Some Implications of the Gel Point Concept to the Chemistry of Alkyd Resins

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Synopsis

This study explored the effects of chemical composition, extent of polyesterification and possible side-reactions upon the rheological behavior of a variety of oil-modified, glyceryl phthalate alkyds in both melt and in dilute solutions with several solvents. Correlative data were obtained on molecular weight and on other aspects of solubility and drying properties important to paint technology. Viscometric data proved very useful in relating variances of reaction degree with usage properties of these polymeric materials. Those data suggest a viewpoint of the gel point mechanism which enhances practical utility of polyesterification theory. This hypothesis proposes that alkyd synthesis is not a homogeneous reaction throughout, and that phase separation creates a colloidal dispersion in the reacting mass long before gelatification occurs. Classical polyesterification theory can predict the event of initial phase separation; other process variables affect the relative stability of the transition colloid which ultimately coalesces into the final gel structure. Practical properties of alkyds in paint vehicles can be adjusted to satisfy varying requirements by arresting the reaction at different levels before or in the transition region. Measurements of melt viscosity and intrinsic viscosity are especially sensitive and convenient probes for control of process and product in terms of this concept.

"Alkyd" is a general term which identifies one of the most important systems of vehicles used in the paint and ink industry. Alkyd resins are complex polymers derived from polyesterification of a variety of polybasic acids, polyols, and natural or synthetic monofunctional acids. Although the physical properties of these film-forming resins are governed mainly by composition, variances in the synthesis process also have large effects.

This family of polymers has been studied in great detail so as to develop a complex empirical art directed to many practical applications. Because the industrial usages of these polymers require that they be stable in solvent solutions at all stages of their processing history up to the time they are dried in films, the polymerization reactions must be checked at relatively low levels of molecular weight.[27] On the other hand, stopping the reaction too early will result in a molecular weight which is too low, and this will prolong greatly the time required to bake or air dry liquid paint films to a hard gel.[2,19,25,27]

Some theoretical studies have been made to determine whether the theory of polyesterification based upon statistical concepts[7-9] could be used to predict the extent of reaction where gelatification occurred during the syn-

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theses of these types of polymers.[22]   Many earlier investigators have con-
cluded that the complexity of side reactions occurring in the syntheses of
these resins makes it difficult to apply theoretical concepts in predicting the
gel point.   Commonly, some empirical correction factors are applied to cor-
rect exact equations for uncertainties coming from the supposedly greater
chemical complexity of alkyd synthesis reactions.   The history of this
point of view has been reviewed by Levy.[22]

In most industrial practice theoretical predictions are ignored alto-
gether and empirical procedures, like measurements of "stroke-cure"
times or of viscosity are used to track the approach to the gel point.   Rel-
atively small variations of the process schedule in the vicinity of the gel
point result in large differences in the rates of film formation, tensile prop-
erties of films, and the storage stability of paints made from these poly-
meric vehicles.[27]

A number of observations in this laboratory over the course of several
years suggested that the anticipated complexities of the alkyd polymer
system might be overestimated.   Possibly, the difficulties experienced in
interpreting the process events near the gel point of the synthesis schedule
might be due to poor experimentation rather than to inappropriateness
of theory.   To investigate this possibility, an intensive effort was made to
establish reproducible procedures for syntheses of some typical alkyd poly-
mers.   The course of events occurring in the process were diagnosed with
more refined analytical tools than are used commonly for process control in
the industrial art.

Here we will attempt to show that manufacture of these polymers can be
effected using reproducible and well controlled processes.   Under these cir-
cumstances, precise data can be obtained for some physical properties of
these polymers which provides some interesting insights regarding the
mechanism and significance of the gel point in the synthesis process.

POLYMER SYNTHESIS

Materials

Materials used were industrial chemicals available from the supplier
listed in Table I.   No differences in quality or reproducibility of results
were observed when materials of the same specifications were obtained from
two or more sources of supply, or as different lots from the same supplier.

Reactors

Exploratory stages of resin preparation were carried out in a 2-liter,
cylindrical, glass flask fitted with a domed and flanged lid, containing ports
to admit a stainless steel agitator, a thermometer, nitrogen bubbler, and
a condenser tube.   The condensate was drained into a Dean-Stark receiver
where water of condensation was withdrawn and solvent was returned
through an overflow port into the reactor.   This equipment was difficult

TABLE I

Material	Supplier
Phthalic anhydride	Allied Chemical and Dye Corp., or Koppers Chemical Co., or Monsanto Chemical Co.
Glycerine, synthetic	Shell Chemical Co., or Proctor and Gamble Co.
Lauric acid (Neo Fat 12)	Armour Industrial Chemical Corp.
Dimer acid (Emery 629-11-R)	Emery Industries, Inc.
Linoleic acid (Baker 9, 11 acids)	Baker Castor Oil Co.
Xylene (commercial grade)	Standard Oil Company of Ohio.

to manage reproducibly and sampling at intermediate stages of reaction caused excessive depletion.

Hence, the more precise work was done in a 10-gal., type 316, stainless-steel reactor. The reactor was agitated by a six-bladed, turbine impeller of 5 in. diameter. Improved turbulence was promoted by placement of three 0.75-in. baffles mounted vertically on the reactor walls about 120 degrees apart. The agitator was driven with an infinitely variable, hydraulic drive to provide agitation speeds of 0–600 rpm. Most reactions were carried out at 300 rpm.

The reactor was purged with dry nitrogen introduced below the agitator shaft at a rate of 0.2 ft.³/min. Vapors from the reactor were passed through a 5-ft. long, 3-in. diameter rectification column filled with Berl saddles. The column was jacketed so it could be heated or cooled, and a cold finger condenser was provided at the top to allow for adjustments of reflux. Analysis of the condensate and cold traps showed the reflux efficiency was sufficient to reduce losses of volatile reactants to a negligible level even when the maximum quantity of water of reaction was passing with the solvent into the condenser.

Vapors from the rectification column were passed through a multitube water condenser of 4 ft.² area. The condensate was then drained into a continuous decantor where water of reaction separated and the supernatant solvent overflowed through a port into the reaction vessel. With this decantor it was possible to maintain solvent concentration in the reactor nearly constant during the 20–25 hr. duration of reaction time. Two 2-in. sight glasses were provided for visual examination of the reacting mass Heat was supplied through electrical strip heaters of 3600 w. capacity mounted under the insulation on the outside wall of the reactor. Heating was regulated by a proportional control device. In addition, a stainless-steel coil having 1.08 ft.² of area was wound as three loops of coil midway between the agitator shaft and walls of the reactor. This coil could be connected to a supply of 140 psig steam or cold water, hence the reactor could be heated or cooled rapidly.

Samples were removed at intervals through a 0.38-in. valve on the bot-

tom of the reactor. At the time of removal, solvent was stripped from the specimen by holding a vacuum on the flask into which the sample was dropped. This sample collector was a two-liter, glass, resin kettle with the cover mechanically sealed to the sample-valve outlet. A high vacuum was drawn through a carbondioxide-cooled, side-arm condenser, which collected the solvent as it was flashed from the sample. The sampling procedure consisted of: (1) purging the sample line, (2) placing a pan as a sample container on the bottom of the stripping chamber, (3) evacuating chamber, (4) opening sample valve slightly to drain samples slowly over about a 5-min. interval, and (5) holding sample under vacuum for approximately 5 min. Solvent level in the stripped resin was less than 0.3%. This was a significant step in resin characterization. Solvent can be removed from cooled samples only with great difficulty. Samples up to 1 qt. in size in the solvent-free condition were taken hourly from the reactor using these techniques.

Reproducibility of Polymer Synthesis

Early synthesis by Levy[22] carried out in 2-liter glass reactors without solvent in the reaction mixture showed very poor reproducibility. Several variations of the schedule of addition of reactants were tried. For example, instead of charging all ingredients at once, either the glycerol and fatty acid were reacted for a few hours before the phthalic was added, or the glycerol was heated to the reaction temperature and then both oil acids and phthalic anhydride were added in the molten state. None of these variations of procedure were successful in eliminating batch-to-batch variations in reaction rate and in analysis of the product obtained. In the absence of solvent it was difficult to prevent losses of volatile reactants during synthesis. Also insoluble reaction products occurred early in the reaction which persisted as a separate phase throughout the reaction period. The precipitates are sometimes called "phthalic gel" by alkyd manufacturers. Both of these problems were eliminated when 15% of xylene was added to the reaction mixture. In the reaction here described, duplicate runs were found to produce resins of reproducible analysis and viscosity. Because of the advantage of reproducibility, all polymers described here were prepared in a 10-gal. reactor with about 15 parts of xylene per 100 parts of reactive constituents.

A Model Alkyd Structure

To begin this research we hoped to find a reference alkyd composition to which all other variants could be referred in correlating effect of compositional changes on properties. The starting point in the search for a model alkyd resin used glycerol, phthalic anhydride, and lauric acid in mole ratios of 1:1:1. In turn, while two of the reactants were held at the 1:1 molar ratio, the third was varied through the following ranges: (a) glycerol 1–25 moles, (b) phthalic anhydride 1–5 moles, (c) lauric acid 0.4–1 mole. Many

of these variants would not gel and some of them gelled at a very early stage in the reaction. The composition containing 0.4 mole of lauric acid and one mole each of phthalic and glycerol gelled only after reaching a very high extent of reaction in terms of carboxyl groups. This was selected as the reference to which all other variants would be compared in studying the effect of compositional and process variables on polymer properties.

