STUDIES ON POLYMERIZATION AND RING FORMATION.
I. AN INTRODUCTION TO THE GENERAL THEORY OF CONDENSATION POLYMERS

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Polymerization frequently leads to substances of very high molecular weights, and the problem of the structure of high polymers is attracting a great deal of attention, especially because such important materials as rubber, cellulose, proteins and resins either are high polymers or have certain properties which are common to high polymers.

The conditions which Berzelius[1] was concerned to recognize by the term polymer were the presence of the same atoms in the same proportions in compounds having different molecular weights. These conditions are satisfied by the members of a great many thousand pairs of compounds which are not now regarded as polymers. Thus, of the compounds paracetaldehyde, butyric acids and hydroxycaproic acids, only the first would now be considered a polymer of acetaldehyde, although there is nothing in the conditions of the Berzelius definition to exclude the others. Hence, whatever the term polymer may mean now, it does not mean precisely what Berzelius intended, and the conditions which he set up are not sufficient to define it. In current attempts to define this term[2] it is still stated that a polymer and its monomer must have the same atoms in the same proportions. But this condition is not satisfied by the polyoxymethylenes (see Table I) which are universally considered to be polymers of formaldehyde. It seems desirable, therefore, to attempt to formulate a definition which will be in so far as possible in accordance with both the current usage and the essential facts.

The structures of a good many polymers, including some of very high molecular weights, are known either completely or in part and an examination of their formulas shows some interesting relationships (see Table I). They are characterized by a recurring structural unit, so that if this is represented by —R—, the structure of these polymers may be represented in part by the general formula —R—R—R—R—R—R—R—R—, etc., or $(—R—)_n$. In this formula n may be small as in paracetaldehyde ($n = 3$), or it may be very large as in the polyoxymethylenes. The end valences may be united as they are in paracetaldehyde to form a ring, or they

[1] Berzelius, *Jahresbericht*, **12**, 63 (1833).

[2] Hess, "Chemie der Zellulose," Leipzig, **1928**, p. 577; Meerwein, Houben-Weyl, "Die Methoden der organischen Chemie," Leipzig, **1923**, Zweite Auflage, dritter Band, p. 1013; Staudinger, *Ber.*, **58**, 1074 (1920).

may be saturated by univalent groups such as H— and —OH to form an open chain of the type H(—R—)$_n$OH as they are in α-polyoxymethylene. It seems probable that cellulose and silk fibroin are of this type, and in any event it may be observed that no high polymer is certainly known to be cyclic.[3]   There are polymers which do not conform to the type (—R—)$_n$ but those which do will be called linear whether the chain is open or closed; and the subsequent discussion is concerned only with these.

The structural units —R— are bivalent radicals which, in general, are not capable of independent existence.   The presence of a recurring structural unit is, of course, characteristic of most organic compounds (e. g., —CH$_2$— in aliphatic compounds), but in the case of polymers there exists a molecule, the monomer, corresponding to the structural unit, and from which the polymer may be formed or to which it may be degraded.

Examination of the formulas of Table I will show that two types of polymers may be distinguished.   In the first type, which includes paracetaldehyde, rubber, polystyrene and polyoxymethylenes, the molecular formula of the structural unit is identical with that of the monomer, i. e., the formula of the structural unit, —R—, is isomeric with that of monomer.   In the second type, which includes the polyethylene glycols, cellulose and silk fibroin, the molecular formula of the structural unit differs from that of the monomer by H$_2$O, i. e., the monomer is H—R—OH. The transformation of polymers of the first type into their monomers is brought about simply by heating, and the reverse transformation (polymerization) occurs spontaneously or by the action of catalysts.   In the second type, degradation to the monomer occurs by hydrolysis, and if the reverse process were to take place it would require the elimination of water among many molecules.   This would be polyintermolecular condensation.[4]

These two classes will be distinguished as (1) addition or A polymers. The molecular formula of the monomer is identical with that of the structural unit.   The monomer can be obtained from the polymer by thermolysis or the polymer can be synthesized from the monomer by self-addition.   (2) Condensation or C polymers: the molecular formula of the monomer differs from that of the structural unit.   The monomer can be obtained from the polymer by hydrolysis or its equivalent or the polymer can be synthesized from the monomer by polyintermolecular condensation. Polymerization then is the chemical union of many similar molecules

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[3] However, Staudinger, in his latest papers, favors the view that polystyrene and rubber are very large rings, Ber., **62**, 241 (1929).

