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STUDIES ON POLYMERIZATION AND RING FORMATION. IV. ETHYLENE SUCCINATES

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Ethylene succinate as a typical example of a condensation polymer[1] has been submitted to further study with the view of gaining more information in regard to its structure. The presence of the structural unit,[1] I, in this ester has been established by the methods used in its synthesis,[2,3] by its chemical behavior, and by its analytical composition.[2,3]

$$—O—CH_2—CH_2—O—OC—CH_2—CH_2—CO— \qquad (I)$$

Of the various polymeric forms described in this paper, the apparent molecular weights indicate average values of 6 and 23, respectively, for the number of structural units contained in each molecule of the lowest and highest polymers. It is assumed that these units are joined together in a linear fashion by real primary valences, as in II. Since it is very improbable that there are free valences at the ends of the resulting chains, the problem of the structure of these polymers resolves itself into finding whether the end valences are mutually saturated with the formation of very large rings or are saturated by univalent groups of some kind.

$$—O—(CH_2)_2—O—OC—(CH_2)_2—CO—O—(CH_2)_2—O—OC—(CH_2)_2—CO—O—(CH_2)_2—O—OC—(CH_2)_2—CO—, \text{ etc.} \qquad (II)$$

Any of the reactions by which this ester is prepared offers the formal possibility of establishing either rings (closed chains) of 8, 16, 24, ...(8)n members or of open chains corresponding to each of these rings. The observed molecular weights indicate the presence of 50 to 180 atoms in each chain. This fact and the physical properties of the ethylene succinates indicate the absence of more than traces of rings of less than 32 members. Since the same theoretical considerations[4,1] which predict the improbability of the formation in bifunctional reactions of rings of 8 to 32 members apply *a fortiori* to still larger rings, an open chain seemed much more probable than a cyclic structure, and our efforts were directed toward the detection of the univalent groups which would constitute the ends of the open chains. We have proved the presence of such groups, and the open-chain structure for the polymeric ethylene succinates is clearly established.

Neutral Ethylene Succinate.—This ester is prepared by heating suc-

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[1] Carothers, THIS JOURNAL, **51**, 2548 (1929).

[2] Vorländer, *Ann.*, **280**, 167 (1894).

[3] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929).

[4] Mohr, *J. prakt. Chem.*, **98**, 348 (1918).

cinic acid with excess glycol at 180° until the distillation of water ceases and then removing the excess glycol by heating in high vacuum at 200–250°. The ester is purified by crystallization and melts at 102°.[5]

Its apparent molecular weight is about 3000.

If this ester is an open chain, its method of formation and its observed molecular weight would lead one to assign to it the structure III, and it

$$\mathrm{H{-}[O{-}(CH_2)_2{-}O{-}OC{-}(CH_2)_2{-}CO{-}]_{22}{-}O{-}(CH_2)_2{-}OH} \qquad \text{(III)}$$

should therefore show the reactions of a dihydric alcohol. The possibility of applying to it many of the typical reactions for the detection of primary alcohol groups was excluded for one reason or another. Thus the presence of ester linkages excluded any reactions which might result to hydrolysis. The fact that the compound is hygroscopic and insoluble in ether made it useless to attempt to apply any such methods as the Zerewitinoff. The compound crystallizes from acetic anhydride and is apparently unchanged even on long boiling in this solvent in the presence of catalysts, but in so large a molecule acetylation might occur without any apparent change in physical properties, and the amount of acetic acid which would be liberated on hydrolysis of even a completely acetylated product would be so small as to make its estimation difficult. The ester reacts very slowly and incompletely with phosphorus tribromide.

Six grams of the ester heated for five hours in 30 cc. of boiling chloroform with 6 cc. of phosphorus tribromide after thorough washing and repeated crystallization was found to contain 0.58% Br.

The ester was also recovered apparently unchanged after treatment with phenyl and naphthyl isocyanates under various conditions. These failures appear to be due to a reluctance of the hydroxyl groups to react, and they are not altogether surprising in view of the diminished reactivity which is frequently associated with increased molecular size.

