Synthesis and Properties of Some Alkyds of More Complex Carboxyl Functionality

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Synopsis

Syntheses are described where dimer fatty acid (C_{36}), or anhydrides of trimellitic, or pyromellitic, or dodecenylsuccinic acids are substituted in part for components of a model polymer derived from 1 mole each phthalic anhydride and glycerol, and 0.4 mole of linoleic acid. These polymers are compared at several degrees of polyesterification with respect to endgroup analysis, melt and intrinsic viscosity, and fractionation and emulsification behavior in water–solvent mixtures. The data suggest that predictions of the gel point in terms of functionality concepts are of general value only for defining the reaction degrees where insoluble molecules can first appear. The experimental event of gelatification can be delayed to varying degrees by different types and concentrations of inert solvent. The extent of reaction where molecular complexity can give a gellable polymer in the absence of solvency retardation occurs near the theoretical gel point and can be located by inspection of functions relating either melt or intrinsic viscosity to molecular weight. Significant differences in polymer structure have a very small effect on this parameter, nor is there much evidence to show preferential reactivity of similar functional groups associated with different structures. Other data here cited demonstrate some practically useful facts regarding how composition and molecular weight affect solvency behavior; however, no general correlations were found which relate solubility behavior to quantities here measured.

In common usage in the paint industry, the term "alkyds" identifies a large class of polymers derived by esterification of mixtures of mono and dibasic acids with simple or mixed polyols having an average hydroxyl functionality greater than two. The monobasic acid may be abietic, benzoic, or a variety of synthetic acids. Most commonly it is an 18-carbon, vegetable oil, fatty acid, either saturated or unsaturated.

For these polyesters, the theory of polyesterification as developed by Carothers,[1] Kienle,[2] and Flory[3,4] has not been used extensively to give guidance to polymer design or process control. To apply these theories for purposes like predicting gel point and molecular weight, the chemical reactions producing the polymer must be clearly defined and side reactions should play an insignificant role. For many years, apparent failures in applying the theory were attributed to complications produced by uncontrollable side reactions, such as varying degrees of olefinic polymerization.

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In recent years, Levy[5] proved that many industrial syntheses which incorporate inert solvent suppress such side reactions, and some other explanation needs to be found for lack of success in fitting experimental results to theoretical predictions.

Moore[6] built upon Levy's findings. He showed that the theory,[3] which estimates the extent of reaction where infinite network polymers are possible, did predict when some quantity of insoluble gel will first form. For polymers derived from phthalic anhydride, glycerine, and lauric or linoleic acids, Moore showed also that mass gelatification did not occur coincidently with the first formation of insoluble polymer. From considerable evidence he inferred that a very long interval along the extent of reaction coordinate could separate the time when insoluble polymer first formed and the final event of gelatification of the reacting mass.

The concept of the existence of a transition region where dispersed gel is stable cannot be generalized without more data. This fact was inferred from a study of only one family of the very large group of alkyd polyesters. Polymers of this type were not used by Flory[3,4] to confirm his theory, nor are all alkyds so simple in structure. In many highly functional polyesters, such a transition interval might not exist or it might be of negligible duration. Hence, to test the generality of this concept, it seemed desirable to explore the synthesis process for some more complex alkyd types.

This program involved taking as a basis for reference the well-characterized alkyds described earlier[7] and modifying their structure through intro-

TABLE I

Pattern of Modification of a Reference Model Alkyd Polymer with Acidic Reactants
(per mole of glycerol)

	Modifier, moles/mole glycerol		
Substituent type	Substituent	Phthalic anhydride (PA)	Linoleic acid (LA)
None (standard)	0.0	1	0.4
Dimer acid (DA)[a]	0.2	1	0.2
	0.4	1	0.0
Dodecynl succinic anhydride (DSA)	0.2	1	0.2
	0.4	1	0.0
Trimellitic anhydride (TMA)	0.2	0.8	0.4
	0.4	0.6	0.4
	0.6	0.4	0.4
Pyromellitic anhydride (PMA)	0.1	0.9	0.4
	0.2	0.8	0.4
	0.3	0.7	0.4

[a] Dimer Acid is the Diels-Alder reaction product of mixed dienoic and trienoic, 18-carbon, vegetable oil fatty acids. The principal constituent is a dimeric acid. Small quantities of higher polymers of greater functionality may be present, depending on conditions of reaction and extent of purification of the product.

duction of more complex types of polyfunctional acids. Four dibasic acids were chosen as modifiers. The pattern of modification is shown in Table I.

These modifications should affect significant changes in polymer structure and solubility behavior. The reaction rate coefficients for different carboxyl functions should also be different. This possibility of asymmetric reactivity, which is aggravated here, has also been suggested as a reason for difficulties in predicting gel point according to simple polyesterification theory.[8]

EXPERIMENTAL PROCEDURES

Materials

All chemicals used were of industrial grade obtained from the suppliers listed below: phthalic anhydride, Allied Chemical and Dye Corp., Kopper Chemical Co., and Monsanto Chemical Co.; trimellitic anhydride, Amoco Chemical Co.; pyromellitic dianhydride, E. I. du Pont de Nemours and Co.; glycerine (synthetic), Shell Chemical Corp.; linoleic acid (Baker 9-11 Acid), Baker Castor Oil Co.; dimer acid (Emery 629-11-R), Emery Industries, Inc.; and dodecenyl succinic anhydride, Allied Chemical Corp. These were all used without further purification.

Resin Preparation

Exploratory preparations of polymers, particularly to determine the solvent effect on gel point, were carried out in two-liter, glass flasks fitted with a stainless steel agitator, thermocouple, nitrogen sparger, and an efficient reflux condenser which discharged condensed solvent and water into a receiver. Here, water of condensation was separated periodically and the supernatant solvent was returned through a constant level overflow into the reactor. A thermocouple in the flask was connected to a Wheelco temperature controller, and the temperature of the reaction mixture was controlled automatically by regulating power supply to the heating mantle around the flask.

Later work to prepare a few polymers for detailed study was carried out in a 10-gal. stainless steel reactor of the same design as described earlier.[9] Samples of polymer at varying degrees of reaction were collected as described before for the standard alkyds.[6,9] Determinations of endgroups, melt viscosity, intrinsic viscosity, ebulliometric molecular weight (in chlorobenzene), and solvent precipitations to recover various molecular weight fractions were performed as described before.[7,9]

COMMENTS ON POLYMER SYNTHESIS

Tables II–V describe the compositions and some conditions of synthesis in a two-liter, resin flask. These runs were made to study the effect of solvent on gel point. These exploratory data provided also a guide to

more precise studies of synthesis reactions in the 10-gal. stainless steel reactor.

