

Changes in the Reactivity of Functional Groups During Polyesterification: A New Approach to Polymerization in Fatty-Acid-Modified Polyesters (Alkyd Resins)

D. H. SOLOMON, B. C. LOFT, and
JEAN D. SWIFT, *Division of Applied Mineralogy,
C.S.I.R.O., Melbourne, Victoria, Australia*

Synopsis

Gel-point calculations based on the theory of polyesterification proposed by Flory do not agree with the experimental values even when Bobalek's concept of gel point as the first formation of infinite molecules (microgel) is used. Resins covering the range 30-60% oil length were prepared and examined by electron microscopy for the presence of microgel particles. The extent of reaction at which microgel forms is discussed in relation to the concept of equal reactivity. The conditions necessary for the formation of microgel particles and the significance of these observations to the basic assumptions used in developing the theory of polyesterification are discussed.

The basic theory of polyesterification has undergone only minor changes since it was first proposed by Flory as a result of his pioneering studies in which he compared the formation of simple esters with polyesterification reactions.¹ The conclusions reached on the kinetics of polyesterification, on the reactivity of functional groups in polymer forming reactions, on the most probable molecular weight distribution for a polyester at a given extent of reaction, and on the importance of ester interchange and related reactions, are based almost entirely on experimental results obtained on bifunctional or linear systems.

The concepts developed for linear systems have been applied to nonlinear polymers; for example, equations have been proposed for the calculation or prediction of the gel point²⁻⁵ of a polyfunctional system, and for the calculation of the most probable molecular weight distribution.¹ Many other investigators have elaborated on Flory's initial efforts on nonlinear polymers and in some form or other, Flory's concepts have been applied to most polyesters.

Alkyd resins (polyesters modified by a natural or synthetic monobasic acid, often a fatty acid) and related polyesters, represent what is probably the most important class of nonlinear polyesters; they are of immense commercial importance to the paint and plastics industries, and because of this, the theory related to their formation and properties has been studied

intensively. Thus, one of the major problems investigated in alkyd resin formulations has been the prediction of the gel points; the belief is widely held that the optimum properties of an alkyd resin are developed at, or near, the gel point.^{5,6} For reasons of stability and reactivity, it is usually desirable to adjust a formulation so that it gels at a low acid number, that is when the extent of reaction in terms of acid groups is high, and an accurate prediction of the gel point of a formulation could save, and even eliminate, many unnecessary experiments. However, the calculated or predicted gel points rarely correspond with the observed physical gelation of the polyester; this disparity has led to many modifications to the equations used to calculate the gel point, and to suggestions that intramolecular reactions are competing with those involved in polymer formation. Recently, Bobalek et al.² have further suggested that the deviations between predicted and actual gel points are partly a result of not distinguishing clearly between the formation of some molecules with an infinite network, and the physical gelation of the polymer. Flory's calculated gel point corresponds to the extent of reaction at which molecules with infinite networks should form, and most workers in this field have assumed that this is when the polyester physically gels. However, Bobalek et al.² and Solomon and Hopwood⁷ have shown that molecules with an infinite network form prior to physical gelation and that these molecules are dispersed in a continuous phase of low molecular weight polymer. This dispersed polymer has been termed microgel. Hydroxyl groups are buried in the microgel particles and are not available for esterification reactions, for urethane formation by the addition of isocyanates, or for ether formation with melamine formaldehyde resin.⁸ These observations are of the utmost importance to the further successful commercial development of alkyd resins since it has already been shown that the film properties of an alkyd resin of a given chemical composition are related to the microgel content; preliminary studies have indicated that processing conditions can markedly influence the amount and type of microgel particles formed.^{2,7}

This paper is concerned with the conditions necessary for the formation of microgel particles, and with a discussion of the significance of these observations to the basic assumptions used in developing the theory of polyesterification.

Experimental

The equipment used for the preparation of the alkyd resins, and the methods used to characterize the polymers have been described in previous papers.^{7,8}

Alkyd resins were made from formulations chosen so that they covered the range of greatest commercial interest. The formulations varied from 60% down to 33% oil length.

The gel points of the formulations were calculated from equations which have been developed using the concepts proposed by Flory and Carothers. The details of the results of the characterization of the resins and of the calculated gel points are given in Tables I-III.

The polymerization of glycerol/phthalic anhydride and trimethylolpropane/adipic acid at mole ratios of 2/3 and 1/1 was studied. At all stages of the reaction up until the physical gelation of the mixture the measured hydroxyl values corresponded with the calculated values. No microgel particles were visible in the electron microscope.

The influence of solvent on the formation of microgel particles, and on the physical gelation of the reaction mixture was studied on the system lauric acid/trimethylol propane/adipic acid at a mole ratio of 1/2/2. The results are given in Table IV.