Reaction occurred completely in the expected sense with succinic and with *p*-bromobenzoic anhydrides at elevated temperatures. These reactions led to the dibasic acid which agreed in properties and composition with the Formula IV, and to a *p*-bromobenzoyl ester which agreed in composition with Formula V.

$$\mathrm{HO{-}OC{-}(CH_2)_2{-}CO{-}[{-}O{-}(CH_2)_2{-}O{-}OC{-}(CH_2)_2{-}CO{-}]_{23}{-}OH} \qquad \text{(IV)}$$

$$p\text{-}\mathrm{BrC_6H_4{-}CO{-}[{-}O{-}(CH_2)_2{-}O{-}OC{-}(CH_2)_2{-}CO{-}]_{22}{-}O{-}(CH_2)_2{-}O{-}OC{-}C_6H_4Br}\text{-}p \qquad \text{(V)}$$

Preparation of IV.—Twelve grams of neutral ethylene succinate was heated with 3 g. of succinic anhydride at 175–180° for three hours. The reaction mixture was washed three times with hot water, dried, precipitated from chloroform with ether and crystallized 6 times from acetone. Its properties identified it as the dibasic acid IV, which would be formed by the reaction of each hydroxyl group of III with one molecule of succinic anhydride.

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[5] Capillary tube melting point. See Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929), for a description of the peculiar melting point behavior of this compound.

The ester III melted at 102°, had an apparent molecular weight of about 3000, was neutral and did not form a sodium salt. IV prepared from III melted at 98° and had an apparent molecular weight of 3110 (method of Menzies and Wright in ethylene chloride, observed values 3170, 3040) and a neutral equivalent of 1708. The action of sodium bicarbonate on IV led to a sodium salt which melted at 104° and contained 1.23% of sodium. The analytical data are given in Table I.

Preparation of Di-*p*-bromobenzoyl Derivative of III.—Two and one-half grams of III was heated for five hours with 0.75 g. of *p*-bromobenzoic anhydride at 175–185°. The reaction mixture was dissolved in chloroform and precipitated by ether, washed with hot water, dried and precipitated from acetone by ether. It melted at 93°. Analysis showed it to be the expected di-*p*-bromobenzoyl derivative, V, of III.

Anal. Calcd. for V as $C_{176}H_{172}O_{84}Br_2$: C, 49.30; H, 5.20; Br, 4.84. Found: C, 49.47, 49.39; H, 5.59, 5.60; Br, 4.84, 5.01, 4.88, 4.91.

Acidic Ethylene Succinates.—If glycol and succinic acid would react completely in the proportions in which they are brought together, it would be possible to prepare chains of various lengths by using the glycol and acid in various ratios. In a number of experiments various excess amounts of succinic acid were allowed to react with glycol. The reactants were heated together at 180° until no more water was evolved and the temperature of the bath was then raised to 200–240° for one to five hours to make the reaction as complete as possible. Only traces of acid and glycol appeared in the distillates. The residues were always acidic and, when the excess of acid was large, always contained some unchanged succinic acid. Moreover, products of high molecular weight could be isolated from these residues even when the ratio of acid was as high as 2:1. This showed that under the conditions of these experiments complete control of the length of the chain produced was not possible by adjustment of the ratios of the reactants. On the other hand, this factor had some influence in controlling the lengths of these chains, and by making use of such control as it offered, together with fractional crystallization, it was possible to isolate samples of material representing chains of various lengths, each of which was quite homogeneous in its physical behavior. A comparison of the analytical data and molecular weights for these acidic ethylene succinates clearly indicates that their structure may be represented by VI, in which x has various average values for different fractions.

$$\mathrm{HO{-}OC{-}(CH_2)_2{-}CO{-}[{-}O{-}(CH_2)_2{-}O{-}OC{-}(CH_2)_2{-}CO{-}]_x{-}OH} \quad \text{(VI)}$$

VIa, $x = 6$ VIb, $x = 9$ VIc, $x = 12$

Preparation of VI, a, b and c.—Ethylene glycol, 41 g., and succinic acid, 93.5 g. (20% excess), were heated at 200–210° for four hours, and the residual water was then removed as completely as possible by heating *in vacuo*. The residue was dissolved in chloroform and precipitated with ether. The powder which resulted from the drying of this precipitate weighed 92.2 g. and melted at 87.5–90°. It was extracted several times with boiling water. The residue (59 g.) was dissolved in chloroform and precipitated by ether. It melted at 90°. This constituted fraction VIc. The hot aqueous extracts on cooling deposited 11 g. of solid which after drying melted at 73–74°.