[4] The term condensation is used here to name any reaction which occurs with the formation of a new bond between atoms not already joined and which proceeds with the elimination of elements (H$_2$, N$_2$, etc.) or of simple compounds (H$_2$O, C$_2$H$_5$OH, NH$_3$, NaBr, etc.).   Examples are the Wurtz reaction, Friedel–Crafts reaction, esterification, etc.

either (A) without or (C) with the elimination of simpler molecules (H_2O, HCl, NaCl, NH_3, etc.).[5]

Assuming that polyintermolecular condensation exists, the above examples and definitions and their implications provide ample reason for referring to this process as a type of polymerization. These examples, of course, do not provide any proof that this process as distinct from and independent of A polymerization does exist. This proof will appear incidentally in the following discussion, which is concerned with the general principles involved in the formation of condensation polymers.
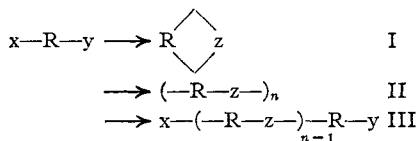
Polyfunctional Compounds.—Polyintermolecular condensation requires as starting materials compounds in which at least two functional groups are present in the same molecule (e. g., hydroxy acids, HORCOOH, might lead to poly-esters, HORCOORCOORCOORCOORCOORCO—, etc.; amino acids, to poly-amides, NH_2RCONHCONHRCONHR-CONHRCONHRCO—, etc.).

Among compounds having more than one functional group, those of the type x—R—y may be called bifunctional, $R''x_3$, trifunctional, etc. In these formulas R stands for a bivalent radical (R'' for a trivalent radical) and x and y for functional groups capable of reacting with each other in a known fashion to form the new functional group z. Thus x—R—y ⟶ —R—z—, where —R—z— evidently represents a structural unit which will appear in the product and which may be present 1, 2, 3, . . . n times. Reactions of this type will be called bifunctional regardless of the number of molecules involved. Reactions of the type x—R—x + y—R'—y ⟶ —z—R—z—R'— may be called bi-bifunctional. All such reactions may, at least by hypothesis, pass through the stage x—R—x—R'—y which is equivalent to x—R—y, and for purposes of discussion they may therefore be classed as simple bifunctional reactions. Reactions of the type $R'x_3$ + Ry_2 ⟶ *product* will be called tri-bifunctional. Similarly there may be tetra-bifunctional, tri-trifunctional reactions, etc., and all these may be classed together as polyfunctional reactions. The present discussion is concerned only with bifunctional reactions.

Bifunctional Reactions.—These always present two possibilities: they may be intramolecular or intermolecular. If intramolecular they can

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[5] It would not be difficult to suggest examples in which a single polymer might belong to either or to both of these classes depending upon the method by which it was synthesized. So far as cellulose is concerned there is little to justify its classification as a C rather than as an A polymer other than the criteria which are set forth in the above definitions, and these may at present appear somewhat arbitrary. Thus even if cellulose were synthesized by the dehydration of glucose, this might occur by the formation of a glucosan which subsequently polymerized by self-addition. It may be observed, however, that of the two trimethylglucosans which might conceivably polymerize in this way to form trimethylcellulose, one is known and does not polymerize, and the other is probably incapable of existence on stereochemical grounds. See Freudenberg and Braun, *Ann.*, **460**, 288 (1928).

lead only to the simple monomeric ring I. If intermolecular they may lead either to a polymeric ring II or to a polymeric chain III.

$$x{-}R{-}y \longrightarrow R \underset{\diagdown\diagup}{\overset{\diagup\diagdown}{}} z \qquad\qquad I$$

$$\longrightarrow ({-}R{-}z{-})_n \qquad\qquad II$$

$$\longrightarrow x{-}({-}R{-}z{-})_{n-1}{-}R{-}y \; III$$

These obviously represent three possibly competing reactions.

