

### Summary

The nuclear synthesis of olefins through the  $\beta$ -bromo ethers has been used in a systematic survey of the hexenes. Ten of the thirteen structurally possible members of this family have been prepared, including those previously unknown. The method is shown to be applicable to the synthesis of monoalkyl, symmetrical and unsymmetrical dialkyl ethylenes. It is believed the method will ultimately prove applicable also to the trialkyl and tetraalkyl ethylenes.

The confusion which has existed in the physical constants of the olefins is beginning to disappear. A definite relation is shown to exist between the physical properties and molecular structure of the hexenes. Certain rules have been formulated relating the boiling points, densities and refractive indices of the hexenes to their structure.

Eight bromohexyl ethyl ethers, three hexenes and five dibromohexanes are herein described for the first time.

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[CONTRIBUTION NO. 72 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT  
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## STUDIES OF POLYMERIZATION AND RING FORMATION. X. THE REVERSIBLE POLYMERIZATION OF SIX-MEMBERED CYCLIC ESTERS

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Reactions leading to the formation of high polymers have received considerable attention during the past few years both because of their inherent interest as representatives of a realm that has been relatively little explored, and because of their bearing on the formulation of naturally occurring macromolecular materials. In this connection the behavior of six-membered cyclic esters is of peculiar interest: they combine with themselves, in many cases spontaneously at the ordinary conditions, to form polymers of high molecular weight, and this transformation is reversible. Since these esters are generally free from unsaturation, their self-combination must have its origin in some peculiarity of the heterocyclic system. Six-membered heterocycles are quite common among naturally occurring materials and are closely associated with natural polymers (sugars and polysaccharides, diketopiperazines and polypeptides); it is therefore reasonable to assume that the behavior of the cyclic esters lies closer to the natural processes that result in the formation of macromolecular substances than does the polymerization of unsaturated compounds, such as styrene, which have been more extensively studied.

Several isolated examples of the reversible polymerization of six-mem-

bered cyclic esters have been recorded in the literature but the question of the mechanism of this phenomenon has received very little attention. In the present paper, we report some observations bearing on this point.

**Previous Work.**—Fichter and Beisswenger<sup>1</sup> first reported that "δ-valerolactone (I) is characterized by a remarkable and surprising phenomenon: it polymerizes after a short time; the initially mobile oil becomes gradually thicker and finally solidifies to a crystalline mass." The polymer after recrystallization melted at 47–48°. Attempts to determine its molecular weight gave values ranging from a five- to a seven-fold polymer. Later the same transformation was observed by Hollo,<sup>2</sup> who also records the spontaneous polymerization of the lactone (II) of hydroxyethylglycolic acid.

Bischoff and Walden<sup>3</sup> in 1893 described the transformation of glycolide (III) under the influence of heat or a trace of zinc chloride into a polymeric solid melting at 220°. On being distilled in a vacuum it was reconverted to the monomer, melting at 86–87°.

Drew and Haworth<sup>4</sup> have obtained the lactone (IV) of 2,3,4-trimethyl-l-arabonic acid in crystalline form (m. p. 45°) and observed that, in the presence of traces of hydrogen chloride, it is converted into a crystalline polymeric powder which has a considerably higher melting point, a lower solubility, and a lower specific rotation than the monomer. Its molecular weight (about 2000) indicates that it is derived from about ten molecules of the monomer. At 175° it distills completely *in vacuo*, and the distillate consists of pure lactone. Drew and Haworth<sup>5</sup> favored a linear polyester structure for this polymer.

Trimethylene carbonate (V) was first described by Carothers and Van Natta.<sup>6</sup> The monomer is a very soluble crystalline solid melting at 47°. If it is heated to 130° for a few minutes with a trace of potassium carbonate, the mobile melt suddenly becomes very viscous and evolves a small amount of gas. The colorless, viscous sirup on cooling solidifies to a stiff mass which shows an apparent molecular weight of about 4000. When this mass is heated in a vacuum it distills almost quantitatively, and the distillate consists of pure monomer.

Monomeric ethylene oxalate (VI) was first described by Bischoff and Walden,<sup>7</sup> who obtained it as a crystalline solid melting at 143° by distilling the product of the action of ethylene glycol on monoethyl oxalate.

