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Possible Mechanisms in Thermal Polymerization of Vegetable Oils. II. Polymer Formation^{1,2}

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THE RESEMBLANCE between thermal polymerization of vegetable oils and polycondensation reactions has been pointed out by many workers (1, 4, 8, 13). However, in some cases, the extent of reaction was estimated from bulk viscosity measurements that, except during the early stages of bodying, were shown to bear a nonlinear relation to monomer disappearance (14) or from iodine number determinations that lose reliability with an increasing extent of reaction. In the present paper, polymer formation was followed, using a molecular still in which monomeric glycerides were separated from polymer and trimeric acyl groups from esters of higher complexity. Disappearance of unsaturation was followed by hydrogenation in dilute solution. Reaction temperature has been shown to affect polymer formation (3, 9, 13, 14, 16). Therefore an attempt has been made to assess the influence of temperature on polymerization mechanism.

The kinetics of the polymerization of methyl esters of unsaturated fatty acids have been studied by Paschke and Wheeler (8, 9) and by Rushman and Simpson (10). Paschke and Wheeler developed the idea that initially nonconjugated dienoic and trienoic acyl groups polymerize by way of a Diels-Alder type of reaction that is preceded by isomerization of the double bonds to the conjugated position. Nonconjugated acyl groups were shown to react with conjugated material. The latter workers have shown that polymerization of methyl linoleate is kinetically of the second order and proceeds more readily than diene conjugation. Second-order kinetics were also found by Sims (12) in a study of dilution polymerization of linseed oil. Further work is reported here in which the behavior of tung and oiticica oils, con-

taining large amounts of conjugated trienoic acids in the *trans* configuration, is contrasted with linseed and safflower oils where the unsaturation is initially *cis* and nonconjugated.

Materials and Methods

Linseed, safflower, tung, and oiticica oils were polymerized in an all-glass apparatus kept under constant positive pressure of oxygen-free nitrogen (12). The oil was degassed before being added to the polymerization vessel that was swept with nitrogen throughout the reaction. Samples were collected in an evacuated receiver, cooled under nitrogen, and kept under refrigeration in nitrogen-filled bottles. The nonconjugated oils were alkali-refined and bleached before heating whereas the conjugated oils were polymerized without prior purification.

Some samples of heated oils were hydrogenated at atmospheric pressure in dilute cyclohexane solution, using a platinum on silica catalyst (15). Details of the preparation of esters from glycerides, their hydrogenation, and their distillation have been reported elsewhere (14).

Content of polymeric glycerides and acyl groups was determined by micromolecular distillation (11); concentration of dimer was expressed in weight percentage, identical with base mole percentage, the molar percentage of monomer units that have dimerized. Where necessary, apparent concentration of monomeric and polymeric glycerides and acyl groups was corrected for the presence of thermal decomposition products. With oiticica oil as much as 16% of a sample distilled in the mono- and di-glyceride range. The results were therefore calculated on a true glyceride basis. With the other oils the differences were of the order of 3% or less and were not applied to the results.

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To permit expression of the data in terms of rate law parameters, the following relations were used.

p = extent of reaction
 = fraction of the functional groups reacted in given time

$(1-p)$ = fraction of unreacted functional groups.

When the kinetic parameters are expressed percent-age-wise, the above functions bear the following relations to them:

a = initial concentration of reactant = 100%

x = % reacted in given time

$(a-x)$ = % reactant remaining = $100(1-p) = a(1-p)$

$p = x/a$ and $1/(1-p) = 100/(100-x)$.

The first-order expression thus becomes $v = k(1-p)$, and that for a second-order reaction, of the type $2A = B$, $v = k(1-p)^2$.

The density of linseed and safflower oils was determined at 25, 100, 200, and 250°C., using Pyrex pycnometers. Specific volumes of the oils were then calculated and used to estimate molarity at reaction temperatures.