The question now arises, what factors will determine which of these possible courses a bifunctional reaction will take? It is obvious, for example, that in general dilution would favor intra- over intermolecular reaction.[6] Temperature and catalysts might favor either one or the other. It appears, however, that structural and stereochemical factors will usually be more important than any others. That is, though it may be possible in some bifunctional reactions to control the choice between intra- and intermolecular reaction by suitable adjustment of experimental conditions, this choice will, in general, be almost completely determined by the nature of the reacting molecules.

The effects of these factors may be stated as follows.   (1) If the product of intramolecular reaction would be a ring which, on stereochemical grounds, is incapable of existence, reaction will be intermolecular.   This is apparently the case with p-$NH_2C_6H_4CH_2CH_2Cl$, which reacts with itself intermolecularly,[7] and not as had previously been supposed[8] with the formation of the so-called dihydro-p-indole.[9]   The utility of this very obvious principle is somewhat diminished by the fact that, in the present state of stereochemical knowledge, it is sometimes impossible to predict whether a given ring system will be capable of existence or not.

(2) Bifunctional reactions which can lead to the formation of 5- or 6-rings almost invariably proceed intramolecularly.   This well-established fact is responsible for the existence of the majority of the very large number of 5- and 6-rings which is known.

(3) Bifunctional reactions which, if intramolecular, could lead only to larger-than-6-rings, generally proceed intermolecularly and lead to polymeric products.   If this rule were free from any exceptions, it would necessarily follow that the polymeric products would always be of the open-chain type, III.

Although a great many bifunctional reactions have been studied in the hope of forming large rings, our information as to the precise nature of the

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[6] Cf. Ruggli, Ann., 392, 92 (1912), where the recognition of this principle made possible the synthesis of large rings containing an acetylenic linkage.

[7] Ferber, Ber., 62, 183 (1929).

[8] V. Braun and Gawrilow, ibid., 45, 1274 (1912).

[9] For some other examples, see Titley, J. Chem. Soc., 2571 (1928).

TABLE I
POLYMERS

Polymer		Monomer	Mer or structural unit
Polystyrene ?-CH₂-CH·CH₂-CH-CH₂-CH·CH₂-CH-CH₂-..-CH-CH₂-CH·CH₂-CH-CH₂-CH-CH₂-? (C₆H₅ on each CH)	heat ⇌	**Styrene** $CH=CH_2$ $\mid$ C_6H_5	$-CH-CH_2-$ $\mid$ C_6H_5
Rubber ?-CH₂-C=CH-CH₂-CH₂-C=CH-CH₂-..-CH₂-C=CH-CH₂-CH₂-C=CH-CH₂-? (CH₃)	heat ⇌	**Isoprene** $CH_2=C-CH=CH_2$ $\mid$ CH_3	$-CH_2-C=CH-CH_2-$ $\mid$ CH_3
α-Polyoxymethylene $HO-CH_2-O-CH_2-O-..-CH_2-O-CH_2-O-CH_2-O-CH_2-OH$	heat ⇌	**Formaldehyde** $H_2C=O$	$-CH_2-O-$
β-Polyoxymethylene $HSO_3-O-CH_2-O-CH_2-O-CH_2-O-..-CH_2-O-CH_2-O-CH_2-O-H$	heat ⇌	$H_2C=O$	$-CH_2-O-$
Polyethylene glycols $HO-CH_2-CH_2-O-CH_2-CH_2-O-..-CH_2-CH_2-OH$	HOH →	**Ethylene glycol** $HO-CH_2-CH_2-OH$	$-CH_2-CH_2-O-$
Silk fibroin NH₂-CH₂-CONH-CH-CONH-CH-CO-..-NH-CH₂-CONH-CH-CONH-CH-CO- (CH₃)	HOH →	**Glycyl alanine** $CH_2-CONH-CH-COOH$ $\mid \qquad\qquad \mid$ $NH_2 \qquad\quad CH_3$	$CH_2-CONH-CH-CO-$ $\mid \qquad\qquad \mid$ $NH- \qquad\quad CH_3$
Cellulose (ring structural formula with CH₂OH, CH, OH, CH, groups)	HOH →	**Glucose** (ring structural formula, CH₂OH, HO-CH, CH-OH, CH, OH, OH)	(ring structural formula, CH₂OH, CH, CH-O-, CH, OH, OH)

