The Polyhydric Alcohol–Polybasic Acid Reaction. III. Further Studies of the Glycerol–Phthalic Anhydride Reaction[1]

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Since the appearance of the first paper of this series,[2] the polyhydric alcohol–polybasic acid reaction has become the basis for a large number of industrial products. Several excellent scientific treatments have been published covering the simple bi-bi functional or non-convertible type polyester polymerides, that is, those obtained from dihydric alcohols and dibasic acids.[3] The glyceryl phthalate reaction,[4] however, still remains the only convertible or higher functional saturated polyester polymeride to which scientific attention has been directed in spite of the clarification that a study of other similar systems should have offered to the problem of resin formation.

In the previous paper on glyceryl phthalate, the data seemed to indicate that the reaction was simple esterification. Such being the case, it followed that all polyester polymerides might be studied by carefully determining the rate and amount of water formed as the reaction proceeded, then directly calculating acid values and percentage esterifications therefrom. Several of the recent investigations on glyceryl phthalate,[5] however, raised some doubt as to the validity of this deduction that only esterification was involved. It was decided, therefore, prior to investigating other polyester systems, to reinvestigate thoroughly the glyceryl phthalate reaction under more rigidly controlled conditions than was done previously, to collect continuously all the products evolved, and to examine in detail resin samples representative of the progress of the reaction.

Recently several kinetic treatments, particularly for the non-convertible polyester polymer-

ides, have been presented principally by Chalmers,[6] Dostal, Mark and Raff,[7] Alatman and Kedrinski,[8] Flory,[9] and Davies.[10] These treatments, with the exception of that by Davies, have all been made on fairly limited experimental data. Very little has been done kinetically, however, with the convertible polyester polymerides, especially when the reaction is carried out under conditions as usually encountered in practice, that is, where the condensation products are removed as formed. In obtaining our experimental data an attempt was made so that sufficient evidence would be available to allow subsequent presentation of a kinetic treatment.

Experimental

Apparatus and Procedure.—After considerable experimentation and many changes, during which time a number of physical factors governing polyester reactions were examined and placed under control, an apparatus was finally developed wherein polyester formation could be carried out under carefully controlled and exactly reproducible conditions and in which the water formed could be instantly and accurately determined. Because this apparatus will be referred to in later papers of this series, it will be described at this time in some detail. The apparatus is illustrated in Fig. 1.

In the experiments on glyceryl phthalate the charge used was such as to theoretically produce $1/4$ mole of resin calculated as glyceryl triphthalate, i. e., $1/2$ mole or 46.0 g. of glycerol, $3/4$ mole or 111.0 g. of phthalic anhydride. In the relating experiments with other polybasic anhydrides, the charges were adjusted to yield an equivalent volume. Whenever polybasic acids were employed, because of the limitation effected by the size of the water-collecting chamber (E) and the increased volume of water evolved, a charge approximately one-half that employed for the anhydride experiments was used.

The water evolved could, of course, have been determined gravimetrically by using a suitable absorbent medium in an absorbent train attached to the outlet of the reaction flask. This would, however, have required continual weighings which would have made rapid readings very difficult. Therefore, a volumetric method was employed. It was essential in the design of the water-collecting chamber that immediately any water was evolved in the reaction flask (A) it was condensed and appeared

(1) Portion of a dissertation submitted to the Graduate Faculty of Rutgers University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(2) Kienle and Hovey, THIS JOURNAL, **51**, 509 (1929).

(3) Carothers and Arvin, ibid., **51**, 2566 (1929); Dostal and Raff, Monatsh., **68**, 117 and 188 (1936); Flory, THIS JOURNAL, **59**, 466 (1937); Kogan, J. Applied Chem. Russ., **10**, 900 (1937); Davies, Trans. Faraday Soc., **34**, 410 (1938); Bradley, Kropa and Johnson, Ind. Eng. Chem., **29**, 1270 (1937).

(4) Hönel, Paint, Oil, Chem. Rev., **91**, 19 (1931); Savard and Diner, Bull. soc. chim., **51**, 597 (1932); Kogan, C. A., **31**, 7047 (1937); Carothers, Trans. Faraday Soc., **32**, 39 (1936); Schlenker, Allgem. Oel- u Fett-Ztg., **29**, 658 (1932); Wornum, J. Oil Colour Chem. Assoc., **16**, 231 (1933); **17**, 119 (1934); Houwink and Klaassens, Kolloid. Z., **70**, 329 (1935).

(5) Bozza, Giorn. Chim. Ind. Applicata, **14**, 294 and 400 (1932); Scheiber, "Kunststoffe," Leipzig, 1934, pp. 217.

(6) Chalmers, THIS JOURNAL, **56**, 912 (1934).

(7) Dostal, Mark and Raff, Ind. Eng. Chem., **29**, 595 (1937).

(8) Alatman and Kedrinski, C. A., **31**, 6219 (1937).

(9) Flory, THIS JOURNAL, **59**, 466 (1937).

(10) Davies, Trans. Faraday Soc., **34**, 410 (1938).

in (E). The calibrated tube used to read the water evolved in (E) had, therefore, to be as close to the reaction flask as possible and the condensation in (E) had to occur with little or no time lag. Furthermore, many of the polybasic acids, particularly in the early stages, possessed subliming tendencies. It was therefore necessary that (E) be filled with a liquid which would dissolve and remove any of such sublimate that might be formed and carried over by the inert gas. It was also recognized that whatever liquid was used in (E), water must be insoluble therein and readily form a sharp distinct meniscus. After considerable experimentation, it was found that a mixture of three parts by volume of toluene to one part by volume of acetophenone was a suitable liquid to use.

It was realized that the gas flow and speed of stirring might have an important effect on the rate of the polyester reaction. These factors were therefore investigated and both were found to be important. In order to obtain reproducible results, a certain optimum definite gas flow and speed of stirring had to be used.

The gas flow was adjusted by observing the rate at which the gas bubbled through the sulfuric acid drying bottle (H). It was found that a rate of three bubbles per second was the optimum for use. With this gas flow, a stirring rate of 400 r. p. m. for stirrer (S) was found to be satisfactory.