In another similar experiment the acid and glycol were heated for two hours at 190–210° under ordinary pressure, and then immediately extracted several times with boiling water (3 × 300 cc.). The residue amounted to 10.5 g. After solution in chloroform and precipitation by ether, it melted at 82–83°. This constituted fraction VIb. On cooling, the aqueous extract deposited considerable white solid. This after precipitation from chloroform by ether melted at 73°. This material together with the fraction from the previous experiment melting at the same temperature constituted fraction VIa. By evaporation of the aqueous extracts from this experiment there was obtained another fraction melting at 86°. The analytical data for this fraction indicated that it lay between the 73° and the 82° fractions.

Fraction IV was prepared from III in the manner already indicated.

The analytical data for these fractions (see Table I) indicate that we are here dealing with a polymeric series in which the average values for the degree of polymerization vary from 6 up to 23. These fractions closely resemble each other in physical properties: they have the same appearance under the microscope, and they show similar solubility relations. All the fractions are soluble in cold chloroform and in hot 50% alcohol. The lowest fraction is quite soluble in hot water and the higher fractions only very slightly soluble. The melting points rise with increasing degree of polymerization.

All these fractions form sodium salts on treatment with sodium bicarbonate, and these resemble very closely in properties the acids from which they are derived. Thus they are readily soluble in cold chloroform and in warm acetone. They are only slightly soluble in cold water. All of them, however, are readily soluble in warm water, and in this respect the higher members are sharply differentiated from the corresponding acids. The magnitude of the change in properties which is produced by the transformation of the slightly polar carboxyl group into the completely polar sodium salt will be expected to vary with the size of the chains to which these groups are attached, but we found it somewhat surprising, nevertheless, that these sodium salts should melt only a few degrees above the melting points of the corresponding acids. This difference diminishes continuously with the increase in length of the chain and in the highest polymer, IV, amounts to only 6°.

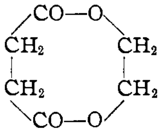
The general plan of the structure of these acid esters is clearly established by the formation of the sodium salts. Attempts to prepare other derivatives from acids met with little success. Treatment with thionyl chloride and with phosphorus pentachloride under various conditions furnished products which contained chlorine, but it could not be established that these materials were really acid chlorides. Attempts to prepare amides by heating the sodium salts of the acids with *p*-toluidine hydrochloride led to the formation of N-*p*-tolyl succinimide. Heating the sodium salts with *p*-bromophenacyl bromide led to the formation of derivatives, but these contained less than the calculated amount of bromine. Thus the sodium salt of VIa led to a derivative, m. p. 73°, containing 8.66% of bromine, while the calculated value for a di-(*p*-bromophenacyl) ester of VIa is 11.61% Br. Similarly, the sodium salt of VIc led to a *p*-bromophenacyl derivative containing 4.12 instead of the calculated 7.13% of bromine.

Table I

Acidic Ethylene Succinates

Sample	M. p., °C.	Neut. equiv.	Mol. wt. calcd. from neut. equiv.	Mol. wt. found in boiling ethylene chloride	X = structural units per molecule	Mol. wt. calcd. from formula	Anal calcd., % C	Anal calcd., % H	Anal. found, % C		Anal. found, % H		Sodium salt M. p., °C.	Sodium salt Anal., sodium Calcd.	Sodium salt Anal., sodium Found
VIa	73	508	1016	1070	6	982	48.86	5.44	48.42	48.58	5.57	5.29	91	4.48	4.26
VIb	82	672	1344	1380	9	1414	49.22	5.56	48.84	48.88	5.74	5.62	97	3.16	3.13
VIc	90	898	1795	1582	12	1847	49.38	5.57	49.34	49.37	5.86	5.81	100	2.43	2.29
IV	98	1708	3417	3110	23	3432	49.66	5.58	49.41	49.44	5.70	5.69	104	1.32	1.23