In the solvent process, one function served by the solvent is to wash down the sublimed phthalic anhydride from the condenser so as to prevent the

TABLE II

Gel Point Determinations Where Part of Phthalic Anhydride is Replaced with Trimellitic Anhydride in System (Phthalic Anhydride + Trimellitic Anhydride): Glycerin: Linoleic Acid = 1:1:0.4 (Mole Basis)

No.	Composition (mole ratio PA/ TMA)	Reaction conditions			Acid no.		% Reaction at gel pt.	
		Solvent 1%	Temp., °F.	Time, min.	At $p=0$	At gel pt.	Theory[a]	Exptl.
1	0.8/0.2[a]	Xylene (30)	340	220	404	55	85.7	86.5
2	0.6/0.4[b]	Xylene (30)	300–340	310	424	90	82.8	78.8
3	0.4/0.6[b]	Xylene (30)	300–340	140	452	148	80.8	67.4
4	0.6/0.4[b]	Xylene (15)	320–400	95	424	190	82.8	55.2
5	0.4/0.6[b]	Dioxane (30)	300–340	225	452	131	80.8	71.2
6	0.8/0.2[a]	DMF (30)	340	1440	404	(4)[c]	85.7	(99)
7	0.9/0.1[a]	DMF (15)	340	1440	393	(8)	87.3	(98)
8	0.8/0.2[a]	MIBK (15)	340–370	200	404	56	85.7	86.2
9	0.6/0.4[a]	MIBK (15)	340–380	180	424	93	82.8	78.0

[a] Calculated by Carother's equation.

[b] Experiments 2, 3, 4, 5, failed to give a clear and homogeneous polymer before gelation occurred.

[c] Values in parenthesis indicate final levels of reaction attained where reaction was not terminated by gelatification.

TABLE III

Gel Point Determinations Where Part of Phthalic Anhydride is Replaced with Pyromellitic Anhydride (or Pyromellitic Acid) in System (Phthalic Anhydride + Pyromellitic Anhydride or Acid): Glycerin: Linoleic Acid = 1:1:0.4 (Mole Basis)

No.	Composition (mole ratio PA/ PMA)	Reaction conditions			Acid no.		% Reaction at gel pt.	
		Solvent 1%	Temp., °F.	Time, min.	At $p=0$	At gel pt.	Theory[a]	Exptl.
10	0.9/0.1[b,c]	Xylene (30)	340	410	404	32	85.7	92.0
11	0.8/0.2	Xylene (15)	340	150	430	101	82.7	76.6
12	0.7/0.3[b]	Xylene (60)	300	210	438	146	80.0	66.5
13	0.9/0.1[b]	Xylene (15)	410	75	404	86	85.7	78.7
14	0.8/0.2[b]	Xylene (15)	400	120	419	85	82.7	79.8
15	0.8/0.2[b]	Dioxane (15)	340	150	419	98	82.7	76.5
16	0.8/0.2[b]	DMF (15)	340	210	419	84	82.7	80.0
17	0.9/0.1[c]	MIBK (25)	380	230	407	60	85.7	85.4
18	0.8/0.2[c]	MIBK (50)	350	360	430	100	82.7	76.8

[a] By Carother's equation.

[b] Pyromellitic acid was used instead of anhydride.

[c] Experiments 10, 17, 18 only yielded polymers of acceptable clarity before gelation occurred.

TABLE IV
Gel Point Determinations Where Part of Linoleic Acid is Replaced with Dimer Acid in
System Phthalic Anhydride:Glycerine:(Linoleic Acid + Dimer Acid) = 1:1:0.4
(Mole Basis)

| No. | Composition (mole ratio DA/LA) | Reaction Conditions | | | Acid no. | | % Reaction at gel pt. | |
		Solvent 1%	Temp., °F.	Time, min.	at $p=0$	At gel pt.	Theory[a]	Exptl.
19	0.2/0.2	Xylene (15)	330	450	357	42.0	85.7 (79.1)	88.3
20	0.4/0[b]	Xylene (15)	330	420	337	70.0	82.8 (73.1)	79.2

[a] Calculated by Carother's equation. Figure in parenthesis is calculated by Flory theory.

[b] In experiment 20, the polymer failed to clarify up to the gel point as happened in other experiments in Tables III and IV.

TABLE V
Gel Point Determinations Where Part of Linoleic Acid is Replaced with Dodecenyl
Succinic Anhydride in System Phthalic Anhydride:Glycerine:(Linoleic Acid +
Dodecenyl Succinic Anhydride) = 1:1:0.4 (Mole Basis)

| No. | Composition (mole ratio DSA/LA) | Reaction conditions | | | Acid no. | | % Reaction at gel pt. | |
		Solvent 1%	Temp., °F.	Time, min.	At $p=0$	At gel pt.	Theory[a]	Exptl.
21	0.02/0.2	Xylene (30)	400	270	418	60	85.7 (79.1)	83.2
22	0.4/0[b]	Xylene (30)	300	555	453	59	82.8 (73.1)	91.0
23	0.2/0.2[b]	Xylene (30)	400	180	418	53	85.7 (79.1)	87.3

[a] Calculated by Carother's Equation. Figure in parenthesis is calculated by Flory Theory.

[b] Dodecenyl succinic anhydride is added later in processes. In run 21, it is introduced at the start together with other constituents.

loss of this reactant. Also, the solvent dissolves both reactant and products more rapidly, hence the conditions of heterogeneous reaction which can exist in the early melt-out stages are minimized.

Replacement of Phthalic Anhydride by Trimellitic Anhydride and Pyromellitic Anhydride

Xylene was tried as the solvent, but the minimal amount required was 30% compared to the 15% which was sufficient for preparation of the standard alkyd.[9] As shown in Table II, even at the 30% level of solvent concentration, no more than 0.2 mole of phthalic anhydride could be replaced

by trimellitic anhydride without causing the reaction mixtures to become heterogeneous.

Dioxane, dimethylformamide (DMF), and methyl isobutyl ketone (MIBK) were also tried. Slight improvements were obtained with dioxane, as indicated by delay in the gel point. However, the product was still a cloudy and heterogeneous resin. Dimethylformamide proved to be an excellent solvent, and the reactions proceeded to 98 and 99% extent of reaction without gelatification. Dioxane and dimethylformamide are completely miscible with water, hence the water failed to separate in the decanter designed to return the water-free solvent to the reactor; hence solvent distilled in process with water had to be replaced with fresh solvent. Methyl isobutyl ketone is a good solvent for the polymer, and a poor solvent for water. A clear, homogeneous resin was obtained using 15% of this solvent in the reaction mixture, and the continuous solvent return from the distillation receiver can be managed as with xylene.

When pyromellitic anhydride was substituted for part of the phthalic (Table III), xylene could be used as solvent only if no more than 0.1 mole of the phthalic was replaced by the tetrabasic acid. For greater quantities of pyromellitic, clear homogeneous resin could be obtained only with the use of stronger solvents like dioxane, dimethylformamide, and methyl isobutyl ketone.

