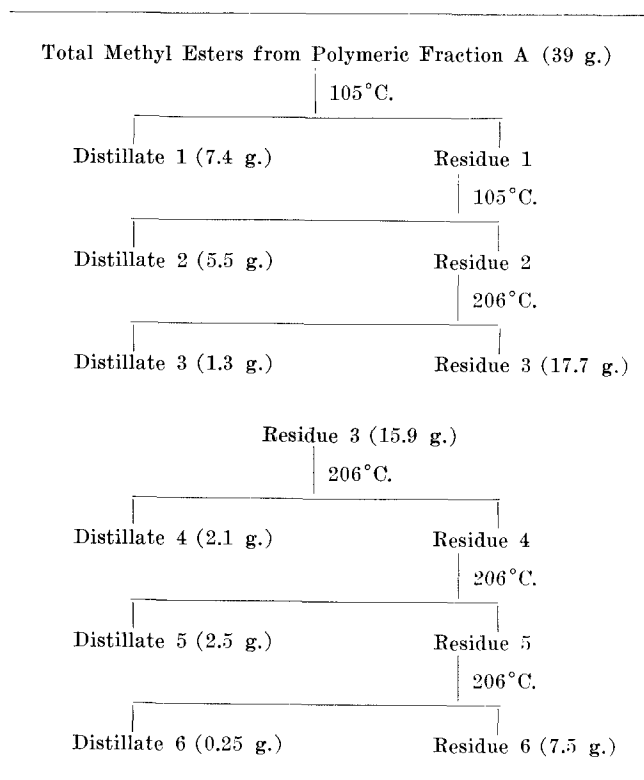
^a Ethyl alcohol solvent.

^b Assuming $E_{1\text{cm.}}^{1\%} = 1,000$ for diene (23) and $E_{1\text{cm.}}^{1\%} = 2,060$ for triene (26).

^c Wijs one hour.

^d Method of Menzies and Wright (25).

exactly as in the case of the non-polymer; the results are shown below and in Table III.



The losses by hold-up were higher than in the case of the methyl esters of the non-polymeric fraction owing to the greater viscosity of the fractions. Distillates 4, 5, and 6 and Residue 6 contained linked chain material; the total amount of linked chain material was approximately 33% of the esters after making allowances for distillation losses and assuming that only dimeric and monomeric esters are present. This figure is obtained by assuming that hold-up losses are evenly distributed among the various components and may therefore not be of high accuracy; nevertheless it is near that expected from the approximately dimeric complexity of Polymeric Fraction A. It will be noted that the proportion of linked chain material even in the polymers of low molecular weight is very much higher than in the non-polymeric fraction.

As in the methyl esters of the non-polymeric fraction all fractions contained conjugated unsaturation, which in the case of Distillate 5 represented a total of 23% of the fraction having this structural feature. A noteworthy point is the large diene conjugation in Residue 6, which consists chiefly of linked chain material.

Summary

1. Present-day knowledge of the composition and mode of formation of stand oils is briefly reviewed.

2. One pilchard stand oil of low viscosity has been separated by molecular distillation into non-polymeric and polymeric triglycerides.

3. The non-polymeric triglycerides contain a very low proportion of fatty acid chains linked together in contradiction of a published hypothesis.

4. The polymeric triglycerides have been separated into three broad sub-fractions, the number average molecular weights of which have been determined by an isothermal distillation method.

5. The polymeric triglyceride sub-fraction of lowest molecular weight was shown to contain an appreciable proportion of linked fatty acid chains.

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