MEASUREMENTS OF PROPERTIES

Dilute Solution Viscometry

Samples to be used for intrinsic viscosity measurements were vacuum-stripped during sampling as described earlier. The resin was then dissolved, while still hot, into methyl ethyl ketone to a concentration of 50 wt.-%. This solution was filtered through fine sintered glass filters. Aliquots were transferred from this master solution to number 50 Ubbelohde viscometers. Progressive dilutions were made directly in the viscometer by the addition of known amounts of solvent. Dilute solution viscosities were measured at eight dilutions ranging from 10 to 0.3 g./dl. of solution. The exact concentration of the master solution was obtained by weighing the non-volatiles residual after an aliquot volume was dried first under atmospheric conditions until most of the solvent was removed, and then held in a vacuum oven at 105°C. for 10 hr. At least two and more often as many as four solutions were prepared for dilution and measurement in the viscometer. The same techniques were used to determine the concentration dependence of dilute solution viscosity in solvents other than the ketone except that the master solutions were made by shaking the cold, solvent-free resin with the other solvent. Efflux times were recorded to ±0.1 sec. All measurements were made at 30 ± 0.02°C. Kinetic energy corrections calculated from viscometer dimensions were found to be small and were ignored.

The intrinsic viscosity can be defined in either of two ways:[23]

$$[\eta] = \lim_{c \to 0} \eta_{sp}/C \tag{1}$$

or

$$[\eta] = \lim_{c \to 0} (\log \eta_r)/C \tag{2}$$

where η_r is relative viscosity and C is the concentration in grams per deciliter.

The first is perhaps the most commonly used, but the second is easier to extrapolate to infinite dilution because $(\log \eta_r)/C$ is less dependent on concentration. Commonly, the units of concentration are grams per deciliter of solution. By expressing the concentration in units of grams of polymer per deciliter of solvent (C') in eq. (2), the values of $(\log \eta_r)/C'$ become nearly independent of concentration for dilute solution concentration of 1–10 g./dl.

of solvent.   The intrinsic viscosity for these alkyds can be determined by
measuring relative viscosity for a single concentration in the linear range of
concentration.

For a number of higher molecular weight polymers, the following relation-
ship between weight-average molecular weight M and intrinsic viscosity
has been found to apply:[9,17,18]

$$[\eta] = KM^a \qquad (3)$$

where $[\eta]$ is the intrinsic viscosity, and K and a are characteristic constants
of the polymer and solvent.   This expression was used to correlate intrin-
sic viscosity and degree of polymerization values determined by endgroup
analysis.   The validity of this expression has been discussed at length by
Bobalek, Lee, and Moore.[1]

Melt Viscosity

Melt viscosities were determined in a capillary extrusion viscometer sim-
ilar to the familiar melt indexer used for thermo-plastics.   The body of
the viscometer consisted of a stainless-steel cylinder, 6 in. in length, having
a 0.5-in. diameter concentric hole bored through its entire length.   One
end of the cylinder was threaded to receive interchangeable 0.5 in. thick,
stainless-steel plugs with different size capillaries.   Clamps were provided
on the cylinder to hold it vertical during operation.   The entire assembly
was covered with a 0.5-in. thick layer of heat-conducting cement, wound
with resistant, heating wire, again covered with heat-conducting cement,
and finally insulated.   Temperature control was maintained by embedding
a Fenwall thermal switch in the heat conducting cement surrounding the
cylinder.   The thermal switch activated a proportional controlling device
which regulated the amount of current passing through the nichrome heat-
ing element.   Temperature was continuously recorded on a Leeds-North-
rup Speedomax H recorder connected to a thermocouple which had been
welded to the cylinder near the capillary plug.   Temperature was main-
tained within $\pm 1°C.$ of the desired setting.

A stainless-steel piston guided by two Teflon O rings maintained to slide
with minimal friction through the 0.5-in. cylinder was used to develop an
extrusion pressure.   One end of the piston was threaded so different weights
could be placed on it, thus changing the extrusion pressure.   Polymer sam-
ples were preheated in an oven to the control temperature on the viscom-
eter and poured into the cylinder.   At the same time the piston was
placed into a hole provided in the thermostated block.   At least 10 min.
was allowed for the piston and the sample to reach thermal equilibrium
before the weighted piston was forced onto the top of the melt.   The ma-
terial extruded during measured time intervals was collected in tared alu-
minum dishes and weighed.   At least three samples were taken at each
temperature and piston weight.

The apparent melt viscosity and shear stress at the capillary wall were

then calculated from the Hagen-Poiseuille equation for laminar flow in a tube of circular cross section:

$$\eta_a = \pi R^3 t_w / 4Q$$

and

$$t_w = PR/2L \tag{4}$$

where η_a is apparent viscosity, R is capillary radius, t_w is shear stress at capillary wall, Q is volumetric extrusion rate, P is pressure, and L is capillary length.

The resin density necessary for this calculation was determined as will be discussed later.

A statistical analysis of the error involved in repetitive melt viscosity determinations demonstrated that individual determinations could differ from the mean by as much as $\pm 10\%$. By carefully selecting the size of capillary and weights for a given sample, and using the mean viscosity from three independent determinations, the error was reduced to less than five percent at the 95% confidence limit.

Calibration of the orifice was accomplished using a standard Dow Corning Co., Number 200, silicone fluid, the viscosity of which was known to three significant figures at each temperature of interest. Kinetic energy corrections were calculated from viscometer dimensions. These corrections were considerably less than the 5% error inherent in the viscosity measurements and were neglected.

To appraise the non-Newtonian properties, the apparent fluidity was calculated as a function of the shear stress at the capillary wall. Use of three different piston weights allowed the apparent fluidity to be measured at three levels of shear stress. Plots of the logarithm of apparent fluidity as a function of shear stress were found to yield straight lines for the resins investigated here. For Newtonian fluids, this line has zero slope. For non-Newtonian materials the slope becomes greater as the sample departs more and more from Newtonian behavior.

Density Determinations

Wide mouth, Pyrex pycnometers purchased from Fisher Scientific Co., (Cat. No. 1–711) were used for density determination. The calibrated and dry pycnometers were filled with resin at room temperature. When the pycnometers were heated, the resin expanded and flowed out of the hole at the top. One pycnometer filling could be used for density determinations at several successively higher temperatures. The pycnometer was brought to equilibrium in ovens where temperature could be maintained constant to within $\pm 2°F.$ up to $500°F.$ Two hours were allowed to attain thermal equilibrium at each temperature before the pycnometers were wiped clean, allowed to cool, and weighed. By this method, densities could be determined to at least three significant figures, which was sufficiently accurate for the calculations made with eq. (4).

Cloud Point

Dilute solutions of alkyd resin in acetone were titrated with water as a precipitant. Agitation was provided by a magnetic stirring device, and all titrations were carried out in a controlled temperature room at 22 ± 0.5°C. Titrations were carried to a visual endpoint, indicated by the first appearance of haze in an intense beam of light passing through the sample.

Fractionation

Solutions (2%) were made with both methyl ketone and acetone as solvents. Fractional precipitation was induced by incremental addition of methanol for the first cuts. Here the very high molecular weight fractions were precipitated. Methanol–water mixtures of increasing water content were added to fractionate the lower molecular material.[21] After each incremental addition of precipitating solvent to the solution in a separatory funnel, the mixture was warmed with an infrared lamp until turbidity disappeared, and then allowed to cool and stand undisturbed at 22 ± 0.5°C. for at least 24 hr. Most often, several days were required before the precipitate settled and the supernatant solution lost turbidity. The solution was then withdrawn from the funnel, and the curdy precipitate was collected, vacuum-dried, and dissolved in solvent for intrinsic viscosity determinations. Because the fractions were sometimes very small, the use of single-point measurements was necessary in many instances.[1]

Molecular Weight

Titration of unreacted carboxyl in samples withdrawn at intervals from the reactor was used to determine degree of polymerization. As pointed out by Flory[7,8] and Stockmayer,[29,30] number-average molecular weights may be determined from elementary stoichiometry. We must assume, however, that ring closure or other intramolecular reactions do not occur, that reactant losses can be neglected, and that the weight of endgroups can be neglected (or accounted for) in assigning a standard weight to the average repeating unit. Neglecting the contribution of endgroups introduces an error which becomes small as molecular weight increases. The second assumption has been reduced in importance through control of the synthesis process. The possibility of a ring closure complication will be considered later.

The same approach as employed by Flory[7] was used to derive the following expression for number-average molecular weight for the model alkyd composed of glycerol (B groups), phthalic anhydride and fatty acid (A groups) in molar ratios of $1:1:0.4$.

Let N_A = total A functional groups; N_B = total B functional groups; ρ = ratio of difunctional A groups to total A groups; P_A = extent of reaction for A groups; P_B = extent of reaction of B groups; $r = N_A/N_B = P_B/P_A$.

Then

$$\text{total number of units} = N_B/3 + N_A(1 - \rho) + N_A\rho/2 \qquad (5)$$
$$\text{total number of links} = N_A P_A$$

and

$$\text{DP} = \frac{\text{total number of molecular units}}{\text{total number of molecules}}$$

so

$$\text{DP} = \frac{[N_B/3 + N_A (1 - \rho) + N_A\rho/2]}{[N_B/3 + N_A(1 - \rho) + N_A \rho/2] - N_A P_A} \qquad (6)$$

Dividing through by N_A and substituting r for N_A/N_B yields

$$\text{DP} = \frac{2/r + 6 - 3\rho}{2/r + 6 - 3\rho - 6 P_A} \qquad (7)$$

For our standard alkyd $r = 0.8$, $\rho = 0.833$; substituting these values into eq. (7) yields

$$\text{DP} = 1/(1 - P_A) \qquad (8)$$

and

$$M = (M_0)\text{DP} \qquad (9)$$

To convert DP into number-average molecular weights, we must know the weight of the average repeating unit, M_0. To do this, let:

$$M_0 = FM_F + PM_P + GM_G/F + P + C \qquad (9a)$$

where F = number moles of fatty acid; P = number moles of phthalic anhydride; G = number moles of glycerine; and M_F, M_P, M_G are respectively the molecular weight of reactants corrected for loss of volatiles.

Assigning values of 132.11 to M_P, 89.49 to M_G, and 183.31 to the lauric acid (M_F), will make M_0 equal to 122.8. With lineoleic acid M_0 is 136.1.