Mechanism of the Formation of Ethylene Succinate.—The formation of an open-chain poly-ester of the type exemplified by II might occur in either one of two ways. (1) The cyclic monomeric ester VII might first be formed, and this might then undergo A polymerization (self-addition) with the formation of II. (2) II might be formed directly from the acid and the glycol (C polymerization) by a series of successive reactions. That poly-esters of this general type may be formed by the first mechanism is clearly indicated by the fact[6] that the monomeric form of trimethylene carbonate can be isolated by the distillation of its polymer, and, by heating, the monomer can be changed to the polymeric form. This is also true of other poly-esters, but, so far as our information extends now, only of those in which the monomer is a 6-membered ring. The 5-ring esters do not polymerize; the poly-esters whose monomers would be larger-than-6-rings are not depolymerized; and, although monomers of this type are known[7] and are stable, none of them has ever been prepared by a bi-functional reaction. The general theory underlying these facts has already been discussed.[1,6]



VII

The evidence that ethylene succinate is formed by Mechanism 2 (C polymerization) rather than 1 is fairly conclusive. Experimental evidence

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[6] Carothers and Van Natta, This Journal, **52**, 314 (1930).

[7] Ruzicka and Stoll, *Helv. Chim. Acta*, 11, 1159 (1928).

in support of Mechanism 2 may be found in the fact that the molecules of ethylene succinate are open chains with functional groups at the ends. The supposition that the monomeric ring VII is first formed involves the tacit assumption that 8-rings are readily formed, but are unstable, whereas fact and theory alike indicate that such rings are formed only with great difficulty, but are stable when they have been formed. We have made a good many attempts to isolate the monomeric 8-ring, VII. All of these attempts have failed, and all of the observations which we have made are best interpreted on the assumption that the long chains are built up by a series of successive reactions and that rings are not formed at any stage of the process. Some light is thrown at one or two points on the details of the mechanism of the reaction by the following observations.

When glycol was allowed to react with succinic acid in the proportions of 1 to 2 moles, the product was found to be a mixture composed chiefly of unchanged succinic acid and poly-ester of fairly high molecular weight. The compound, $HO—OC—(CH_2)_2—CO—O—(CH_2)_2—O—OC—(CH_2)_2—CO—OH$, which might be expected to form under these stoichiometrical conditions was not found.

Neutral ethylene succinate was prepared by heating the acid with excess glycol and, after some time, distilling off the excess glycol as completely as possible at high temperature and under greatly reduced pressure. Under these conditions the formation of some di-β-hydroxyethyl succinate, VIII, might be expected. This ester was in fact formed, and it distilled

$$HO—(CH_2)_2—O—OC—(CH_2)_2—CO—O—(CH_2)_2—OH \qquad \text{(VIII)}$$

out of the reaction mixture when this was heated *in vacuo*. It was obtained in a state of approximate purity by redistillation in a carefully cleaned all-glass apparatus under high vacuum.

Di-(β-hydroxyethyl)-succinate.—Sixty-two grams of ethylene glycol (1 mole) and 39.3 g. of succinic acid ($^1/_3$ mole) in a pyrex Claisen flask fitted with ground-glass stoppers and provided with a receiver were heated for six hours by means of an oil-bath at 174–180°; 8.8 g. of water, b. p. 100–102°, n^{28}_D 1.3323, collected in the receiver. The residue was heated *in vacuo* finally to a temperature of 250° at 0.015 mm., until distillation ceased. The residue was a pale yellow viscous liquid which readily solidified on cooling. It was dissolved in 100 cc. of warm chloroform and precipitated as a powder by the addition of 250 cc. of benzene. After drying, this powder weighed 36 g. (0.25 g. equivalent). Its instantaneous melting point was 98° and its slow melting point 105.5°. The distillates were redistilled and yielded 9.97 g. or 0.648 mole of water, 33.9 g. or 0.548 mole of glycol and 14.5 g. or 0.07 mole of di-(β-hydroxyethyl) succinate. The total esters (0.7 mole + 0.25 g. equivalent) accounted for 0.32 mole of the 0.333 mole of succinic acid used, and these esters plus the glycol recovered accounted for 94.6% of the glycol used, while the water isolated was 87.5% of the calculated amount.

The di-(β-hydroxyethyl) succinate was never isolated in a state of purity. When distilled in a carefully cleaned all-glass (pyrex) Claisen flask, it boiled at 176–180° at 0.001 mm. as a colorless viscous liquid, leaving only a trace of residue.