The experimental technique was first carefully to weigh out the acid or anhydride into the reaction flask (A). The apparatus was then assembled and the proper amount of polyhydric alcohol carefully introduced into the dropping funnel. In order to prevent any contamination from the exterior and in order thoroughly to seal the apparatus, all the ground glass joints on assembling were lubricated with a small amount of glycerol. The apparatus, once assembled, was placed in the constant temperature bath (D) and with gas very slowly flowing through, heated until the polybasic acid or anhydride was at the temperature at which it was intended to carry out the reaction. The polyhydric alcohol in the dropping funnel, in the meanwhile, was brought to this same temperature by means of a free flame played on the outside thereof. When both the polybasic acid or anhydride and the polyhydric alcohol were at the reaction temperature, the gas was stopped momentarily and the polyhydric alcohol run into the flask. This addition was taken as the zero time for the reaction. Upon the completion of the addition of the polyhydric alcohol, which rarely took more than fifteen seconds, the glass stopper of the dropping funnel was closed and the gas flow adjusted to the proper rate.

When phthalic anhydride was used, because of its subliming tendency, a small amount was transferred by the gas stream to the toluene–acetophenone in the water-collecting chamber. The actual amount thus carried over was determined at the end of any run by analyzing the toluene–acetophenone mixture.

As water was evolved, it was transferred immediately into the water-collecting chamber where it was condensed, dropping to the bottom of the collecting tube where the amount given off could be accurately read as a function of the time of reaction. The small amount of water vapor carried in the gas stream was trapped by means of the anhydrone, the increase in weight of the anhydrone being

determined for each run, at regular intervals, by removing the absorption bottle (G₂) and weighing it. In order to eliminate any possibility of loss during the weighing operation, a second pre-weighed (G₂) absorption bottle was used as a replacement, while the first absorption bottle was out of the system. The increase in weight of the anhydrone was thus plotted as a function of time, from which curve corrections were made to the amount of water evolved as read in the collecting tube, giving the true water evolved.
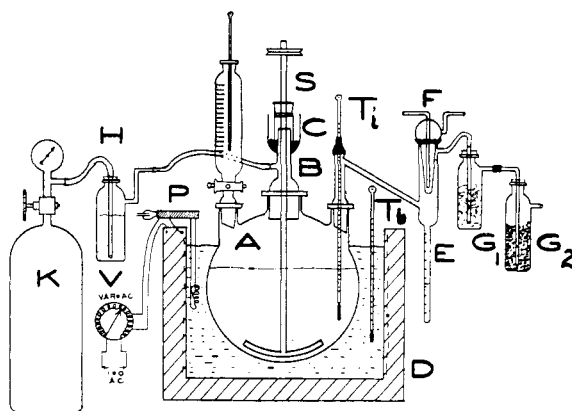

Fig. 1.—Apparatus for preparation of glyceryl phthalate. A, Pyrex reaction flask (500 cc.); B, adapter with side-arm; C, mercury seal stirrer (S); D, constant temperature wax bath; E, 10-ml. water-collecting chamber; F, condenser; G₁, absorption bottle (glass wool); G₂, absorption bottle (anhydrone); H, gas drier (sulfuric acid); K, gas cylinder (nitrogen or carbon dioxide); P, de Khotinsky thermo-regulator; V, variac (General Radio Company).

In order to prevent any condensation of moisture in the upper part of the reaction flask, adapter (B), or that part of the water-collecting chamber connected to the reaction flask, all these parts were heated during a run by continually playing a Bunsen burner thereon.

It was thus possible to carry out reproducible polyester formation reactions accurately and determine the rate at which the water was evolved. It was also possible to carry out these reactions so that samples could be taken out at regular intervals and the reactions studied by subsequently studying the composition of these samples at the various stages. And, finally, it was possible to carry any of the desired polyester resin-forming reactions along to some particular predetermined end-point and to be reasonably assured that the rate at which that end-point was achieved was, to all purposes, the same as passed through in carrying out the complete reaction.

Materials.—The phthalic anhydride for this investigation was resublimed c. p. phthalic anhydride obtained from the Selden Division, American Cyanamid Company, which material itself had already been sublimed in its preparation.

The glycerol was obtained by twice distilling Procter and Gamble c. p. water-white glycerin at 6 mm. pressure in an atmosphere of nitrogen. A small portion was then frozen rapidly in carbon dioxide and alcohol with continual

stirring until small crystals were obtained. These crystals were used to seed the specially distilled glycerol and the entire product crystallized by maintaining in a sealed container and a thermostat set at 17°. This crystallized glycerol was then brought to room temperature and the first portion melted, decanted and discarded. The remaining portion was used in the experiments. Its constants were: specific gravity at 20°, pycnometer corrected for vacuum, 1.2631; index of refraction at d_{20} 1.4741. This compared with the data given by Bozart and Snoddy[11] for 100% glycerol: *specific gravity at 20° 1.2633; index of refraction at d_{20} 1.4740.*

The Reaction at 200°

The glycerol–phthalic anhydride reaction was studied in detail at 200°. This temperature was chosen because experience showed that at 200° the reaction progressed at a rapid rate but not at such a rapid rate that it could not be followed accurately; also, it represented an average tempera-

TABLE I

GLYCERYL PHTHALATE (ANHYDRIDE)

Experiment 39: complete experimental data at T, 200°. Glycerol, 46.0 g.; phthalic anhydride, 111.0 g.; temperature of mixing, 200°.