The above formulas for the polyoxymethylenes, polystyrenes and rubber have been well established especially by the work of Staudinger and his students: *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); **59**, 3019 (1926); **60**, 1782 (1927); **61**, 2427 (1928); **62**, 241, 263 (1929); *Ann.*, **447**, 97, 110 (1926); *Z. physik. Chem.*, **126**, 425 (1927); *Kautschuk*, 237 (1927). For the formulas for cellulose, silk fibroin and rubber see Freudenberg and Braun, *Ann.*, **460**, 288 (1928); Meyer and Mark, *Ber.*, **61**, 593, 1932, 1939 (1928); Meyer, *Naturwissenschaften*, **42**, 790 (1928). The formulas for cellulose and silk fibroin are not, of course, regarded as finally established.

products of these reactions is very meager. That they do not usually proceed intramolecularly follows from the fact that very few large rings are known. It is true that such reactions frequently do not proceed at all under conditions which, in analogous cases, lead to the formation of 5- and 6-rings; but the formation of the latter often proceeds under conditions which do not permit intermolecular reaction even among unifunctional compounds (compare the formation of γ-lactones in the presence of a large excess of water, with the esterification of acetic acid). There are, however, a good many types of reaction which are intermolecular among simple compounds, which are practically free from side reactions, and which by suitable adjustment of experimental conditions may be forced to completion. It should be possible to conduct reactions of these types even when bifunctional, so as to obtain analytically homogeneous products whether they proceed intramolecularly or not. These simple principles have been repeatedly applied to bifunctional reactions in this Laboratory, and they have seldom failed to lead to analytically homogeneous products. Moreover, where the formation of 5- or 6-rings was excluded by the nature of the reacting materials, these reactions have, *without exception*, led to *high polymers*. This fact provides a possible explanation for the meagerness of the information which is available concerning the precise nature of the products of such bifunctional reactions. High polymers frequently have properties which make their investigation very difficult. Moreover, if a chemist is expecting a reaction to lead to materials of simple properties, he is usually inclined to regard the appearance of a resinous or sirupy product which neither can be crystallized nor distilled as signifying only that the experiment has failed. When the products of such reactions have been capable of purification and have shown the expected analytical composition, they have frequently been assumed to be dimeric (and cyclic) for no other reason than that they were obviously not monomeric. In this connection it should be emphasized that substances of very high molecular weights may nevertheless be microcrystalline and very soluble (see the following paper).

Some of the points discussed above are illustrated by the following examples.

Anhydrides of the acids of the series $HOOC(CH_2)_xCOOH$ are known in which x has all values from 1 to 8 inclusive. Of these only succinic and glutaric anhydrides are monomeric. These are, respectively, 5- and 6-rings. The other anhydrides which, if monomeric, would be 4-, 7-, 8-, 9-, 10- and 11-rings, are all highly polymeric.[10]

[10] For malonic anhydride see Staudinger and Ott, *Ber.*, **41**, 2214 (1908). For the other anhydrides see Voerman, *Rec. trav. chim.*, **23**, 265 (1904). The cryoscopic data which Voerman presents on phenol solutions have no bearing on the molecular weights of the anhydrides, since even succinic anhydride reacts rapidly with phenol to form phenyl succinate; Bischoff and von Hedenström, *Ber.*, **35**, 4076 (1902). Farmer and Kracov-

Hydroxy-acids of the series $HO(CH_2)_xCOOH$ may condense with themselves. Only those in which x is 3 or 4 yield monomeric lactones.[11] These lactones are 5- and 6-rings, respectively. This series of acids now includes those in which x has all values from 8 to 16 inclusive.[12] The lactones corresponding to the acids in which x has the values 12 to 16 are also known,[12b] as well as the 17-membered lactone of the unsaturated acid, hexadecene-(7)-ol-(16)-acid-(1).[13] All of these lactones are perfectly stable substances and can be distilled without decomposition;[14] and yet none of these lactones has been synthesized by a bifunctional reaction.[15] They were synthesized by the oxidation of the corresponding cyclic ketones with persulfuric acid. By heating the acids, products are indeed obtained which have the same analytical composition as the lactones, but[12a] they are "polymeric-like." The properties of the known lactones of this series indicate that lactones cannot be intermediates in the formation of these polymers. The formation of these must, therefore, involve C polymerization.