Samples of polymerized linseed and tung oils were fractionated by the method of Bernstein (2), which consisted essentially of extraction at +3°C. with three successive batches of solvent and protection from oxidative polymerization by 0.1% hydroquinone and a nitrogen atmosphere. By using a rotating evaporator to remove the solvent, the samples could be stripped at temperatures no higher than 50°C. Last traces of solvent were removed under high vacuum at room temperature. Molecular weights of the fractions were determined by the Signer method of isothermal distillation, using ether as the solvent (5).

Experimental and Results

Index of Extent of Polymerization. Extent of polymerization can be estimated in two ways, from decrease in unsaturation or from disappearance of monomer. The first method was tested by using hydrogenation in dilute solution to determine the decrease in unsaturation. The results (Table I) show

TABLE I
Effect of Heating Time on Hydrogenation Iodine Value

Linseed Oil ^a		Safflower Oil ^b		α -Tung Oil ^c		β -Tung Oil ^c		Oiticica Oil ^d	
Hour	HIV	Hour	HIV	Hour	HIV	Hour	HIV	Hour	HIV
0.00	185.0	0.00	145.0	0.00	237.2	0.00	235.0	0.00	189.2
0.05	181.7	0.15	141.1	0.03	236.2	0.05	231.4	0.25	169.5
1.0	153.5	1.0	131.3	0.75	227.9	0.75	205.0	0.50	153.2
2.0	135.9	2.0	112.5	1.50	219.3	1.50	175.0	0.75	137.6
2.5	123.4	3.0	92.6	2.25	209.0	2.25	1.00	128.7
3.0	111.0	4.0	80.8	3.00	194.4				
4.0	91.9	5.0	70.0	3.75	176.3				
5.0	75.9	6.0	61.0						

^a 310°C., ^b 320°C., ^c 203°C., ^d 230°C.

that the linseed oil has lost more than one double bond per molecule; division of change in hydrogenation iodine value (HIV) by 86.6 seems unreliable (1).

Extent of reaction from hydrogenation data was therefore calculated by using two denominators: total unsaturation as found in the 0-hr. sample and 86.6. When the data were used in second-order, rate plots ($p/[1-p]$ vs. t), curved lines were obtained in all cases when 86.6 was the denominator. When total

unsaturation was used in the calculations however, straight lines were obtained with oiticica oil and α -tung oil at 203°C. whereas α -tung oil at 270°C., linseed and safflower oils gave linear plots only after a short, initial curved portion. The data for β -tung oil, heated at 203°C., gave a curved plot in this case.

When the data were applied to first-order, rate plots, $\log(1-p)$ vs. t , curved lines were obtained in all cases when extent of reaction was calculated, using 86.6 in the denominator. On the basis of total unsaturation, safflower and linseed oils yielded linear plots while tung and oiticica oils gave curves.

To permit estimation of the extent of reaction from the disappearance of monomeric glycerides, samples of oils were distilled molecularly (Table II) and the

TABLE II
Polymer Formation in Heated Oils

Linseed 240°C.							
Time, hr.	1.0	13.0	24.0	48.0	61.0	80.0	95.0
% PG	1.01	5.58	10.6	21.4	27.3	30.4	38.5
% PAG	0.46	3.73	5.96	10.3	12.6
Linseed 310°C.							
Time, hr.	0.15	0.50	1.0	2.0	2.5	3.0	4.0
% PG	7.00	20.0	30.2	55.1	58.2	61.3	67.5
% PAG	3.06	7.00	13.6	24.5	28.5	31.3	36.1
Safflower 320°C.							
Time, hr.	0.15	1.0	2.0	3.0	4.0	5.0	6.0
% PG	5.00	31.8	53.0	65.1	72.3	75.4	76.4
% PAG	2.24	14.1	28.0	39.1	47.6	52.8	58.7
α -Tung 203°C.							
Time, hr.	0.08	0.75	1.5	2.25	3.00	3.75	
% PG	5.23	27.5	43.0	55.4	60.1	63.0	
% PAG	2.28	14.3	22.7	30.9	34.1	39.8	
β -Tung 203°C.							
Time, hr.	0.15	0.80	1.50	2.25	3.00		
% PG	10.6	41.4	54.9	62.0	67.0		
% PAG	6.62	25.8	35.5	39.9		
Oiticica 195°C. ^a							
Time, hr.	0.0	1.0	2.0	3.0			
% PG	40.2	51.5	52.2	63.6			
% PAG			