Time, min.	Temp., °C.	Water evolved, cc.			Acid value[a]
		V_0	G_1	V_3	
0	200	..	..	..	535.7
1	236	..	..	..	
2	227	0.10	..	0.10	
3	222	0.40	..	0.40	247
4	217	0.85	..	0.85	241
6	212	1.42	..	1.42	229
7	210	1.72	..	1.72	223
8	208	2.02	..	2.02	218
9	206	2.28	..	2.28	213
10	203	2.50	..	2.50	208
11	203	2.62	..	2.62	206.5
12	202	2.85	..	2.85	201
13	202	2.93	..	2.93	200
14	201	3.12	..	3.12	197
16	201	3.30	..	3.30	193
18	200	3.52	..	3.53	188
20	200	3.72	0.01	3.73	184.5
22	199	3.92	..	3.93	182
24	199	4.17	..	4.19	176
26	199	4.30	..	4.32	173
28	199	4.48	..	4.50	170
30	200	4.68	.03	4.71	166
32	200	4.82	..	4.85	164
36	201	5.12	..	5.16	157
40	201	5.40	..	5.45	153
45	200	5.72	..	5.78	147
50	200	6.10	.08	6.18	143.5
55	200	6.30	..	6.39	141
60	199	6.52	..	6.61	139
65	199	6.70	..	6.82	136
70	200	6.90	..	7.03	134
75	200	7.10	..	7.24	133
80	200	7.15	.16	7.31	132

(11) Bozart and Snoddy, *Ind. Eng. Chem.*, **19**, 506 (1927).

Experiment No. 40

Time	Temp.	V_0	G_1	V_3	Acid value
0	200	..	..	..	535.7
1	230				
	233				
	228	Trace		..	
2	225	0.20		0.20	...
3	220	.40		.40	247
4	216	.85		.85	240
5	212	1.30		1.30	232
6	211	1.55		1.55	227
7	209	1.80		1.80	222
8	208	2.02		2.02	218
9	206	2.20		2.20	214.5
10	204	2.38		2.38	210.8
11	204	2.55		2.55	208
12	202	2.65		2.65	206
14	202	2.90		2.90	201
16	201	3.18		3.18	195
18	200	3.45	.01	3.46	190
20	200	3.70		3.71	185
22	200	3.90		3.91	181.5
24	200	4.12		4.14	177
28	200	4.50	.02	4.52	169
30	200	4.63		4.65	166
35	200	5.03		5.07	158.5
40	200	5.41		5.46	152
45	200	5.72		5.78	147.5
50	200	6.02		6.09	144
55	200	6.30	.09	6.39	140.5
60	200	6.50		6.60	139
65	200	6.80		6.90	135.5
70	200	6.90	.12	7.02	134
75	200	7.08		7.21	132.5
80	200	7.15		7.31	131
86	200	7.38		7.55	128.5
90	200	7.46	.19	7.65	127
95	201	7.56		7.76	126

[a] Calculated at each point from the water evolved–acid value curve, which curve was established carefully by a large number of individual determinations.

ture at which alkyd resins are prepared commercially.

Studies were made to determine whether the reaction could be carried out quantitatively. A large number of experiments revealed that the loss in weight obtained after the reaction had been completed equalled the sum of the amount of water evolved and collected in the water-collecting chamber, plus such correction as it was necessary to make for the water carried off by the inert gas, and the amount of phthalic anhydride that had been carried over into the toluene–acetophenone mixture.

In order to determine whether or not the liquid which was collected and measured in the water-collecting chamber was actually water, at the end of one of the runs the entire contents of the water-collecting chamber was placed in a separatory

funnel. After allowing sufficient time for complete separation, the lower layer was then removed and examined. It was neutral to litmus and tasteless. The index of refraction was determined in an Abbe refractometer and found to be n^{22}D 1.333 which agrees very well with the value
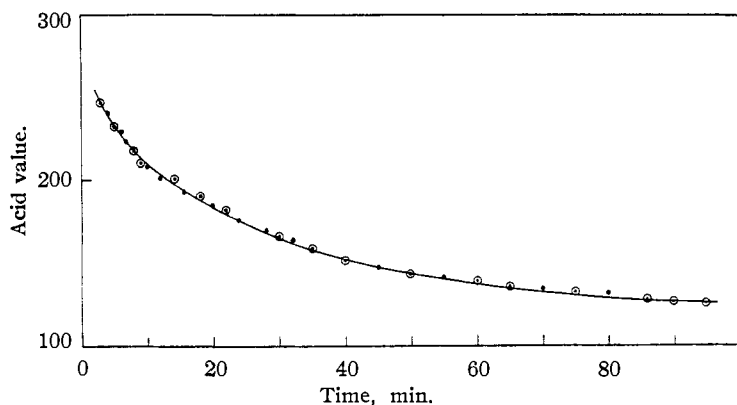

Fig. 2.—Glyceryl phthalate: variation of acid value with time at $T = 200°$; ●, expt. 39; ⊙, expt. 40.

for pure water as given in the "International Critical Tables."

It was observed, as in previous studies of this reaction, that when the reactants were brought together at 200°, an almost instantaneous exothermic interaction occurred, the temprature rising approximately 35°. In this interaction, no evolution of water was obtained, but the acid value dropped from an initial one of 535.7 to approximately 267. In other words, an initial 50% esterification occurred.

A detailed study of the water evolved–acid value relationship was undertaken. In order accurately to establish this relationship, it was necessary to make individual experimental runs to certain water evolved values and, on the resulting samples, to determine the acid values, having previously established the fact that experimental runs carried to the same water evolved values gave substantially identical acid values. This gave a series of samples of sufficiently large size that such properties as ultimate composition, molecular weight, viscosity characteristics, etc., could then be determined readily as a function of the progress of the reaction. But it was necessary to be certain that no change occurred in the samples on standing. A study was therefore made of what effect aging for several weeks had on the samples from various stages of the reaction. Except for a slight change in the early stages, the samples were apparently unaffected.

The complete water evolved–time data for the reaction at 200° are given in Table I. The corresponding acid values attained are included. As the reaction proceeded, the bath temperature (T_b), the temperature of the reaction itself (T_i), and the amount of water collected in the water-collecting chamber (V_0), were recorded carefully at every time interval that readings were taken. From the water-correction curve, V_0 was corrected to give V_a, the actual amount of water evolved. It is obvious that at the temperature of 200° very little correction in V_0 is necessary.