Amino acids of the series $NH_2(CH_2)_xCOOH$ are known in which x has the values 3, 4, 5 and 6. When x is 3 and 4, intramolecular anhydride formation occurs spontaneously at the melting point of the acids, the products being the 5- and 6-membered rings, pyrrolidone and piperidone.[16]

ski have recently obtained adipic anhydride in a monomeric form, *J. Chem. Soc.*, 680 (1927).

[11] On this point no data are available for those in which x is 5 and 6 [THIS JOURNAL, **46**, 2838 (1924); *Ber.*, **60**, 605 (1927); *ibid.*, **33**, 864 (1900)]. The analogous acids, $CH_3CHOH(CH_2)_2CH(CH_3)CH_2COOH$ [Baeyer and Seuffert, *ibid.*, **32**, 3619 (1899)] and $C_2H_5CHOH(CH_2)_4COOH$ [Blaise and Kohler, *Compt. rend.*, **148**, 1772 (1909)], have been prepared, and by heating are converted at least partially into the 7-membered lactones. The acid $C_2H_5CHOH(CH_2)_5COOH$ has also been prepared. On heating, it also loses water, but the 8-membered lactone is not formed. The product is a lactide-like material which cannot be distilled without decomposition (Blaise and Kohler).

[12] (a) Lycan and Adams, THIS JOURNAL, **51**, 625 (1929); (b) Ruzicka and Stoll, *Helv. Chim. Acta.*, **11**, 1159 (1928). Since this paper was written a great deal of further information concerning these acids has become available in the paper of Chuit and Hausser, *ibid.*, **12**, 463 (1929).

[13] Kerschbaum, *Ber.*, **60**, 902 (1927).

[14] This indicates that large heterocyclic rings are not less stable than their lower homologs. Their physical properties are such as would be expected from the known properties of their lower homologs. The mere presence of a large ring does not result in the development of any of those unusual secondary, residual, or supermolecular forces which are sometimes supposed to confer "polymeric" properties on relatively simple molecules.
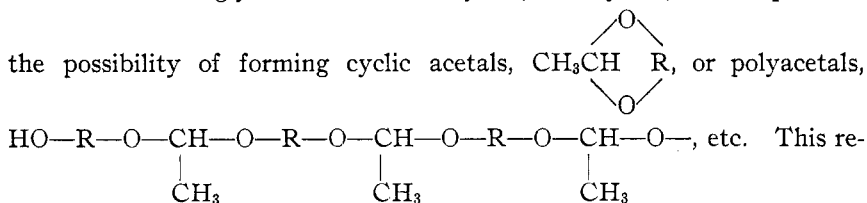
[15] Kerschbaum (ref. 13) records various attempts to prepare ambretollid by the methods commonly used for the preparation of lactones. By heating the acid he obtained traces of an oil which had the odor of the lactone. (It is powerfully odorous.) The product was, however, for the most part, a gelatinous material *soluble in alkali.* For the usefulness of the method proposed in German Patent Application 150,677, see Ruzicka and Stoll, ref. 12 b.

[16] Gabriel, *Ber.*, **22**, 3338 (1889); Schotten, *ibid.*, **21**, 2240 (1888).