^a Corrected for 31.6, 16.3, 15.9, 13.0% material of M.W. 880
 PG = polymeric glycerides.
 PAG = polymeric acyl groups.

data expressed in two ways. From the formation of polymer, residual monomer was calculated and plotted as $1/(1-p)$ and also $\log(1-p)$. With linseed oil both plots curved; the first-order plot curved after an initial linear period, and the second-order plot became straight after an initial curved portion. Safflower oil appeared to give a first-order plot exclusively. With tung oil the second-order plot was straight whereas the first-order plot was curved. Alternatively, residual monomer was plotted against time, and the kinetic order was obtained by use of the fractional, half-life period method (7). The results of this analysis (Table III) are in agreement with those obtained above.

TABLE III
Reaction Orders from Formation of Polymeric Glycerides, Using Fractional Half-life Period Method

Fraction Reacted	Linseed		Safflower		α -Tung		β -Tung 203°C.
	220°C.	310°C.	280°C.	320°C.	203°C.	270°C.	
0.2	1.09	1.04	0.98	0.98	2.08	2.3	2.20
0.3	1.41	1.62	1.07	2.11	1.8	2.59
0.4	2.06	2.43	1.22	2.35	2.66

Ratios of Polymeric Acyl Groups to Polymeric Glycerides. Ratios of polymeric acyl groups to polymeric glycerides were calculated from the data in Table II and plotted in Figure 1 as functions of the

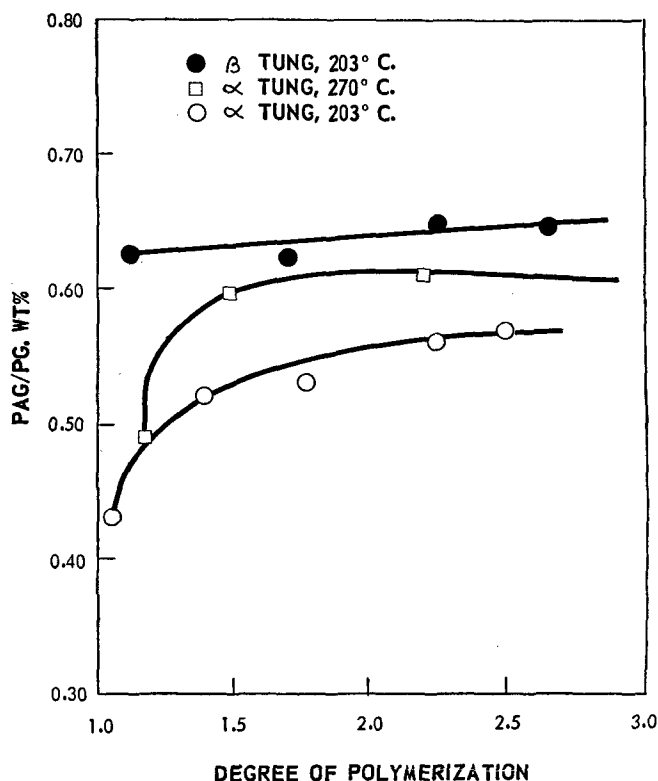


Fig. 1. Ratio of polymeric acyl groups to polymeric glycerides as a function of degree of polymerization: tung oil.

Open symbols: α -tung oil
Closed symbols: β -tung oil

degree of polymerization, $1/(1-p)$. With unisomerized (α -) tung oil at low temperatures, the ratio increased slowly from a value of about 0.4, reaching 0.55 at a D.P. of about 2. Isomerized tung oil, heated at 203°C., had a high initial value for the ratio that changed very little as the degree of polymerization increased. Unisomerized tung oil, heated at 270°C., behaved in an intermediate manner.

The ratios found with safflower and linseed oil also show (Fig. 2) a difference in behavior between oils heated at high and low temperatures. At high polymerization temperatures the ratio increased from a value slightly greater than 0.4; the rate of ratio increase apparently became greater as the degree of polymerization became larger. Use of high reaction temperatures resulted in a larger ratio except during the early stages of the reaction. Up to approximately 20% reaction (D.P. = 1.25), linseed oil, polymerized at low temperatures, and safflower oil at 280°C. had a high initial polymeric acyl group content.

