POLYMERIZATION[1]

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TABLE OF CONTENTS

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This review is concerned with reactions that result in the combination of simple molecules to form materials of high molecular weight, and especially with the nature of such reactions and the structure and properties of the products. For the sake of comparison, the structures of certain natural polymers concerning which it is possible to make definite statements are briefly considered also. The literature on the subject of high polymers is most profuse, and from the theoretical side it has until very recently been contradictory and confused. For these reasons the present discussion is of necessity rather selective and critical. (For other general discussions of certain aspects of this field the reader may consult references 1 to 7 and 18.) It is necessary also to define especially the sense in which certain terms are to be used.

I. DEFINITIONS

1. *Current definitions*

It is generally agreed by organic chemists (9) that polymerization is chemical combination involving the operation of primary valence forces, and that the term polymer should not be used (as it frequently is by physical and inorganic chemists) to name loose or vaguely defined molecular aggregates. Beyond this, however, there is not much agreement. The word polymer was introduced by Berzelius (12) nearly a century ago to recognize the fact that two compounds may have the same composition but different molecular weights, and he classified polymerism as a special type of isomerism. The accepted meaning of these terms has subsequently undergone considerable change, but current textbook definitions always state that a monomer and its polymer have the same composition, and it is usually either stated or implied that the process of polymerization is peculiar to unsaturated compounds and consists in self-addition. But recently discovered facts show that these conditions really are not satisfied in many instances to which the terms polymer and polymerization are applied. The formula of α-polyoxymethylene, for example, is not $(CH_2O)_x$, but $(CH_2O)_xH_2O$ (110).

It is true also that many compounds which are not unsaturated are capable of reacting with themselves to form products of high molecular weight, and that such reactions are quite commonly called polymerization. For example, benzyl chloride in the presence of aluminum chloride:

$$x\ C_6H_5CH_2Cl \rightarrow (C_7H_6)_x + x\ HCl$$

One can assume that the first step in this reaction is the elimination of HCl to yield the radical $C_6H_5CH{=}$, which, being unsaturated, is capable of reacting with itself by addition. On the other hand, it may be that this is simply a polymolecular Friedel Crafts reaction, the first step being the formation of $C_6H_5CH_2$-$C_6H_4CH_2Cl$, which is capable of reacting with itself by the same mechanism and finally yielding a very long chain in which the chlorine content is negligible. If the usual definitions are adopted, this reaction can properly be called polymerization only if it proceeds by the first mechanism. Curiously enough, one actually finds in the literature cases in which the fact that a reaction is called polymerization is used to prove that the first step must be the formation of an unsaturated intermediate capable of reaction with itself by addition. It is perhaps unnecessary to say that the questions of the composition of high polymers and the mechanism of their formation are frequently rather intricate and cannot be solved in advance by definition.

2. Proposed definitions

It is more practical and useful (and also more consistent with actual usage) to define polymerization as any chemical combination of a number of similar molecules to form a single molecule. A polymer then will be any compound that can be formed by this process or degraded by the reverse process: formaldehyde can be regenerated from polyoxymethylene by the action of heat; ethylene glycol can be obtained from polyethylene glycol by hydrolysis; cellulose can be hydrolyzed to glucose; and rubber can be formed by the reaction of isoprene with itself.

3. Linear and non-linear polymers

The simplest and perhaps the most numerous and important high polymers are characterized structurally by the fact that their molecules are long chains built up from a repeating radical or unit. This type of structure may be represented by the general formula,

$$\ldots\ldots -A-A-A-A-A-A-A-A-A- \ldots\ldots$$

The repeating radical —A— is called the *structural unit.* The number and nature of these units determine the nature of the molecule. To complete this formula it is necessary to specify the disposition of the terminal valences; they may conceivably be mutually joined to form a cyclic structure or saturated by univalent groups. Whether the chain is open or closed, polymers of this class will be called *linear polymers.* It should be added that linear high polymers are usually mixtures containing chains of different lengths.

If the polymer is derived from a single compound the structural units of the chain will in general be identical, but the mutual reaction of two or more compounds that are chemically similar but not identical may lead to chains made up from two or more different units. Such products will be called linear mixed polymers.[2] Many polypeptides and proteins belong to this class. Non-linear polymers also exist; they can be formed, for example, by the cross linking of long chains into two- or three-dimensional structures.

4. Types of compounds capable of polymerizing

The step-by-step synthesis of long molecular chains containing a repeating unit is illustrated by Fischer's famous synthesis of polypeptides. Reactions of polymerization, however, lead to the formation of polymeric chains in a single operation. The capacity for self-combination of this kind is found among simple molecules of three different types: (*a*) unsaturated compounds;

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[2] The term heteropolymer has also been suggested (23).

(*b*) cyclic compounds; (*c*) polyfunctional compounds. These are illustrated by the following examples.

(*a*) $$\underset{\text{Formaldehyde}}{n\,CH_2{=}O} + H_2O \rightarrow \underset{\alpha\text{-Polyoxymethylene}}{HO{-}CH_2O{-}CH_2O{-}\ldots{-}CH_2O{-}CH_2O{-}CH_2O{-}H}$$

(*b*) $$\underset{\text{Ethylene oxide}}{n\,\underline{\left|CH_2CH_2O\right|}} + H_2O \rightarrow \underset{\text{Polyethylene glycol}}{HO{-}CH_2CH_2O{-}CH_2CH_2O{-}\ldots{-}CH_2CH_2O{-}H}$$

(*c*) $$\underset{\text{Ethylene glycol}}{n\,HO{-}CH_2CH_2O{-}H} - (n-1)H_2O \rightarrow \underset{\text{Polyethylene glycol}}{HO{-}CH_2CH_2O{-}CH_2CH_2O{-}\ldots{-}CH_2CH_2O{-}H}$$[3]

In each of these examples the product molecule is made up of a repeating series of identical units. Each unit corresponds with one molecule of the starting material. The latter, therefore, is called the monomer (*mer* = part). Ethylene glycol and ethylene oxide are both monomers since, although they differ in structure and composition, their molecules contain one $—CH_2CH_2O—$ unit each. Similarly diethylene glycol, $HO—CH_2CH_2O—CH_2CH_2O—H$, is a dimer.

5. *Types of polymerization*

Molecules can combine to form larger molecules either by addition or by condensation,[4] and two corresponding types of polymerization may be recognized. The formation of polyoxymethylene from formaldehyde is addition or *A* polymerization. The formation of polyethylene glycol directly from ethylene glycol

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[3] The direct polyintermolecular dehydration of ethylene glycol to polyethylene glycol not involving the intermediate formation of ethylene oxide is perhaps somewhat hypothetical. It is used here merely as a formal illustration.

[4] The term condensation is used here to name any reaction that occurs with the formation of a new bond between atoms not already joined and proceeds with the elimination of elements (hydrogen, nitrogen, etc.) or of simple compounds (water, ethyl alcohol, ammonia, sodium bromide, etc.). Examples are the Wurtz reaction, Friedel Crafts reaction, esterification, etc. See Kempf in Houben-Weyl, ref. 6, Volume II, p. 717.

is condensation or *C* polymerization.[5] This second type of polymerization, although its existence as a general phenomenon has only recently been recognized (18), is especially simple both practically and theoretically since it involves the known behavior of typical functional groups.