Values for P_A can be determined directly from titration of the resin, where A_0 is the acid number (milligrams KOH per gram polymer) at zero reaction, and A is the acid number after reaction, then

$$P_A = (A_0 - A)/A_0 \qquad (10)$$

Acid numbers were determined by dissolving resin samples in an equal volume mixture of benzene and ethanol, and then titrating to the phenolphthalein endpoint with standardized base. The correctness of the endpoint of phenolphthalein titration was verified by potentiometric titrations with a glass–calomel electrode system. Dimethylformamide was used as the solvent for several samples to investigate the effect of a stronger solvent on the acid values. The acid values obtained with dimethylformamide solvent were the same as obtained in benzene–ethanol.

The validity of molecular weights determined from end group analysis using the values here cited for M_0 was confirmed by Moore.[24] He found that molecular weights obtained by using refined ebullioscopic techniques agreed to $\pm 5\%$ with values obtained from endgroup analysis up to a DP of 30, after which endgroup analysis seemed to overestimate the molecular weight (Fig. 17).

Drying Times

Several of the unsaturated alkyds of different degrees of reaction were modified with metal catalysts, and drying times were measured. These alkyds were diluted to 40 wt.-% solids with an equal volume mixture of xylene and butanol. The catalyst was added so the system contained 1.0% lead, 0.02% manganese, and 0.02% cobalt metals based on resin solids. The metals were added as mixed acid (tallate) soaps.

The catalyzed solutions were aged for 24 hr. in filled bottles; then 0.004-in. thick wet films were deposited with a film gauge on clean glass plates. The film was considered dry when a cigarette paper pressed onto the film for 50 sec. under a 100-g. weight failed to stick or rip away with noticeable tack. The films were examined every 10 min. for the first 2 hr., every hour for the next 6 hr., then every 12 hr. until dry. Six progressive stages of drying were recorded.

Suppression of Drying Oil Polymerization During Alkyd Synthesis

It is commonly assumed that drying oil polymerization is an unavoidable reaction of alkyd synthesis. To evaluate the importance of this side reaction, two alkyd resins were prepared having similar molecular composition except that one contained an unsaturated fatty acid (lauric) while the other contained a saturated fatty acid (linoleic). Melt viscosities of such polymers are shown in Figures 2–5. When these viscosities are plotted on the same graph, as shown in Figure 6, all polymers fall on the same curve.

If drying oil polymerization were taking place, it seems reasonable to expect some significant influence on melt viscosity. Likewise, Figures 11 and 13 illustrate intrinsic viscosities for saturated and unsaturated alkyds respectively. The linoleic modified alkyd shown in Figure 13 has slightly higher values of intrinsic viscosity at any given DP which might be expected because the linoleic acid side chain is slightly larger than that from the lauric acid. However, the slopes are identical, which does not seem reasonable if we assume fatty acid polymerization has occurred and thereby changed the branching complexity of the linoleic modified polymer.

Two syntheses were carried out by Levy[22] in duplicate. Glycerine, phthalic anhydride, and linoleic acid were reacted in the molar ratios of 1:1:0.4 for the first, in the second 0.06 moles of the linoleic acid was replaced by 0.06 moles of linoleic acid dimer. All four syntheses were carried out under the same conditions. Intrinsic viscosity values of the first

two alkyds were 0.106 and 0.106 dl./g.; values for the dimer-modified alkyd jumped to 0.151 and 0.150 dl./g. This further illustrates that the presence of small amounts of polymerized fatty acids in alkyds can cause a great increase in intrinsic viscosity. However, under the process conditions here employed, the dimeric acids had to be added to the formula. Monomeric linoleic acids did not appear to dimerize to an appreciable extent as a side reaction of this process.

As further evidence to this point, wet analysis techniques of Levy[22] involving saponification, separation of fatty acids, and vacuum-fractional distillation of the fatty acid showed no trace of polymerized fatty acids due to his synthesis conditions. Polymerized fatty acids could be recovered almost quantitatively if such were substituted for 10 wt.-% of total fatty acids charged to alkyd synthesis.

These observations show that drying oil polymerization does not take place to a significant degree under the conditions of alkyd synthesis here employed. This may not always be the case in other synthesis processes. It is interesting, however, that this side reaction can be suppressed to produce standard alkyds where oil polymerization is negligible. This can be useful in future work directed explicitly to study drying oil polymerization where it does occur in alkyds. This was not the main concern, however, in this study.

RESULTS AND DISCUSSION

What is the Gel Point?

During the course of these studies, a concept was developed which seemed to explain experimental observations while remaining in accord with the theory of gel point derived by Flory who applied statistical principles to some simplifying assumptions.[7−9]

To orient this discussion, a model for the gelation mechanism will be presented first as a hypothesis. This will later be supported by interpreting a variety of data here reported. As experimental results are discussed, other possible explanations conflicting with this hypothesis will be considered.

The concept of gelation here proposed is shown in Figure 1. As molecular weight increases, a critical extent of reaction is reached, where the formation of infinite network types of molecules becomes probable. This is the theoretical "gel point" as predicted by Flory's theory.[7−10] The exact size of molecular aggregates or particles is not known; here they will be called microgel. The microgel particles (either very large molecules or aggregates of molecules) are dispersed in the lower molecular weight polymer which remains as the continuous phase. These colloidal particles or microgel are stabilized in suspension, perhaps by a micellar type arrangement of the more polar molecules or by adsorption of a double layer. The stabilization mechanism is not of concern here. As a result of this

FIRST FORMATION OF INFINITE
NETWORK, THEORTICAL
GEL POINT

PHASE INVERSION, PHYSICAL
GELATION

INCREASE IN NUMBER
OF GEL PARTICLES

GELLED
RESIN

POLYMER BULK

GEL
PARTICLES
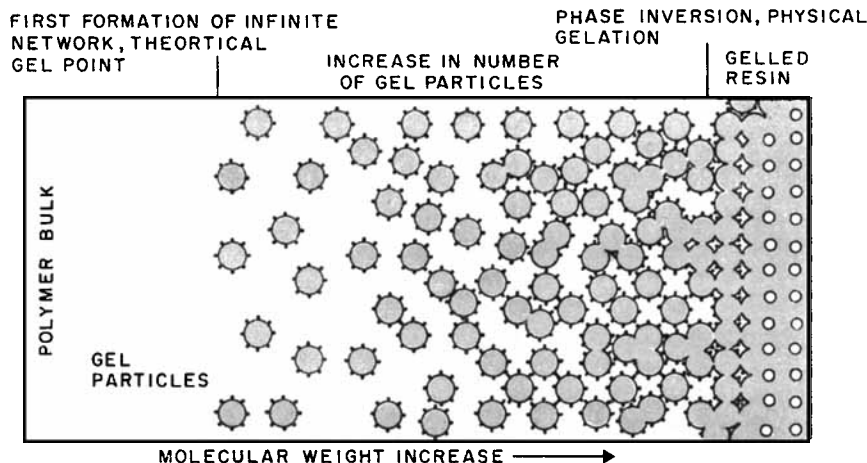
MOLECULAR WEIGHT INCREASE ⟶

Fig. 1. Proposed model for gelation process.

stabilization after phase separation, the microgel particles are unlikely to react with each other at an appreciable rate, and reaction with smaller molecules of the continuous phase is greatly retarded because of this phase heterogeneity.

As esterification proceeds, the number of particles increases, but because of the limited possibilities of particle growth, the size of each remains at colloidal dimensions. Finally a point is reached where the number of microgel particles becomes so large that they can no longer be kept completely separated by the repulsive action of the stabilizing layer in the now restricted volume of the continuous phase. At this point, microgel particles will coalesce or flocculate. At this point they can react with one another so as to stabilize a loose aggregate structure, as happens, for example, in gelation of latex dispersions. At this time a phase inversion occurs, and the flocculated microgel builds the continuous phase which includes the residual fluid phase sorbed into its internal structure. This phase inversion causes a steep rise in viscosity and immobilization of fluid flow.

The discussion which follows considers how this model of the gelation process is consistent with the data obtained to characterize change in polymer properties at difficult levels of reaction.

Relationship Between Melt Viscosity and Number-Average Degree of Polymerization

The equation[6]

$$\log \eta_A = A + \beta M_n^{1/2} \tag{11}$$

has been found useful in correlating melt viscosity and number-average molecular weight for alkyd resins. Data are shown in Figures 2–6. Similar equations have been used to correlate melt viscosity with weight-
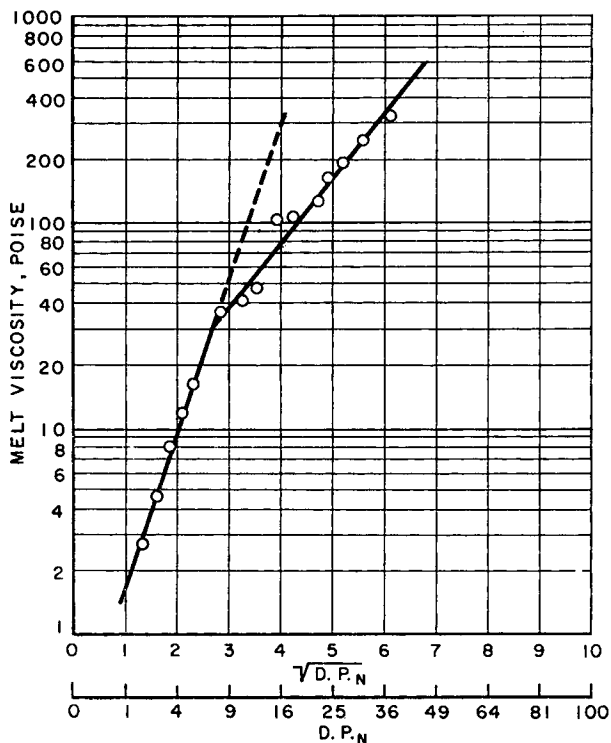
Fig. 2. Relationship of melt viscosity and number-average degree of polymerization for a glycerol:phthalic:lauric alkyd (1:1:0.4) containing $10 \pm 2\%$ xylene. Determination at 150°F. and extrapolated to zero shear stress.

average molecular weight.[6]   When molecular weight is low and molecular weight is rather narrow, as shown in earlier studies,[26] $\bar{M}_n$ and $\bar{M}_w$ will not be too far apart.