When x is 5 the acid is, on heating, converted to the extent of 20 to 30% of the theoretical into the 7-membered lactam. "The rest of the acid is converted into a viscous gelatinous mass which could be obtained in a state of only approximate purity and which, according to the analysis, is isomeric with the 7-membered lactam; that is, it is a polymeric product."[17]   Where x is 6 no trace of the corresponding lactam could be obtained by heating the acid, although this lactam (suberone-isoxime) is a known and stable substance.[18]   By heating the acid a product was obtained having the same composition as this lactam, but it was an undistillable solid, insoluble in most solvents.[17]

The compounds $Br(CH_2)_xNH_2$, where x is 4, 5 and 6, react with themselves with the formation of secondary amines containing the structural unit $(-CH_2-)_xNH-$.   Where x is 4 and 5 the products are the monomeric 5- and 6-rings, pyrrolidine and piperidine.[19]   Where x is 6 the amount of the monomeric base (7-ring) formed was too small to permit purification.[20]   The product was for the most part an oil which solidified to a waxy solid.   It could not be distilled in vacuum without decomposition, and though no molecular weight determination is recorded, v. Braun seems inclined to regard it as dimeric.   Its properties are obviously more consistent with a more highly polymeric structure.

An interesting example of a bi-bifunctional reaction is found in the reaction between glycols and acetaldehyde (or acetylene).   This presents the possibility of forming cyclic acetals, $CH_3CH \langle \begin{smallmatrix} O \\ O \end{smallmatrix} \rangle R$, or polyacetals,

$$HO-R-O-CH(-CH_3)-O-R-O-CH(-CH_3)-O-R-O-CH(-CH_3)-O-, \text{ etc.}$$

This reaction has been studied by Hill and Hibbert.[21]   Ethylene and trimethylene glycols gave in excellent yields the cyclic acetals which are 5- and 6-rings. Tetramethylene glycol gave in poor yield a volatile compound which was apparently the monomeric cyclic acetal containing a 7-ring.   A considerable part of the product was an undistillable sirup.   The products from octamethylene and decamethylene glycols were also undistillable sirups. No molecular weight determinations are recorded.   Hill and Hibbert

[17] V. Braun, *Ber.*, **40**, 1840 (1907).

[18] B. p. 156° at 8 mm.   It is, however, not prepared by a bifunctional reaction, but from cycloheptanone oxime by the Beckmann rearrangement.   Wallach, *Ann.*, **312**, 305; **309**, 18 (1899).

[19] V. Braun and Beschke, *Ber.*, **39**, 4121 (1906); Blank, *ibid.*, **25**, 3044 (1892); V. Braun and Steindorf, *ibid.*, **38**, 172 (1905).

[20] V. Braun and Steindorf, *ibid.*, **38**, 1083 (1905); v. Braun, *ibid.*, **43**, 2853 (1910).

[21] Hill and Hibbert, THIS JOURNAL, **45**, 3108, 3124 (1923).   See also Franke and Gigerl, *Monatsh.*, **49**, 8 (1928).

recognized of course that these sirups might have the polymeric linear structure indicated above, but seemed inclined to regard them as simple rings of a peculiar kind.

The only reaction which has led to the formation of large carbon rings from open-chain compounds is the action of heat on certain salts of dibasic acids.[22] In no case are these large rings the chief products of this reaction, nor can it be established that they are primary products, since the reaction takes place at high temperature. If polymeric products were formed they would be decomposed thermally. High polymers could not appear in the distillate from which the products are isolated, because high polymers cannot be distilled. These features sharply distinguish this reaction from other truly bifunctional reactions which might, but which do not, so far as our information goes, lead to rings of the same type.[23]

Any theory which attempts to explain why 5- and 6-rings are formed very readily and larger rings with very great difficulty must take into account the fact that these larger rings are not less stable than the smaller. A satisfactory theory is already available. The Baeyer strain theory in its original form is made untenable by the existence of the higher cycloparaffins, and has been replaced by the Sachse–Mohr theory which permits the existence of non-planar and strainless rings and which has besides a great deal of other evidence in its support.[24] The features of this theory essential to the present argument are exceedingly simple. They involve the assumption of the tetrahedral angle in the carbon valences and of free rotation about each carbon–carbon single bond in a chain. No description of stereochemical relations can be as convincing as a demonstration with suitable models.[25] Such models show that there is a certain inevitability in the formation of 5- and 6-rings and a large degree of fortuity in the formation of larger rings. This question has been considered in some detail by Mohr.[26] Regarding the possibility of the forma-

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

[23] For example, the action of metals on a dihalide, $Br(CH_2)_xBr$. Thus decamethylene bromide reacts rapidly and very smoothly with metallic sodium, but no cyclodecane is formed. See Franke and Kienberger, *Monatsh.*, **33**, 1189 (1912). This reaction will be discussed in a later paper.