6. Condensation polymerizations and bifunctional reactions

A general class of condensation polymerizations is represented by the equation

$$\text{x—R—y} + \text{x—R—y} + \text{x—R—y} + \ldots\ldots \rightarrow \text{x—R—z—R—z—R—} \ldots$$

In the formula x—R—y, R is a bivalent radical and x and y are functional groups capable of reacting with each other to form the known functional group z. Thus if x is HO and y is COOH, z will be CO—O. The compounds x—R—y are called bifunctional compounds and their reactions, bifunctional reactions. Reactions of the type, x—R—x + y—R′—y → *product*, may be included in this class.

Bifunctional reactions present the possibility of following various courses. (*a*) They may be intramolecular at the first stage. The product will then be the cyclic monomer

$$\lfloor\underline{\text{R—z}}\rfloor.$$

(*b*) Reaction may be intermolecular at the first stage and intramolecular at some subsequent stage. The product will then be a cyclic polymer

$$\lfloor\underline{(\text{—R—z—})_n}\rfloor.$$

(*c*) Reaction may be exclusively intermolecular. In this case the product will be an open chain of the type x—R—z—R—z . . . . —R—z—R—y. These possibilities may be illustrated

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[5] The term condensation polymerization was at one time applied by Staudinger (38) to addition polymerizations that involve the migration or displacement of a group or an atom, but its use in this sense has never become general. In view of its obvious propriety for the purpose, it was adopted by the writer (18) as a name for polyintermolecular condensation.

by the hydroxy acids of the series $H—O—(CH_2)_n—CO—OH$. The self-esterification of these might lead to the simple lactones

$$\lfloor\underline{O—(CH_2)_n—CO}\rfloor,$$

or to cyclic polyesters

$$\lfloor\underline{[O—(CH_2)_n—CO]_p}\rfloor$$

or to open chain polyesters

$$H[O—(CH_2)_n—CO]_pOH.$$

All three of these possibilities can be realized.

II. CONDENSATION POLYMERIZATION

1. *Polyesters*

Bifunctional esterifications are especially suitable for the study of condensation polymerization, because esterification is a reversible reaction, and it is entirely free from side reactions under conditions that are easy to realize.

a. The self-esterification of hydroxy acids. It is well known that hydroxy acids react with themselves to form cyclic esters when there is the possibility of forming a five- or a six-membered ring: γ- and δ-hydroxy acids lead to the corresponding lactones, and α-hydroxy acids yield the cyclic dimers. Thus glycolic acid reacts with itself to form glycolide:[6]

$$2\ HO—CH_2—COOH \rightarrow \lfloor\underline{O—CH_2—CO—O—CH_2—CO}\rfloor + 2\ H_2O$$

The γ-lactones are stable substances, but the δ-lactones and glycolide and its analogs on being heated are rapidly transformed into polyesters of high molecular weight. This peculiar behavior of the six-membered cyclic esters is considered in more detail in a later paragraph.

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[6] But it is by no means certain that the glycolide is ever formed through the steps glycolic acid → glycolylglycolic acid → glycolide. Dietzel and Krug (19) have shown that in the self-esterification of lactic acid the primary steps are: lactic acid → lactyllactic acid → polylactyllactic acids. Lactide when it is formed results from the depolymerization of these polylactyllactic acids.

No information is available concerning the behavior of the simplest ϵ-hydroxy acid, hydroxycaproic acid, but the corresponding bromo acid when treated with sodium ethylate in alcohol solution gives a poor yield of the seven-membered lactone (37). The chief product is an undistillable material, undoubtedly polyester. ϵ-Hydroxycaprylic acid, $C_2H_5—CHOH—(CH_2)_4—COOH$ is partly converted into the corresponding seven-membered lactone on being heated, but the next member of this series, $C_2H_5—CHOH—(CH_2)_5—COOH$, under the same conditions gives only an undistillable residue (24).

Larger lactones containing rings of fourteen to eighteen atoms are known (25), and also β-lactones (four-membered rings) (26, 27). All of these are fairly stable compounds, but none of them has ever been prepared directly from the corresponding acid.[7]

The attempt to prepare self-esters from simple β-hydroxy acids results merely in dehydration to the unsaturated acid, but in hydroxypivalic acid, $HO—CH_2—C(CH_3)_2—COOH$, this usual behavior is impossible because of the absence of any α-hydrogen. The self-esterification of this acid has been studied by Blaise and Marcilly (28). It occurs at 200°C. or at lower temperatures in the presence of certain catalysts. The product is a microcrystalline powder insoluble in most organic solvents. It forms sodium salts insoluble in cold water, and it is readily hydrolyzed to hydroxypivalic acid. These facts clearly indicate a structure of the type

$$HO-CH_2-C(CH_3)_2-COO-[-CH_2-C(CH_3)_2-COO-]_n-CH_2-C(CH_3)_2-COOH$$

and on the basis of molecular weight and analytical data Blaise and Marcilly assign to n the value 4.

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[7] Kerschbaum (36) records various attempts to prepare the lactone of ambrettolic acid (hexadecene-7-ol-16-acid-1) from the acid obtained by hydrolyzing the naturally occurring lactone. By heating the acid he obtained a small amount of oil which, from its odor, was inferred to contain lactone. The chief product, however, was a non-volatile material soluble in alkali. Neither Chuit and Hausser (29) nor Lycan and Adams (30) report any evidence for the presence of lactone in the self-esters prepared from higher ω-hydroxy acids. Unpublished experiments made in this laboratory have failed to reveal the presence of any lactone among the products of the dehydration of ω-hydroxypentadecanoic acid.

In regard to the higher ω-hydroxy acids, Chuit and Hausser (29) have recently synthesized the entire series from HO—$(CH_2)_7$—COOH to HO—$(CH_2)_{20}$—COOH. All these acids readily undergo self-esterification on being heated. The products are not the corresponding lactones (which in several cases are known), but solid acidic materials whose properties are consistent with the general formula HO—R—CO—O—R—CO—. . . . —O—R—COOH. Similar products obtained by the self-esterification of higher hydroxy acids have also been investigated by Bougalt and Bourdier (31) and by Lycan and Adams (30).

The presence of a terminal carboxyl group in each of these products proves that the ester formation is exclusively intermolecular. It should be possible, therefore, by regulating the degree of completeness of the esterification to obtain molecules of various lengths and, in particular, to obtain exceedingly long molecules. Such molecules are of especial interest in connection with the study of high polymers, since the nature of the acid used absolutely determines the structural unit of the polyester.

b. Polyesters from dibasic acids and glycols. The study of bifunctional esterifications from this standpoint was first undertaken by the writer and his collaborators (32 to 35). Dibasic acids and glycols were used as starting materials since these are more readily accessible than hydroxy acids, and they also permit more numerous structural variations in the ester product.