Replacement of Linoleic Acid by Dimeric Acid or Dodecenyl Succinic Anhydride

Both of these modifier acids are viscous liquids at room temperature and are easily soluble in xylene. Dimeric acids are the Diels-Alder adducts formed in polymerizing mixtures of dienoic and trienoic fatty acids. The composition and structure can be somewhat variable from lot to lot. When 15% xylene was used as solvent, no more than half of the 0.4 mole of linoleic acid in the standard alkyd could be substituted by its acid equivalent of dimeric fatty acid (Table IV). A further increase in amount of the dimeric acid resulted in a heterogeneous resin carrying suspended gel at low degrees of reaction.

About 30% of xylene was used in preparation of the dodecenyl succinic anhydride-modified resins (Table V). At this level of solvent dilution, clear homogeneous resins were obtained even when all of the linoleic acid (0.4 mole) was replaced with dodecenyl succinic anhydride.

Comments on the Pilot Plant Synthesis

To allow for better comparisons of new structures with the model alkyds of Levy and Moore,[9] only those variations of more complex polymers shown in Tables VI and VII were prepared in the pilot plant where 15% xylene made possible a process which yielded eventually polymer which seemed free of suspended gel or unmelted reactants. This was the solvent level which allowed for operating the process close to the conditions used for synthesis of the reference alkyds.

TABLE VI
Reactant Compositions Tried in Pilot Plant Reactor[a]

	Reactant compositions, moles/mole glycerol					
No.	PA	PMA	TMA	LA	DA	DSA
24	1.0	—	—	0.2	0.2	—
25	1.0	—	—	—	0.4	—
26	1.0	—	—	0.2	—	0.2
27	0.9	0.1	—	0.4	—	—
28	0.8	0.2	—	0.4	—	—
29	0.8	0.2	—	0.4	—	—
30	0.8	—	0.2	0.4	—	—
31	0.6	—	0.4	0.4	—	—

[a] Xylene (15%) was used in nos. 24–28, methyl isobutyl ketone (15%) was used in nos. 29–31.

TABLE VII
Some Process Details for Syntheses in Pilot Plant Reactor

		Time, min.		% Reaction		
No.	Temp., °F.	Total	To clear point	At end point	Expected at gel pt.	Appearance of final product
24	330	480	300	82	88	Reddish, clear
25	330	300	300	83	79	White, cloudy
26	310	345	60	83	83	Clear
27	325	330	330	84	92	Slightly cloudy
28	315	120	120	73	77	Very cloudy
29	300	255	180	74	77	Solid residues
30	310	240	120	72	86	Clear
31	310	330	240	71	78	Clear

Samples were withdrawn periodically from the bottom of the reactor. At the early stages of reaction, the resins were often cloudy. As the reaction proceeded, the samples became more clear and apparently homogeneous.

When 0.2 mole of linoleic acid was substituted by dimer acid, the resin became homogeneous after 5 hr. of reaction. But when all of the 0.4 mole of linoleic acid in the original standard alkyd was totally substituted by dimer acid, a clear resin, free of obvious gel particles, was obtained at extents of reaction of 82.8%, which is beyond the experimental gel point observed for the same nominal composition in the synthesis conducted in two-liter resin flask. Under pilot plant conditions, the control of solvent concentration in the reaction zone is less variable. This may have much to do with the efficiency of solvent in delaying the gel point.

For the preparation of trimellitic anhydride-modified resin, 15% of methyl isobutyl ketone was used as the solvent. Clear, homogeneous resins were obtained with 0.2 and 0.4 moles of trimellitic anhydride substi-

tuted for part of the 1 mole of phthalic in the standard formula. At the low level of substitution (0.2 mole for 0.2 mole of phthalic), nearly equivalent results were obtained with 30% xylene. Only the resin prepared in xylene solvent will be compared later with the original model polymer.

It was more difficult to prepare clear, homogeneous resin when phthalic anhydride was substituted by pyromellitic anhydride. A homogeneous resin could not be obtained at all at any extent of reaction short of the gel point when xylene was used as solvent even at concentrations of 30%. Better results were obtained with 15–20% of methyl isobutyl ketone, but even here some turbidity persisted to more advanced levels of reaction than with the trimellitic-modified polymers, and the degree of turbidity varied between batches.

Determination of Extent of Reaction in the Pilot Plant Syntheses

The extent of reaction with respect to carboxyl groups is calculated as $P_A = C_{A_0} - C_A/C_{A_0}$, where C_{A_0} is taken conveniently as the acid number (milligrams of KOH per gram of polymer) at zero reaction and C_A is remaining acid number after some reaction.

The corresponding hydroxyl numbers C_{B_0} or C_B (milligram of KOH equivalent to the acid which would be required to esterify the free hydroxyl functions in a gram of polymer) can also be determined to track extent of reaction.

Since the measured hydroxyl number includes hydroxyl in excess of carboxyl functions, this has to be corrected to equivalence with acid number when calculating the extent of reaction from analysis of this endgroup. The extent of reaction in terms of potentially reactable hydroxyl groups $P_B' = C_{B_0}' - C_B'/C_{B_0}'$, where C_{B_0}' and C_B' are corrected for the stoichiometric excess of hydroxyl functions in the system.

Calculations of the P_A, P_B' and the ratios P_A/P_B' at different extents of reaction are listed in Table VIII for some of the pilot plant preparations.

As shown in Table VIII, the P_A/P_B' ratio is not always unity for dimer- and pyromellitic-modified alkyds. The difference seems to be greater than experimental error. With advancement of the reaction, the ratio approaches unity. Possibly a nonhomogeneous distribution of reactive molecules between solid, liquid, and vapor phases occurs in the reaction system in early stages. During this period, sampling the polymer melt alone does not abstract a composition which is representative of the total charge to the reactor.

When superficial observation indicated that the reflux contained very little glycerol, and when the fluid phase seemed to be free of suspended insolubles, then the ratio of P_A/P_B' approached unity in the polymer phase sampled from the bottom of the reactor.

Calculation of Number-Average Degree of Polymerization ($\overline{X}_n$)

In general, the same approach as described by Flory[3] was followed in calculating the number-average degree of polymerization. Because dif-

TABLE VIII
Ratio of Acid Number to Hydroxyl Number at Increasing Extent of Reaction

No.	Polymer type	Acid no.	Hydroxyl no.	P_A	P_B'	P_A/P_B'
24	DA-modified	357.0	411.0	0.0	0.0	—
		91.1	170.6	74.6	67.4	1.11
		81.5	156.3	77.2	71.5	1.08
		71.0	141.0	80.2	75.8	1.06
		65.0	122.9	81.8	78.9	1.04
26	DSA-modified	418	482	0.0	0.0	—
		163.2	220.5	60.8	62.6	0.972
		142.5	199.8	65.8	67.5	0.975
		115.6	172.2	72.3	74.1	0.976
		97.2	156.6	76.6	77.8	0.984
		80.0	139.8	80.0	81.8	0.987
		71.4	128.5	83.5	84.6	0.987
30	TMA-modified	403.0	465.0	0.0	0.0	—
	(0.2 mole)	188.0	211.2	53.5	62.9	0.852
		155.5	195.5	61.6	66.8	0.922
		132.1	182.7	67.2	70.2	0.958
		115.0	171.8	71.6	72.8	0.984
31	TMA-modified	423.0	453.0	0.0	0.0	—
	(0.4 mole)	148.0	163.7	65.1	68.4	0.952
		137.9	149.8	67.6	71.7	0.943
		127.8	139.6	69.9	74.1	0.943
		117.8	131.7	72.3	76.0	0.952

ferent authors can approach the calculation in a variety of ways[10] the method used here will be described in some detail.