[24] See Hückel, "Der gegenwärtige Stand der Spannungstheorie," *Fortschritte Chem. Physik und physik. Chem.*, Band 19, Heft 4, 1927.

[25] Ordinary (preferably quite small) wire tetrahedra may be joined by short pieces of rubber tubing in such a way that the arms which are being connected over-lap. This provides free rotation about the union, but prevents bending. This method of union insures that any model which is built up is practically strainless (*i. e.*, the tetrahedral angle is always retained) and at the same time is sufficiently mobile to illustrate the multiplicity of forms which long chains and large rings can assume.

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

tion of a cyclic ketonic ester by the internal condensation of sebacic ester he says:

The molecule of sebacic ester is a very long chain. The multiplicity of forms which this molecule can assume is extraordinarily great. It is clear that by the random collisions of the molecules, fewer molecules of sebacic ester will in unit time assume the form necessary for ring closure than is the case with adipic ester under the same conditions, since this contains in its molecule only four methylene groups, and four less points of rotation than does sebacic ester. To bring the two ends of the sebacic ester molecule together in the least forced fashion apparently requires a very small amount of energy or none at all. Unfortunately, however, we have not the means arbitrarily and with the least possible expenditure of energy to bring about the desired change in form of the molecules and to hinder the undesired. In this connection we are left entirely to chance, that is, to random collision, which will bring about a given form the more rarely the more forms are possible, *i. e.*, the longer the chain between the two carboxyl groups.

In perhaps two dozen cases it is well established that a bifunctional reaction proceeds fairly smoothly with the formation of a larger-than-6-ring. These cases include more 7-membered than larger rings, and more aromatic than aliphatic compounds. The Sachse–Mohr theory would lead one to expect that the formation of 7-rings would not be very much more difficult than the formation of 6-rings. The bifunctional reactions discussed in the examples offered above all involve purely aliphatic compounds, and for the most part the chains are unsubstituted. In most of these examples the formation of a 7-ring occurs to a certain extent, and the formation of the corresponding 8-ring not at all. It appears that in such 7-atom chains the probabilities of intra- and intermolecular reaction are about equal. The addition of one more atom to the chain diminishes the probability of intra- with respect to intermolecular reaction to such an extent that only the latter appears. These relations may be somewhat modified by the presence of substituents on the chains and even by the nature of the reacting groups in ways which it is, at present, impossible to predict. It is evident, however, that if two atoms of such a chain are adjacent atoms of a benzene ring their position with respect to each other is fixed, and the chances of intramolecular reaction are greater than in an analogous simple chain of the same length. (The latter will have one more axis of rotation than the former.) It is therefore not surprising that in $NH_2(CH_2)_6Cl$ intramolecular reaction occurs only to a slight extent, and in $o\text{-}NH_2C_6H_4(CH_2)_4Cl$ almost quantitatively.[27] Other similar examples might be cited.

There is also some evidence to indicate that even simple substituents such as methyl groups on a chain may increase the tendency toward the formation of larger rings.[28] Researches in the diphenyl series have established that substituent groups suitably placed may completely inhibit

[27] v. Braun and Bartsch, *Ber.*, **32**, 1270 (1899).

[28] See "Annual Reports of the Progress of Chemistry," **1927**, p. 100; Moyer and Adams, THIS JOURNAL, **51**, 630 (1929).

rotation about a nearby single bond, and a similar effect in aliphatic chains is at least conceivable. Any restriction of the freedom of rotation of the atoms of a chain would, on the basis of the Sachse–Mohr theory, increase the chances of ring formation.