Figure 2 shows data obtained from a glycerol–phthalic anhydride–lauric acid alkyd reacted in molar ratios of 1:1:0.4 at a temperature of 325 $\pm$ 5°F.   Viscosities were measured in concentrated solutions containing $10 \pm 2\%$ xylene at 150 ± 2°F.

Melt viscosities for the same series of alkyds are shown in Figure 3, where solvent was first removed by vacuum stripping.   These samples contained less than 0.3% xylene.   The solvent concentration here may be less than the 0.3% which is the minimum threshhold which can be detected positively by weight-loss methods.   Viscosity was measured at 200 $\pm$ 2°F.   For this process series, the reaction temperature varied from 321°F. at the start to 350°F. at completion of the reaction.

Viscosities shown in Figures 4 and 5 are from two duplicate runs in which the saturated lauric acid has been replaced by unsaturated linoleic acid with the molar ratios or reactants being maintained at 1:1:0.4 glycerol:phthalic anhydride:linoleic acid.   These alkyds were vacuum-stripped
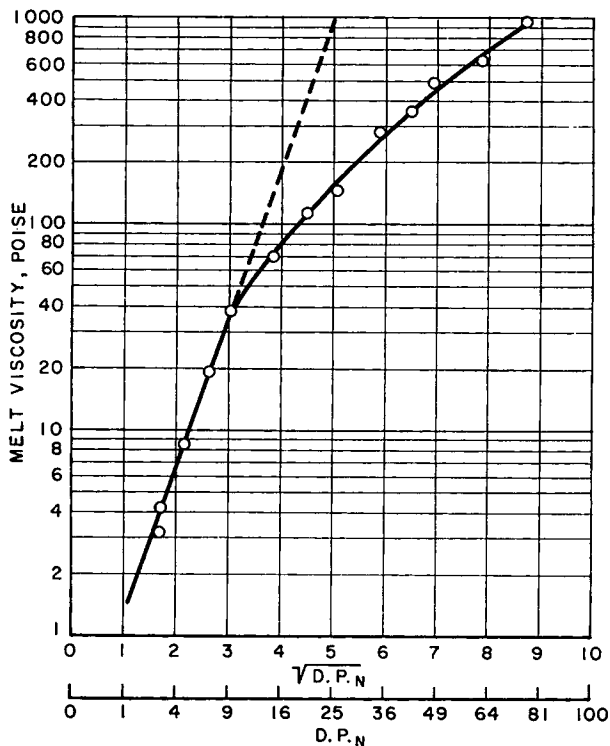
Fig. 3. Relationship of melt viscosity and number-average degree of polymerization for a glycerol:phthalic:lauric alkyd (1:1:0.4) containing less than 0.3% xylene. Determination at 200°F. and extrapolated to zero shear stress.

and retained less than 0.3% of the xylene which was present in concentration of 15% during the reaction. Viscosities were measured at 200 ± 2°F., and reaction temperature ranged from 320 at the start to 355°F. at the terminus of the process.

On examination of Figures 2–5, it is apparent that the linear relationship between log of melt viscosity and square root of degree of polymerization $(DP)^{1/2}$ is obeyed until $(DP)^{1/2}$ reaches a value of about 3. Later work by Fox and Flory[12,14] has suggested that a more universal correlation between molecular weight and bulk viscosity results when the logarithm of the molecular weight is plotted as a function of logarithm of bulk viscosity. More recently, Fox[15,16] has found that an upward break occurs in this log–log plot when a critical level of molecular weight is exceeded. This he called the critical entanglement point where molecules must not only overcome the "molecular friction" in sliding past one another, but must also disentangle. When the data of Figures 3–5 were plotted on a log–log plot, the downward break was found to persist, with the slope changing abruptly from 2.10 to 1.53 at a DP of 8.5.

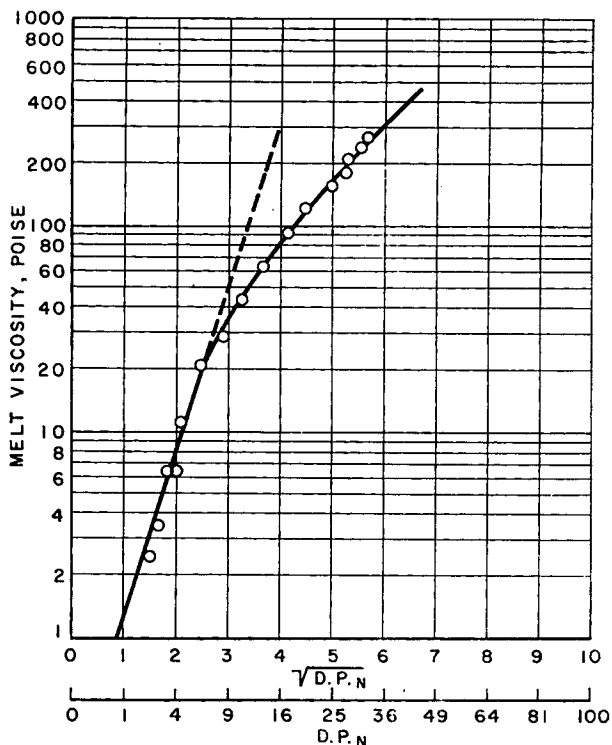When the data from Figures 3–5 were plotted together, as shown in

Fig. 4. Relationship of melt viscosity and number-average degree of polymerization for a glycerol:phthalic:linoleic alkyd (1:1:0.4) containing less than 0.3% xylene. Determination at 200°F. and a shear stress at the capillary wall of 7.54×10^4 dynes/cm.[2].

Figure 6, they were observed to fit a single line, the downward break being even more apparent. This behavior is in reverse of the direction of Fox's predictions, and seems also to contradict our initial expectation that the slope of the curve should become more steep when the gel point was near. Several explanations might be advanced to explain these unexpected facts.

The apparent anomaly might be attributed to losses of acid during the course of the reaction or to the presence of an increasing amount of intramolecular condensation. These factors would effectively defunctionalize or block molecular weight development. Because DP calculations are based on analysis of the unreacted endgroups, extraneous losses of acid functionality would cause us to overrate the value for DP. If the calculated value for DP is in error on the high side, the horizontal scale would be extended causing an apparent but unreal change in slope.

This explanation does not seem plausible. To obtain a synthesis which yielded resins showing reproducible analysis for carboxyl, hydroxyl, and other constituents,[22] it was necessary to use a solvent in the synthesis. The most important result of using a solvent cook under precision control was to reduce the loss of reactants to a degree which couldn't be detected by
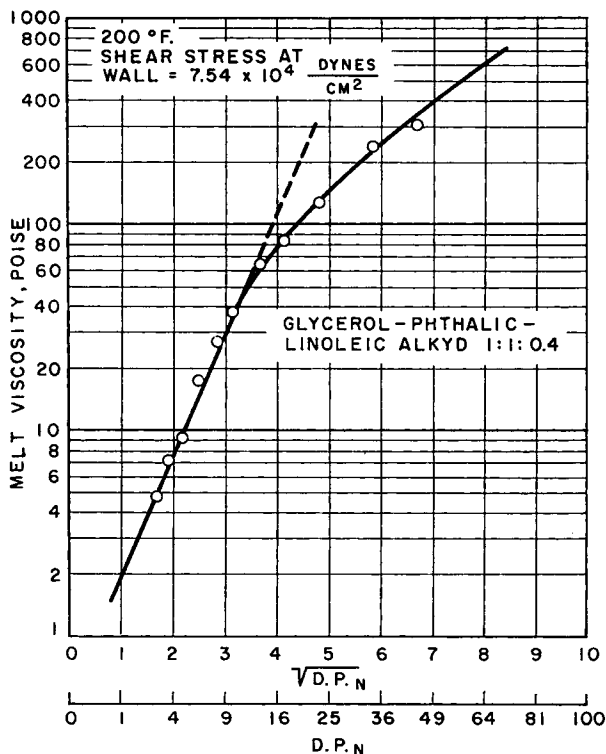
Fig. 5. Relationship of melt viscosity and number-average degree of polymerization for a glycerol:phthalic:linoleic alkyd (1:1:0.4) containing less than 0.3% xylene. Determinations at 200°F. and a shear stress at the capillary wall of 7.54 × 10⁴ dynes/cm.²

total analysis of the finished resin or by collection of volatiles in traps cooled with liquid nitrogen. For example, when water of reaction was collected, less than 0.005% of the total acid charged appeared in the water condensate or on the walls of a series of cold traps used to scrub the nitrogen stream flowing from the reactor.

The possibility of intramolecular reaction exists, but it is doubtful that its effect on molecular weight could be large enough to explain the magnitude of the deviations shown here in the melt viscosity correlations. If intramolecular condensation is proceeding as a competitive reaction, it must be consuming functional groups at some fairly uniform rate. It is possible to estimate by graphical methods the number of functional groups which would need to be consumed to explain the observed viscosity deviations which are indicated by the horizontal deviations of experimental data from the dotted lines in Figures 2–6 which extrapolate the curves from lower molecular weights. This has been done for the data presented in Figure 2.

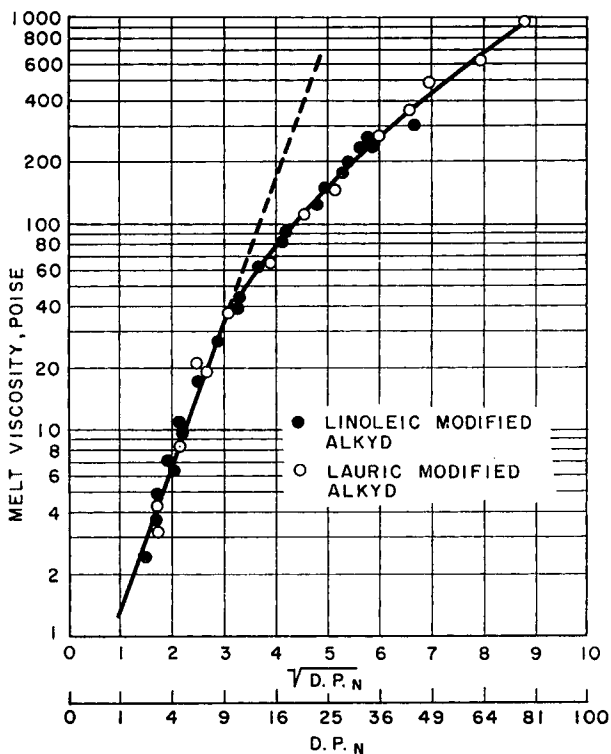Results shown in Table II demonstrate that the number of functional

Fig. 6. Cumulative plot of relationship of melt viscosity to number-average degree of polymerization for alkyds shown in Figs. 3–5.

groups that would have to be utilized in intracondensation remains nearly constant. If this is the explanation, all intramolecular condensation must have occurred early with no gains in later stages of reaction where this should be more probable.