<sup>1</sup> Fichter and Beisswenger, *Ber.*, **36**, 1200 (1903).

<sup>2</sup> Hollo, *ibid.*, **61**, 895 (1928).

<sup>3</sup> Bischoff and Walden, *ibid.*, **26**, 262 (1893).

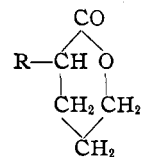
<sup>4</sup> Drew and Haworth, *J. Chem. Soc.*, 775 (1927).

<sup>5</sup> Cf. Haworth, "The Structure of Sugars," Edward Arnold and Co., London, 1929, p. 78.

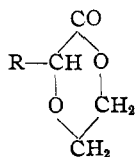
<sup>6</sup> Carothers and Van Natta, *THIS JOURNAL*, **52**, 314 (1930).

<sup>7</sup> Bischoff and Walden, *Ber.*, **27**, 2939 (1894).

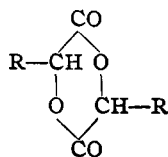
Later Bischoff<sup>8</sup> obtained less soluble, higher melting forms of ethylene oxalate, and showed that these on distillation were converted into the 143° form. Bischoff also observed that the melting points of the ethylene oxalates change on standing, and suspected that these changes might be due to a reversible polymerization, but he reported no comparative molecular weight data. The relation of the various forms of ethylene oxalate to one another has lately been studied by Carothers, Arvin and Dorough.<sup>9</sup> It was found that the flat, diamond-shaped crystals of the monomer completely disintegrate during the course of a few days, yielding a microcrystalline powder which consists of a mixture of polymers. From this mixture by careful extraction with cold solvents two definite fractions can be isolated. One of these melts at 159° and has an apparent molecular weight of about 3000; the other fraction, which is probably much more highly polymeric, melts at 173° and is too insoluble for molecular weight determinations. These isolated fractions on standing lose their identity: they revert spontaneously within a few days to more complicated mixtures which usually contain appreciable amounts of monomer. The polymeric ethylene oxalates can be converted into the monomer (with considerable loss) by vacuum distillation. Propylene oxalate (VIa) (m. p. 142°) is converted by the action of heat into an insoluble, microcrystalline polymer melting at 178°.<sup>9</sup>



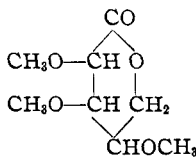
I, R = H  
Ia, R = *n*-C<sub>3</sub>H<sub>7</sub>



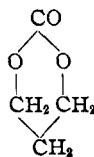
II, R = H  
IIa, R = C<sub>2</sub>H<sub>5</sub>



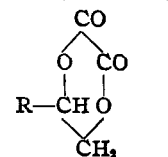
III, R = H  
IIIa, R = CH<sub>3</sub>



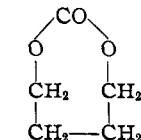
IV



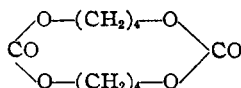
V



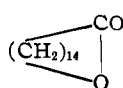
VI, R = H  
VIa, R = CH<sub>3</sub>



VII



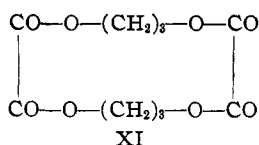
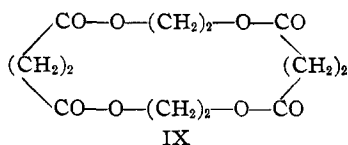
VIII



IX

<sup>8</sup> Bischoff, *Ber.*, **40**, 2803 (1907).

<sup>9</sup> Carothers, Arvin, and Dorough, *THIS JOURNAL*, **52**, 3292 (1930); cf. Bergmann and Wolff, *J. prakt. Chem.*, **128**, 229 (1930); and Carothers and Van Natta, *Ber.*, **64**, 1755 (1931).



**Generality of the Phenomenon.**—The examples cited above show that the capacity to undergo reversible polymerization is quite common among six-membered cyclic esters. The presence of substituent groups, however, has a considerable effect and, in general, a depressing effect, on this tendency. The unsubstituted esters I, II and VI polymerize spontaneously at ordinary temperature in the complete absence of any added catalyst; substituted esters on the other hand, such as Ia, IIa, IV and VIa, require the action of heat, or catalysts, or both, and in some cases polymerization fails altogether.