For the resin in which the fatty acid component was substituted by dibasic acids, let N_A and N_B be, respectively, the total number of equivalents of functional groups of A type (acid), and of B type (hydroxyl). Then let ρ be the ratio of number of equivalents of A groups contained in bifunctional molecules to the total equivalents of A groups coming from all molecules charged. Where P_A is the extent of reaction of A group (estimated from acid value determinations) and r is the ratio N_A/N_B, then the total number of unit structures available for building molecules is equal to $(N_B/3) + N_A (1 - \rho) + (N_A/2)\rho$. The total number of ester links is $N_A P_A$. If $\bar{X}_n$ is defined as the ratio of total number of units to total number of molecules of P_A, then

$$\bar{X}_n = \frac{(N_B/3) + N_A(1 - \rho) + (N_A/2)\rho}{(N_B/3) + N_A(1 - \rho) + (N_A/2)\rho - N_A P_A}$$

Dividing through by N_A and substituting r for N_A/N_B, gives:

$$X_n = \frac{(2/r) + 6 - 3\rho}{(2/r) + 6 - 3\rho - 6P_A}$$

Here $\bar{X}_n$ is expressed only as a function of input composition to the reactor and acid value determined after some reaction.

To illustrate, for resins 24 and 26 which were prepared in 10-gal. reactor from phthalic anhydride, glycerine, linoleic acid, and dimer acid or dodecenyl succinic acid, in molar ratios of 1:1:0.2:0.2, r is $^{13}/_{15}$, ρ is $^{12}/_{13}$, and $1/\bar{X}_n = 1 - ^{13}/_{12} P_A$.

Again, for the resin in which part of the phathalic anhydride was substituted by trifunctional groups, let ρ = ratio of A equivalents in monofunctional molecules to total A equivalents, ρ' = ratio of A difunctional molecules to total A, ρ'' = ratio of A in trifunctional molecules to total A; then the total number of units is $N_A\rho'/2 + N_A\rho''/3 + N_A\rho/1 + N_B/3$, the total number of links is $N_A P_A$, and

$$\bar{X}_n = \frac{N_A\rho'/2 + N_A\rho''/3 + N_A\rho/1 + N_B/3}{N_A(\rho'/2) + N_A\rho''/3 + N_A\rho/1 + N_B/3 - N_A P_A}$$

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

$$\bar{X}_n = \frac{3\rho' + 1\rho'' + 6\rho + 2/r}{3\rho' + 1\rho'' + 6\rho + 2/r - 6P_A}$$

For resin 31, for example, which was made from phthalic anhydride, trimellitic anhydride, linoleic acid, and glycerine in molar ratio of 0.6:0.4:-0.4:1, we find that r is $^{15}/_{15}$, ρ' is $^3/_7$, ρ'' is $^3/_7$, ρ is $^1/_7$; hence $1/\bar{X}_n = 1 - /_6 P_A$.

To convert $\bar{X}_n$ into number-average molecular weights, we must calculate the average weight of the repeating unit. This can be determined from knowledge of the composition and mechanism of polymerization. For example, in dimer acid-modified alkyd: let L, D, P, G be the number of moles, respectively, of linoleic acid, dimer acid, phthalic anhydride and glycerine. Then let M_L, M_D, M_P, M_G be respectively the molecular weights of each corrected for loss of endgroups, and let M_0 be the molecular weight of the average repeating unit. M_0 equals $LM_L + DM_D + PM_P + GM_G$, divided by the total number of moles. Since for linoleic acid, M_L is 263, and for dimer acid, M_D is 543, and for phthalic anhydride, M_P is 132, and for glycerine, M_G is 89.6, then $M_0 = 161$.

The osmotic pressure molecular weights of the final process samples of each alkyd type were measured by ebulliometry and compared with the values calculated as above indicated from end group analysis. Table IX shows that the molecular weight determined by ebulliometry in chlorobenzene agrees with that calculated from acid number determination to about 11%. Similar agreement was reported for the standard alkyd of Table I[9] at lower molecular weights.

Fractionation of Polymer

The highest molecular weight samples of several of the alkyds produced in the 10-gal. reactor were fractionally precipitated in methyl ethyl ketone by

TABLE IX
Molecular Weight Calculated from Endgroup Analysis and from Boiling-Point
Elevation of Chlorobenzene

No.	Standard polymer modified with	Molecular weight	
		Endgroup analysis	B. P. elevation
24	Dimer acid	1401	1263
26	Dodecenylsuccinic	1419	1382
30	Trimellitic (0.2 mole)	629	698
31	Trimellitic (0.4 mole)	920	932
1	Standard	728	720
2	"	1220	1350
3	"	2700	2560
4	"	4600	2900

adding water. Each fraction, representing precipitate recovered at different levels of water addition, was dried in vacuum at room temperature. Acid number and hydroxyl number of the fractions were determined, and the ratio P_A/P_B' was calculated, as described earlier, for each fraction. The intrinsic viscosities were determined also. The data are shown in Table X. In Table X, the last fraction which could not be precipitated by addition of water in amounts well in excess of the volume of ketone appears as the fraction lost. This highly soluble fraction amounted to 28% and 45%, respectively, for the dimer acid and dodecenyl succinic acid modified alkyds. For the trimellitic-modified alkyds, the highly water-soluble fraction was in excess of 58 and 40%, respectively, for the low and high levels of trimellitic content.

Examination of acid number, hydroxyl number, and intrinsic viscosity in Table X suggests that precipitation fractionation does separate species of the different molecular weight rather than species broadly different in copolymer composition. The ratio of carboxyl to hydroxyl endgroups changes rather slowly with declining molecular weight. The polymer in the recoverable fractions seems to be homogeneous in composition and to have the composition expected if incorporation of all reactants charged was random. There is no suggestion of compositional variations which might come from some carboxyl compounds reacting more readily than others.

Correlation of Intrinsic Viscosity with Degree of Polymerization

The number-average degree of polymerization was correlated with intrinsic viscosity in methyl ethyl ketone according to the equation:[7]

$$[\eta] = K\bar{X}_n{}^a$$

Table X shows that molecular weight distribution is narrow for all except resin 24, the dimer-modified alkyd.