TABLE II

The Relative Number of Functional Groups (Δ Acid Number) Which Would Need To Be Utilized in Intramolecular Condensation if Ring Closure Is To Explain Melt Viscosity Deviations at Later Stages of Reaction in Figure 2

$(DP_n)^{1/2}$	$\Delta (DP_n)^{1/2}$	Δ Acid no.
3.38	0.35	11
3.52	0.5	14
4.21	0.92	14
4.68	1.2	15
4.96	1.3	14.5
5.20	1.5	14.5
5.60	1.7	14.2
6.1	2.0	13.8
6.5	2.2	13.0

Also, if the melt viscosity were due to any factor that caused the apparent values of DP to be erroneously high, intrinsic viscosity plots using the same DP data should show the same sort of downward deviation. Intrinsic viscosity plots, shown in Figures 12 and 13 for the same alkyds, show no irregularities until a DP of 30 is reached, where an upward deviation occurs suggesting a sharp increase in weight-average molecular weight. The upward deviation in the intrinsic viscosity data will be discussed later.

Flory's[7] theory predicts that infinite network structure should begin to form at a degree of polymerization of 11.15, which is very close to the point where deviations in slope occur in bulk viscosity curves (Figs. 2–6).

Supposing that the infinite network structure predicted by theory (which here we call microgel) is formed where predicted by Flory's theory[7] as suggested earlier, the microgel particles will separate as a dispersed phase. Their molecular weight will be much higher than that of the polymer bulk, and their solubility parameter will be markedly different, resulting perhaps in particles made up of nonextended molecules dispersed in a continuum of low molecular weight polymer. The compacting of large molecules into the dimensions of a colloidal particle would decrease the hydrodynamic resistance to flow which might have been presented if these larger molecules remained extended in homogeneous solution. Essentially, the largest molecules are being fractionated from the polymer bulk to form microgel particles which have a comparatively small contribution to melt viscosity when present in low concentration.

Thus, the sudden appearance of microgel particles could coincide with a decrease in melt viscosity below the value expected if all molecular species were making their maximum contribution as extended molecules. This type of deviation is suggested by Figures 2–6.

Very dilute solutions do not exhibit nonlinearity in the 5–30 D.P. region, as shown in Figures 12 and 13. To determine how low the per cent solids could be taken before this nonlinearity ceased, a series of concentrated solution viscosities were run in xylene and xylene–ethanol. These measurements were made with a Ferranti-Shirley viscometer (discussed in detail by Moore[24]) at 30 ± 1 °C. As shown in Figure 7, polymers in xylene solution continue to exhibit nonlinearity even below 40% solids. However, in an equal volume blend of xylene–ethanol, a linear plot prevails up to concentrations as high as 50%.

The appearance of non-Newtonian flow characteristics at advanced degrees of reaction may indicate the appearance of larger, more complicated molecules. As shown in Figures 8 and 9, dependence of melt viscosity on shear rate does not develop until reaction is advanced to a DP of 20–25. It is particularly interesting that non-Newtonian behavior is seen to develop very close to the DP where plots of intrinsic viscosity against DP show also a steep change in slope (Figures 12, 13). Both measurements indicate development of a new factor in fluid structure. Non-Newtonian flow was not detected in the concentration solution viscosities which are shown in Figure 7.
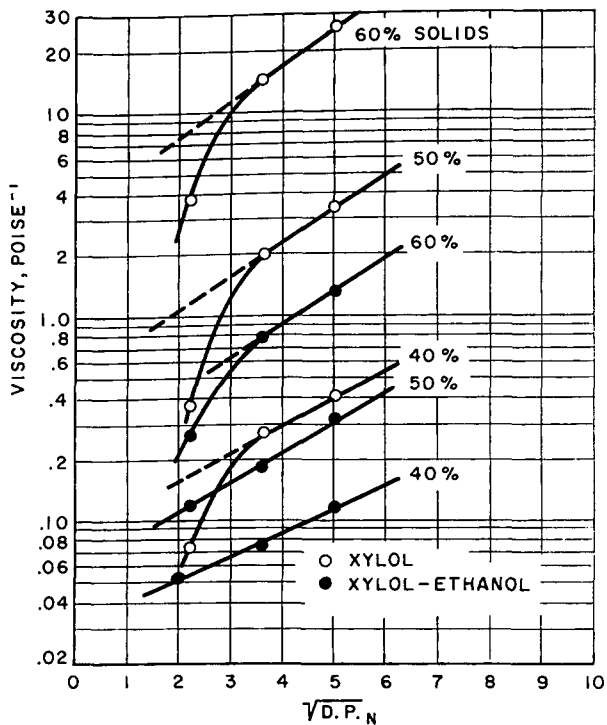
Fig. 7. Effect of number-average degree of polymerization on concentrated solution viscosity. Glycerol, phthalic, linoleic alkyd in xylene, and 50–50 (by weight) xylene–ethanol; determination at 30°C.

Drying Studies

It is a common industrial observation that if a resin synthesis is not carried close to the point of gelatification, then drying or film forming properties are less than optimum. This was confirmed in our laboratory. Figure 10 shows how drying times vary with advancing degree of polymerization for a series of linoleic modified alkyds.

As DP approaches 9, a dramatic decrease occurs in the time required to dry films to a tack-free condition. Increasing the DP beyond this critical point speeds drying somewhat more, but the relative gains are less. Finally after a DP of about 30 is reached, only a very slight reduction in drying time can be had by further advance in DP.

To explain these data we can infer that either directly or indirectly some nucleation process affects drying rate. If the drying is slow when nucleating sites are in low concentration, then the first few nuclei to form should have a tremendous influence on rate of film formation. Subsequent increases in nucleation sites should have a proportionally smaller effect. For example, addition of ten nuclei to a mass already having ten nuclei would result in a 100% increase, while addition of the same number to a mass
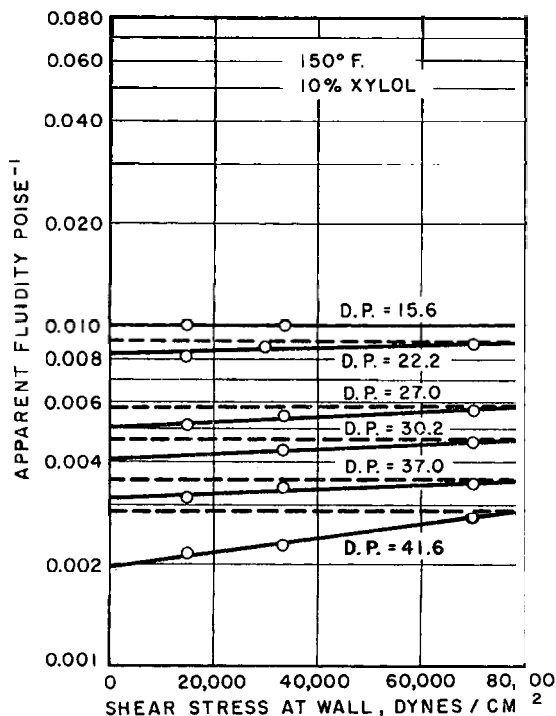
Fig. 8. Effect of shear stress at capillary wall on apparent fluidity for the lauric-modified alkyd of Fig. 2 containing 10% xylene.

containing 1000 nuclei would result in only a 1% increase. The appearance of microgel particles, where theory[7] predicts probability of infinite network formation, may coincide with the DP where the alkyd first develops capability to dry at a rapid rate if appearance of such complex molecules is important to the drying process. This conjecture is supported by the data. The DP where a high gain in drying rate begins to develop coincides with the DP range where the unexpected downward deflection occurs in the curves which relate logarithm of melt viscosity to the square root of DP (Figs. 2–7).

To determine whether small amounts of this "nucleation species" has a greater effect on drying times than does a general increase in average molecular weight, two alkyds were mixed together. A relatively low molecular weight material of DP of 10 was mixed with a high molecular weight type of DP of 34. The results are plotted in Figure 11. Addition of as little as 20% of the high DP material reduces drying time to about 15% of what was characteristic for the low molecular weight polymer. Further increase in quantity of the high DP alkyd causes relatively little further gains on the drying rates.