A number of substituted  $\delta$ -valerolactones (I) have been described in the literature, but without any record of their polymerization. We have therefore prepared  $\alpha$ -*n*-propyl- $\delta$ -valerolactone (Ia) as described in the experimental part. Although  $\delta$ -valerolactone was found to be completely polymerized to a waxy solid after twenty-nine days at room temperature, the new  $\alpha$ -*n*-propyl- $\delta$ -valerolactone was still unchanged after twelve months, nor did it show any signs of polymerization after being heated to  $80^\circ$  for one month. However, when heated to  $80^\circ$  for one month in the presence of a trace of potassium carbonate or zinc chloride, it became more viscous, and its apparent molecular weight rose to 1100–1200.

Hollo<sup>2</sup> records the spontaneous polymerization of the lactone (II) of hydroxyethylglycolic acid, but makes no mention of the polymerization of its  $\alpha$ -alkyl derivatives (II, R = C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub> and *iso*-C<sub>3</sub>H<sub>7</sub>) which he prepared at the same time. We have made attempts to polymerize the lactone (IIa) of hydroxyethyl- $\alpha$ -hydroxybutyric acid. Sixteen hours of heating at  $140$ – $160^\circ$  failed to produce any change in the viscosity or the color of the pure lactone. Under the same conditions in the presence of a trace of potassium carbonate, only a slight increase in viscosity occurred.

Bischoff and Walden<sup>10</sup> state that lactide (IIIa) does not polymerize under the conditions that result in the polymerization of glycolide (III). We find, however, that at  $250$ – $275^\circ$  the polymerization of lactide is quite rapid: in two hours a sample was transformed into a resinous mass which showed an apparent molecular weight of about 3000. A similar effect can be obtained at much lower temperatures, *e. g.*,  $140$ – $150^\circ$ , if potassium carbonate is present.

We have also examined some of the higher homologs of lactide. The cyclic esters derived from  $\alpha$ -hydroxycaprylic and from  $\alpha$ -hydroxypalmitic

<sup>10</sup> Bischoff and Walden, *Ann.*, 279, 71 (1894).

acids were prepared and heated for various periods both in the presence and absence of catalysts. Evidences of polymerization could be found only at temperatures sufficiently high to produce considerable decomposition.

Finally, it may be mentioned that although ethylene oxalate polymerizes spontaneously at the ordinary temperature, propylene oxalate undergoes a similar transformation only at considerably elevated temperatures.<sup>9</sup>

**Peculiarity of the Phenomenon.**—Among cyclic esters the capacity to undergo reversible polymerization in the manner illustrated by the examples cited above is peculiar to six-membered rings. The  $\gamma$ -lactones and other five-membered cyclic esters show no tendency to polymerize, and no corresponding polymers are known. Thus, we have heated samples of pure  $\gamma$ -butyrolactone both with and without catalysts (zinc chloride, potassium carbonate) at 80° for twelve months; none of the samples showed any detectable increase in viscosity. We have also made various attempts to polymerize ethylene carbonate, but these attempts were all unsuccessful, although the corresponding six-membered ring, trimethylene carbonate (V), is readily polymerized.<sup>11</sup>

It appears also that cyclic esters of more than six members show no tendency to polymerize spontaneously. Information on this point is somewhat incomplete. No aliphatic cyclic esters of nine to thirteen atoms have been described. In fact no practical means for the preparation of such esters are yet known. In general, the attempt to prepare cyclic esters of more than six atoms from open chain compounds leads to linear polymers.

Thus the six-atom ring trimethylene carbonate (V) is readily obtained by heating diethyl carbonate with trimethylene glycol, and subsequently distilling the product *in vacuo*, but when diethyl carbonate is similarly treated with tetramethylene glycol, the product is a polymeric material that is not capable of being distilled *in vacuo*, *i. e.*, it cannot be depolymerized; only at temperatures above 300°, it undergoes complete thermal decomposition and yields a complicated mixture of products among which are found very small amounts of the dimeric fourteen-membered ring VIII.<sup>6</sup> Attempts to detect the presence of the monomer VII have been unsuccessful. Similar behavior is observed with trimethylene oxalate<sup>9</sup> and ethylene succinate.<sup>12</sup> The preparation of these esters leads to linear polymeric products of high molecular weight. No smooth depolymeriza-

<sup>11</sup>  $\beta$ -Lactones have not been specifically examined from this standpoint, but it appears likely in view of some observations recorded by Johansson [Lunds Universitets Årsskrift II, [2] 12, 3 (1916)] that simple lactones of this class undergo irreversible polymerization under the action of heat.