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 46.58; H, 6.88. Found: C, 45.76, 45.70; H, 6.86, 6.95.

Treatment with *p*-nitrobenzoyl chloride in pyridine yielded a di-(*p*-nitrobenzoate) as white needles from alcohol; m. p. 90–91°.

Anal. Calcd. for $C_{22}H_{20}O_{12}N_2$: C, 52.35; H, 3.97. Found: C, 52.36, 52.36; H, 4.19, 4.14.

The di-(phenylurethan) formed by the action of phenyl isocyanate on di-(β-hydroxyethyl) succinate and crystallized from a mixture of benzene and petroleum ether melted at 113°.

Anal. Calcd. for $C_{22}H_{24}O_8N_2$: C, 59.45; H, 5.41. Found: C, 59.40, 59.56; H, 5.53, 5.52.

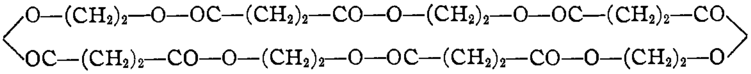
When heated slowly *in vacuo* di-β-hydroxyethyl succinate was completely converted into neutral (polymeric) ethylene succinate and ethylene glycol, the former appearing in the distillate and the latter remaining in the distilling flask. This process evidently involves an ester interchange: glycol is eliminated between two molecules of the dihydroxy ester with the formation of a new dihydroxy ester containing two of the structural units of ethylene succinate. Repetition of this process finally results in such a molecule as III. It is evident that so long as one of the products of a possible ester interchange can be eliminated in this way, no merely stoichiometrical factors can set up a limit to the length of the molecules which might be produced. Nevertheless a fairly definite limit exists: polyintermolecular esterification has never led us to molecules of greater average length than about 200 atoms. No doubt various factors are involved in this point. There can be no question that the reactivity of functional groups diminishes with the size of the molecules which contain them. It is apparently this factor which accounts for the failure of the ester III to react with many of the typical reagents for hydroxyl groups. Moreover, as Staudinger has frequently emphasized,[8] the thermal stability of molecules must diminish with increase in their size. These two factors act in opposition. To force the completion of the reaction between succinic acid and glycol we have used high temperature (250°) to increase reaction velocity and high vacuum to remove the water as completely as possible. The ester produced under these conditions has a molecular weight of about 3000. It is interesting to observe that in the thermal polymerization of styrene the product formed at 250° also has an apparent molecular weight of about 3000, while the polystyrenes formed at lower temperatures have much higher molecular weights. And so also the A polymerization of trimethylene carbonate described in the previous paper,[6] although it also involves an ester interchange, leads to a poly-ester with a molecular weight considerably above 3000, since the reaction consists merely in self-addition and proceeds rapidly at 100°.

[8] See Staudinger, *Ber.*, **59**, 3019 (1926).

Dimeric Ethylene Succinate.—Tilitschejew[9] has reported the isolation of a new ethylene succinate from the volatile materials formed by heating the product of the action of succinic acid on glycol (m. p. 88–89°) to 340–390° under 3–4 mm. pressure. The new product was distinguished from the usual form not only by its different melting point (129–130°), but by its definite macrocrystallinity. Cryoscopic data on acetic acid solutions of the new ethylene succinate indicated a double formula and, since Vorländer had already reported[10] that the old form was dimeric, Tilitschejew regarded his new ester as an isomer of the old. It has now been established that the usual form of ethylene succinate is not dimeric, but much more highly polymeric; the new compound cannot, therefore, be simply an isomer of the old. Aside from this, however, repetition of Tilitschejew's experiments has completely verified the correctness of his claims as to the nature of the new compound. It crystallizes in thin plates melting sharply at 130°. The analytical data clearly indicate that it is dimeric ethylene succinate.

Anal. Calcd. for $(C_6H_8O_4)_2$: C, 50.00; H, 5.50; mol. wt., 288; saponification equivalent, 72. Found: C, 49.85, 50.00; H, 5.60, 5.57; mol. wt., in boiling ethylene chloride, 302, 299; in freezing benzene 279; saponification equivalent, 71.97, 71.95, 71.66.