Esters derived from dibasic acids and glycols can be prepared by any of the typical reactions ordinarily used in the preparation of simple esters, e.g.:

(*a*) $HO-R-OH + HOOC-R'-COOH \rightarrow -O-R-O-CO-R'-CO- + H_2O$

(*b*) $HO-R-OH + EtOOC-R'-COOEt \rightarrow -O-R-O-CO-R'-CO- + EtOH$

(*c*) $HO-R-OH + C_6H_5OOC-R'-COOC_6H_5 \rightarrow -O-R-O-CO-R'-CO- + C_6H_5OH$

(*d*) $HO-R-OH + ClCO-R'-COCl \rightarrow -O-R-O-CO-R'-CO- + HCl$

(*e*) $Br-R-Br + AgOCO-R'-COOAg \rightarrow -O-R-O-CO-R'-CO- + AgBr$

In these equations —O—R—O—CO—R′—CO— represents the structural unit of the product. The studies have proved that the nature of the ester is completely determined by the number of atoms in the chain of the unit: if this number is five, the product is monomeric and cyclic (i.e., it contains only one unit); if the number is six, the product can be obtained in both monomeric and polymeric forms and these are interconvertible; if the number is more than six, the product is exclusively polymeric.

The preparation of an ester of this last class may be illustrated by the action of succinic acid on ethylene glycol.[8] Succinic acid mixed with a slight excess of glycol is heated in a distilling flask. At about 160–175°C. rapid esterification sets in, accompanied by the liberation of water. When no more water is evolved the temperature is raised to 220–250°C. and the pressure is reduced below 1 mm., whereupon most of the excess glycol distils. The ester product is completely non-volatile and remains in the distilling flask in the form of an exceedingly viscous liquid. When this is cooled it solidifies to a hard, brittle, opaque, white mass. This can be dissolved in cold chloroform and precipitated as a granular powder by the addition of ether or benzene. It can be recrystallized from hot ethyl acetate or a large volume of hot acetone. The recrystallized ester melts at about 102°C. A product having the same physical properties can be prepared in the same way by the action of diethyl succinate or diphenyl succinate on ethylene glycol. The reaction then consists in ester interchange and the volatile product liberated is alcohol or phenol.

By the method of direct esterification or by ester interchange the esters listed in table 1 have been prepared. They are without exception highly polymeric, the molecular weights being on the average in the neighborhood of 3000. Molecular weights of several of the esters have been determined in a variety of solvents and by both freezing and boiling point methods, and within the limits of experimental error the same values have been found.

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[8] The preparation of ethylene succinate by reaction between the acid and glycol was first carried out by Lourenco (17). Later Davidoff (40) and Vorländer (41) prepared it by various methods, and the latter investigator assigned to it the formula of a sixteen-membered cyclic dimer. His molecular weight determinations were apparently in error. The dimeric ester is now known (42, 34) and its properties are quite different from those of Vorländer's ester, which closely resembles the polymeric ester prepared from the acid and the glycol.

These esters show considerable similarity in their physical properties. They are completely non-volatile and all of them dissolve quite readily in cold chloroform. Those derived from the higher glycols or acids also dissolve in cold benzene, and in the solid state they are less hard and more wax-like than ethylene succinate. In spite of their high molecular weight and lack of complete homogeneity all these esters except the phthalates are crystalline. The melting points vary slightly from one preparation to another of a given ester and usually cover a range of about 2°.

The ethylene succinate described above is neutral, and its composition and molecular weight indicate the average formula[9]

$$HO—[(CH_2)_2—O—CO—(CH_2)_2—CO—O]_{22}—(CH_2)_2—OH,$$

i.e., it is an open chain derived from twenty-two molecules of acid and twenty-three molecules of glycol.

The hydroxyls at the end of this chain do not readily react with the usual reagents for alcohol groups; their sluggish behavior in this respect is characteristic of many high molecular weight materials. However, on being heated to a fairly high temperature with *p*-bromobenzoic anhydride the ester yields a di-*p*-bromobenzoyl derivative identified as such by its bromine content. The ester also reacts with molten succinic anhydride and yields an acidic ester whose neutral equivalent and observed molecular weight agree with the formula I d.

$$\text{(I)}\ HO—CO—(CH_2)_2—CO—[—O—(CH_2)_2—O—CO—(CH_2)_2—CO]_x—OH$$

$$\text{I a, } x = 6;\ \text{I b, } x = 9;\ \text{I c, } x = 12;\ \text{I d, } x = 23.$$

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[9] The molecules of this product certainly do not all have the same length, but on the other hand it appears to be much more nearly homogeneous than any products ever obtained by addition polymerization (polystyrene, etc.). In its qualitative solubility behavior it resembles a chemical individual, and fairly elaborate fractional crystallizations have failed to separate it into portions showing any considerable difference in their properties. The reason for its relatively great homogeneity lies in the conditions of its formation, which are such as to force much smaller molecules to react with themselves, but are not sufficiently drastic to cause the formation of much larger molecules. Under other conditions polymeric mixtures having a wide range of molecular weights can be obtained.

TABLE 1

Polyesters from glycols and dibasic acids

COMPOUND	FORMULA OF STRUCTURAL UNIT	ATOMS IN CHAIN OF STRUCTURAL UNIT	AVERAGE OBSERVED MOLECULAR WEIGHT	AVERAGE NUMBER OF STRUCTURAL UNITS PER MOLECULE	PHYSICAL PROPERTIES
Tetramethylene carbonate....	$—O—(CH_2)_4—O—CO—$	7	1400	11–12	Microcrystalline powder, m.p. 59°
Pentamethylene carbonate....	$—O—(CH_2)_5—O—CO—$	8	2700	20–22	Microcrystalline powder, m.p. 44–46°
Hexamethylene carbonate.....	$—O—(CH_2)_6—O—CO—$	9	2800	18–21	Microcrystalline powder, m.p. 55–60°
Decamethylene carbonate.....	$—O—(CH_2)_{10}—O—CO—$	13	1800	8–10	Microcrystalline powder, m.p. 55°
Ethylene succinate...........	$—O—(CH_2)_2—O—CO—(CH_2)_2—CO—$	8	3000	20	Microcrystalline powder, m.p. 108°
Ethylene adipate.............	$—O—(CH_2)_2—O—CO—(CH_2)_4—CO—$	10	2900	17	Microcrystalline powder, m.p. 50°
Hexamethylene succinate.....	$—O—(CH_2)_6—O—CO—(CH_2)_2—CO—$	12	3400	14	Microcrystalline powder, m.p. 57°
Ethylene sebacate............	$—O—(CH_2)_2—O—CO—(CH_2)_8—CO—$	14	4000	13	Microcrystalline powder, m.p. 79°
Trimethylene sebacate........	$—O—(CH_2)_3—O—CO—(CH_2)_8—CO—$	15	3100	12	Microcrystalline powder, m.p. 56°
Decamethylene adipate.......	$—O—(CH_2)_{10}—O—CO—(CH_2)_4—CO—$	18	3000	10	Microcrystalline powder, m.p. 77°
Decamethylene sebacate......	$—O—(CH_2)_{10}—O—CO—(CH_2)_8—CO—$	22	3000	8	Microcrystalline powder, m.p. 74°

