pared from the bromoacid chloride as well as that from the bromination of the amide in carbon tetrachloride. No trace of the α-sulfonyl acid was observed when the filtrate from the reaction mixture was acidified. Addition of silver nitrate solution gave silver bromide, indicating some hydrolysis of the halide.

Into 50 ml. of boiling 5% sodium hydroxide solution was sprinkled 2.86 g. of IV. The mixture was boiled about five minutes until only a faint test for ammonia was obtained. It was then chilled, acidified with nitric acid and extracted with ether. The aqueous portion gave a heavy precipitate with silver nitrate, indicating a large removal of bromine. The ether extracts were evaporated and gave a small quantity of oil that did not solidify at −15°. The amount of oil was less than 1 ml.

Two grams of II was sprinkled into 50 ml. of boiling 5% sodium hydroxide solution. The material formed opaque globules and only traces of ammonia were evolved. The mixture was refluxed for five minutes, chilled and filtered. The entire residue was unchanged amide.

Summary

Compounds reported to be N-bromo-α-sulfonylamides by Tröger and Hille have been shown to be α-bromo-α-sulfonylamides. The most satisfactory method of preparation of α-bromo-α-sulfonylamides was by direct bromination of α-sulfonylamides in moist carbon tetrachloride. Members of this series were also prepared by direct bromination of the amides in glacial acetic acid and by bromination of α-sulfonyl acid chlorides, followed by reaction with ammonia. The reactions of α-bromo-α-sulfonylamides showed that the sulfone group was similar to other labilizing groups in causing hypohalite characteristics in α-halo derivatives.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

The Polyhydric Alcohol–Polybasic Acid Reaction. V. The Glyceryl Succinate and Glyceryl Maleate Polyesters

BY R. H. KIENLE AND F. E. PETKE

Although the glycol succinate reaction has been studied in some detail, no quantitative data have been published for the glyceryl succinate and the glyceryl maleate polymerization reactions. Glyceryl succinate was first prepared by Van Bemmelen.[1] It has been referred to frequently in resin literature[2] but the only published quantitative data on the polyester seem to be those of Hönel.[3] No such data appear to have been published for glyceryl maleate. In the present investigation, data are presented for the formation of these polyesters, succinic acid and succinic anhydride being used to prepare glyceryl succinate, and maleic anhydride to prepare glyceryl maleate.

The apparatus and technique used have already been fully described.[4] The purification and chemical constants of the glycerol employed similarly have been given. The maleic anhydride used was American Cyanamid Company chemically pure material, redistilled. The succinic acid and succinic anhydride were the chemically pure grade of Selden Division, American Cyanamid Company. The glycerol–succinic acid reaction was carried out at 190° in order that the data might be comparable with the recently published glyceryl phthalate (acid) investigation. The glycerol–maleic anhydride and glycerol–succinic anhydride reactions were carried out at 160°, since the reactions proceeded too rapidly at 190°.

Experimental Data

The detailed data obtained for the glycerol–maleic anhydride, glycerol–succinic anhydride, and glycerol–succinic acid reactions are listed in Figs. 1, 2 and 3, respectively.

Figure 4 gives the acid value–water evolved relationship for all three reactions. When the theoretical acid value–water evolved curves are inserted in this plot, assuming only interesterification has occurred, it is found, in the case of glyceryl maleate, that the water evolved experimentally was at all times greater than theory, while in the case of both the glyceryl succinate reactions, the water evolved was at all times less than the theoretical. The equation for determining this theoretical relationship is

$$A_t = \frac{56.1(V_f - V_t)}{18(W - V_t)}$$

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(1) Van Bemmelen, *J. prakt. Chem.*, **69**, 84 (1856).

(2) Ellis, "The Chemistry of Synthetic Resins," Vol. I and II, Reinhold Publishing Corp., New York, N. Y.

(3) Hönel, *Paint Oil Chem. Rev.*, **91**, 19 (1931).

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

where A_t is the acid value at time t, V_t the water evolved at time t, V_f the total water evolved at 100% esterification, and W the total weight of reactants used. This equation is the exact form of an approximate equation used in the previous papers of this series.