The change in acid value as a function of time, T, 200°, is plotted in Fig. 2, the complete data for experiments 39 and 40 being included. It is evident that both runs give exactly the same curve, showing that the reaction is accurately reproducible. In Fig. 3, the water evolved–time curve is plotted similarly.

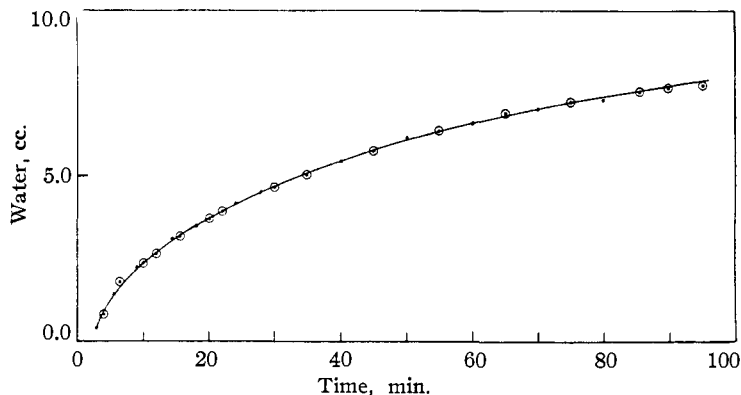From these two curves, Fig. 4 has been con-

Fig. 3.—Glyceryl phthalate: variation of water evolved with time at $T = 200°$; ●, expt. 39; ⊙, expt. 40.

structed which shows the water evolved–acid value relationship. In addition, the experimentally determined values of a number of individual runs also have been given. It will be seen that these individual values quite accurately fit the curve obtained by combining Figs. 2 and 3, showing that the water evolved–acid value relationship
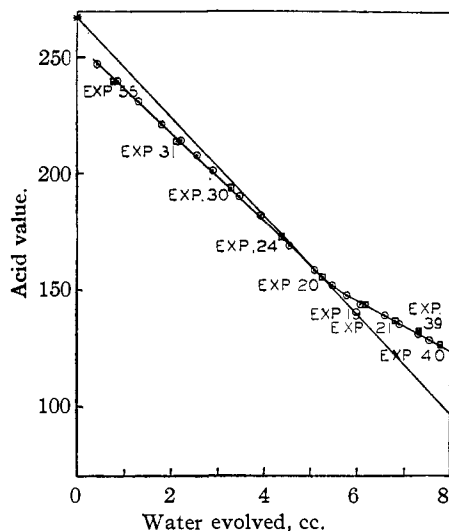
Fig. 4.—Glyceryl phthalate (anhydride):
water evolved—acid value relationship.

is the same whether obtained by the method of individual runs or by the graphical method of combining the complete acid value–time run with the water evolved–time run. In Fig. 4 there is shown also the theoretical relationship between the volume of water evolved and the acid number on the assumption that, immediately after 50% esterification had been attained without loss of water, subsequent resinification occurred with evolution of water and with only esterification occurring at all times. The equation representing this theoretical relationship is

$$A = 378.9 \frac{P - P_c}{W - P_c} - 3110 \frac{V}{W - T} \qquad (1)$$

wherein A is acid number; P, weight of phthalic anhydride used; W, the total weight of ingredients; T, total weight loss in experiment; V, cc. of water evolved; and P_c, weight of phthalic anhydride lost in the experiment.

It is evident, when Fig. 4 is examined, that in the early stages of a glyceryl phthalate reaction there is less water evolved than is required on the assumption that only esterification has taken place. In the later stages of the reaction, more water is evolved which suggests that over this portion of the reaction some anhydride formation occurs.

Numerous attempts were made to treat water evolved and acid value data for glyceryl phthalate kinetically. It is sufficient to indicate at this point that no simple kinetic relationship was found applicable to the entire data.

In order to get some idea of the "beyond the

gel" state, an experiment was made in which the rate of water evolution was followed well beyond the gel state. That portion of the data which covers the portion of the reaction just prior to and beyond gelation, is shown in Fig. 5. The point at which gelation occurred is indicated clearly by an arrow. It is evident from this curve that condensation continues beyond gelation with such change of rate as takes place seemingly resulting from the physical limitations of intercontact of the molecules brought about by the state of arrested motion that occurred at gelation.
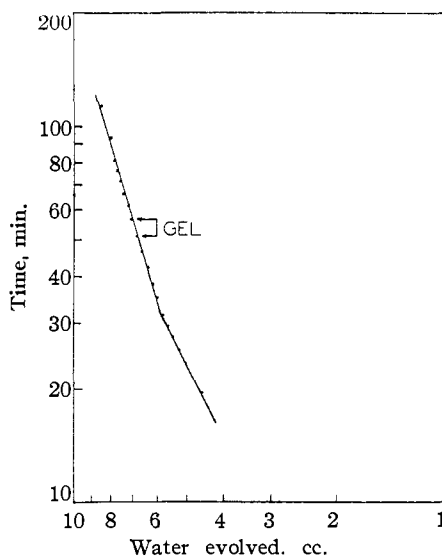

Fig. 5.—Glyceryl phthalate: water evolved, V_0, before and after gelation.

Effect of Temperature

The reaction was studied over the temperature range 160–215°. A number of individual experiments revealed that over this temperature range the same acid value is attained for any given water loss independent of the temperature. This having been established, detailed quantitative water evolved–acid value–time runs were carried out at 160, 185 and 215°. The data obtained, as well as those given in Table I, are plotted as a log acid value–log time relationship in Fig. 6.

In Table II are summarized for the various temperatures, the time for gelation to occur and the water evolved. It will be noted that the amount of water evolved at gelation appears to be independent of the temperature. Using the gel point, therefore, as a common reference state for the reaction, the heat of activation has been calculated and found to be 21,600 cal. per g. mole.