Ethylene phthalate	$—O—(CH_2)_2—O—CO—C_6H_4—CO—$	8	4800	25	Hard, transparent resin
Trimethylene phthalate	$—O—(CH_2)_3—O—CO—C_6H_4—CO—$	9	3100	14	Soft, transparent resin
Hexamethylene phthalate	$—O(CH_2)_6—O—CO—C_6H_4—CO—$	12	1800	7	Soft, transparent gum
Decamethylene phthalate	$—O—(CH_2)_{10}—O—CO—C_6H_4—CO—$	16	2100	7	Very viscous, transparent sirup
Trimethylene oxalate	$—O—(CH_2)_3—O—CO—CO—$	7	2000	15	Microcrystalline powder, m.p. 88°
Hexamethylene oxalate	$—O—(CH_2)_6—O—CO—CO—$	10	1100	7	Microcrystalline powder, m.p. 66°
Decamethylene oxalate	$—O—(CH_2)_{10}—O—CO—CO—$	14	1200	6	Microcrystalline powder, m.p. 79°
Polyester from hydroxydecanoic acid	$—O—(CH_2)_9—CO—$	11	5000	20	Microcrystalline powder, m.p. 76° (30)

Similar acidic esters of lower molecular weight have also been obtained by partial esterification of glycol with an excess of succinic acid and fractional crystallization of the product. The observed molecular weights and neutral equivalents of the fractions corresponding to various values of x in formula I are indicated in table 2.

The presence of these terminal groups proves that the esterification of succinic acid by ethylene glycol is intermolecular at every stage.[10] The reaction evidently involves a series of condensations resulting in the production of ester molecules of progressively greater length. The first product might be

TABLE 2

Acidic ethylene succinates

FORMULA	MELTING POINT	MOLECULAR WEIGHT		SODIUM SALT	
		Calculated from neutralization equivalent	Found by ebullioscopy	Melting point	Molecular weight calculated from sodium content
	°C.			°C.	
I a	73	1020	1070	91	1030
I b	82	1340	1380	97	1460
I c	90	1800	1580	100	2010
I d	98	3400	3110	109	3740

$$HO(CH_2)_2OCO(CH_2)_2COOH,$$

and the second

$$HO(CH_2)_2OCO(CH_2)_2COO(CH_2)_2OCO(CH_2)_2COOH.$$

Moreover, since both glycols and dibasic acids have a tendency to esterify at both ends simultaneously, it is reasonable to suppose that similar chains will be present, some of which are terminated

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[10] Lycan and Adams (30) also present convincing evidence of the open chain structures of polyesters derived from ω-hydroxydecanoic acid. They isolated fractions whose molecular weights estimated by titration with alkali ranged from 1000 to nearly 9000. All of these fractions formed potassium salts which were completely soluble in warm water.

at both ends by carboxyl and others by hydroxyl. It is evident that an exceedingly large number of species may be involved in the ester equilibrium.[11] But as the amount of water participating in the equilibrium is diminished by its constant removal, the smaller molecules are forced to couple with each other until finally practically none of them remains. A further simplification of the kinds of molecular species present in the product is effected by using an excess of glycol, since this makes all the terminal groups alike. For this purpose, it makes no difference how large an excess of glycol is used, provided the reaction mixture is finally heated for some time in a high vacuum, since under these conditions the reaction can be propagated by ester interchange. Thus it is possible to isolate the monomeric ester, *bis*-β-hydroxyethylsuccinate,

$$HO—(CH_2)_2—O—CO—(CH_2)_2—CO—O—(CH_2)_2—OH,$$

and this on being heated to 200°C. in a vacuum loses glycol and is converted into the neutral polyethylene succinate of molecular weight 3000 already described. In view of this fact it is obvious that the accidental mutilation of the terminal groups (e.g., the loss of OH or CO_2) cannot in itself prohibit the progress of the coupling; the reaction can progress by ester interchange involving the last ester linkage.

Apparently the ultimate factors that set the attainable limit on the length of polyester molecules are purely physical. As the molecular weight becomes greater, the reaction product becomes more viscous and the rate of diffusion of the volatile product (water or alcohol) to the surface becomes slower and slower.[12] Moreover as the reaction progresses, the mobility of the reacting molecules diminishes and the relative concentration of the reactive groups becomes smaller. All of these factors affect the rate and some of them affect the position of equilibrium, but the molecular weight at which a practical limit is reached will depend upon the

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[11] The kinetics of the reaction between phthalic anhydride and ethylene glycol have been studied by Kienle and Hovey (43).

[12] At least in the crystalline state polyesters adsorb water and hold it very tenaciously.

temperature and pressure, the area and thickness of the reacting mass, etc., and by a suitable adjustment of these factors it is possible to obtain polyesters having very much higher molecular weights than those listed in table 1 (51).

2. Bifunctional Wurtz reactions and Friedel Crafts reactions

The action of sodium on polymethylene bromides, $Br(CH_2)_xBr$, leads in certain cases to the formation of cyclic hydrocarbons. Cyclopropane, cyclopentane, and cyclohexane have been prepared in this way. On the other hand, the action of sodium on decamethylene bromide does not yield any cyclic hydrocarbons.

In the presence of absolute ether this reaction proceeds very smoothly (44, 45). The product, which is for the most part insoluble in ether, consists of a complex mixture formed by the coupling of various numbers of molecules of the halide with each other, e.g.,

$$Br(CH_2)_{10}Br + 2\ Na + Br(CH_2)_{10}Br + 2\ Na + Br(CH_2)_{10}Br \rightarrow$$
$$Br(CH_2)_{30}Br + 4\ NaBr.$$

At the same time, owing to the participation of the ether in the reaction, most of the terminal bromine atoms are replaced by hydrogen.[13] This reduction of the terminal groups can finally be carried to completion by the action of sodium in boiling butyl ether, and the product then consists of a mixture having the general formula

$$H{-}[(CH_2)_{10}]_x{-}H$$

in which the values of x range from 1 to at least 10. The various members of this mixture up to and including n-$C_{70}H_{142}$ can be separated and isolated in a state of purity by fractional evaporation in a molecular still followed by crystallization. The identity of these fractions is established by their melting points and their

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[13] In its mechanism the Wurtz reaction undoubtedly involves as its first step the formation of the sodium compound RNa (46). This normally couples with another molecule of the halide, but if ether is present it may be destroyed by the reaction

$$RNa + (C_2H_5)_2O \rightarrow RH + C_2H_4 + C_2H_5ONa\ (47).$$

x-ray diffraction patterns. There is no evidence of the presence of any materials in the mixture not belonging to the series

$$H—[(CH_2)_{10}]_x—H.$$

About 25 per cent of the total product consists of members standing above $C_{70}H_{142}$. These are not capable of being distilled, and they cannot be separated from each other by fractional crystallization. The average molecular weight of this material indicates that it must contain hydrocarbons at least as high as $C_{100}H_{202}$.