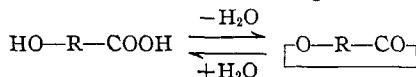
<sup>12</sup> Carothers and Dorough, *THIS JOURNAL*, 52, 711 (1930).

tion of these polymers can be effected by the action of heat; but at high temperatures they undergo complete thermal decomposition, yielding a complicated mixture of gaseous, liquid and tarry products containing very small amounts of the cyclic dimers which are, respectively, fourteen and sixteen-membered rings (XI and IX). The corresponding monomers have never been obtained.

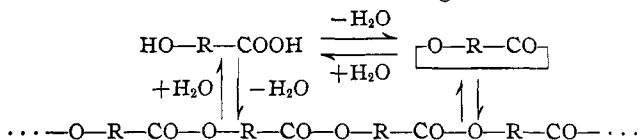
The following observations indicate the relatively great stability of the large cyclic esters. Specimens of dimeric trimethylene oxalate (XI), dimeric ethylene succinate (IX), and exaltolide (X) have been preserved in the laboratory for two years without showing any signs of change. The last two of these compounds have been heated in sealed tubes at 170° for a considerable period of time. After twelve hours they were quite unchanged; after forty-three hours they had become slightly colored and their melting points slightly lowered, but signs of appreciable polymerization were absent.<sup>13</sup>

The peculiar position of the six-membered esters is shown in the following outline, in which, for simplicity, the starting material in each case is represented as an hydroxy acid.

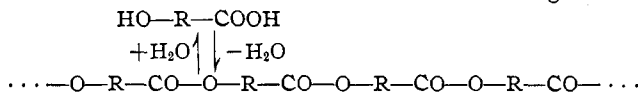
(A) The structural unit is five atoms long



(B) The structural unit is six atoms long



(C) The structural unit is more than six atoms long



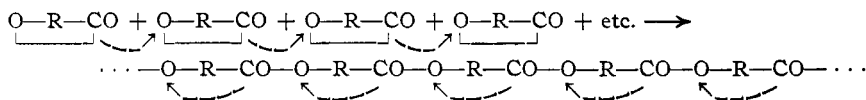
Under B it should be mentioned that the reversible relation between the monomer and the polymer complicates the problem of deciding in a given case which of these is the real primary product of the dehydration of the hydroxy acid. In any event the conditions of the dehydration

<sup>13</sup> We do not intend to suggest that the polymerization of large cyclic esters is impossible. In fact, since such esters can be hydrolyzed to the corresponding hydroxy acids, it is evident from equation C that such a polymerization can probably be effected under some conditions. The process would consist in hydrolysis of the cyclic ester to the hydroxy acid and the dehydration of this to the polyester. Both of these steps might occur in a single operation under appropriate conditions, *e. g.*, at elevated temperature in the presence of a small amount of water plus mineral acid. But the experiments described above do demonstrate that the large cyclic esters, at least qualitatively, are very different from the six-membered esters.

usually favor the polymerization of the monomer, so that the latter is isolated only by vacuum distillation of the actual reaction product. Dietzel and Krug<sup>14</sup> have presented evidence to show that the self-esterification of lactic acid leads directly only to polylactyl lactic acids and that lactide, when it is produced, results from the depolymerization of these poly esters. On the other hand, it is established, at least in certain instances,<sup>4</sup> that  $\delta$ -lactones may be formed as such directly from the corresponding hydroxy acid. No doubt in most cases, depending upon the conditions, either the monomer or the polymer may be formed as the primary product.