The concept that very high molecular weight molecules or colloidal particles must be present at least in small concentrations before drying
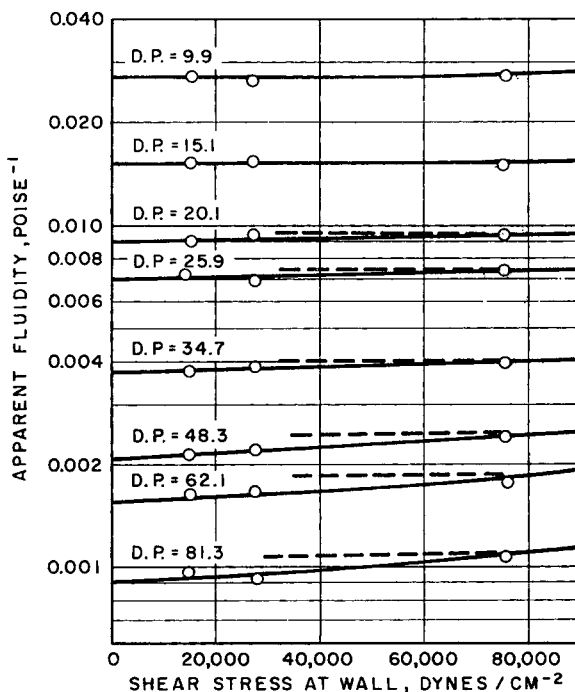
Fig. 9. Effect of shear stress at capillary wall on apparent fluidity for the lauric-modified alkyd of Fig. 3 containing less than 0.3% xylene. Determinations of viscosity at 200°F.

properties optimize explains the utility of a number of practices in the industrial art. For example, the usual practice of carrying the synthesis very close to gelation as practiced industrially and discussed by Berryman[2] could provide a large number of nucleating particles. Drying time advantages are gained also when an alkyd is styrenated. This may be due to the nucleating characteristics of the larger copolymer molecules which seem to exist in colloidal dispersion in these vehicles.[30] The high polymer alkyd technique proposed by Kraft[19,20] could introduce nucleating sites in long oil alkyds. Kraft recommends withholding a portion of the monofunctional fatty-acid and reacting other constituents to higher molecular weight before adding the remaining acid and continuing reaction to a low residual acidity. The nucleating species of polymer could be introduced by this procedure.

Kraft's technique was tried during the course of this research. An alkyd of the molar proportions 1:1:0.4 of glycerol, phthalic anhydride, and linoleic acid, respectively (oil length = 35.3%), was cooked to an acid number of 9.28. By adding 0.4 moles of fatty acid, the oil length was increased to 53.6%. Two reactions were carried out; in the first, the 1:1:0.4 alkyd prepolymer (acid number 9.28) was charged to a reactor along with sufficient linoleic acid to bring the molar proportion to 1:1:0.8; in the
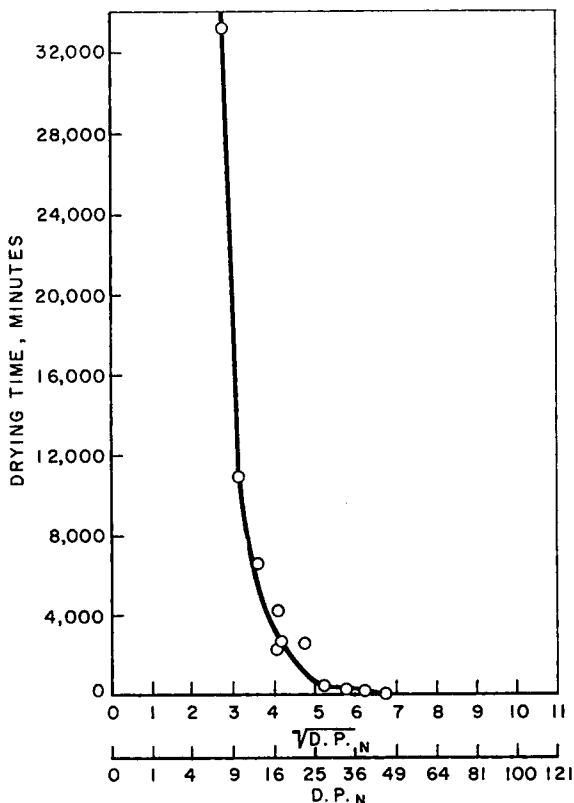
Fig. 10. Effect of advancing degree of polymerization on drying time of linoleic alkyd. Dried at 22°C. from 4 mil wet film.

second, monomeric glycerine, phthalic anhydride, and linoleic acid were charged in molar proportions 1:1:0.8. In all cases the prepolymer batch maintained a much higher viscosity at corresponding acid numbers and finally gelled at an acid number of 10.7. Viscosity of the second polymer remained low, with no signs of gelation at an acid number of 9.50. If the interpretation we suggest in our hypothesis of Figure 1 is correct, the success of Kraft's technique indicates a high order of stability for dilute concentrations of the constituent we call microgel.

The exact role that microgel plays in the drying process is not completely understood. It is tempting to attribute the increased drying rate to the great increase in drying oil functionality which the microgel particles must possess. This may play a role; however, oxygen absorption studies indicate that some other mechanism is also involved. It has been shown[24,25] that the rate of oxygen absorption increases as molecular weight becomes larger. This cannot be explained as due to an increase in functionality, because the rate of oxygen uptake depends on total saturation of fatty acids and not on how they are distributed between alkyd molecules of different
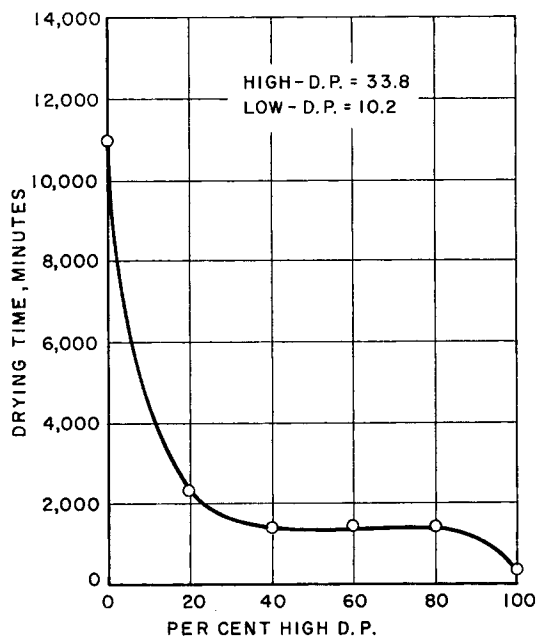
Fig. 11. Drying time for mixtures of a high and low DP linoleic alkyd. Dried at 22°C. from a 4 mil wet film.

size. It has been proposed[25] that the faster oxygen absorption rate is the result of a decrease in the termination rate of the free radical oxidation process. The termination rate may be affected to a greater degree by the event of gelation than are the initiation and propagation rates of this chain reaction series system. Any physical circumstance which causes gelation to occur earlier in the drying schedule will retard rates of termination of free radicals more than rate of oxygen uptake and polymerization are retarded. This will promote increased rates of oxygen absorption. High molecular weight especially when coupled with colloidal nucleation of the gelatification step can speed the rate of development of a gel structure so as to create earlier in the process the heterogeneous reaction environment which results in retardation of free radical termination. Hence, this nucleation not only speeds gelatification, which manifests itself as hardening of the film, but it creates also a reaction environment in the film where oxygen uptake and oxidatively promoted polymerization reactions by a free-radical mechanism are subjected to less retardation by the now slower termination step.

Intrinsic Viscosity Data

Because intrinsic viscosity measurements at all degrees of polymerization were very reproducible, average values from replicate runs are plotted together in Figures 12, 13. Figure 12 shows data for the lauric-modified

alkyds represented in Figures 2 and 3, and Figure 13 shows data for linoleic-modified alkyds of Figures 4 and 5. The intrinsic viscosity can be related to molecular weight over a considerable range of DP by the equation:

$$[\eta] = K(DP)^a$$

Sharp deviations from this relationship occur at values of DP near 30. This is true in both oxidizing and nonoxidizing alkyds, which suggests that either olefinic polymerization does not occur in the linoleic alkyd or, if so, this complication is not indicated by intrinsic viscosity measurements. Deviations from linearity of the curves of Figures 12 and 13 occur at the same DP where non-Newtonian behavior becomes obvious in the melt viscosity data (Figs. 8 and 9). Moore[24] shows also that curves corresponding cloud point with DP also show a break at about the same DP. The polymers develop optimum film drying rates (see Fig. 10) at about this same DP. Referring to Figure 1, we suggest that at values of DP where intrinsic viscosity increases steeply, indicates a sufficient accumulation of
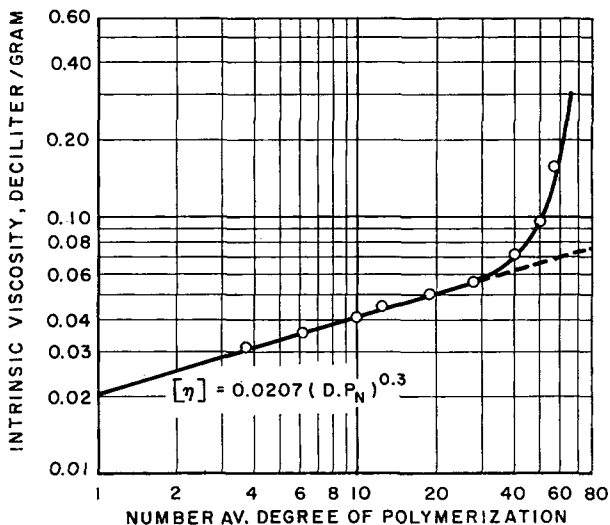

Fig. 12. Relationship of intrinsic viscosity and number-average degree of polymerization for lauric-modified alkyd. Intrinsic viscosity measured in methyl ethyl ketone at 30 ± 0.01°C.

dispersed microgel colloid so that coalescence of dispersed microgel or gelatification can occur. The microgel particles formed early in the process, near a DP of about 10, can be swollen or extended by solvents which have greater solvency than has low molecular weight fraction of the polymer which is the continuum in the melt. The solvent extends these molecules in dilute solution and hence the effect on intrinsic viscosity follows the regular molecular weight correlation over a greater range of molecular

weight in solution than occurs in the melt where phase separation is not delayed. Ultimately values of DP are reached when coalescence of particles and their interaction develops larger molecules and more complex molecular structure which no longer can be brought into homogeneous solution even by strong solvents in dilute solutions. At this time, a break occurs in the slope of the curve relating DP and intrinsic viscosity. At this same level of complexity, non-Newtonian behavior occurs in the melt, and cloud-point titrations show a minimal value.
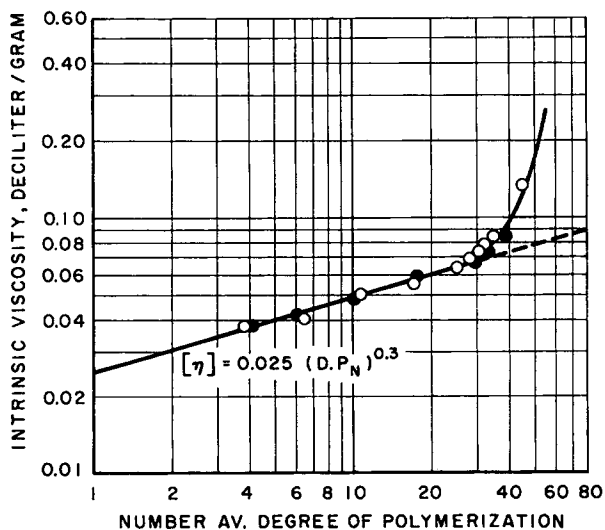

Fig. 13. Relationship of intrinsic viscosity and number-average degree of polymerization for linoleic-modified alkyd. Measurements in methyl ethyl ketone at 30 ± 0.01°C.