The following results of unpublished studies made by Dr. R. A. Jacobson in this laboratory are more or less closely related to those described above. The action of metallic sodium on *p*-dibromobenzene in absolute ether leads to a product corresponding in composition to the formula $Br—C_6H_4—(C_6H_4)_6—C_6H_4Br$. When the reaction is carried out in boiling toluene the product formed corresponds approximately in composition and molecular weight to the formula $Br—C_6H_4—(C_6H_4)_{12}—C_6H_4Br$. Both of these products are readily soluble in benzene. *p*-Xylylene bromide, $BrCH_2—C_6H_4—CH_2Br$, when treated with sodium in hot toluene, yields a very insoluble hydrocarbon which does not melt below 350°C. Apparently a very large number of *p*-xylylene units participate in this coupling.

Benzyl chloride in the presence of aluminum chloride or ferric chloride (see 10) reacts with itself to form resins of high molecular weight. This is evidently a bifunctional Friedel Crafts reaction involving the progressive coupling of successively longer chains with the elimination of hydrogen chloride. Depending upon the conditions of their formation these resins are fusible and soluble, or infusible and insoluble. Molecular weight values indicate that the fusible resins are formed from fourteen to twenty-five molecules of benzyl chloride. The infusible resins are no doubt much more highly polymeric. Benzyl fluoride in the presence of a trace of acid reacts very vigorously with itself in a similar manner (11).

3. *Other bifunctional reactions*

The number of possible types of condensation polymers is practically unlimited. Although very few of these possibilities have received any considerable study, the following examples at least indicate that the formation of such polymers is the usual result of bifunctional reactions when structural features preclude the formation of a five- or a six-membered ring.

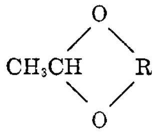
a. Polyamides. The acids $NH_2(CH_2)_3COOH$ and $NH_2(CH_2)_4COOH$ are readily dehydrated to the corresponding monomeric lactams (48). There is no record of either of these being caused to polymerize. The next higher member yields two products (49, 50a). One of these (20–30 per cent) is the lactam (seven-membered ring), a distillable crystalline material; the other is a polyamide, an undistillable hard, waxy material insoluble in most solvents except concentrated hydrochloric acid, phenol, and hot formamide. It can be hydrolyzed quantitatively to the amino acid. Molecular weight determinations indicate the presence of at least ten structural units in its molecule. The formation of this polymer is due to direct intermolecular condensation and the formation of the lactam is an independent reaction, for the latter cannot be polymerized under the conditions that lead to the production of the former. The acid $NH_2(CH_2)_6COOH$ on being dehydrated yields exclusively a product that is polymeric (50), although the corresponding monomeric lactam has been prepared by another method and is a stable substance (164). The acid $NH_2(CH_2)_{10}COOH$ also yields only polyamide (51).

A number of polyamides have been prepared by Dr. J. E. Kirby in this laboratory by the action of dibasic acids on aliphatic diamines. These materials are all much less soluble, and when crystalline have much higher melting points than the analogous polyesters (51).

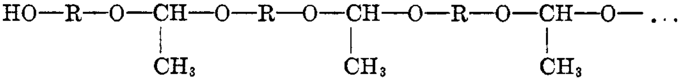
b. Polyamines. v. Braun observed (52) that the compound $NH_2(CH_2)_6Cl$, unlike its immediate lower homologs, when it reacts with itself yields only a very small amount of the volatile cyclic base. The chief product is an undistillable, waxy solid, but this has never been studied in detail.

The formation of quaternary ammonium salts from various compounds of the series $(CH_3)_2N(CH_2)_nBr$ has been studied (53). The products have been assumed to be cyclic monomers or dimers, but it still remains to be demonstrated that none of them are linear polymers.

c. Polyacetals. The reaction between glycols and acetaldehyde (or acetylene) presents the possibility of forming cyclic acetals,



or polyacetals



$$\mathrm{HO{-}R{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}R{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}R{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}O{-}\ldots}$$

This reaction has been studied by Hill and Hibbert (8). Ethylene and trimethylene glycols gave in excellent yields the cyclic acetals which are five- and six-atom rings. Tetramethylene glycol gave in poor yield a volatile compound which was apparently the monomeric cyclic acetal containing a seven-atom 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, but it may be assumed that the undistillable products are polymeric. An analogous compound prepared in this laboratory (51) from benzaldehyde and diethylene glycol had an apparent molecular weight of about 1370.

d. Polyanhydrides. Dibasic acids of the series $HOOC(CH_2)_x$-COOH are readily converted into the corresponding anhydridess. Malonic anhydride, the first member of the series, is polymeric (54). The next two members, succinic and glutaric anhydrides, are known only as the monomeric five- and six-membered rings. The anhydrides of all the higher acids are polymeric.[14] The

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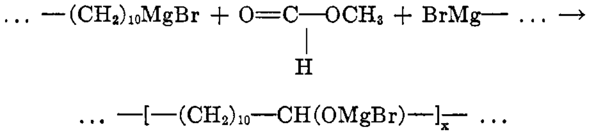
[14] The known examples are anhydrides of adipic, pimelic, suberic, azelaic, sebacic (55) and hexadecamethylene dicarboxylic (51) acids. These if monomeric would be respectively seven-, eight-, nine-, ten-, eleven-, and nineteen-membered rings. Adipic anhydride can be obtained in both a monomeric and a polymeric form (56).

monomeric anhydrides are macrocrystalline, readily distillable solids; the polymeric anhydrides are non-volatile microcrystalline powders or waxes, and they are less soluble than the monomeric anhydrides. Both types are very reactive, but qualitatively their chemical behavior is not the same. The monomers react with aniline to give pure monoanilide; the polymers give a mixture of acid, monoanilide, and dianilide in the ratio 1:2:1. This is precisely in accordance with the calculated behavior of a very long chain having the general structure.

$$CO{-}R{-}CO{-}O{-}CO{-}R{-}CO{-}O{-}CO{-}R{-}CO{-}O{-}\text{ etc.}$$

e. Grignard reactions. Bifunctional Grignard reagents such as $BrMg(CH_2)_5MgBr$ are capable of reacting with bifunctional reactants (dialdehydes, diketones, simple esters, etc.). The products may be rings or long chains. Several five- and six-atom rings have been prepared in this way, and in poor yield one seven-atom ring (57). In this laboratory it has been found (51) that decamethylene dimagnesium bromide reacts readily with methyl formate:



$$\ldots\ {-}(CH_2)_{10}MgBr + O{=}\underset{\displaystyle H}{\underset{|}{C}}{-}OCH_3 + BrMg{-}\ \ldots \rightarrow$$

$$\ldots\ {-}[{-}(CH_2)_{10}{-}CH(OMgBr){-}]_x{-}\ \ldots$$

The final product is a microcrystalline solid readily soluble in various organic solvents and melting at about 120°C. Its chemical and analytical behavior shows that it is the expected linear polyalcohol containing about eight of the structural units $-(CH_2)_{10}-CHOH-$.