TABLE II

EFFECT OF TEMPERATURE

Temp., °C.	Time, min. gelation	Water evolved, cc.
160	860	7.98
185	255	7.99
200	105	7.99
215	50	7.98

Physical and Chemical Variations as Reaction Progresses

Analytical.—In Table III are summarized the analytical data of the various glyceryl phthalate samples prepared in the 200° temperature studies. The methods used in determining the acid value and saponification value already have been described[2]; carbon and hydrogen were determined by the standard micro-chemical methods now in use for these elements.[12] The values given for the sample marked "gel" are only approximate. The sample marked "degelled" was prepared by taking a portion of the gelled resin, placing in a Pyrex tube, sealing the tube and heating in an oven overnight at a temperature of approximately 150°. A fusible, amber, resinous product resulted which was now soluble in acetone and which cured only very, very slowly when a small portion was placed on a hot-plate at 200°. Data on the degelled sample are included for whatever bearing such data might have on the later theoretical speculations.

TABLE III

ANALYTICAL DATA

VARIOUS GLYCERYL PHTHALATES (ANHYDRIDE) AT 200°

Expt.	Acid value	Saponification value	%, E	H_2O, cc. V_a	Ultimate analyses C, %	H, %
55	240	536	55.2	0.85	..	..
29	204.5	536.7	61.9	2.70	58.6	4.74
27	193.1	537.8	64.2	3.30	58.9	4.52
28	183.8	537	65.9	3.80	59.3	4.59
24	172.7	542.5	68.2	4.37	59.7	4.71
20	155.4	549.8	71.8	5.25	59.4	5.01
21	136.6	551	75.0	6.80	59.2	4.43
40	126.0	552	77.2	7.76	60.2	4.37
Gel	(107)	556.8	..	7.99	60.0	4.39
Degel	141.8	538.9	73.6	..	59.7	4.44

Infrared Spectra.—Infrared spectra on the samples described in Table III and covering the range from 1–15 μ have been measured. The details of this investigation will be reported else-

(12) Acknowledgment is made to Dr. G. L. Royer for carrying out these determinations.

where.[13] The spectra showed that the glyceryl phthalate samples for the various acid values fell into groups rather than varying continuously, the spectra of the several samples in a given group being quite similar one with another.

Of special interest in the infrared investigation were the spectra of the degelled samples. These were found to be similar to the corresponding polymeride of the same acid value obtained when approaching gelation, making the assumption that gelation is the result of the formation of a gigantic molecule very questionable.
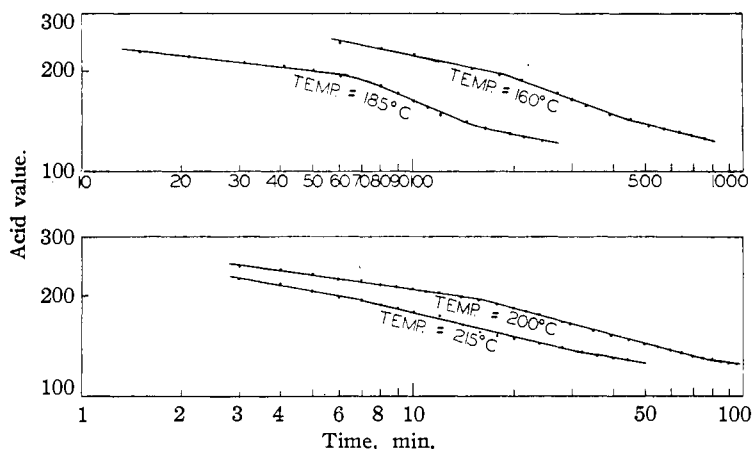

Fig. 6.—Glyceryl phthalate: acid value–time isotherms.

Molecular Weight.—For the determination of the average molecular weights, a cryoscopic solvent was sought in which the polyesters were all very soluble, in which water was immiscible, and in which duplicate values, unaffected by moderate changes in concentration of resin used, could be obtained. Acetophenone ($K = 5650$) was found to answer these requisites. In the experimental data presented, carefully distilled acetophenone was employed throughout, its suitability being checked with specially purified naphthalene.

The average molecular weights found for the various glyceryl phthalate samples are given in Table IV together with the concentrations at which the measurements were made and the depressions observed. In Fig. 7, these average molecular weights are plotted against the corresponding acid values.

How the molecular weight would vary with the acid value if any ideal (2,3) continuous interesterification alone occurred is shown as the so-called theoretical curve in Fig. 7. The deviation of the

(13) R. H. Kienle and R. B. Barnes, Presented before American Chemical Society Meeting at Chapel Hill, N. C., April, 1937.

TABLE IV

AVERAGE MOLECULAR WEIGHTS
GLYCERYL PHTHALATES (ANHYDRIDE)
SOLVENT: ACETOPHENONE

Expt.	Acid value	Concn., %	ΔT,°C.	M
55	240	5.38	0.713	418
29	204	3.12	.402	437
28	184	3.94	.463	482
24	173	5.46	.565	545
20	155	4.36	.420	590
21	137	4.52	.325	790
40	126	3.02	.152	1120
Degel	142	3.98	.227	680

actual data from the theoretical shows that other molecular species in variance with simple interesterification must be forming. The fact that the experimental curve falls below the theoretical, and in keeping with the general evidence that the reaction is essentially esterification, strongly suggests intraesterification. These average molecular weights must be dovetailed with the other data such as acid value, water loss, etc., in modifying the reaction and structural consideration.
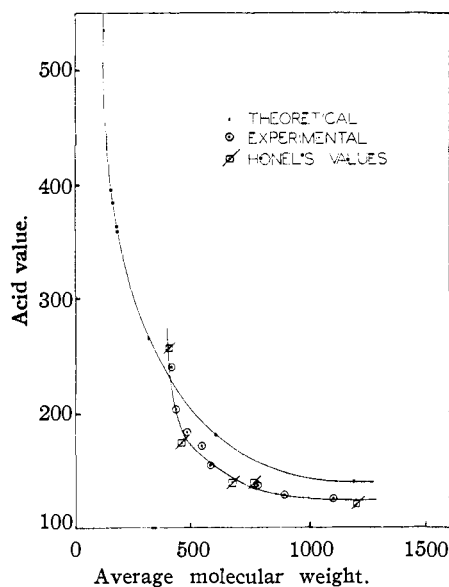

Fig. 7.—Glyceryl phthalate.