As DP is advanced beyond the critical point where deviations from linearity occur in plot of log $[\eta]$ versus DP, storage stability of alkyd solutions is rapidly lost and drying rates are improved only slightly. For example, for a 40% xylene solution of alkyd of DP of 28, the drying time was 8 hr., and skin formation in the half-filled storage container was negligible even after 6 months. As DP was advanced to 34, drying time dropped to 5 hr.; however storage stability was much reduced. Skin formation was severe in less than 2 months. As a DP of 39, drying time was reduced further to 4 hr. As a penalty for this small gain, storage stability was impractically short. A thick skin formed over the alkyd solution in less than a week. For practical reasons, it is necessary to halt the reaction below some critical value of DP so that storage stability is adequate to allow commercial handling of the product.

In view of the practical importance of being able to detect the beginning of this microgel coalescence point, some simpler analytical methods were examined. Cloud-point determinations, as reported by Moore,[24,26] pro-

vided a reasonable means of detecting this point; however, differentiation was not as sensitive as with intrinsic viscosity.

As usually practiced, intrinsic viscosity measurements are tedious because solutions of several dilutions need be measured to make possible the extrapolation of the correlation functions to zero concentration. This labor can be reduced greatly to a point where such measurements are convenient
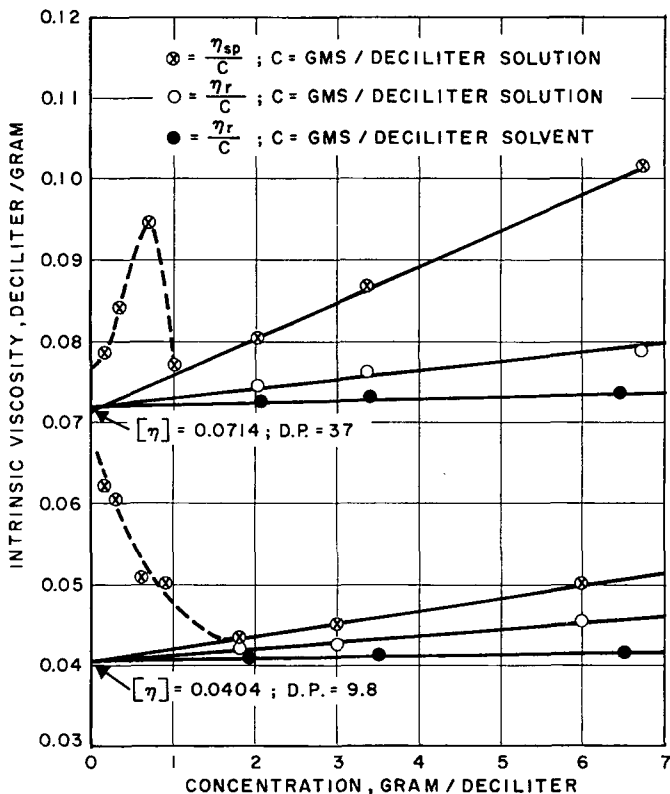

Fig. 14. Three graphical techniques used to obtain values for intrinsic viscosity from dilute solution viscosity data. Data for lauric alkyd in methyl ethyl ketone at 30 ± 0.01 °C.

for process control by using the single-point technique. The feasibility of doing so is suggested by the data of Figures 14 and 15, and is discussed in more detail by Bobalek, Lee, and Moore.[1]

Fractionation of an alkyd expected to contain coalesced microgel particles has been carried out, and the data are shown in Table III. Intrinsic viscosity measurement of fractions indicates that 10–15% of the polymer contains very high molecular material, while the residual 80% or more of the polymer has a very low molecular weight. This confirms the hypothesis that the amount of high molecular weight polymer required to promote fast drying rates need not be very large.
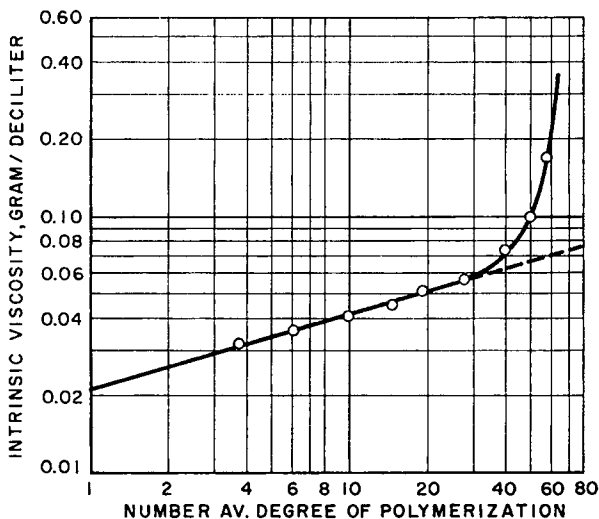
Fig. 15. Relationship between number-average degree of polymerization and intrinsic viscosity as determined by the one-point method for a lauric-modified alkyd. All measurements made at polymer concentrations near 2 g./100 ml. solvent.

As was expected, when the highest molecular weight fraction representing 20% of the total was removed through fractionation, the residual linoleic alkyd lost all ability to air dry to a hard film even though the capacity to absorb oxygen was still very high.

TABLE III

Intrinsic Viscosities of Fractions Obtained from a Glycerol-Based Alkyd having an Intrinsic Viscosity of 0.154 dl./g.

Fraction number	Intrinsic viscosity, dl./g	Weight per cent in fraction
1	1.03	3.68
2	0.86	3.63
3	0.535	5.49
4	0.405	3.26
5	0.35	3.03
6	0.223	6.59
7	0.149	8.64
8	0.119	3.28
9	0.075	2.83
10	0.065	2.80
11	0.058	3.71
12	0.0475	53.06

Gelation

When this research project was in the exploratory stage, it was noted by Levy[22] that the presence of solvent during synthesis would invariably re-

tard gelation. That is, the gel point in a solvent-free synthesis mixture (fusion process) occurred at a lower degree of polymerization than when same synthesis was carried out in the presence of solvent (solvent process). If reaction was advanced in a solvent cook beyond what would cause gelation in a comparable fusion process, then vacuum distillation of part of the solvent from such mixture of even low temperature would cause gelation to occur within a few minutes. Several additional hours of reaction would be required to reach the gel point at reaction temperatures if all the solvent was retained.

Classical gelation theory offers no adequate explanation as to why process variables should effect the gel point, while experience has demonstrated that process variables are highly significant. For alkyds, theory predicts gelation should occur before it is observed. The discrepancy has been explained by Stockmayer[29] and Brett[7] as due to side reactions for which the theory cannot correct, such as intramolecular condensation (ring closure). The data here cited show that assumptions regarding side reactions can explain only a small part of the observed deviations from theory.

Case[4] has predicted a delayed gel point from kinetic arguments, using the concept of reactant dissymmetry. This approach was investigated experimentally by Moore[24] and Chiang,[32] who concluded that the data for polymerization kinetics were inconsistent with the basic assumptions underlying this explanation.

At this point a closer look was taken at the basis of the theory which predicts gel point.[9] The equations developed by Flory are capable of predicting the extent of reaction at which a finite probability exists for formation of an infinite network (i.e., where a the branching coefficient exceeds some critical value a_c).

It was further pointed out by Flory that values of a greater than a_c do not indicate that all of the molecules are part of the same infinite network. Rather, theory predicts that sol and gel portions coexist up to the point where all functional groups have reacted and all the polymer is in one large molecule. The sol portion of a polymer was defined as that fraction which contains no molecules belonging to an infinite network. As reaction continues past the point of incipient gelation, it is predicted that a gel fraction will form and rapidly increase in size. Transfer of the high molecular weight species from the sol to the gel portion causes the average molecular weight of the residual sol fraction to drop progressively to lower values. Finally only monomer is present in the sol phase. As these last molecules in the sol portion become part of infinite networks, gelatification is truly completed.

Flory[7] defines an infinite network as one which which has macroscopic dimensions. Although this concept implies that an "infinite" network molecule is large compared to the size of ordinary molecules, the physical meaning of large size is not defined. The fact that molecules making up the gel portion are extremely large when compared to polymer molecules of the sol portion does not demand that the large molecules be insoluble and in-

fusible (that is, "gelled" in the usual sense of the word). Clarification of this detail is the basis for the model proposed in Figure 1.