In the formation of bifunctional Grignard reagents some coupling always occurs: dibromides of the formula $Br(CH_2)_nBr$ yield considerable amounts of $BrMg(CH_2)_{2n}MgBr$ and progressively smaller amounts of higher coupling products. It is a curious fact that this reaction does not occur intramolecularly even in the case of pentamethylene bromide where it would lead to the formation of a five-membered ring (154).

The coupling of simple Grignard reagents can be effected by the action of iodine, and this method has been applied by Grignard and Tcheoufaki to acetylene dimagnesium bromide (155). Products having the following formulas were isolated:

$$HC{\equiv}C{-}C{\equiv}CI;\ HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}I;$$

and also a form of carbon, which probably resulted from a continuation of the initial reaction in the same sense.

The attempt to prepare a Grignard reagent from *p*-xylylene bromide, $BrCH_2C_6H_4CH_2Br$, leads (51) to an insoluble hydrocarbon having the composition

$$(-CH_2C_6H_4CH_2-)_x.$$

The value of x is probably very large.

f. Sulfur and selenium compounds. The action of sodium sulfide on alkylene halides of the formula $X(CH_2)_nX$ leads to considerable yields of the expected cyclic products $(CH_2)_n{>}S$ only when these are five- or six-membered rings (162). Ethylene bromide gives white amorphous insoluble products (161); when prepared under certain conditions these are capable of being depolymerized by heat to yield the cyclic dimer, diethylene disulfide. Monomeric ethylene sulfide has been prepared by Delepine (86) by treating ethylene thiocyanate with sodium sulfide. It polymerizes spontaneously on standing. The chief product of the action of sodium sulfide on trimethylene halides is an amorphous polymer, although a small amount of the cyclic trimethylene sulfide can be obtained under certain conditions (87). Hexamethylene iodide also yields an amorphous polymer as the chief product (163, 87). v. Braun suggests that its formula is probably

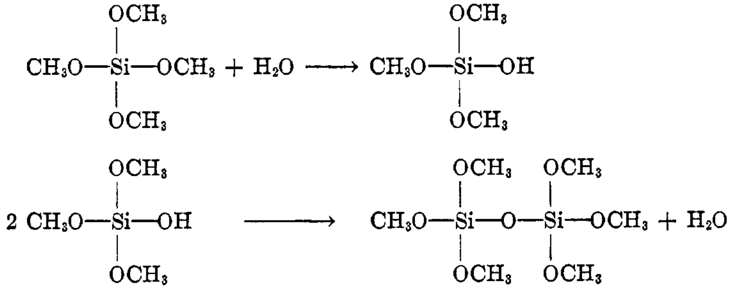
$$I(CH_2)_6 \cdot S \cdot (CH_2)_6 \ldots . S(CH_2)_6I,$$

but no estimates of its molecular weight have been presented.

The amorphous material formed from ethylene chloride and sodium sulfide is capable of being molded into a product which is very resistant to solvents and somewhat resembles rubber in its properties. One may infer that its molecular weight is very high. In recent patents (159) it is claimed that similar products can be obtained from alkylene halides generally.

Morgan and Burstall (160) state that the interaction of sodium selenide and the requisite alkylene dibromide leads readily to the production in good yields of cyclic seleno hydrocarbons containing five- or six-membered rings, but trimethylene bromide and sodium selenide give little cycloselenopropane. The main product is a sixfold polymer melting at 38–40°C.

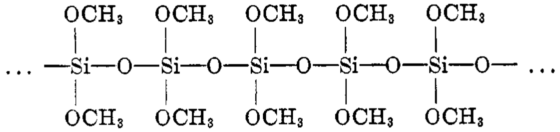
g. Miscellaneous. A curious spontaneous progressive coupling is found in the action of water on methyl orthosilicate. The reaction may be formulated as follows:



$$\mathrm{CH_3O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}OCH_3 + H_2O \longrightarrow CH_3O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}OH}$$

$$\mathrm{2\ CH_3O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}OH \longrightarrow CH_3O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}OCH_3 + H_2O}$$

Partial hydrolysis and coupling of this dimeric product lead to a tetramer, and so on. By suitably adjusting the initial ratio of water to ester it is possible to obtain samples representing various degrees of polymerization. The lower members have been isolated as chemical individuals by fractional distillation (156). The intermediate members are viscous undistillable liquids soluble in organic solvents. Solutions of these polymers are used in the preparation of paints having unusual properties (60). Films prepared from these paints harden by a continuation of the initial progressive hydrolysis and coupling, which yields as the final product pure silica. This synthesis incidentally furnishes an elegant proof of the three-dimensional polymeric structure of silica. The OCH_3 groups are responsible for the coupling, which results in the formation of long chains from the monomeric ester.

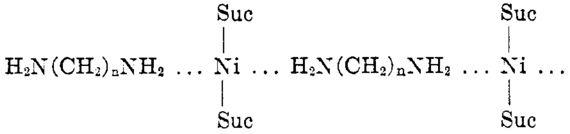


$$\mathrm{\ldots{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\underset{\underset{\textstyle OCH_3}{|}}{\overset{\overset{\textstyle OCH_3}{|}}{Si}}{-}O{-}\ldots}$$

Since each silicon atom in these chains still bears two OCH_3 groups, the coupling can continue in the other dimensions, yielding finally a three-dimensional lattice in which each silicon atom is joined (through oxygen) to four others.

Metallic sodium acts on compounds of the type R_2SiCl_2 yielding chain structures composed of $—SiR_2—SiR_2—$ groups (157). These products are for the most part amorphous and glue-like.

The specially pronounced tendency toward the formation of five- and six-membered rings is frequently manifested in complex coördination compounds (148) and complex formation frequently fails when it would involve the formation of larger rings. Ethylene and trimethylene diamine yield crystalline nickelotriene succinimide compounds of the formula $[\mathrm{Nien_3}]\mathrm{Suc_2}$ and $[\mathrm{Nitr_3}]\mathrm{Suc_2}$, but the compounds from tetra- and penta-methylene diamines are amorphous and, according to Tschugaeff (114), they must be represented as chains of unknown length:



$$H_2N(CH_2)_nNH_2 \ldots \underset{\underset{\mathrm{Suc}}{|}}{\overset{\overset{\mathrm{Suc}}{|}}{\mathrm{Ni}}} \ldots H_2N(CH_2)_nNH_2 \ldots \underset{\underset{\mathrm{Suc}}{|}}{\overset{\overset{\mathrm{Suc}}{|}}{\mathrm{Ni}}} \ldots$$

Bifunctional couplings probably occur in many reactions of oxidation and reduction. Busch and Schmidt have shown (22) that the catalytic reduction of aryl halides under some conditions proceeds to a considerable extent as follows:

$$2\ C_6H_5Br + 2\ H \rightarrow C_6H_5—C_6H_5 + 2\ HBr$$

When the same reaction is applied to *p*-diiodobenzene, terphenyl, $C_6H_5 \cdot C_6H_4 \cdot C_6H_5$, and *p*, *p*′-diphenyldiphenyl are obtained.