Approximate Polymer Distribution. To determine the approximate polymer distribution, solvent fractionation was performed on four samples of oil: low

TABLE IV
Polymer Distribution, % by Wt.

	Linseed Oil		Tung Oil	
	$p=0.454^a$	$p=1.79^a$	$p=0.268^a$	$p=0.746^a$
Monomer ^b	72.6	33.8	43.9	28.4
Dimer ^b	16.1	11.8	32.1	15.0
Trimer ^b	9.2	10.4	14.5	13.0
Tetramer.....	2.9	8.1	3.8	8.7
Tetramer.....	Nil	35.9	15.8	34.9

^a Extent of reaction calculated from loss in unsaturation.

^b Mn by isothermal distillation.

and high viscosity linseed and low and high viscosity tung oils. Molecular weights of the monomer, dimer, and trimer fractions were determined, and a rough polymer distribution was calculated. The results (Table IV) show that whereas the monomer peak in linseed oil is but slowly reduced, tung oil monomers are rapidly converted to dimers which, in turn, react further.

Discussion

In general, nonconjugated oils display first-order characteristics during the early part of the polymerization reaction whereas conjugated oils react in an apparently second-order manner. However both reactions become complicated on or before 50% reaction; more acyl groups are used up per glyceride molecule polymerized, and from the hydrogenation data more than one double bond per molecule is involved during polymerization.

Two aspects of the hydrogenation data deserve comment. Oxidation of the samples could be responsible for the observed consumption of more than one mole of hydrogen per mole of fatty acid, and difficult-to-saturate double bonds in polymer molecules could give the impression of too great an extent of reaction. The samples were not checked for peroxide value before hydrogenation, nor were infrared spectra measured afterwards. However extreme care was taken to avoid oxidation of the samples, and an excess HIV of 23 (column 1, Table I) is equivalent to a peroxide value of 950 millimoles per kg.

An analysis was made of the effect on the shape of the rate plots of a continuously increasing error in HIV. Because of the form of the functions, the second-order expression is more sensitive to error

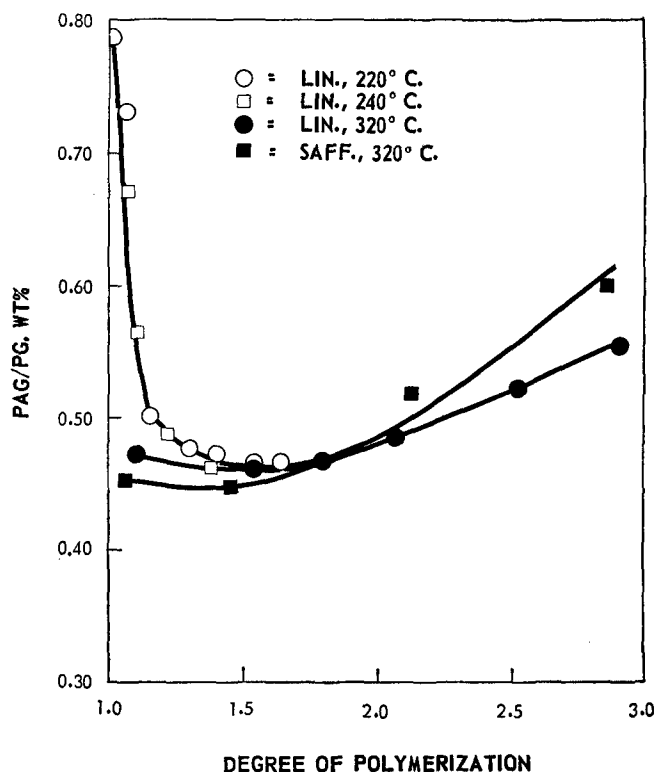


Fig. 2. Ratio of polymeric acyl groups to polymeric glycerides as a function of degree of polymerization: linseed and safflower oil.

than the first-order expression, and, in either case, greater sensitivity is obtained when p is calculated by using the smaller denominator. The curvature of the lines obtained when the hydrogenation data were tested support the suggestion that difficult hydrogenation was encountered. However the same trends in reaction order were found in the molecular distillation data.