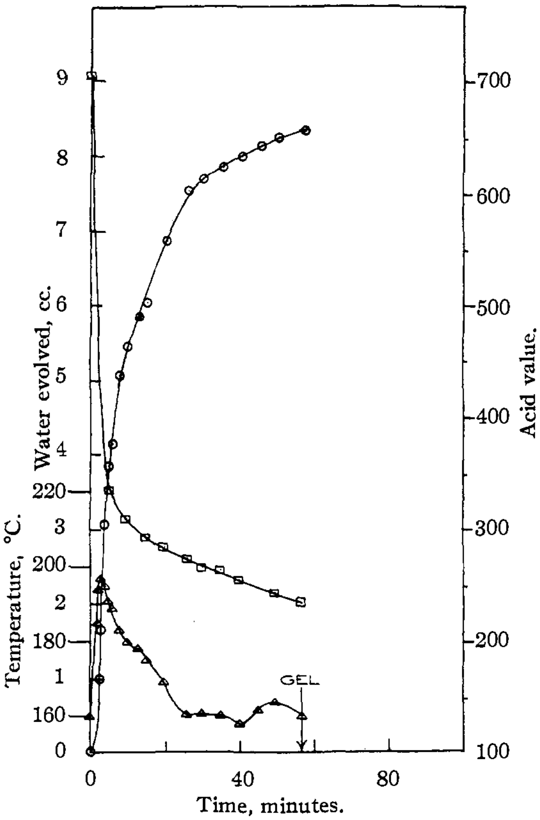

Fig. 1.—Reaction data. Glyceryl maleate: proportions, glycerol 69.0 g., maleic anhydride 110.3 g., temperature of mixing 160°, ◬, temperature, ⊡, acid value, ⊙, water evolved.

The log acid value–log time curves for the three reactions are shown in Fig. 5. It is interesting to note that the general shape of these curves is similar to the corresponding plots for glyceryl phthalate (anhydride) and glyceryl phthalate (acid). The changes of slope observed in the curves of the present investigation appear to occur at degrees of esterification corresponding to those previously noted for the glyceryl phthalates.

Table I

		Glyceryl maleate (anhydride)	Glyceryl succinate (acid)	Glyceryl succinate (anhydride)
Acid value		231	189	183.6
Saponification value		729	739.5	737.6
% Esterification		68.5	74.5	75.0
Average molecular weight		1050	1075	1085
Ultimate analysis	C, %	46.9	46.7	46.7
	H, %	4.6	5.2	5.4

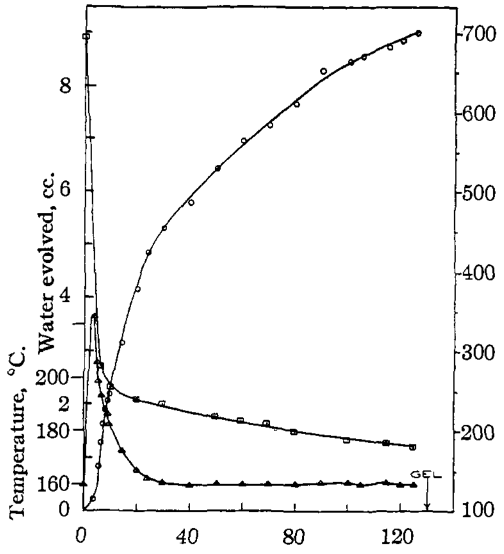

Fig. 2.—Reaction data. Glyceryl succinate (anhydride): proportions, glycerol 69.0 g., succinic anhydride 112.5 g., temperature of mixing 160°, ◬, temperature, ⊡, acid value, ⊙, water evolved.

Analytical Data.—Samples taken just prior to gelation in each reaction were found to be soft, rather flexible, very light amber colored resins.

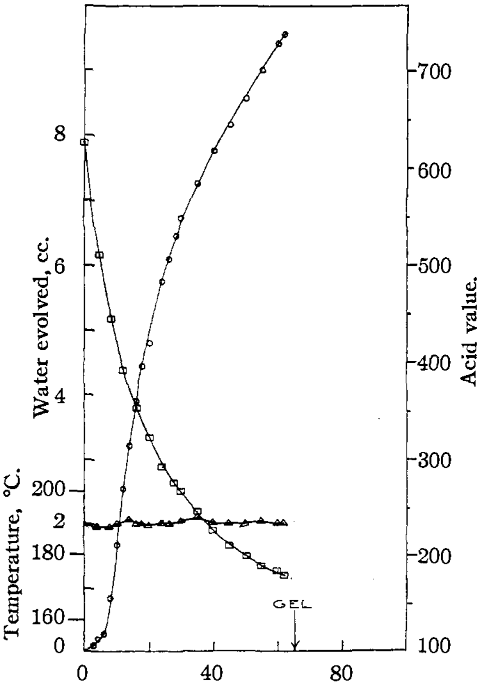

Fig. 3.—Reaction data. Glyceryl succinate (acid): proportions, glycerol 23.0 g., succinic acid 44.3 g., temperature of mixing 190°, ◬, temperature, ⊡, acid value, ⊙, water evolved.