A preliminary stage in the oxidation of aniline to aniline black is the formation of long chains of the following type (20),

$$C_6H_5 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH_2.$$

In a similar way the oxidation of phenols may lead to the formation of polyphenylene ethers (21). Substituted polyphenylene ethers of high molecular weight are obtained by the condensation polymerization of silver salts of halogenated phenols (173).

4. Stereochemical factors involved in condensation polymerization

Bifunctional reactions always present the possibility of following two courses—they may lead to ring closure, or to progressive coupling—but the very numerous studies of such reactions have been concerned almost exclusively with ring closure. The possibility of progressive coupling has frequently been ignored or rejected as unlikely, and highly improbable cyclic structures have occasionally been assigned to products on the ground merely that they were the result of bifunctional reactions. In other cases the actual products have been discarded simply because they were obviously not the expected cyclic products. This attitude has certainly been partly responsible for the comparative meagerness of the literature on condensation polymers. The examples cited in the previous paragraphs show, however, that bifunctional reactions may proceed in a strictly normal fashion by progressive coupling and result in the formation of large molecules, and that, considering any particular homologous series, this type of reaction is the rule and ring closure is the exception.

This is not an especially astonishing conclusion. Intermolecular reaction is a perfectly general phenomenon; intramolecular reaction is a peculiar and special kind of happening. This is immediately evident from the consideration that if two groups are to react they must meet, i.e., they must approach each other very closely. If the groups are not present in the same molecules, such approach is always possible as long as the molecules are free to move about. But two groups, x and y, that are present at opposite ends of a single molecule are capable of approaching each other only if the architecture of the molecule permits, and even if such approach is permissible it does not necessarily follow that it will occur, or if it occurs that it will be effective. Meanwhile the x groups of this molecule are continually colliding with y groups of other similar molecules. From this standpoint progressive coupling in bifunctional reactions is inherently more probable, generally speaking, than ring closure, and the latter, if it occurs to the exclusion of the former, must be peculiarly favored by some special factors.

The reasons for the great difference in the relative ease with which different types of rings are formed has been the subject of much speculation, and two factors that have frequently been assumed to be of self-evident importance are the relative energy content of the rings and their stability or degree of strain. There is, however, no theoretical justification for this assumption (58), and the facts show that neither of these factors can possibly be decisive. Thus, the action of sodium on propylene bromide yields cyclopropane, not cyclohexane, although the latter has a much lower energy content per unit and is less highly strained than the former.

On the other hand spatial relations in the reacting compound must of necessity have a great influence on the possibility of ring formation. The atoms of the benzene ring, for example, and all the atoms joined directly to it lie in the same plane (59), and to link the two *para* positions of the ring together through a chain of less than four or five accessory atoms would require a very improbable degree of distortion. Many attempts have been made to bring about such linkings, but the supposedly successful examples have proved on reëxamination to be fictitious (62). The same thing is true (61) of alleged examples of ring closure through the p and p' positions of diphenyl.

The stereochemistry of simple aliphatic chains is a rather complicated matter. Ruzicka's discovery that large aliphatic rings are no less stable than small ones is impossible to reconcile with the Baeyer strain theory, and the latter has been superseded by the Sachse-Mohr theory (66) which permits the existence of large rings in non-planar and strainless forms and is supported by a great deal of other evidence besides. The essential assumption in the Sachse-Mohr theory is simply the usual one that the four valences of the carbon atom are directed toward the corners of a tetrahedron and that there is free rotation about each single bond in a chain. Space models embodying these features can easily be made by joining small wire tetrahedra with rubber tubing in such a way that the arms that are being connected overlap. Rings constructed with such models show graphically that a five-atom ring is uniplanar and free from strain; a six-atom ring is highly strained unless two of the atoms are allowed to lie in a different plane from the other four; larger rings if they are to exist must be multiplanar and strainless, and they possess a mobility which makes it possible for them to assume a great multiplicity of shapes.[15]

The variety of possible configurations of an open chain is much greater than in a ring and it increases rapidly with the length of the chain. In the crystals of fatty acids and paraffins the chains probably are rigidly extended into a zigzag structure (13); but a model of such a chain is exceedingly flexible and mobile, and it seems very improbable that in the liquid condition or in solution the molecules retain their rigidly extended form. No doubt certain possible configurations are more probable than others, but there is at present no means of knowing just what these are.[16] It is clear, however, that the relative probability of close approach of the ends of a chain diminishes very rapidly as the length of the chain increases. Owing to the fewness of their separate points of rotation, five- and six-atom chains can assume relatively few configurations. In fact, if a space model of such a chain is supported at one of the bonds the entire structure can be rotated in such a way that the freely moving and unsupported ends collide at each rotation. This shows that there is a certain inevitability in the closure of such chains. Longer chains on the other hand can assume an extraordinary multiplicity of shapes without any close approach of the ends. The ends of the model can be brought together arbitrarily without any resistance, but as Mohr has pointed out (66) in the molecule itself one is dependent upon

[15] Apparently the shape that they actually tend to assume involves the close approach of opposite sides of the ring; the ring consists essentially of two parallel chains joined at the end (67, 144, 145).

[16] Attempts to decide this question by studies of x-ray diffraction (88), electric moment (63), ionization constant (65), and numerous other properties (143) have led to the following rather contradictory conclusions: (*a*) the chains are straight zigzags; (*b*) they are straight zigzags except for the five-atom chain which is coiled; (*c*) they have a helicoidal configuration which brings the first and fifth atoms very close together and introduces an anomaly in properties when the length of the chain is five, ten, or fifteen atoms. None of these configurations provides any mechanism for the close intramolecular approach of the ends of chains longer than six atoms.

random collision,[17] "which will bring about a given form the more rarely the more forms are possible, i.e., the longer the chain."

One obvious and important implication of this theory is that a cyclic strucure for linear high polymers is very improbable. The formation of such polymers usually depends upon the absence of any tendency toward ring closure in the early stages of the coupling, and the probability of ring closure will diminish as the length of the chain increases. This implication is also in accord with the facts. It is true that cyclic formulas have been assigned to various high polymers by Staudinger and by other investigators, but none of these formulas has been established.[18] On the other hand, in a variety of instances open chain structures have been experimentally proved.

The presence of substituents and the nature of the terminal groups may be expected to modify the stereochemical behavior of chains. Thus, if two atoms of 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

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[17] It seems quite possible that this dependence upon random collision is not inherently necessary. It may be that some selective control over molecular form is possible by the use of the orienting effects at surfaces, and such factors may perhaps come into play in the synthesis of large rings in nature. This suggests the possibility of some very interesting studies of a novel kind in surface chemistry.

[18] In this connection merely negative evidence, e.g., the failure to detect terminal groups, is worthless. Terminal groups may become lost or mutilated, or they may be present and yet fail to react. High polymers are frequently very sluggish in their chemical behavior.