Under C it should be mentioned that although attempts to prepare seven-membered cyclic esters from dibasic acids and dihydric alcohols lead only to poly esters,  $\epsilon$ -hydroxy acids appear to be dehydrated with the simultaneous formation of polymer and monomer.<sup>15</sup> There is, however, no record of the interconversion of these two forms, and the higher  $\omega$ -hydroxy acids yield linear polymers exclusively.<sup>16</sup>

**Mechanism of the Phenomenon.**—The smooth reversibility of the polymerization of the six-membered cyclic esters and the absence of double-bond unsaturation at first suggested that here, if anywhere, might be found the missing models of that hypothetical phenomenon, association polymerization, to which for a time the peculiarities of natural polymers were widely attributed.<sup>17</sup> This thought was considerably weakened, however, when Dr. J. W. Hill presented in the closely analogous case of adipic anhydride, a direct and decisive proof of the structural difference between monomer and polymer.<sup>18</sup> No similar proof is possible in the esters under consideration; nevertheless, all the evidence together conclusively favors the mechanism suggested by Carothers and Van Natta,<sup>6</sup> namely, that the polymers are linear polyesters and that both the polymerization and its reversal proceed by a process of ester interchange. This is indicated in the equation



<sup>14</sup> Dietzel and Krug, *Ber.*, **58**, 1307 (1925).

<sup>15</sup> Marvel and Birkheimer, *THIS JOURNAL*, **51**, 260 (1929); Blaise and Koehler, *Compt. rend.*, **148**, 1773 (1909).

<sup>16</sup> No exception to this statement has been observed among the numerous esters we have prepared from dibasic acids and glycols, but we have lately found that in the self-esterification of  $\omega$ -hydroxydecanoic acid in the absence of solvent, appreciable amounts of the cyclic dimeric ester are formed. This has already been prepared by a different method and described by Lycan and Adams [*THIS JOURNAL*, **51**, 3450 (1929)].

<sup>17</sup> Abderhalden, *Naturwissenschaften*, **12**, 716 (1924); Bergmann, *ibid.*, **13**, 1045 (1925); Pringsheim, *ibid.*, **13**, 1084 (1925); Hess, *Ann.*, **435**, 1 (1924).

<sup>18</sup> Hill, *THIS JOURNAL*, **52**, 4110 (1930).

The peculiar position occupied by the six-membered cyclic esters may be explained, as we have already suggested,<sup>6</sup> by stereochemical factors: rings of six atoms are strained (or may pass through positions of strain); rings of five atoms or more than ten atoms are strainless. In the cyclic esters the strain can be relieved by the process of ester interchange, which results in polymerization. The resulting polymers (from the six-membered esters) are easily depolymerized owing to the high probability of the close approach of atoms six atoms apart in a chain. Polyesters whose depolymerization would result in larger monomeric rings are not depolymerized; the probability of the close approach of the requisite atoms is too slight.

The interchange mechanism for the polymerization of the six-membered esters is supported by the following facts: (1) The polymers have the same apparent analytical compositions,<sup>19</sup> and saponification equivalents as the corresponding monomers, and they yield the same products on hydrolysis.

(2) The products of the polymerization of the six-membered cyclic esters closely resemble in their physical properties the polymers formed by the action of dibasic acids on glycols, or by the self-esterification of the higher  $\omega$ -hydroxy acids. It has been definitely established that these polymers are linear polyesters; the chains are open and are terminated by hydroxyl and/or carboxyl groups.<sup>12, 20</sup>

(3) Both the forward and the reverse transformations are catalyzed by acids and bases, typical ester-interchange catalysts.

(4) The speed of the polymerization runs parallel with the susceptibility to hydrolysis. The much greater susceptibility of  $\delta$ -lactones to hydrolysis as compared with analogous  $\gamma$ -lactones is well known. The hydrolysis constant for  $\delta$ -valerolactone (I) is more than twice that of its  $\alpha$ -methyl derivative,<sup>2</sup> and the former polymerizes spontaneously while the latter does not. Similar relations hold for the lactone of hydroxyethylglycolic acid (II) and its  $\alpha$ -alkyl derivatives.<sup>2</sup> The hydrolytic constants for glycolide in its two stages are, respectively, 0.0179 and 0.119, while the corresponding values for lactide are 0.00313 and 0.0611.<sup>21</sup> The former polymerizes much more readily than the latter. Ethylene oxalate, which polymerizes with extraordinary facility, is so sensitive to hydrolysis that, like an acid, it can be titrated directly with moderately warm dilute alkali.