The constants K and a for the range of molecular weights where the equation fits the data are shown in Table XI. In the log–log plot to determine

TABLE X

Analysis of Precipitation Fractions of Polymers Nos. 24, 26, 30, and 31

| Polymer and Fraction[a] | 100 × | | | $[\eta]_{MEK}$, | $\bar{X}_n$ | % of |
No. F_n	P_A	P_B'	P_A/P_B'	dl./g.		Total
24-F_1	(90.5)	(77.3)	(1.17)	(0.145)	(50.0)	14.60
24-F_2	(90.4)	(73.8)	(1.22)	(0.133)	(48.0)	8.14
24-F_3	(89.4)	(69.7)	(1.28)	(0.124)	(33.3)	5.29
24-F_4	88.5	84.9	1.04	0.083	24.4	13.49
24-F_5	87.5	85.5	1.02	0.071	19.2	11.34
24-F_6	85.5	81.7	1.05	0.055	13.5	7.91
24-F_7	82.9	78.1	1.06	0.049	9.8	10.10
24-F_8	76.6	—	—	0.045	7.7	1.22
24-F_0	81.8	78.9	1.04	0.063	8.2	100.0
26-F_1	(90.2)	(89.2)	(1.01)	(0.063)	(43.5)	4.21
26-F_2	(90.1)	(88.3)	(1.02)	(0.062)	(41.6)	8.65
26-F_3	(89.1)	(86.6)	(1.03)	(0.053)	(28.6)	9.34
26-F_4	88.5	86.4	1.02	0.052	24.4	4.28
26-F_5	88.2	86.0	1.03	0.051	22.7	4.04
26-F_6	87.3	84.6	1.03	0.050	18.2	10.64
26-F_7	86.4	81.6	1.06	0.044	15.4	7.26
26-F_8	84.6	79.3	1.07	0.044	11.9	5.82
26-F_0	83.5	84.6	0.99	0.042	10.4	100.0
30-F_1	(89.6)	(90.2)	(0.99)	(0.077)	(33.3)	5.70
30-F_2	(86.0)	(84.1)	(1.02)	(0.094)	(14.5)	4.31
30-F_3	85.1	80.3	1.06	0.065	12.7	10.06
30-F_4	81.4	76.2	1.07	0.060	8.48	9.00
30-F_5	80.4	74.4	1.08	0.052	7.69	7.49
30-F_6	79.1	73.8	1.08	0.046	6.94	6.14
30-F_0	71.6	72.8	0.99	0.042	4.46	100
31-F_1	(93.8)	(80.2)	(1.17)	(0.051)	(—)	2.60
31-F_2	(82.4)	(79.8)	(1.03)	(0.054)	(25.0)	18.4
31-F_3	78.6	73.2	1.07	0.052	11.9	27.3
31-F_4	75.5	69.5	1.08	0.058	8.34	10.9
31-F_5	66.6	—	—	0.054	4.46	0.9
31-F_0	72.3	76.0	0.95	0.047	6.41	100

[a] $\sum_{n=1}^{n} \cdot F_n/F_0$ is 0.72 for No. 24; 0.54 for No. 26; 0.43 for No. 30, $n = 1$ and 0.60 for No. 31 (F_0 is unfractionated polymer). The weight loss unaccounted for is polymer soluble in equivolume mixtures of methylethyl-ketone and water. Data numbers in parentheses are doubtful because polymer in these fractions could not be redissolved completely in MEK after precipitation fractionation.

constants of this equation, a sharp deviation upward occurs beyond some advanced degrees of polymerization in all except for the dimer-modified polymer (resin 24). The significance of this break point at higher values of $\bar{X}_n$ will be discussed later.

TABLE XI
Correlation Constants for Relating of Degree of Polymerization ($\bar{X}_n$) with Intrinsic Viscosity [η] at 30°C. in Dimethylformamide and Methyl Ethyl Ketone by Equation:
$$[\eta] = A\bar{X}_n{}^b$$

| No. | Modifier | MEK | | DMF | | Critical $\bar{X}_n \pm$ |
		$100A$	$10b$	$100A$	$10b$	0.5^a
24	Dimer acid (0.2 mole)	4.7	2.2	2.9	3.1	> 8
26	Dodecenyl succinic (0.2 mole)	2.0	2.2	2.2	2.1	8
30	Trimellitic (0.2 mole)	2.8	1.8	2.8	2.4	4
31	Trimellitic (0.4 mole)	3.1	2.1	3.0	3.1	5
	None	2.5	3.0	—	—	30

[a] For $\bar{X}_n$ greater than $\bar{X}_n$ (critical), the curve of log [η] vs. log $\bar{X}_n$ is no longer linear, and takes a steep positive curvature.

Solubility Properties as Shown by Intrinsic Viscosity in Various Solvents

The size and hydrodynamic resistance of a polymer molecule in solution depends on the quality of the solvent; the better the solvent, the larger is the apparent size of this molecule. This more extended state is indicated by a greater intrinsic viscosity in the better solvent of a group being compared. From this viewpoint, dimethylformamide seemed to be better solvent than methyl ethyl ketone for all the polymers except for the dimer modified type.

In general, alkyd resins having a greater number of carboxyl groups should be more extended in relatively basic solvents such as dimethylformamide. However, in dimer acid-modified alkyd, the acid–base interaction which is expected to promote molecular extension in dimethylformamide does not seem to prevail. Methyl ethyl ketone which ordinarily is the better solvent for nonpolar molecules is the better solvent for this polymer. Possibly, interference with hydrogen bonding occurs because the bulky structure screens the carboxyls; or it may be that some carboxyls are a much weaker acid in this particular structure.

Table XII shows the intrinsic viscosities of several of the more complex alkyds in methyl ethyl ketone, dimethylformamide, 97:3 MEK–water mixture and chloroform.

TABLE XII
Intrinsic Viscosities in Various Solvents at 30°C.

| No. | Modifier for standard polymer | $\bar{X}_n$ | [η], dl./g. | | | |
			MEK	DMF	MEK:H$_2$O 93:3	CHCl$_3$
24	Dimer acid	8.70	0.0625	0.0591	0.0653	0.0806
26	Dodecenyl succinic	10.41	0.0421	0.0516	0.0421	0.0523
30	Trimellitic (0.2 mole)	4.46	0.0421	0.0422	0.0458	0.0567
31	Trimellitic (0.4 mole)	6.41	0.0472	0.0531	0.0500	0.0543
	None (standard)	4.9	0.133	—	0.174	0.163

TABLE XIII
Intrinsic Viscosities in MEK–Water Mixtures at 30°C.

No.	Modifier	$\bar{X}_n$	[η] of MEK–H₂O mixtures, dl./g.					
			No H₂O	1% H₂O	2% H₂O	3% H₂O	5% H₂O	10% H₂O
24	DA	8.70	0.0625	0.0621	0.0633	0.0654	0.0630	0.0597
26	DSA	10.41	0.0421	0.0421	0.0423	0.0421	0.0424	0.0419
30	TMA	4.46	0.0421	0.0425	0.0431	0.0458	0.0433	0.0444
31	TMA	6.41	0.0472	0.0497	0.0482	0.0500	0.0506	0.0592
	None (standard)	49	0.133	0.160	0.170	0.173	0.167	0.138

Where intrinsic viscosity in 97:3 MEK–water mixture is higher than in pure methyl ethyl ketone. This might be explained by the hypothesis that water may associate by hydrogen bonding with the carboxyls to reduce hydrogen bonding between polymer molecules. This could make the hydrated polymer more soluble in a solvent which is mostly ketone.