Discussion

The results in Tables I-III clearly show that in alkyd resins molecules with an infinite network are formed at much lower extents of reaction than is predicted by equations based on Flory's or Carothers' assumptions. A significant difference between the alkyd resins and nonlinear polyesters which did not contain a fatty acid residue (e.g., glyceryl phthalate, trimethylol propane adipate) was also noted; in alkyd resins the microgel particles increase in size over a considerable extent of reaction whereas the fatty acid free polyesters undergo a sudden change from a soluble polymer to a physically gelled mass.

One of the basic assumptions inherent in the equations used to calculate the gel point of the alkyd resins is that "the intrinsic reactivity of a functional group remains independent of molecular size." Since some molecules form a network structure sooner than is predicted by these equations it follows that the functional groups in these molecules have reacted at a faster rate than expected. In other words at some stage of the polyesterification the increase in molecular size has resulted in an increased rate of esterification for some molecules.

To explain the above conclusion the following model is proposed for polyesterification in alkyd resins; subsequently other evidence will be considered in relation to this model.

In the early stages of polymerization (average D.P. 2-4), some molecules will have a composition in which the fatty acid/polyester ratio is such that it will give them potential surface activity. These molecules will then form micelles, and it is at the surface of these micelles that rapid polyesterification occurs with the eventual formation of microgel particles.* The functional groups in the microgel particles then exhibit greatly reduced activity in polyesterification since they are no longer in the same phase as the other reacting entities. (Previous evidence has suggested that the hydroxyl groups are "buried" inside the microgel.⁷)

The influence of solvents on the gel points of an alkyd resin supports the above theory. The results in Table IV taken in conjunction with those of Bobalek et al.² show that all solvents retard gelation but that the more polar solvents, such as dimethylformamide, are more effective in this re-

* The concept of gelation proposed by Bobalek et al.² is used here; that is the point at which molecules with an infinite network first form. This point may occur some time before phase inversion and physical gelation.

TABLE I
The Polyesterification of Formulations with Mole Ratios of Fatty Acid/Polyol/Dibasic Acid = 1/1.36/1.11

Formulation	Extent of reaction, ^a %	Measured hydroxyl value	Calculated hydroxyl value	Difference between measured and calculated hydroxyl value, mg. KOH/g.	Diameter of microgel particles ^b	Calculated gel points <i>P_A</i>			
						Bobalek et al. ^c	Jonason ^d	Patton ^e	Yoshida ^f
Linoleic acid/ trimethylol propane/ adipic acid	73	0.89		18	Up to 0.2 μ	92%	96%	>100%	>100%
	81	0.86		20	0.1 to 0.2 μ				
Linoleic acid/ trimethylol propane/ phthalic anhydride	69	0.96		7	Up to 0.5 μ	92%	98%	>100%	>100%
	83	0.95		8	0.5 to 1.0 μ				
Linoleic acid/ glycerol/phthalic anhydride	71	0.95		9	Up to 0.1 μ	92%	98%	>100%	>100%
	82	0.91		13	Up to 0.15 μ				
	90	0.86		25	0.1 to 0.2 μ with a few up to 0.5 μ				

Linoleic acid/glycerol/ adipic acid	66	0.94	13	Up to 0.15 μ	92%	96%	>100%	>100%
Lauric acid/ trimethylol propane/ adipic acid	81	0.91	14	0.1 to 0.2 μ	92%	96%	>100%	>100%
Lauric acid/ trimethylol propane/ adipic acid	80	0.91	14	0.1 to 0.2 μ	92%	96%	>100%	>100%
Lauric acid/ trimethylol propane/ phthalic anhydride	91	0.86	18	0.1 to 0.2 μ	92%	98%	>100%	>100%
Lauric acid/ trimethylol propane/ phthalic anhydride	73	0.94	11	Up to 0.5 μ	92%	98%	>100%	>100%
Lauric acid/glycerol/ phthalic anhydride	80	0.91	14	0.5 to 0.75 μ	92%	98%	>100%	>100%
Lauric acid/glycerol/ phthalic anhydride	72	0.94	13	Up to 0.15 μ	92%	98%	>100%	>100%
Lauric acid/glycerol/ adipic acid	81	0.91	15	Up to 0.2 μ	92%	96%	>100%	>100%
Lauric acid/glycerol/ adipic acid	65	0.96	9	Up to 0.15 μ	92%	96%	>100%	>100%
Glyceryl mono- linoleate/glycerol/ phthalic anhydride	75	0.95	12	0.1 to 0.2 μ	—	>100%	>100%	>100%
	65	0.59	66	0.1 μ				
	75	0.51	68	0.1 to 0.5 μ				
	84	0.41	70	0.2 to 1.0 μ				

^a The extent of reaction is expressed in terms of the carboxyl groups.

^b The resin samples were examined under the electron microscope; the magnification used was 7,500, the beam current was 1 μ amp. and the potential on the electron gun was 100 kv.