Attempts to partially saponify this ester were unsuccessful—a part of the ester was recovered unchanged and the remainder was degraded to sodium succinate and glycol. Nevertheless, it seems fairly certain that this compound is the 16-membered ring, IX. No alternative formula seems



(IX)

plausible. It is very improbable that this compound is present as such in the polymeric ester from which it is prepared. The dimer is quite soluble in hot absolute alcohol; the neutral polymer is quite insoluble. Continuous extraction of the polymer with hot absolute alcohol resulted in the solution of only a very small amount of material and this had the properties of the polymer not of the dimer. The dimer must therefore be formed during the process of thermal decomposition. The transformation of polymeric trimethylene carbonate into monomeric ethylene carbonate described in the previous paper[6] proceeds smoothly and practically quantitatively at about 200°. The formation of the dimeric tetramethylene carbonate, described in the same paper, and of dimeric ethylene succinate occurs only at a much higher temperature. Large amounts of gaseous and liquid products are formed as well as considerable

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[9] Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **57**, 143–150 (1925); *Chem. Zentr.*, I, 2667 (1926).

[10] Vorländer, *Ann.*, **280**, 167 (1894).

carbonaceous residue. The yields of the dimers are quite small, *e. g.*, 3–4% of the theoretical under the best conditions (Tilitschejew, however, reports 5.5%). In these respects the reaction resembles that used by Ruzicka for the preparation of the large cyclic ketones.[11] As yet we have not succeeded in isolating any monomeric ethylene succinate from the products of this reaction.

Ethylene Succinate and the Association Theory of High Polymers.—The discussion in this and the previous papers will, it is hoped, have amply demonstrated the adequacy of the ordinary structural theory of organic chemistry to deal with the poly-esters, a fairly complicated class of high polymers.

A possible explanation of the structure of the poly-esters which has not yet been considered is the following. The chemical unit or molecule of ethylene succinate is the monomeric 8-ring, VII. Because of the great strains in this structure, or for some other reason, it exhibits exceptionally strong residual or lattice forces, so that the osmotic unit becomes an aggregate of a great many of these ultimate chemical units. There is such a complete lack of any general theoretical justification for this view that there would be no need to consider it in connection with the poly-esters were it not that in the field of natural polymers such as cellulose, rubber, etc., in various slightly differing forms it has been defended at great length by so many investigators.[12]

Among the many facts which are quite incompatible with any association theory of the structure of poly-esters, the following deserve special mention.

(1) All of the known cyclic esters containing larger-than-6-rings are stable substances with definite properties corresponding with their simple formulas. They do not show any tendency to associate in solution.

(2) The polymeric esters corresponding to these monomers show no tendency to dissociate.

(3) In the polymeric ethylene succinates the chemical and osmotic units have been shown to be identical within the limits of experimental error, *i. e., ebullioscopic data give the same values for the molecular weights that are given by the determination of hydroxyl or carboxyl.*

The association theory is not clearly enough defined to permit any more crucial tests than these, but the following experiment at any rate agrees with these in the conclusions to which it leads.

If two different association polymers (A)n and (B)m are mixed in solution or in the liquid state so that they constitute a single phase, then

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[11] Ruzicka and co-workers, *Helv. Chim. Acta*, **9**, 230, 249, 339, 389, 399, 499, 715, 1008 (1926); **10**, 695 (1927); **11**, 496, 670, 686, 1159, 1174 (1928).

[12] See for example Bergman, Knehe and Lippmann, *Ann.*, **458**, 93 (1927); Hess, Trogus and Friese, *ibid.*, **466**, 80 (1928); Schlubach and Elsner, *Ber.*, **61**, 2358 (1928); Pummerer, Nielsen and Gündel, *ibid.*, **60**, 2167 (1927).

since $(A)n \rightleftarrows nA$ and $(B)m \rightleftarrows mB$, the resulting mixture should be composed at least in part of $(AB)_p$.