The intrinsic viscosities in chloroform are the highest. The explanation of why chloroform is a superior solvent for these alkyds is not clear. Hydrogen bonding between solvent and polymer should be less here than in dimethylformamide. The greater solvent power of chloroform must derive from other types of chemical interaction.

The effect of water in ketone on the intrinsic viscosity of several polymers follows no expected pattern. Some data are shown in Table XIII and plotted in Figure 1.

In general, the viscometric data suggest that solubility behavior in solvents is affected strongly by both composition and by molecular weight
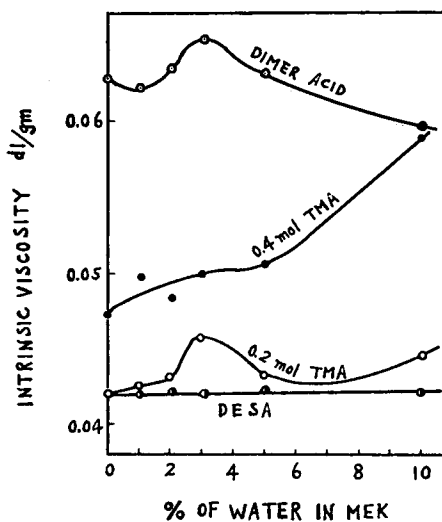

Fig. 1. Intrinsic viscosity of modified alkyd in MEK–water mixed solvent

of the polymer and also by the composition of the solvent. Since solubility considerations govern phase separation and gelatification phenomena in polymers, it should not be surprising that solvents should exert a powerful influence in modifying the course of the polyesterification reactions, and in particular, have an influence on when the gel-point will occur. Any theory which predicts gel point without accounting for the solubility effect must be incomplete. How to account for it theoretically is not yet clear. The importance of doing so, however, is indicated by the experimental observations here cited regarding the solvent effect on the gel point.

Melt Viscosity

Results of melt viscosity determinations are shown in Table XIV. On examination of Figures 2–4, it is seen that the curve relating log η_M to square root of molecular weight seems to be nearly linear for low $\bar{X}_n$ and

TABLE XIV

Melt Viscosity η_M at 200 ± 2°F. (93.3 ± 1.1°C.) for Alkyd Samples of Varying Degree of Reaction After the Clear Point (Pilot Plant Synthesis)

No.	Modifier	$\bar{X}_n$	η_M, poise
	None (standard)	2.5	2.4
		3.1	3.4
		4.0	6.4
		6.5	20.4
		8.7[a]	28
		13	61
24	DA	4.3	2.3
		5.2	4.5
		6.1[a]	7.5
		8.7	12
26	DSA	2.9	1.6
		3.5	2.2
		4.6	3.0
		5.9	6.0
		8.0[a]	12
		10.4	14
30	TMA	2.4	0.59
		3.0[a]	2.2
		4.1	2.9
		4.5	3.5

[a] At these values of $\bar{X}_n$, curves plotting log η_M versus $\bar{X}_n^{1/2}$ become nonlinear, and show a decline in slope.

shows a sharp downward curvature at about $\bar{X}_n$ of 6.5 and 7.7, respectively, for the dimer acid and dodecenyl succinic anhydride alkyds. The curvature may be near an $\bar{X}_n$ of 3–4 for the trimellitic anhydride-modified alkyd. These three alkyds were prepared at the same solvent content, in the same reactor, and under the same conditions as the standard alkyds to which these structures are compared. Here the downward curvature occurred
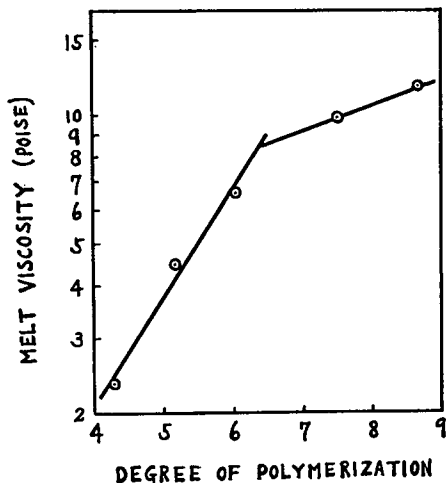
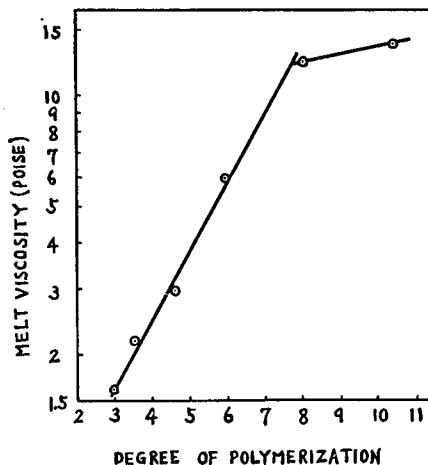Fig. 2. Melt viscosity of dimer acid-modified alkyd.

Fig. 3. Melt viscosity of dodecenyl succinic anhydride-modified alkyd.

near $\bar{X}_n$ of 9 which was near the theoretical gel point of the standard alkyd (made from 1 mole each of glycerol and phthalic and 0.4 mole of lauric or linoleic). The downward curvature for the alkyds of Figures 2 and 3 occurs near the theoretical gel points of $P_A = 0.79$ predicted by Flory's theory. In Figure 4, the same may be true of the TMA alkyd, but for reasons of experimental difficulty the data are too scanty to indicate this as clearly.