^c The gel points were calculated using eq. (13) on p. 654 of ref. 2.

^d The gel points were calculated using eq. (3) on p. 130 of ref. 3 for the diacid, and eq. (17) on p. 134 of ref. 3 for the phthalic anhydride.

^e The gel points were calculated using eq. (9) on p. 43 of ref. 5.

^f The gel points were calculated using eq. (15) on p. 109 of ref. 4.

TABLE II
The Polyesterification of Formulations with Mole Ratios of Fatty Acid/Polyol/Dibasic Acid = 1/2/2

Formulation	Extent of reaction, %	Measured hydroxyl value	Calculated hydroxyl value	Difference between measured and calculated hydroxyl value, mg. KOH/g.	Diameter of microgel particles	Calculated gel points P_A			
						Bobalek, et al.	Jonason	Patton	Yoshida
Lauric acid/tri-methylol propane/adipic acid	72	0.94	0.94	11	0.2 to 0.4 μ	85%	87%	100%	97%
	81	0.89	0.89	17	0.25 to 0.5 μ				
	87	0.83	0.83	21	0.25 to 1.0 μ				
	92	Resin gelled		—	—				
Linoleic acid/glycerol/phthalic anhydride	62	0.87	0.87	28	0.25 to 0.5 μ	85%	91%	100%	97%
	74	0.80	0.80	34	0.5 to 1.0 μ				
	88	0.61	0.61	45	0.75 to 1 μ with a few up to 2 μ				
	98	Resin gelled		—	—				
Linoleic acid/glycerol/adipic acid	65	0.91	0.91	19	0.2 to 0.3 μ	85%	87%	100%	97%
	76	0.86	0.86	24	0.3 to 0.5 μ				
	80	0.82	0.82	28	0.5 to 1.0 μ with a few up to 2 μ				
	95	Resin gelled		—	—				
Glyceryl mono linoleate/glycerol/phthalic anhydride	63	0.74	0.74	48	0.5 to 1.0 μ	—	89%	100%	88%
	75	0.59	0.59	61	1.0 to 1.5 μ				
	90	Resin gelled		—	—				
	66	0.82	0.82	33	0.1 to 1.0 μ	—	88%	100%	88%
Glyceryl mono linoleate/glycerol/adipic acid	76	0.73	0.73	42	0.1 to 2 μ	—	—	—	—
	85	Resin gelled		—	—				

TABLE III
The Polyesterification of Formulations with Mole Ratios of Fatty Acid/Polyol/Dibasic Acid = 1/1/1

Formulation	Extent of reaction, %	Measured hydroxyl value	Calculated hydroxyl value	Difference between measured and calculated hydroxyl value, mg. KOH/g.	Diameter of microgel particles	Calculated gel points P ₄			
						Bobalek et al.	Jonason	Patton	Yoshida
Linoleic acid/glycerol/	95	1	1	0	No microgel was observed	82%	93%	100%	>100%
phthalic anhydride	70	0.92	0.92	8	Up to 0.25 μ	82%	86%	100%	>100%
Linoleic acid/glycerol/adipic acid	80	0.85	0.85	11	0.2 to 0.5 μ				
	85	Resin gelled		—					

TABLE IV
The Influence of Solvent on Polyesterification^a

Formulation	Solvent present	Extent of reaction, %	Measured hydroxyl value		Difference between measured and calculated hydroxyl values, mg. KOH/g.	Size of microgel particles
			Calculated hydroxyl value	Calculated hydroxyl value		
Lauric acid/trimethylol propane/adipic acid = 1/2/2	30%	71	0.96	0.96	7	0.1-0.25 μ diameter
	toluene	80	0.91	0.91	14	0.2-0.5 μ diameter
Lauric acid/trimethylol propane/adipic acid = 1/2/2	30% dimethyl formamide	94	Resin gelled		--	--
		70	1.0	1.0	--	No microgel
	80	0.99	0.99	1	Trace only of microgel	
	85	0.97	0.97	4	0.1-0.2 μ diameter	
		95	0.92	0.92	8	Up to 1 μ diameter
		99	0.83	0.83	13	0.5-1.5 μ diameter

^a The calculated gel points are given in Table II.

gard. We suggest that the solvents retard, or in some cases inhibit, micelle formation, and this is the mechanism by which they retard gelation. Previous theories of polyesterification have failed to offer a satisfactory explanation for the influence of solvent on the reaction.²

The monomeric units available for polymer formation also influence microgel formation. Previously, we have noted that in glyceride/glycerol mixtures condensed with phthalic anhydride, microgel is most readily formed when the fatty acid is all present as glyceryl- α -monoester, provided that polyol is also present.⁷ This represents the composition in which all the fatty acid residues are attached to polymer-forming molecules (i.e., the difunctional glyceryl monoester) and consequently this would be expected to give the maximum opportunity for growing molecules to achieve the desired organophilic/organophobic balance.