The process of polyintermolecular condensation finds no mention in treatises on polymerization. This may be due to the fact that such a process is not admitted to exist, or that it is not admitted to be polymerization. The examples cited above, and others to be described later, prove that such a process does exist, and that it may result in the formation of very large molecules. Whether it is to be regarded as polymerization or not will depend upon the definition which is adopted for that term. The definitions offered above include it as a special type of polymerization. This classification finds more to justify it than the analogies which are recognized in these definitions.

The process of A polymerization (the only type which appears to have been generally recognized) results in the formation of large molecules from small; and it has come about that any process which has this result is called polymerization. Since, however, A polymerization is by definition a process of self-addition, chemists have often been misled to the assumption that condensation leads directly only to small molecules, and that if large molecules are formed from small as the apparent result of condensation, this is due to the intervention of some unsaturated molecules capable of undergoing A polymerization.[29] It is quite certain, however, that in many such cases (i. e., in all cases of true C polymerization) no such intermediate products occur. This is a matter of important practical implications. The reactions involved in the formation of A polymers must, in the nature of the case, be for the most part reactions which are peculiar to the process of polymerization. For this reason the mechanism of A polymerization still remains somewhat obscure. Hence, the mere assumption that unsaturated intermediates intervene in a reaction which leads to high polymers contributes little to one's understanding of the mechanism of the process, or the structure of the product. In those cases in which this assumption is wrong its use leads one to regard as complicated and

[29] Thus, Drummond, *Inst. Rubber Ind.*, 4, 43 (1928), states, "Where resins are formed by a preliminary condensation as are the phenol-formaldehyde products, it is logical to assume that in the preliminary reaction, unsaturated atomic linkings are introduced which provide the necessary arrangement for polymerization subsequently to occur." Scheiber, *Chem. Umschau, Fette, Oele, Wachse Harze*, 15, 181 (1928), is even more explicit: "Für den Aufbau organischer Stoffe kommen bekanntlich nur zwei Prozesse in Betracht, und zwar Kondensationen und Polymerisationen. Vorgänge der ersteren Art führen im allgemeinen zu Molekulverbänden beschränkter Grösse—..Bei Polymerisationen hingegen kommt es in manchen Fallen zur Ausbildung extrem grosser Moleküle..."

mysterious a process which may be simple and obvious. C polymerization merely involves the use in a multiple fashion of the typical reactions of common functional groups. Among bifunctional compounds these reactions may proceed in such a way as to guarantee the structure of the structural unit, —R—, in the polymer, (—R—)$_n$, formed. It is one of the immediate objects of the researches to be described in subsequent papers to discover how the physical and chemical properties of high polymers of this type are related to the nature of the structural unit.

Summary

Linear polymers conform to the type —R—R—R—R—R—, etc., which is characterized by a recurring structural unit. The structural unit —R— is a bivalent radical. Two types of polymers are recognized. (1) Addition or A polymers: the polymeric molecule is converted by heat into a monomer having the same composition as the structural unit, or the polymer is formed by the mutual addition of a number of such monomers. (2) Condensation or C polymers: the polymeric molecule is converted by hydrolysis or its equivalent to a monomer which differs in composition from the structural unit by one H_2O (or HCl, NH_3, etc.), or the polymeric molecule is formed from numbers of the monomers by a process of polyintermolecular condensation. Rubber, polystyrene, polyoxymethylene and paracetaldehyde are A polymers. Cellulose, silk fibroin and hexa-ethylene glycol are probably C polymers.

Substances of the type x—R—x and x—R—y are called bifunctional. In these formulas —R— represents a bivalent radical and x and y functional groups capable of reacting with each other in a known fashion to form the new functional group, z. Reactions of the type x—R—y ⟶ *product* are called bifunctional and those of the type x—R—x + y—R—y ⟶ *product* are called bi-bifunctional. Such reactions will lead to compounds containing the structural units —R—z— and —R—z—R—z—. Bifunctional reactions will be intramolecular and will lead to the monomeric product, $R \overset{\textstyle\triangle}{\underset{\textstyle\triangledown}{}} z$ when this can be a 5- or 6-ring. If the monomeric product can only be a larger-than-6-ring, reaction will usually be intermolecular and the product a polymer of the type —R—z—R—z—R—z—R—z—R—z—, etc.

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