Despite their low molecular weight, the techniques of dilute solution viscometry can be applied also to the alkyds of more complex carboxyl functionality. The applicable concentration range over which extrapolations can be made to determine intrinsic viscosity of these alkyds is 3–15
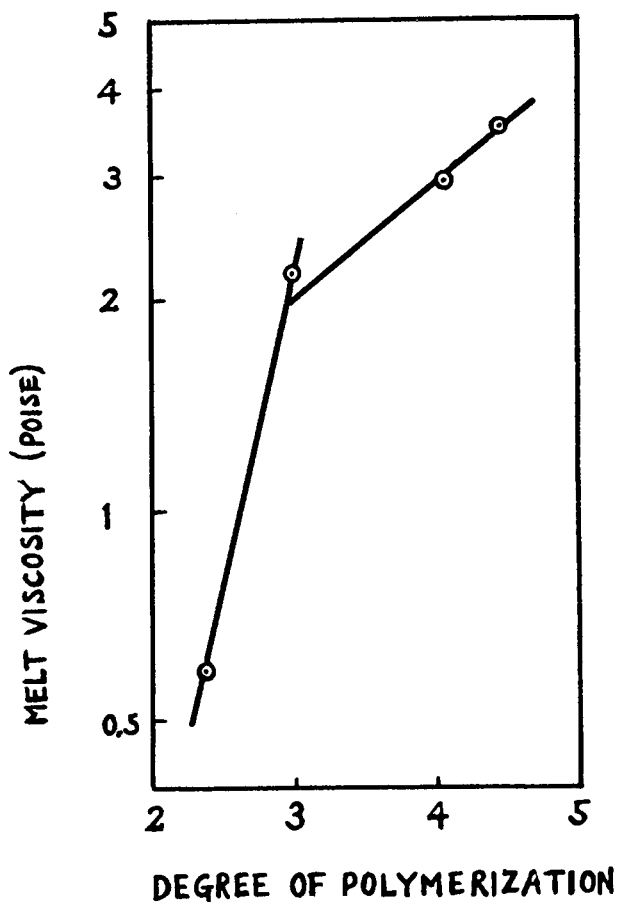
Fig. 4. Melt viscosity of 0.2 mole trimellitic anhydride-modified alkyd.

g./dl., which is more than for the model alkyd and much greater than for most other high polymers. Here also, as for the standard alkyd, the correlation of intrinsic viscosity with degree of polymerization according to the equation $[\eta] = K\bar{X}_n^a$ applies for lower values of $\bar{X}_n$; at higher $\bar{X}_n$, the intrinsic viscosity rises more steeply than this correlation predicts by extrapolation from low $\bar{X}_n$ to higher values. However, the upward curvatures in the log–log plot of the intrinsic viscosity function break sharply at the same degrees of polymerization where downward curvatures occur in the melt viscosity versus $\bar{X}_n$ correlation. For at least the dimer and dodecenyl succinic modifications, this is close to the theoretical gel point.

In the model alkyd, the break points of these two functions occurred at markedly different levels of reaction. The hypothesis was advanced earlier[9] that the difference between $\bar{X}_n$ where these two irregularities occur in the melt viscosity and intrinsic viscosity curves, respectively, is a measure of the extent of the transition region separating the events of first

phase separation of a dispersed colloid from the final event of total gelatification. If this is so for these more complex alkyds, then the transition interval is very short compared to what exists in the simpler alkyds studied earlier by Levy and Moore.[5,6]

Unfortunately, intrinsic viscosity data were not obtained as a function of the degree of reaction where strong solvents were used in the flask synthesis batches. The pilot plant experiments which could have yielded quantities of samples for such measurements were not performed because of technical difficulties. Hence, we cannot be certain whether comparisons of melt viscosity and intrinsic viscosity data would indicate an extended transition region in the stronger solvents. However, this possibility is suggested by noting the general effect of strong solvents in delaying the gel point. The data are shown in Tables II–V.

VARIABLES AFFECTING THE GEL POINT

The gel point is best defined as the extent of the reaction where melt viscosity rises to values where agitation cannot be sustained in the reactor because the system loses fluidity. The gel point is not independent of variables of the reaction process. For example, different solvents change the gel point in resins derived from the same composition of monomer (Tables II–V).

Table II shows that when a small amount of phthalic anhydride is substituted by trimellitic anhydride, then the experimental gel point agrees quite well with the theoretical gel point calculated from Carothers' equations.[1] When the amount of trimellitic was increased, gelatification occurred at much lesser extents of reaction than predicted by Carothers' equation. Raising the temperature in attempts to melt the higher melting point component caused stripping of the solvent, and the reaction mixture gelled. Dioxane delayed the gel point slightly. When dimethylformamide was used as solvent, the reaction proceeded to 99% extent of reaction without gelatification. Dimethyl formamide was a very good solvent for the reactants and also a good dispersing or swelling agent for the crosslinked polymer which must form in the last stage of reaction.

As indicated in Table III, when xylene was used as solvent, the effect of substitution by pyromellitic anhydride on the experimental gel point was quite similar to the effect produced by equivalent quantities of trimellitic anhydride. Because the melting point of pyromellitic anhydride was much higher than that of trimellitic anhydride, and its solubility was less, even strong solvents like dioxane, dimethyl formamide and methyl isobutyl ketone did not prolong the gel point as much as they did for the trimellitic system.

As indicated in Table IV, when dimer acid was substituted for linoleic acid, the experimental gel points were located between the values calculated respectively by the Carothers and the Flory equations.

In the dodecenyl succinic anhydride system, when the dodecenyl suc-

cinic anhydride was added later after some reaction had occurred between anhydride and glycerine, the gel point developed at a higher extent of reaction than when all components were added together.

CONCLUSIONS

This research supports the general concepts developed in earlier investigations[9] to reinforce the following conclusions.

An increasing degree of confidence can be placed in using the quantitative theories of polyesterification to predict the extent of reaction where branching and crosslinking begin to develop at sufficient rate so that gains in molecular complexity become more important than do further gains in molecular weight as an influence on functional properties. In practical applications, the useful properties of this family of industrial polymers as paint vehicles do not become optimum until a point has been reached along the extent of reaction coordinate where this branching complexity leads to some phase separation. Viscometric methods are convenient and generally applicable as a probe for determining when polymers attain to this desirable condition of molecular complexity and phase structure short of gelatification.

The solubility relationship between components of the reaction mixture can be altered either by changing the structure of polymer, or by incorporation of different sorts of solvents. Neither of these approaches will retard significantly the development of molecular complexity. Solubility considerations, however, markedly influence the event of gel formation which follows some time after molecular complexity (and perhaps phase heterogeneity) begins to develop.

Knowledge of these solvent–polymer interactions is important not only for adjusting properties of finished polymers for optimum performance as vehicles for paints, printing inks, and adhesives, but also for development of new or improved processes for preparation of some potentially useful polymers which can be made only with difficulty, or not at all, if the solvency factor is disregarded until after the polymer is made.