**Further Observations.**—Data on some polymers of  $\delta$ -valerolactone are presented in Table I.

<sup>19</sup> But the values for carbon are usually somewhat low and the values for hydrogen somewhat high. This may signify that the chains are open, or it may mean merely that the polyesters in spite of the fact that they are insoluble in water are nevertheless somewhat hygroscopic and difficult to dry.

<sup>20</sup> Lycan and Adams, *THIS JOURNAL*, **51**, 625, 3450 (1929).

<sup>21</sup> Johansson and Sibelius, *Ber.*, **52**, 745 (1919).



TABLE I  
 POLYMERS OF  $\delta$ -VALEROLACTONE

No.	Catalyst	Temp. during polym., °C.	Time	M. p. of polymer, °C.	Mol. wt. of polymer (boiling point in benzene)	
1	None	Room	29 days	35-40	1060	1060
2	None	80-85	13 days	52-53	1270	1330
3	K <sub>2</sub> CO <sub>3</sub>	80-85	5 days	53-54	1840	1820
4	ZnCl <sub>2</sub>	80-85	5 days	52-54	2230	1846
5	None	150	10 hrs.	52-55	2110	2240
6	Over CH <sub>3</sub> COCl	Room	3 days	50-51	1720	1720

The melting points are in general somewhat higher than those reported by Fichter and Beisswenger.<sup>1</sup> The polymer is soluble in a variety of organic solvents and is readily crystallized, *e. g.*, from a mixture of petroleum ether and benzene. When allowed to solidify from a melt it forms an opaque, soft, waxy solid. The crystals are poorly developed; they appear under the microscope as tiny irregular particles.

Polymeric  $\delta$ -valerolactone is acidic. In acetone solution it can be titrated with alkali to a sharp end-point which persists for several minutes. Sample 5 of Table I thus showed a neutral equivalent of 2153 and 2243 in two determinations. The closeness of this value to the observed molecular weights indicates the probable presence of one carboxyl group for each molecule. It is not quite certain that this agreement is not accidental. A product prepared by heating the monomer at 175° showed an equivalent weight of 6320 and a molecular weight of about 1500 (observed 1420 and 1660), but the molecular weight values are under suspicion because of severe foaming. It seems certain however that at least part of the polyester molecules bear carboxyl groups.

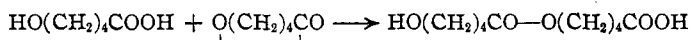
The polymeric  $\delta$ -valerolactone is not homogeneous, but contains molecules of different sizes. Its sodium salts are not soluble in water. A sample of recrystallized polymer formed at ordinary temperature (m. p. 53-56°) showed by titration in acetone an equivalent weight of 3160. The acetone solution was evaporated and the resulting dry sodium salt taken up in hot absolute alcohol, filtered and cooled to crystallize. In this way fractions of different solubilities and sodium content were isolated: (1) 0.38 g. containing 0.22% Na; (2) 0.77 g. containing 0.49% Na; (3) 0.14 g. containing 3.92% Na. The equivalent weights inferred from the sodium contents are: (1) 10,400, (2) 4700, (3) 590. Determination of the molecular weight of fraction 2 by the boiling point in benzene gave the value 3880.

The polyester derived from the lactone (II) of hydroxyethylglycolic acid differs in its behavior from polymeric  $\delta$ -valerolactone. It cannot be titrated to a sharp end-point with 0.1 *N* alkali. Attempts to prepare a sodium salt by treating it with sodium bicarbonate under various condi-

tions have led to mixtures from which two distinct fractions are readily separated. One of these is unchanged polyester entirely free of sodium; the other is the pure sodium salt of hydroxyethylglycolic acid. Thus even so mild an alkali as sodium bicarbonate hydrolyzes the polyester, and it is impossible to determine whether the polymeric molecules bear carboxyl groups. Ethylene oxalate (VI) shows a still more exaggerated sensitivity to alkalis. Trimethylene carbonate (V) appears to be neutral. In this case any terminal carboxyl groups that might arise during the polymerization would be lost spontaneously since they would be linked to oxygen ( $R-O-CO-OH$ ). The momentary liberation of a small amount of gas at the end of the sudden thermal polymerization of trimethylene carbonate is perhaps due to loss of carbon dioxide from acid carbonic ester groups formed in this way.

For  $\delta$ -valerolactone, however, as already indicated, the presence of a terminal carboxyl group in the polymeric molecule is fairly clearly demonstrated.