Viscosity Studies.—As a further possible adjunct to information concerning the molecular changes in the glyceryl phthalate reaction, viscosity measurements were undertaken.

Working in dioxane, Kienle and Race[14] reported the viscosity characteristics of a series of glyceryl phthalate samples at various acid values. A similar investigation was later made by Hou-

wink and Klaassens.[4] There is a fair agreement between the values reported in both these papers for the samples taken at the early stages of the reaction. Houwink and Klaassens, however, were not able to obtain the high value reported by Kienle and Race for the very last stages. But Houwink and Klaassens, in their measurements, used as a final sample one which was a considerable time period away from gelation, while Kienle and Race used a sample just prior to gelation. All of these values reported, however, were low as compared with numerous specific viscosity values given by Staudinger for other synthetic polymerides, such as polystyrene. If the contention of Staudinger, that specific viscosity bears relation to the molecular size, has the importance he attributes thereto, this would indicate that glyceryl phthalate is definitely a small polymeric molecule.

The present measurements were made using c. p. acetone (A. V. = 0) as a solvent at a concentration of 15.0% by weight. The measurements were made in a vacuum capillary type viscometer described by Gregory, Ressweiler and Lampert,[15] and were carried out at 35°. The average values of several determinations have been corrected for the density of the solution in each case. The values obtained for the different glyceryl phthalate samples are given in Table V. It will be noted that until an acid value of less than 137 is reached, only a small steady increase in the specific viscosity is observed. From then on, the increase is rapid in line with Kienle and Race's original observations. The rather rapid increase in specific viscosity that begins at an acid value of approximately 137 indicates that a change in molecular complexity occurs when this acid value is reached. Up to this time, the molecules probably were of such small size that they had some, although little,

TABLE V

VISCOSITY CHARACTERISTICS OF VARIOUS
GLYCERYL PHTHALATE (ANHYDRIDE) SAMPLES

Solvent, acetone; concentration, 15.0% by weight; temperature, 35°; viscosity of acetone, η_0 = 0.00278 poise.

Acid value	$\eta \times 10^5$ poise	Relative viscosity, η_r	Specific viscosity, η_s
204	574	2.065	1.065
193	598	2.150	1.150
184	568	2.044	1.044
173	560	2.018	1.018
155	560	2.255	1.255
137	654	2.350	1.350
123	930	3.420	2.420

(14) Kienle and Race, Trans. Electrochem. Soc., 65, 231 (1934).

(15) Gregory, Ressweiler and Lampert, J. Rheol., 1, 30 (1929)

effect on the viscosity. Beyond this point, the reaction started to produce large enough molecules to be effective in causing a pronounced increase in viscosity.

Monomolecular Films.—It was found that the various glyceryl phthalate samples readily formed monomolecular films. These have been studied in detail and will be reported upon later. Although Moss[16] and Harkins[17] investigated some of the linear polymerides in this manner, as far as is known, no measurements have been reported on convertible polymerides.

By means of the usual method of intercepts, it was possible to determine an area which represented the area per molecule of the average molecular species, A_{max}, present in any given sample. The values of A_{max} and the corresponding acid values are given in Table VI and are shown in curve form in Fig. 8.

Fig. 8.—Glyceryl phthalate: monomolecular area per average molecule as function of acid value.

TABLE VI

AREA PER AVERAGE MOLECULE, A_{max}, OF SEVERAL GLYCERYL PHTHALATES AS MONOMOLECULAR FILMS ON 0.001 N HCl

Acid value	Area/molecule, A_{max} (Å.)²
240	31.1
204	35.5
184	52.0
155	74.0
137	129.2
126	138.8

Fractionation.—While studying the various glyceryl phthalate samples in glacial acetic acid solution, it was observed that when this solution was drowned in a large volume of water, white amorphous precipitates frequently resulted. It was found that if the water was made slightly acid with hydrochloric acid, the precipitate obtained was readily filterable and often granular in nature. Undoubtedly low molecular weight portions were separated from the larger molecules by this treatment. Thus some idea of obtaining the size of the latter seemed a possibility. A fractionation was therefore made, using glyceryl phthalate, A. V. 130.

Fifteen grams of the resin was dissolved in 150 g. of glacial acetic acid. This solution was added slowly to 1500 cc. of water which had been acidified with hydrochloric acid. The resulting precipitate was reslurried in distilled water, washed several times by decantation, filtered, and dried at 60°. The acid value was found to be 92.2, and

(16) Moss, THIS JOURNAL, **56**, 41 (1934).

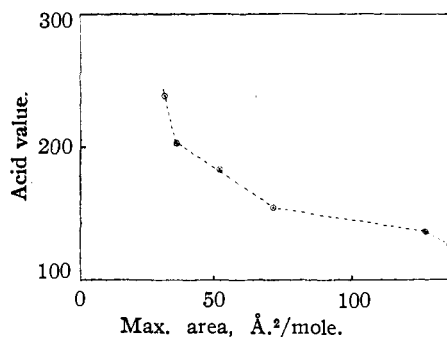(17) Harkins, Ries and Carman, *ibid.*, **57**, 776 (1935).

the molecular weight in acetophenone was 2580. It is interesting to compare these values with the theoretical values calculated if only interesterification were involved. On the assumption that a condition of interesterification equivalent to tetramer formation has occurred, which is required by the molecular weight and other data, the acid value resulting would be 117 and the molecular weight 2384. If intraesterification occurred at one position on the molecule along with the interesterification, the acid value would be 94.5 and the molecular weight 2366. These latter values are in fair agreement with the values found experimentally.

It has been known for some time that if polyester resins are dissolved in acetone, water can be added slowly and, at a certain point, precipitation or turbidity occurs. The amount of water that can be added to any given solution and the character of the precipitate obtained seemingly depend on the extent to which the resin has been carried in its preparation. Thus a solution of a partially formed resin will tolerate a large amount of water and will give a very gummy precipitate while a resin near the gel point will tolerate little water and will yield a precipitate quite granular in character.