The simple version of polyesterification theory used here to predict the onset of infinite branching or first phase separation is based on the simplifying assumptions that reactivity of the functions is independent of the molecular weight of the molecule with which such are associated. It has usually been presumed that corrections would need to be made for asymmetric reactivity, that is for differences in rate coefficients between primary and secondary hydroxyls in glycerol and for differences in reactivity of anhydrides versus corresponding acids, or between carboxyls associated with different molecular structures. Here such corrections were neglected, and the predictions still hold. In rather complex systems, the composition of molecules of most of the high molecular weight fractions are predictable also as a random blend of all species charged. Evidence of selective reactivity, if it occurs at all, seems to disappear at some levels of reaction far short of

the first event of phase separation and certainly long before the gel point in homogeneous polyesterification processes in solvent solutions. This rather unexpected observation suggests that the mechanism of polyesterification is poorly understood. Perhaps other consecutive reactions, like

TABLE XV

Emulsification Properties of 40% Xylene Solutions of Alkyd Polymers in Water Containing Morpholine in Amounts Stoichiometrically Equivalent to Polymer Acidity

Polymer type	Cloud pt., ml. of H_2O[a]	Acid value	% Reaction (P_A)	Emulsion	
				Type[b]	Stability[c]
A. Linoleic dimer					
Low level (0.2 mole)	7.6	105	71	W/O	E
" " "	7.2	83	77	W/O	P
" " "	7.6	72	88	W/O	F
High level (0.4 mole)	0.3	61	82	W/O	P
B. Dodecynlsuccinic					
(0.2 mole)	44	142	66	O/W	F
" "	38	96	77	M	E
" "	30	70	83	O/W	F
C. Trimellitic					
Low level (0.2 mole)	34	166	58	W/O	F
" " "	d	134	66	M	E
" " "	d	114	72	M	E
High level (0.4 mole)	29	130	69	O/W	F
" " "	28	122	71	O/W	E
D. Pyromellitic					
0.2 mole	25	112	73	O/W	P
" "	d	70	84	O/W	F
" "	d	56	87	O/W	E

[a] Cloud, point, which measures sensitivity of highest molecular weight fraction to precipitation by water, is given as volume of H_2O required to produce cloudiness in a 5% solution of polymer in acetone.

[b] W/O is water-in-oil solution; O/W is oil-in-water type; M is an O/W microemulsion which is commonly called a solution because of its low turbidity. Emulsions prepared with a Manton Gaulin Manufacturing Co. (Everett, Mass.) micro homogenizer.

[c] Stability: E = stable for more than 2 weeks; P = dispersion breaks in less than one day; F = some preparations are stable for 2 weeks, some are not (stability is doubtful).

[d] Polymer solution was cloudy at 0 ml. of H_2O.

hydrolysis, alcoholysis, acidolysis, and ester exchange, are very important and have a net effect of submerging such differences.

The theory based on very simple assumptions can be used for predicting gel point of very complex polymers. If asymmetric reactivity occurs at all, its effect on changing compositional structure of different molecular weight fractions is also very small, at least after the reaction is advanced to

the degree where useful polymers are obtained for practical purposes as in formulation of solvent or water-thinned paints.

At the present time, the question is not yet clear as to which practical properties depend on molecular weight *per se*, or which may depend on factors like the apparent homogenization of intramolecular composition as reaction time is prolonged (Table VIII).

The data of earlier studies[9] suggest that properties like oxidation rate of films deposited from solvent solution depends a great deal on molecular weight. In other uses, as in the design of vehicles for water-thinned paint, the relative importance of compositional versus molecular weight parameters is less clear. The data of Table XV suggest some of the difficulties of clarifying this question.

The ease of emulsification and quality of emulsions prepared seems to depend in a complex way on both molecular weight and some other structural differences which develop as the reaction time is prolonged. Emulsification behavior is not related by any obviously direct correlation with solubility behavior as it was rated by other methods described earlier in this paper. Some rough trends may be apparent in noting the pattern of fractionation behavior when water is used as a precipitant. For the present, however, intrinsic viscosity measurements or measurements of compositional parameters like content of unreacted acid or hydroxyl groups are by themselves not a dominant factor in predicting performance with respect to practical considerations like those illustrated in Table XV.

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Résumé

On décrit les synthèses où soit les dimères d'acide gras (C₃₅) soit les anhydrides des acides triméllylique, pyroméllitique ou dodécenylsuccinique sont substitués en partie par un modèle polymérique dérivé d'une môle d'anhydride phtalique, et de glycérol et 0.4 môle d'acide linoléique. Ces polymères sont comparés à divers degrés de polyestérification par l'analyse des groupes terminaux, la viscosité a l'état fondu, la viscosité in-

trinsèque, le fractionnement et le comportement émulsifiant dans des mélanges eau-solvant. Les résultats suggèrent que les prévisions du point de gélification au point de vue de la fonctionnalité ne sont généralement valables que pour la définition du degré de réaction où les molécules insolubles apparaissent en premier lieu. Les moments expérimentaux de gélification peuvent être arrêtés à des degrés variables par différents types et concentrations en solvants inertes. Le rendement de la réaction où la complexité de la réaction peut donner un polymère gélifiable en l'absence du retard dû à la solvatation apparaît près du point théorique de gélification. Il peut être déterminé par un examen des fonctions relatives aux points de fusion et aux viscosités intrinsèques des polymères. Les différences importantes dans la structure des polymères ont un très léger effet sur ce paramètre, même s'il y a une réactivité préférentielle du groupement fonctionnel similaire associé aux différentes structures. D'autres résultats cités ici montrent des faits utilisables pratiquement indiquant comment le pouvoir solvatant influence la composition et le poids moléculaire; cependant aucune corrélation générale ne peut être déduite pour relier la solubilité et les quantités mesurées.

Zusammenfassung

Es werden Synthesen beschrieben, bei denen die Komponenten eines von je 1 Mol Phthalsäureanhydrid und Glycerin und 0,4 Mol Linolsäure abgeleiteten Modellpolymeren zum Teil durch dimere Fettsäuren (C_{36}) oder Anhydride von Trimellit-, Pyromellit- oder Dodecenylbernsteinsäure ersetzt werden. Diese Polymeren wurden bei mehreren Polyveresterungsgraden bezüglich Endgruppenanalyse, Schmelzviskosität und Viskositätszahl sowie Fraktionierungs- und Emulsionsbildungsverhalten in Wasser-Lösungsmittel-Gemischen verglichen. Wie die experimentellen Daten zeigen, ist eine Voraussage des Gelpunktes auf Grund von Funktionalitätsbetrachtungen von allgemeinem Wert nur zur Bestimmung des Umsetzungsgrades, bei welchem die Bildung unlöslicher Moleküle beginnen kann. Das Auftreten der Gelbildung kann experimentell durch Änderung von Art und Konzentration des inerten Lösungsmittels zu verschiedenen Umsetzungsgraden verschoben werden. Der Umsatz, bei welchem der komplexe Charakter des Moleküls in Abwesenheit von Löslichkeitsverzögerung zu einem zur Gelbildung fähigen Polymeren führen kann, liegt in der Nähe des theoretischen Gelpunktes und kann durch eine Betrachtung der Beziehungen zwischen Schmelz- oder Lösungsviskosität und Molekulargewicht festgelegt werden. Dieser Parameter wird durch grosse Unterschiede in der Polymerstruktur nur sehr wenig beeinflusst; auch konnte keine bevorzugte Reaktionsfähigkeit ähnlicher, mit verschiedenen Strukturen verknüpften funktionellen Gruppen nachgewiesen werden. Weitere in dieser Arbeit veröffentlichte Daten betreffen gewisse für die Praxis nützliche Befunde über den Einfluss von Zusammensetzung und Molekulargewicht auf das Löslichkeitsverhalten. Es wurde jedoch keine allgemeine Beziehung zwischen dem Löslichkeitsverhalten und den hier gemessenen Grössen gefunden.

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