The analytical data for these samples are given in Table I.

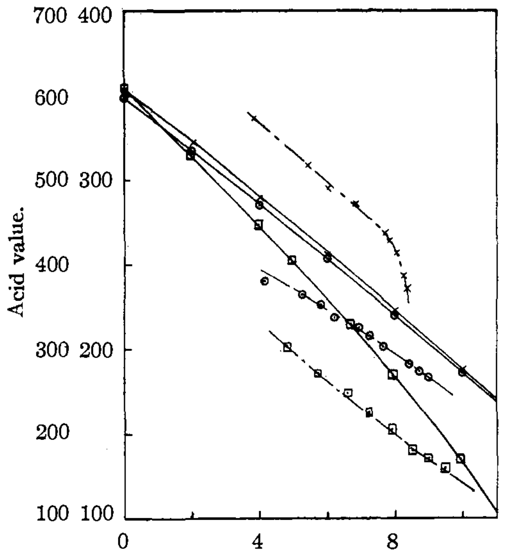

Fig. 4.—Acid value, water evolved relationship: ×, glycerol maleate, ⊙, glyceryl succinate (anhydride), ⊡, glyceryl succinate (acid), —— theory, – – – – experimental.

The infrared spectra from 1–15 μ for these resins have been measured[5] and are plotted in Fig. 6. The spectra show all the necessary linkages for polyester formation together with a suggestion of both conjugation and ring formation in the case of glyceryl maleate.

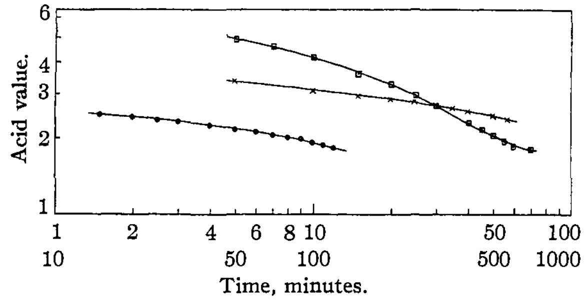

Fig. 5.—Log acid value–log time: ×, glyceryl maleate, $T = 160°$; glyceryl succinate anhydride, $T = 160°$; □, glyceryl succinate acid, $T = 190°$.

The spreading curves for these same polyester polymerides as monomolecular films on 0.001 N hydrochloric acid were determined and are given in Fig. 7. From these curves the areas per molecule were obtained by extrapolation and found to be 31.5 sq. Å. for glyceryl maleate and 80.5 sq. Å. for glyceryl succinate.

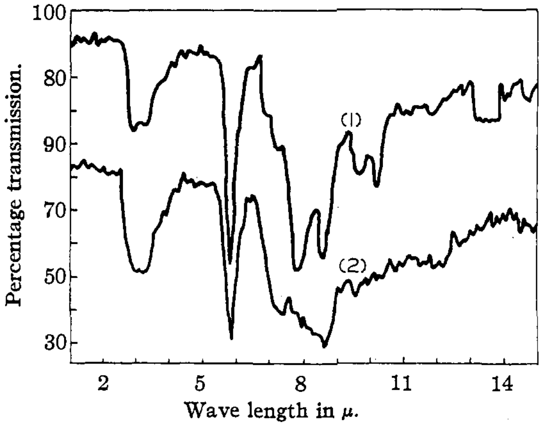

Fig. 6.—Infrared spectra: (1) glyceryl maleate, A. V. 231; (2) glyceryl succinate, A. V. 182.

In Table II there have been summarized pertinent data with respect to the sol–gel transition for the various polyester polymerides thus far reported. Also there have been included in this table the calculated acid values for the dimer and tetramer form of the several polyesters, assuming only interesterification had occurred. It is interesting to note that with the exception of glyceryl maleate, the acid value at which gelation occurs is between the two values.