From monomer disappearance data, specific rate-constants were calculated, first order for linseed and safflower oils and second order for tung and oiticica oils, and substituted in the Arrhenius equation. Energies of activation were calculated and compared (Table V) with those obtained previously (13). The

TABLE V
Activation Energy by Viscosity and Polymer Formation

Oil	Temperature	E (K. cal./base-mole)	
	Range, °C.	viscosity	dM/dt
Linseed.....	220-320	34.4	35.9
Tung.....	195-270	23.2	26.4
Oiticica.....	195-230	22.4

results indicate good agreement between viscosity rate constants and monomer-disappearance, rate-constants when both are measured in the early stages of the reaction. Because oiticica oil gave curved viscosity plots that were not amenable to treatment, the monomer disappearance plots in this paper are the first indication of the order, rate, and activation energy of the polymerization of oiticica oil.

Increasing the polymerization temperature affected the ratio of polymeric acyl groups to polymeric glycerides, an observation made previously (12, 14, 16). As shown in Figures 1 and 2, conjugated oils, particularly when in the all-*trans* configuration, tend to participate in intraglyceride reactions. With nonconjugated oils the ratio was not affected in the same manner. Beyond a D.P. of about 1.5, the ratio appeared to be relatively temperature-independent. In the early stages of polymerization, oils heated at low temperatures appeared to have a large polymeric acyl group content. Although this observation might be attributed to a slower rate of polymerization at lower temperatures, thus permitting more accurate assessment of the polymer content, low ratios were consistently obtained at small degrees of polymerization when the oils were heated at high temperatures.

The high initial ratios of polymeric acyl groups to polymeric glycerides might be the result of early, incomplete randomization of the acyl groups. However Dutton and Cannon (6) have shown that linseed oil has essentially a random distribution of acyl groups. It would therefore seem that at low polymerization temperatures (260°C.) a small amount of intraglyceride reaction may precede interglyceride polymerization.

The differences in kinetic order between the polymerization of nonconjugated and conjugated oils indicate a difference in mechanism. The first-order behavior of linseed and safflower oils might be interpreted as resulting from polymerization following isomerization. Similarly the second-order kinetics observed with the conjugated oils might be considered support for this hypothesis. However, in experiments where an inert diluent was used, second-order kinetics have been observed in the thermal polymerization of methyl linoleate (10) and linseed oil (12).

An explanation of the differences in kinetic order when the oils are heated in bulk can be found in their bulk molarity and in the molecular weight distribution of the polymers. Vegetable oils, by reason of their density and molecular weight, are approximately 1 molar with respect to themselves. Therefore, until the concentration of monomer is reduced by polymerization, they will display pseudo-unimolecular characteristics. Fractionation of samples of linseed and tung oils by the method of Bernstein (2) has shown that, whereas the monomer peak in linseed oil is but slowly reduced, tung oil monomers are rapidly converted to dimers. Consequently the transition from pseudounimolecular behavior is rapid with tung oil and slower with linseed oil.

Summary

From molecular distillation data, and information obtained by hydrogenation in dilute solution, extents of reaction have been calculated for the polymerization of linseed, safflower, tung, and oiticica oils. The hydrogenation data indicate that more than one double bond per molecule can be consumed during polymerization.

The kinetic order of the polymerization of nonconjugated oils increases from an initial value of unity to approach a value of two. With conjugated oils, second-order characteristics were maintained during the course of the bodying. An explanation of this difference in reaction order based on monomer disappearance is presented. Rate constants and overall energies of activation were calculated and compared with those obtained from viscosity measurements. Agreement between the two sets of values was obtained. Oiticica oil, which gives curved viscosity plots that cannot be resolved, has been treated successfully in this manner.

Intraglyceride reactions have been studied, and differences in behavior between nonconjugated and conjugated oils at high and low polymerization temperatures have been observed.

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