Ethylene sebacate (m. p. 78°) and ethylene succinate (m. p. 103°) were melted together and thoroughly mixed. After cooling, the mass was extracted with benzene, which is a solvent for the sebacate but not for the succinate. The residue melted at 103° (unchanged succinate). To the benzene solution petroleum ether was added; the precipitated solid melted at 78–79° (unchanged sebacate). An ester was prepared by the action of glycol on equivalent amounts of succinic and sebacic acids. This was quite different in its properties from either the succinate or sebacate and it was homogeneous in its solubility behavior (m. p. 38–40°; mol. wt. 1540). This demonstrates the existence of a mixed polymer and the absence of any reversible relationship of association between it and the two corresponding simple polymers.

In the 6-ring esters a reversible relationship exists between the monomeric and polymeric forms, and some of the statements made above do not apply to these polymers. But it is possible, nevertheless, to account satisfactorily for the behavior of these esters without the assumption of any special or peculiar kinds of valence.[6]

The view that the ordinary structural theory of organic chemistry is adequate to deal with high polymers has been now for several years ably defended by Staudinger and his collaborators,[13] and recently the same view has been applied in a brilliant fashion to such natural polymers as cellulose, rubber, silk fibroin, etc., by Meyer and Mark.[14] So far as the minor differences[15] in the views of these two groups of investigators are concerned, our own experiments on poly-esters incline us to favor those of Staudinger. That is, we can find no real objection to referring to primary valence chains as molecules, and among the polyesters these molecules are experimentally identical with the osmotic units of their solutions.

The writers are indebted to Mr. W. H. Taylor for the molecular weight determinations and to Mr. G. A. Jones for the determinations of carbon and hydrogen.

Summary

The polymeric ethylene succinate previously described is shown to be a long chain made up of the recurring unit $—O—(CH_2)_2—O—CO—$

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[13] Staudinger and co-workers, *Helv. Chim. Acta*, **5**, 785 (1922); **7**, 23, 842 (1924); **8**, 41, 65, 67 (1925); **9**, 529 (1926); **11**, 1047, 1052 (1928); *Ber.*, **53**, 1073 (1920); **57**, 1203 (1924); **60**, 1782 (1927); **59**, 3019 (1926); **61**, 2427 (1928); **62**, 241, 263, 442 (1929); *Ann.*, **447**, 97, 110 (1926); **467**, 73 (1928); *Z. physik. Chem.*, **126**, 425 (1927); *Kautschuk*, 237 (1927); *Z. angew. Chem.*, **42**, 37, 67 (1929); *Z. Krist.*, **70**, 193 (1929).

[14] Meyer and Mark, *Ber.*, **61**, 593, 1932, 1939 (1928); Meyer, *Naturwissenschaften*, **42**, 790 (1928); *Z. angew. Chem.*, **41**, 935 (1928).

[15] Meyer, *Naturwissenschaften*, **17**, 255 (1929).

$(CH_2)_2$—CO— and bearing hydroxyl groups at its ends. Acidic ethylene succinates made up of similar chains of various lengths and bearing carboxyl groups at their ends have been prepared. Molecular weight determinations of these esters based on ebullioscopic measurements agree with those based on chemical evidence (estimation of hydroxyl or carboxyl).

A study of the ethylene succinate prepared by Tilitschejew verifies his claim that it is dimeric, and this ester is undoubtedly a 16-membered ring.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 55 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS OLEFINS INTO SULFURIC ACID AT 25°[1]

BY HAROLD S. DAVIS[2] AND REUBEN SCHULER[3]

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This paper deals with measurements of the rates at which the gaseous olefins and the vapors of some liquid olefins are absorbed by sulfuric acid of various concentrations at 25°.

The quantity of acid used was always much larger than the molecular equivalent of the amount of olefin taken so that the data apply only to sulfuric acid in the initial stages of saturation, where its character was not perceptibly changed by dissolved olefin reaction products. Thus the absorptions were of the type which take place in gas analysis pipets except that they were carried out at constant volume instead of at constant pressure.

Apparatus.—The apparatus employed to measure the rates of absorption (Fig. 1) consisted essentially of a cylindrical glass reaction chamber connected to a glass manometer tube dipping in mercury. A measured volume of the olefin gas was introduced into the evacuated chamber which contained sulfuric acid. The progress of the absorption was followed by recording the gaseous pressure shown by the height of mercury in the manometer tube at successive periods of time. When desired the chamber could be turned on its major axis at a definite number of rotations per minute (r.p.m.), the manometer tube turning with it. A flexible piece

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