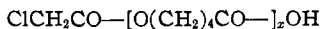
It seems likely that the first step in the polymerization of the cyclic esters involves the intervention of a trace of the corresponding hydroxy acid or one of its derivatives. One can imagine that hydroxyvaleric acid would thus react with valerolactone



The dimeric acid would then react in the same manner with valerolactone to form a trimeric acid, and the reaction would continue in this sense until all of the lactone was exhausted or the chains became too long for further reaction. In this mechanism a foreign acid might equally well participate, and it would be bound in the product as the first unit of the polymeric chain. Experiments in this direction were made with chloroacetic acid.

One gram of  $\delta$ -valerolactone was heated with 0.1 g. of chloroacetic acid for fifteen hours at 150–160°. The reaction mixture, which solidified on standing in a refrigerator, was recrystallized from alcohol and carefully dried. It melted at 42° and contained 3.28% chlorine. It was triturated with an excess of sodium bicarbonate in the presence of a little water, and the product after drying was extracted with warm alcohol. The polyester which separated was thrice recrystallized from alcohol. It now melted at 45–46° and contained 2.3% sodium. The molecular weights calculated respectively from the chlorine and sodium content, assuming a molecule having the formula XII, are 1008 and 1000.

(XII)



In a similar experiment in which one gram of valerolactone was heated with 0.05 g. of chloroacetic acid the initial product melted at 48° and contained 2.06% chlorine. The sodium salt melted at 50–51° and contained 1.35% sodium. The molecular weights calculated from these data are 1720 and 1705.

Chlorine-containing derivatives were also obtained by heating the polymeric lactone with chloroacetic acid. Two grams of polymer and 0.1 g. of chloroacetic acid were heated for ten hours at 150–160°. The product was thrice crystallized from alcohol. It contained 1.75% chlorine, and this corresponds to a molecular weight of 2030. Its neutral equivalent as indicated by titration with alkali was 2083.

These results are at least consistent with the mechanism suggested above. A mechanism involving the mutual coalescence of two molecules of monomer to form a twelve-atom ring and the growth of this through the progressive absorption of more monomeric molecules seems less likely, but some observations lately made in this Laboratory on the polymerization of cyclic anhydrides indicate that this mechanism is not at all impossible.

**Lactone (II) of Hydroxyethylglycolic Acid.**—Preparation: The method of Hollo<sup>2</sup> was slightly modified. The crude mixture containing the sodium salt of the hydroxy acid, sodium chloride and a little glycol was washed with acetone, suspended in absolute alcohol and treated with less than the calculated amount of hydrochloric acid. The precipitated sodium chloride was removed by filtration and the lactone isolated from the filtrate by distillation. In this way it was readily obtained free of chlorine.

When allowed to stand it gradually solidified to a pasty mass. After five weeks the solid was crystallized five times from ethyl acetate. It then melted at 62–64° and showed a molecular weight in boiling benzene of about 460 (observed, 451, 471). This probably corresponds approximately with Hollo's polymer melting at 56–63°.

A polymer formed by heating the lactone at 150° for five hours after being crystallized four times from ethyl acetate melted at 87–89°. It was very soluble in cold chloroform, hot ethyl acetate and hot alcohol, slightly soluble in ether, cold ethyl acetate and water. Molecular weight determinations in boiling benzene gave the values 1647 and 1788.

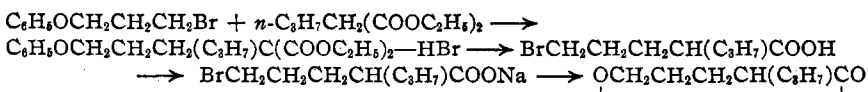
Hollo describes another type of polymer obtained when the sodium salt of the hydroxy acid is treated with an excess of hydrochloric acid. This melts at 66–68°, boils at 216 to 220°, and distils without change at atmospheric pressure.

It seems quite impossible however that a polymer should boil only 5° higher than the monomer (210–215°), and the explanation of Hollo's observation probably lies in the fact that the hydrochloric acid present in the polymer distils with the monomer during depolymerization and the polymerization of the distillate is so powerfully catalyzed that it occurs very rapidly. In our experiments a specimen of polymeric lactone originating from a preparation in which a slight excess of hydrochloric acid was used to liberate the hydroxy acid was observed to distil at 215–216° and the distillate solidified immediately on cooling. The solid product after three crystallizations from ethyl acetate melted at 85 to 87°.