It should be understood clearly that we are proposing that only some molecules lead to microgel in the early stages; others will grow in solution until their molecular weight, and the polarity of the medium, have changed sufficiently to enable microgel particles to separate. Indirect evidence in support of the contention that only some molecules are capable of microgel formation comes from a study of the hydroxyl values of samples taken during the formation of an alkyd resin.

The unavailable hydroxyl groups have been shown to be present in microgel particles and consequently the measured hydroxyl value is a guide to the amount of microgel present. In some alkyd resin formulations there is an initial deviation of the hydroxyl value from the theoretical but as the polyesterification proceeds no further hydroxyl groups are lost,⁷ apart from those which have formed ester links.

Other evidence which supports greater activity in the early stages of polyesterification, at least for some molecules, comes from molecular weight distribution studies on the diethylene glycol-adipic acid reaction;⁹ at low degrees of polymerization the most probable molecular weight distribution is not found. There is less low molecular weight material than predicted by the concept of equal reactivity. This has been taken as evidence that the low molecular weight polymers react more rapidly than those with higher molecular weights. However, in these linear systems, the molecules stay in solution and consequently, interchange reactions are likely and at higher degrees of polymerization the differences between theory and practice are less obvious. With nonlinear systems, however, any molecules which undergo rapid reaction can lead to microgel. These microgel particles are not in solution and interchange reactions do not alter appreciably the size or composition of the particles.

Kinetic analysis of reactions leading to alkyd resin formation would appear to be of limited value in the light of the theory proposed above. First, some of the functional groups enter an environment in which they show enhanced reactivity and then little or no activity. Second, the third-order kinetics found by Flory apply only above 80% esterification;¹ at this point microgel has usually formed and it is most unlikely that the hydroxyl

groups present are all esterifiable. Therefore, the equation developed by Flory cannot be used since it assumes that all groups are available. Third, most alkyd resins have a viscosity in the vicinity of 30 poise; even in the absence of microgel, this makes it difficult to obtain results of sufficient accuracy for kinetic analysis.¹⁰

The authors would like to thank A. F. Wilson for the electron micrographs.

References

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
2. E. G. Bobalek, E. R. Moore, S. S. Levy, and C. C. Lee, *J. Appl. Polymer Sci.*, **8**, 625 (1964).
3. M. Jonason, *J. Appl. Polymer Sci.*, **4**, 129 (1960).
4. T. Yoshida, *Chem. High Polymers, Japan*, **23**, 113 (1966).
5. T. C. Patton, *Alkyd Resin Technology*, Interscience, New York, 1962.
6. D. W. Berryman, *J. Oil Colour Chemists' Assoc.*, **42**, 393 (1959).
7. D. H. Solomon and J. J. Hopwood, *J. Appl. Polymer Sci.*, **10**, 1893 (1966).
8. D. H. Solomon and J. J. Hopwood, *J. Appl. Polymer Sci.*, **10**, 981 (1966).
9. M. T. Pope and R. J. P. Williams, *J. Chem. Soc.*, **1959**, 3579.
10. P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083 (1941).

Résumé

Les calculs de point de gelification basés sur la théorie de la polyestérification proposée par Flory ne concordent pas avec les valeurs expérimentales mêmes lorsque le concept de Bobalek (microgel) est utilisée comme première approximation pour des molécules infinies. Des résines couvrant le domaine de 30 à 60% de longueur ont été préparées et examinées par microscopie électronique concernant la présence de particules de microgels. Le degré de réaction à la formation de microgel est discuté par rapport avec la nature de la réactivité. Les conditions nécessaires pour la formation de particules de microgel et la signification de ces observations pour les hypothèses de base utilisées pour le développement de la théorie de la polyestérification sont soumises à discussion.

Zusammenfassung

Gelpunktsberechnungen auf der Grundlage der von Flory vorgeschlagenen Polyesterbildungstheorie stimmen auch bei Verwendung des von Bobalek benützten Gelpunkt-konzepts als erste Bildung unendlicher Moleküle (Mikrogel) nicht mit den experimentellen Werten überein. Harze wurden im Bereich von 30 bis 60% Öl-Streckung dargestellt und elektronenmikroskopisch auf die Anwesenheit von Mikrogeleilchen untersucht. Das Reaktionsausmass, bei welchem sich Mikrogel bildet, wird in Beziehung zum Konzept gleicher Reaktivität diskutiert. Die für die Bildung von Mikrogeleilchen notwendigen Bedingungen und die Bedeutung dieser Beobachtungen für die bei der Entwicklung der Theorie der Polyesterbildung gemachten grundlegenden Annahmen werden diskutiert.

Received October 21, 1966

Prod. No. 1571