TABLE VII

PRECIPITATION STUDIES OF GLYCERYL PHTHALATE (ANHYDRIDE) AT 20–21°

Sample	A. V.	Weight, g.	Water used, cc.	H₂O/g. to ppt.	Character of ppt.
55	240	1.0125	66.50	65.50	Colloidal
29	204	1.0040	62.40	62.30	Colloidal
27	193	1.0007	46.20	46.20	Soft, gummy
28	184	1.0006	45.25	45.25	Soft, gummy
24	173	1.0036	41.40	41.30	Soft, gummy
20	155	1.0316	33.60	32.60	Soft, gummy
21	137	1.0065	23.36	23.26	Granular
40	126	1.0050	20.50	20.50	Granular

Approximately 1 g. of each of the glyceryl phthalate resins was dissolved in 50 cc. of c. p. acetone, the actual amount used being carefully weighed and recorded. Each solution was then titrated with distilled water to the point at which cloudiness was first observed. It was possible to obtain this end-point to within 0.05 cc. The data obtained are given in Table VII, and plotted in Fig. 9.
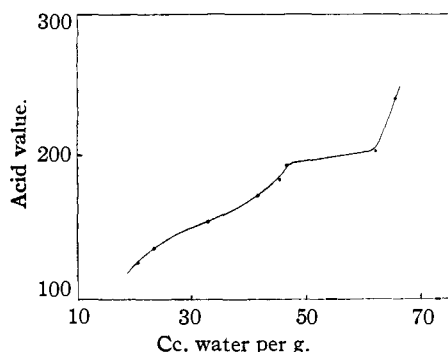
Fig. 9.—Glyceryl phthalate: water required for precipitation.

Theoretical

It has been shown by all the chemical examinations and supported by the infrared spectra data that only C–O–C linkages are formed.[18] Therefore, in modifying the assumption that interesterification was the only reaction involved, the possible secondary reactions to consider were ether formation, anhydride formation, and intraesterification. In the case where equivalent quantities of reactants are involved, as in the present investigation, there was little evidence for ether formation. Anhydride formation and intraesterification, however, appeared to be definite possibilities. A number of glyceryl phthalate samples for which the acid value, saponification value, average molecular weight, and water evolved had been determined were taken and examined as to whether or not possible combinations of polyesters could be postulated, following a common pattern, which would correlate all the data. On the basis of interesterification as the primary reaction with anhydride and intraesterification as secondary reaction possibilities, it has been found possible to derive approximate theoretical compositions which satisfy all of the determined values. In arriving at these calculations, a schematic postulation of the progress of reaction, such as is shown diagrammatically in Fig. 10, was used.

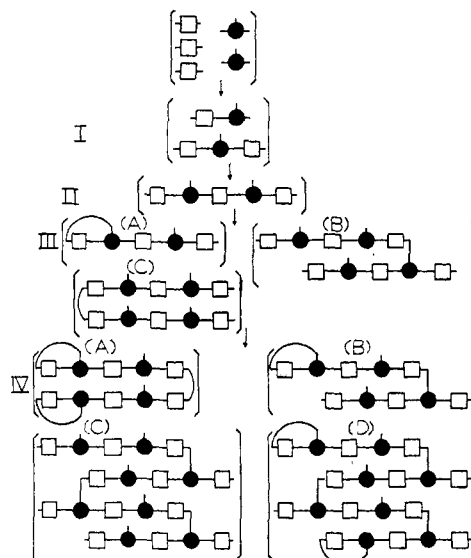(18) Kienle, *J. Soc. Chem. Ind.*, **55**, 229T (1936).

Fig. 10.—Glyceryl phthalate reaction, postulated progress: ratio of 2 moles of glycerol to 3 moles of phthalic anhydride.

Four typical glyceryl phthalate samples have been examined in detail, namely, those with acid values of 235, 184, 137 and 126. It has been possible to propose approximate compositions for each of these samples. These compositions, as well as the agreement between the calculated and the observed analytical data, are given in Table

TABLE VIII

CALCULATED COMPOSITIONS OF VARIOUS GLYCERYL PHTHALATES

Observed	Species (Fig. 10)	Composition Approximate mol. fraction	Calcd.
A. V. = 235			A. V. = 235
V_a = 1.00 cc.	I	0.60	V_a = 1.80
M = 425	II	.40	M = 480
			v = 1.7
M_v = 406			
A. V. = 184			A. V. = 190
V_a = 3.80 cc.			V_a = 4.00
M = 482	I	.40	M = 488
	II	.30	v = 1.5
	IIIa	.30	
M_v = 460			
A. V. = 137			A. V. = 140
V_a = 6.70 cc.			V_a = 6.70
M = 795	II	.33	M = 801
	IIIa	.33	v = 2.0
	IIIb	.33	
M_v = 800			
A. V. = 126			A. V. = 125
V_a = 7.60 cc.			V_a = 7.60
M = 1120	II	.167	M = 1190
Sap. value = 551	IIIa	.167	v = 2.6
	IIIb	.333	Sap. value = 552
	IVa	.084	
	IVb	.083	
	IVc	.084	
	IVd	.083	
M_v = 1150			

VIII. Examination of this table shows that the agreement between the observed and calculated values is surprisingly good.

The value of M_v in this table requires explanation. It will be observed by examining Fig. 10 that every postulated polymeric molecule is a polybasic acid with a characteristic basicity. Thus the basicity of the molecule represented by IIIb is 3. Any given individual glyceryl phthalate sample will, therefore, have an average basicity, v, depending on the number and kind of polymeric molecules present. Carothers[4] has shown in linear systems, in which the basicity of the polymeric molecules remains essentially constant, that the molecular weights can be determined either by the usual methods or from the acid value. When the molecular weight is determined from the acid value, the following equation applies

$$MA_t = 56.1 \times 10^3 v \qquad (2)$$

wherein M is the average molecular weight, A_t is the acid value at time t, and v is the basicity. In linear polyesters, v is 1, therefore v did not appear in Carothers' calculations. But in the convertible polyesters, the value of v is important. In Table VIII the Mv value was obtained by using equation (2), first determining the average value of v from the composition finally suggested, then substituting this together with the acid value experimentally determined, and solving. It is seemingly additional evidence in favor of the compositions suggested that the molecular weights thus calculated agree very well with the average molecular weights, M, actually determined.