This polymer distilled completely, but the distillate was not unchanged polymer. Molecular weight determinations on the distillate made immediately after the completion of the distillation gave the values, 144, 140 and 121 (calcd. for monomer, 102). After two hours the distillate had already begun to crystallize. After twenty-four hours it had solidified, and the solid after recrystallization thrice from ethyl acetate showed a molecular weight of about 900 in boiling benzene (observed, 867, 931).

Polymers originating from preparations in which an excess of hydrochloric acid was carefully avoided behaved in precisely the same way except that the reversion of the distillate was much slower; it remained fluid for twenty-four hours. The melting points of the purified polymers obtained from either source approached 89°.

$\alpha$ -*n*-Propyl- $\delta$ -valerolactone was prepared through the steps indicated in the following equations.



Phenoxypropyl-(*n*-propyl)-malonic diethyl ester: colorless liquid, b. p. (4 mm.) 195–200°;  $d_4^{25}$  1.0246;  $n_D^{25}$  1.4820.

*Anal.* Calcd. for  $C_{19}H_{28}O_8$ : C, 67.85; H, 8.33. Found: C, 68.60, 68.04; H, 8.03, 8.09.

$\delta$ -Bromo- $\alpha$ -*n*-propylvaleric acid: b. p. (5 mm.) 148–150°;  $d_4^{20}$  1.3851,  $n_D^{20}$  1.4730.

*Anal.* Calcd. for  $C_8H_{16}O_2Br$ : C, 43.05; H, 6.72; neutral equivalent, 223. Found: C, 44.33; H, 6.84; neutral equivalent, 220, 222

The high values for carbon are probably due to the presence of some phenol.

$\alpha$ -*n*-Propyl- $\delta$ -valerolactone: b. p. (10 mm.) 118–120°;  $d_4^{20}$  0.9929;  $n_D^{20}$  1.4585.

*Anal.* Calcd. for  $C_8H_{14}O_2$ : C, 67.67; H, 9.85; saponification equivalent, 142. Found: C, 67.59, 67.50; H, 10.01, 10.18; saponification equivalent, 143, 144.

**Preparation of Lactide.**—The preparation of lactide by methods described in the older literature<sup>22</sup> gave poor yields, but excellent results were obtained by the following method based on recent patents.<sup>23</sup> Two hundred grams of commercial lactic acid was heated at ordinary pressure in a Claisen flask by a metal bath at 120° until water ceased to distil. The temperature was then raised to 140° and the pressure reduced to 10 mm. During six hours water continued to distil slowly from the flask. The pressure in the system was reduced to 5 mm. and the temperature raised sufficiently to cause rapid distillation of the lactide, which solidified in the receiver. The yield of crude product was 125 g. It was purified by crystallization from ether; m. p. 128°.

### Summary

Several isolated examples of the reversible polymerization of six-membered cyclic esters have been briefly reported in the literature. Further examples are reported in the present paper, together with some experimental data and speculations on the mechanism of the phenomenon. The following conclusions are reached.

1. The ability to undergo reversible polymerization is generally characteristic of six-membered cyclic esters.
2. Ester rings of five atoms or more than six atoms do not polymerize under the action of heat.
3. The tendency of six-membered cyclic esters to polymerize is closely related to their great susceptibility toward hydrolysis; both tendencies are diminished by the presence of substituent groups.
4. The polymers formed from six-membered cyclic esters are linear polyesters and, at least in certain instances, the chains are open and terminated by hydroxyl and carboxyl groups.
5. Both the polymerization and the depolymerization consist essentially in a process of ester interchange.
6. The peculiar position occupied by the six-membered cyclic esters is readily explained by stereochemical considerations based on the Sachse-Mohr theory.

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<sup>22</sup> Gay-Lussac and Pelouze, *Ann.*, **7**, 43 (1833); Bischoff and Walden, *Ber.*, **26**, 263 (1893).

<sup>23</sup> Chemische Werke, French Patent 456,824 (1913); Grüter and Pohl, U. S. Patent 1,095,205 (1914).