Flory has not developed the equation for defining a in the alkyd resin system considered here. Using a similar approach, however, the appropriate equation[24] has been developed for the alkyd compositions here studied. This is

$$a = \frac{P_B P_A [1 - 2P_B + P_B{}^2 + 2P_B\rho - 2P_B{}^2\rho + P_B{}^2\rho^2]}{1 - 2P_A P_B{}^2 \rho(1 - \rho)} \qquad (12)$$
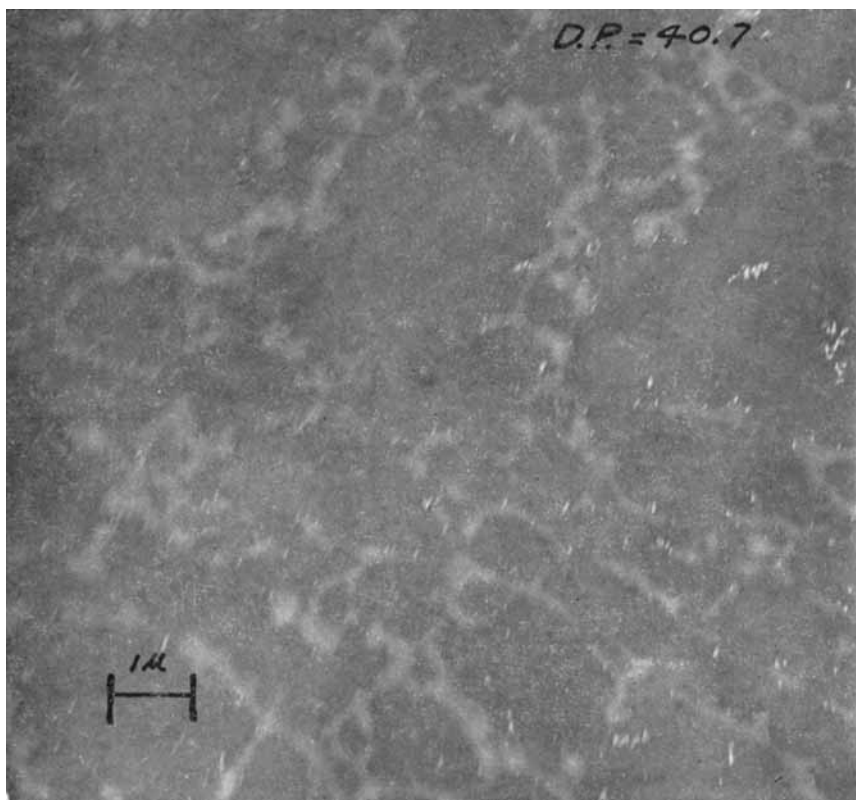

Fig. 16. Electron transmission through thin film (cast from 5% solution in amyl acetate) of alkyd polymer of Fig. 15 at DP of 40 where curve of Fig. 15 breaks from linearity. According to theory here proposed, this is at the microgel coalescence event suggested in Fig. 1. At lesser DP values, the opaque phase (in this photo the brighter structure) appears as dispersed single particles of 0.25–1.0 μ size.

where P_B is the extent of reaction of the hydroxyl, P_A is the extent of reaction of the acid, ρ is the ratio of difunctional acid groups to total acid groups, and r is the ratio of total acid groups to total hydroxyl groups (or $r = P_B/P_A$).

This equation can be reduced to the following form which simplifies the necessary trial and error solution for the critical value of P_A (at $a_c = 0.5$):

$$AP_A{}^4 + BP_A{}^3 - CP_A{}^2 + a_c = 0 \tag{13}$$

where

$$A = -\rho r^3 (1 - \rho)^2 \tag{14}$$

$$B = 2r^2 \rho [1 - a_c(1 - \rho) - \rho] \tag{15}$$

$$C = r\rho \tag{16}$$

Trial and error solution for gel point of the model alkyd yields: $P_A = 0.912$; $DP_n = 11.25$; $(DP_n)^{1/2} = 3.35$. The predicted value of $(DP_n)^{1/2} = 3.35$ is very close to the values where deviations from initial slopes of the
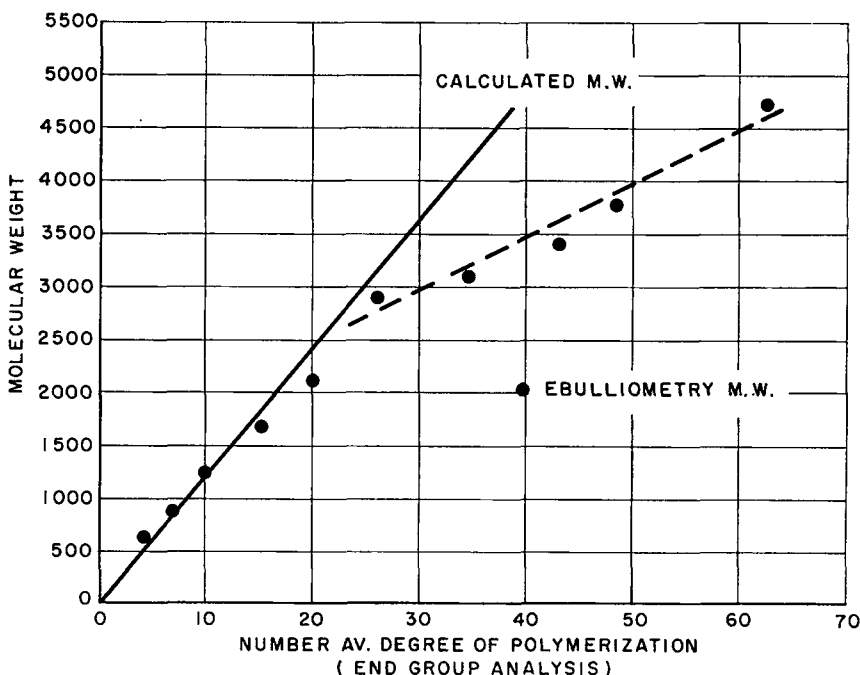

Fig. 17. Data points show number-average molecular weight of lauric-modified alkyd (ebullioscopic in chlorobenzene) compared to molecular weight calculated from end-group analysis (solid line). The flattening of curve beyond DP of about 30 may be due to insolubility of higher molecular weight portion of polymer at advanced degrees of polymerization.

correlation functions occur in Figures 2–6. This coincidence seems to link the microgel appearance event of our hypothesis to the theoretical gel point. Solvency of the phases which can form at this point can affect our perception of this theoretical gel point. Further, by referring to Figure 1,

we can surmise that addition of a solvent should retard final gelatification of the colloidal dispersion and possibly the extent of reaction when microgel first precipitates. This influence of the solvent on gelatification has been explored in further extensions of this study.[32]

The gelation model proposed in Figure 1 presents a hypothesis which seems to establish harmony between fundamental theory and many of the experimental facts of alkyd chemistry. Further evidence of the plausibility of this hypothesis has been presented by Moore.[24] For example, electron microscopy of very thin alkyd films demonstrates appearance of structural details suggesting the appearance of a dispersed second phase at later stages of reaction (Fig. 16). These micrographs suggest that the microgel particles have dimensions in the range of 0.1–1.0 μ, with larger particles occurring more commonly at higher values of DP. Also, filtration of xylene solutions of alkyd suspected of containing solvent-stable microgel through a 0.45-μ Millipore filter substantially lowered the intrinsic viscosity of the filtered polymer in only the four higher molecular weight species shown in Figure 17.

The more important uncertainties which still remain are concerned with understanding the role of the solvent in modifying the sequence of events suggested in Figure 1, and explaining the theory of stabilization of colloidal dispersions and their eventual gelatification of these types of polymers at advanced levels of DP.

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Résumé

On a étudié dans ce travail l'influence de la composition chimique du degré de poly-estérification et d'éventuelles réactions secondaires sur le comportement rhéologique de plusieurs résines phtaliques alkydes de glycérine modifiées aux huiles, aussi bien à l'état fondu qu'en solution diluée dans plusieurs solvants. Des données coordonnées ont été obtenues au sujet du poids moléculaire, et des propriétés de solubilité et de séchage, intéressantes pour la peinture. Les données viscosimétriques se sont avérées très utiles pour établir une relation entre la variation du degré de réaction et les propriétés pratiques de ces polymères. Ces résultats mettent en évidence un point particulier du mécanisme du point de gélification qui augmente l'utilité pratique de la théorie de polyestérification. Dans cette hypothèse on suppose cependant que la synthèse des résines alkydes n'est pas une réaction homogène et que la séparation de phase donne lieu à une dispersion colloïdale dans la masse réactionnelle bien avant la gélification. Dans la théorie classique de polyestérification on peut prévoir le cas d'une séparation de phase initiale. D'autres variations dans le procédé affectent la stabilité relative du colloïde de transition qui finalement se rassemble en une structure sous forme de gel. On peut ajuster les propriétés pratiques des résines alkydes pour des articles paints afin de satisfaire différentes exigences, en arrêtant la réaction à des stades différents, soit avant, soit dans la région de transition. Des mesures de la viscosité à l'état fondu et de la viscosité intrinsèque sont particulièrement sensibles et conviennent au contrôle du procédé et des produits sur la base de ce concept.

Zusammenfassung

In der vorliegenden Arbeit wurde der Einflussder chemischen Zusammensetzung, des Ausmasses der Polyesterbildung und möglicher Nebenreaktionen auf das rheologische Verhalten einer Anzahl öl-modifizierter Glyzerinphthalatalkydharze in der Schmelze und in verdünnter Lösung in einigen Lösungsmitteln untersucht. Eine Korrelation zwischen den Molekulargewichten und anderen Löslichkeitsparametern und den für die Anstrichtechnologie wichtigen Trocknungseigenschaften wurde erhalten. Viskosimetrische Messungen erwiesen sich als recht brauchbar um Unterschiede im Reaktionsgrad zu den Gebrauchseigenschaften dieser Polymeren in Beziehung zu setzen. Die Ergebnisse lassen den Gelpunktsmechanismus unter einem Gesichtspunkt erscheinen, der die praktische Brauchbarkeit der Polyesterbildungstheorie beweist. Es wird dabei angenommen, dass die Alkydharzsynthese nicht durchwegs eine homogene Reaktion ist und dass lange vor Eintritt der Gelbildung durch Phasentrennung eine kolloide Dispersion in der reagierenden Masse entsteht. Die klassische Polyesterbildungstheorie vermag den Eintritt der Phasentrennung anzugeben; andere Prozessvariable beeinflussen die relative Stabilität des intermediären Kolloids, das schliesslich zur endgültigen Gelstruktur koaguliert. Die praktischen Eigenschaften der Alkydharze als Anstrichstoffe können durch Anhalten der Reaktion in verschiedenen Stadien vor oder in der intermediären Phase verschiedenen Anfordernissen angepasst werden. Messung der Schmelzviskosität und der Viskositätszahl ist im Sinne dieses Konzepts eine besonders empfindliche und bequeme Methode zur Kontrolle des Verfahrens und der erhaltenen Produkte.