The compositions of the several glyceryl phthalate samples as calculated are in surprisingly good agreement with the various experimental facts observed. Thus, only when an acid value around 190 is reached in the reaction, do molecules of the species III type seemingly appear. From this point on to approximately an acid value of 135, molecules of the species III type are apparently forming. Further on, molecules of the species IV type, with their three dimensional complexities, begin to appear until finally their concentration is sufficiently great to cause arrested motion, that is, gelation. The grouping of the various samples with respect to the infrared spectra is now understandable. The marked change in the character of the precipitate from a gummy to that of a granular, easily filterable type at an acid value of 137 as acetone solutions are diluted with water is ex-

plained. When the basicities are taken into account and it is assumed that in monomolecular films the point of attachment to water is through the carboxyl groups, which all prior work on complex acids has indicated is the case, the changing character of the monomolecular areas is also understandable. The non-appearance of the complex three-dimensional polyester molecules of the species IV type, until acid values less than approximately 137 are reached, offers an explanation for the change in specific viscosity that was observed in the neighborhood of this acid value. The introduction of the intraesterification and anhydride modification also accounts for the character of the acid value–water loss relationship. In other words, the general schematic postulation of the progress of the reaction presented in Fig. 10 is consistent with the experimental data that have been obtained for glyceryl phthalate.

It must not be concluded that the polyester compositions developed above are being presented as definite fixed structures. Thus it is suggested that in a glyceryl phthalate resin, such as one represented by an acid value of 126, small amounts of polyesters of even higher degrees of polymerization or complexity than those postulated might well be present.

The possibility that the reaction proceeds entirely in a heterogeneous manner, governed completely by the random chance contact of active groups on the interacting molecules, each active group acting independently and in no organized molecular manner, is therefore questioned. When, however, the reaction has proceeded so that essentially tetramers are being formed and the concentration thereof has approximated 33 mole %, gelation occurs seemingly because, at this concentration, a sufficient complexity of three-dimensional molecules has been built up to bring about a state of arrested motion. It follows that gelation in polymerides is not necessarily attendant with the formation of gigantic macromolecules. Macromolecules may appear later, but gelation apparently occurs, or can occur, when there has formed a sufficient concentration of suitably complex three dimensional molecules of a relatively low degree of polymerization which are capable of intertwining. This may be thought of as analogous to a log jam which always results when a certain minimum concentration of logs becomes permanently interlocked.

Other convertible polyester systems also have

been investigated recently. It was found that the data obtained for these systems could be treated in a manner analogous to the glyceryl phthalate data. It is, therefore, suggested that the essential concepts developed herewith are applicable generally to convertible polymeric systems.

Summary

1. The reaction between glycerol and phthalic anhydride was reinvestigated. A special apparatus, designed so that the reaction could be carried out under controlled reproducible conditions, was used.

2. The reaction was studied in detail at 200°. Samples were taken at various stages of the reaction and their acid value, saponification value, ultimate analysis, and molecular weight determined. The infrared spectra, rheological properties, and spreading characteristics as monomolecular films were ascertained for each of the samples.

3. As the reaction proceeded at 200°, it was shown that the water evolved was greater than calculated from simple interesterification considerations.

4. A schematic progress of the reaction is suggested wherein it is proposed that the underlying reactions are essentially interesterification, modified by intraesterification and anhydride formation. Application of these concepts allowed approximate compositions of glyceryl phthalate polymerides to be derived at various stages of polymerization. The several constants calculated from these postulated compositions were found to agree very well with those measured experimentally.

5. Gelation has been shown to occur at a relatively low average molecular weight, suggesting that molecular growth proceeds until a sufficient concentration of intertwined three dimensional molecules has formed, whence arrested motion occurs.

6. Limited data are presented on precipitation and fractionation studies.

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The Polyhydric Alcohol–Polybasic Acid Reaction. IV. Glyceryl Phthalate from Phthalic Acid

BY R. H. KIENLE, P. A. VAN DER MEULEN AND F. E. PETKE

All the studies on the glyceryl phthalate reaction thus far reported in the literature have been carried out with phthalic anhydride. In the present investigation, data are presented wherein phthalic acid was substituted for the anhydride.

The apparatus used and experimental technique employed already have been described fully.[1] The phthalic acid was obtained from resublimed phthalic anhydride (Selden Division, American Cyanamid Company) by dissolving in carbonate free sodium hydroxide solution, then precipitating with hydrochloric acid, thoroughly washing until the wash water tested free from chloride ion, and finally drying carefully at 60° in the air.

The present investigation was carried out at 190°. This temperature was chosen because it was found that at this temperature no anhydride formation occurred during the preheating period employed before the glycerol was added.

(1) Kienle, van der Meulen and Petke, THIS JOURNAL, **61**, 2258 (1939).

Experimental Data

The detailed data obtained for the glycerol-phthalic acid reaction at 190° are given in Table I.

In Fig. 1 the variations of both the acid value and the water evolved with time of reaction have been plotted. In the case of the water evolved-time curve, the observed points of a second independent experiment under identical conditions have been included to show how well the data could be duplicated. On the acid value-time curve, the values obtained from several independent determinations are also shown. Again they fall quite well on the curve.

The log acid value–log time relationship is shown in Fig. 2. It is strikingly similar in shape to the same relationship for glyceryl phthalate (anhydride) except that for glyceryl phthalate (acid) it has been possible to extend the relationship to much higher acid values.

In Fig. 2 changes in slope are observed at ap-