TABLE II

Glyceryl polymeride	Mol. resin	React. temp., °C.	Time, to gel., min.	H_2O evolved, Va	A. V. at gelation (obsd.)	A. V. (calcd.) Dimer	A. V. (calcd.) Tetramer
Phthalate	1/4	160	160	7.99	120	139	117
Succinate	1/4	160	130	6.00	178	182	154
Maleate	1/4	160	57	5.44	230	187	157
Phthalate (acid)	1/8	190	164	10.80	120	139	117
Succinate (acid)	1/8	190	64	9.62	178	183	154

Discussion

In the glyceryl succinate reaction, when acid is used instead of anhydride, no initial temperature rise is observed and time is required to attain 50% esterification. From this point on to gelation, however, the reactions are fairly equivalent,

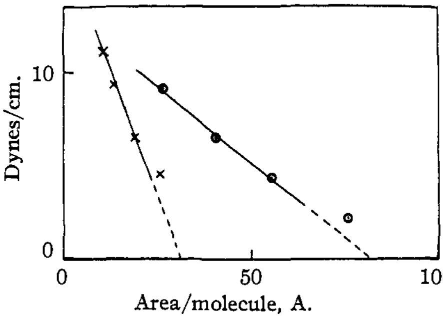

Fig. 7.—Monomolecular film data: $T = 15–16°$; 0.001 N HCl; ×, glyceryl maleate; ⊙, glyceryl succinate.

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[5] Acknowledgment is made to Mr. R. R. Brattain for measuring these spectra.

finally yielding polyesters with similar properties, as is evident from the analytical values shown in Table I. In the glyceryl succinate reaction, regardless of whether acid or anhydride is used, less water is evolved than is required theoretically. This seems to indicate that little more than interesterification is involved and that a portion of the water formed is retained by or dissolved in the polyesters.

The glyceryl maleate reaction is more complicated. From the beginning of the reaction to gelation more water is evolved than is predicted if only interesterification is assumed. The acid value of glyceryl maleate just prior to gelation is much higher than would be expected from the other polyesters examined. The formation of anhydrides and intraesterification, therefore, is required to explain the high acid value and the excess water evolved. Since the total evolved water in the glyceryl maleate is smaller than that resulting from the glyceryl succinate reaction, but the average molecular weights of the two resins at corresponding stages are practically equal, it would seem that addition polymerization also has occurred. The appearance of adsorption bands around 10.0 and 13.0 μ in the infrared spectrum of glyceryl maleate, common to ring compounds,[6] and the much lower spreading area of the glyceryl maleate polyester as compared with the glyceryl succinate polyester are further evidence in favor of the occurrence of addition polymerization.

In a previous paper[7] the importance of the average functionality of a highly functional polymeride with respect to when gelation will occur was discussed. In polyester polymerides, when stoichiometric proportions of reactants are used and optimum conditions of reaction are employed, it has been shown[4] that the average polymeric functionality with respect to the carboxyl groups can be calculated from the equation

$$MA_t = 56.1 \times 10^3 v$$

where v = the basicity of polyester, that is, the average polymeric functionality with respect to carboxyl groups. The calculated and observed values were found to agree very well. Gelation in all highly functional polymeric systems was shown to occur when the average polymeric functionality exceeded 3.0. In the case of glyceryl phthalate, gelation was found to result when v attained a value of 3.3 or just beyond the condition for potential gelation. At this point, not very large molecular weight polyesters are formed, but rather the mole percentage of tetramers or higher polymers has attained a low limited molar concentration sufficient to bring about a state of arrested motion. The glyceryl maleate and the glyceryl succinate data further support this concept. Thus, just before gelation, the average molecular weights are in the order of 1100–1200, while the average polymeric functionality at gelation for glyceryl maleate is approximately 4.3 and for glyceryl succinate is approximately 3.4.

Summary

1. The glyceryl succinate reaction has been investigated using both acid and anhydride. A difference was observed in the early portion of the acid reaction, but after 50% esterification had been reached, the two reactions were essentially similar. Less water was evolved than was required theoretically by interesterification. It has been suggested that part of the water formed was retained by the polyester.

2. The glyceryl maleate (anhydride) also has been studied. In this case more water was evolved than required by theory. This has been attributed to the formation of anhydrides and intraesterification along with interesterification. Data are presented indicating that addition polymerization also occurred.

3. Data for the various polymerides are summarized and gelation is explained in terms of low molecular weight polyester formation.

BOUND BROOK, N. J. RECEIVED OCTOBER 5, 1939

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[6] Coblentz, "Investigation of Infra-Red Spectra," p. 136, Carnegie Institute (1905).

[7] Kienle, *J. Soc. Chem. Ind.*, **55**, 229T (1936).