The tendency to resort to cyclic formulas does not aid in clarifying the problems of high polymers. One can assume that the rubber molecule is an enormously large ring, but rubber is very susceptible to degradation by oxygen, heat, mechanical action, etc., and the first step in such degradation must cause the ring to be ruptured. This product then presents all those problems which the assumption of a cyclic structure was designed to evade.

It seems evident that all polymerizations, whatever their mechanisms, must be progressive stepwise reactions. The simultaneous combination of 100 molecules presents insuperable kinetic difficulties. If this view is correct, ring closure can occur only as the last step in the reaction chain. But at this stage the ends of the chain must be more remote from each other than at any earlier stage, and the opportunities for ring closure must be at a minimum.

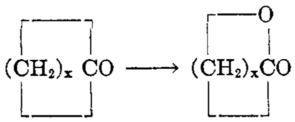
one more axis of rotation than the former.) It is not surprising therefore that the majority of the known seven- and eight-membered rings have at least two of their atoms members of a benzene ring. The compound $NH_2(CH_2)_6Cl$ reacts with itself intramolecularly only to a slight extent, while with o-$NH_2C_6H_4(CH_2)_4Cl$ ring closure is almost quantitative (68). Other similar examples might be cited (50, 163).

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. Researches in the diphenyl series (69) have established that substituent groups suitably placed may completely inhibit rotation about a nearby single bond, and a similar effect in aliphatic chains is at least conceivable. Almost 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 influence of the nature of the terminal groups is seen in the fact that ω-hydroxy acids on dehydration give both lactone and polyester, while attempts to prepare seven-atom cyclic esters from dibasic acids and dihydric alcohols yield only polyesters. Dilution also may be expected to favor ring formation as compared with progressive coupling (70), but all these effects are comparatively small.

a. Large rings. The question arises whether large rings are ever formed as the normal primary products of bifunctional reactions. Meyer and Jacobson in their textbook (147) devote over fifteen hundred pages to five- and six-membered heterocyclic compounds and only seventeen pages to all larger rings. Most of the examples of this class of compounds that they accept as authentic fall into one or more of the following types: the ring contains only seven or eight atoms; two or more atoms of the ring are members of a benzene nucleus; the yields are very poor; the compound is formed by ring widening. There remain a few examples (e.g., the cyclic duplomercaptal derived from acetone and pentamethylene dimercaptan) in which the evidence for a very large cyclic structure is good; but this evidence is no better than that on which the sixteen-membered cyclic formula for ethylene succinate was based (41), and ethylene succinate when reëxamined (32, 34) proved to be a linear polymer of high molecular weight.

Concerning the identity of large rings described by Ruzicka, it is not possible to entertain any doubt at all, but the methods required for the preparation of these materials present some illuminating peculiarities. His lactones were obtained from the corresponding cyclic ketones by oxidation (25),



$$(CH_2)_x\ CO \longrightarrow (CH_2)_xCO$$

i.e., the ring was already established in the starting material. All attempts to prepare the lactones by a bifunctional reaction, e.g., from the hydroxy acids or from the silver salts of the bromo acids were unsuccessful. The ketones themselves (71) were obtained by heating the thorium salts of the dibasic acids to a very high temperature (400–500°C.). These conditions of violence lead to thermal rupture, and, whatever the primary products may be, the ultimate products must, for the most part, be volatile materials of fairly low molecular weight. The cyclic ketones are found mixed with a great variety of other materials among these volatile products. It is at least conceivable that the primary products in this reaction are linear polyketones and that the cyclic ketones are thermolysis products of the polymer.

In this connection it is interesting that large heterocyclic rings can also be obtained by thermolysis of the polyesters. Thus when polyethylene succinate is heated to 300°C. in a vacuum, it decomposes and yields a carbonaceous residue and a gaseous and liquid distillate. From the latter a small amount of the sixteen-membered cyclic dimer can be obtained. Similar cyclic products have been obtained from tetramethylene carbonate, from trimethylene oxalate and from the potassium salt of the acetyl derivative of hydroxydecanoic acid. The anhydride of sebacic acid can also be depolymerized under certain conditions to a cyclic dimer. The properties of these compounds are listed in

TABLE 3

Large cyclic esters and anhydrides

COMPOUND	FORMULA	ATOMS IN RING	MELTING POINT °C.	REFERENCES
Ethylene succinate	$O(CH_2)_2OCO(CH_2)_2CO—O(CH_2)_2OCO(CH_2)_2CO$	16	130	42, 34
Tetramethylene carbonate	$O(CH_2)_4OCO—O(CH_2)_4OCO$	14	173	33
Trimethylene oxalate	$O(CH_2)_3OCOCO—O(CH_2)_3OCOCO$	14	176	64, 35
Dimeric lactone of ω-hydroxydecanoic acid	$O(CH_2)_9CO—O(CH_2)_9CO$	22	95.5	30
Dimeric sebacic anhydride	$OCO(CH_2)_8CO—OCO(CH_2)_8CO$	22	68	51

table 3. Their identity is established by analytical data and repeated molecular weight determinations. They are distinguished from the corresponding polymers by their definite macrocrystallinity and relatively great solubility. The attempts to obtain corresponding monomers which would be seven-, eight-, and eleven-membered rings have been unsuccessful. It seems possible that this failure may be due to purely practical difficulties, but so far as the data go they are in agreement with the fact that Ruzicka found the yields of the cyclic ketones of eight to twelve atoms to be much less than the yields of the larger rings. This fact is not easy to explain on the basis of the simple Sachse-Mohr theory presented above. A possible explanation has recently been offered by Stoll and Stoll (67).

III. POLYMERIZATION INVOLVING CYCLIC COMPOUNDS

1. Six-membered cyclic esters

Among cyclic esters the property of undergoing reversible polymerization is characteristic of and peculiar to the six-membered rings. γ-Butyrolactone cannot be polymerized, and no corresponding polyester is known. Higher lactones, e.g.,

$$\underline{[\mathrm{O{-}(CH_2)_{15}{-}CO}]},$$

are stable substances which show no tendency to polymerize spontaneously, although polymers are the only products of the self-esterification of the corresponding hydroxy acids. On the other hand, δ-valerolactone, a mobile liquid, gradually changes on standing to an opaque solid polymer, and from this the lactone can be regenerated by heating.

Various isolated examples of the polymerization of the six-membered esters have been reported, but only a few of them have been described in any detail. In this laboratory some study (mostly unpublished) has been made of the mechanism of this phenomenon.

The esters now known to exhibit this behavior are listed in table 4. (In most cases neither the molecular weights nor the melting points of the polymers can be regarded as very significant,

TABLE 4

Six-membered cyclic esters and their polymers

MONOMER	FORMULA	MONOMER		POLYMER		REFERENCES
		Melting point	Molecular weight	Melting point	Molecular weight	
		°C.		°C.		
δ-Valerolactone	$\left[\underline{\mathrm{O(CH_2)_4CO}}\right]$	Liquid	114	52–53	2180	72, 51
α-Propyl-δ-valerolactone	$\left[\underline{\mathrm{O{-}(CH_2)_3CH(C_3H_7)CO}}\right]$	Liquid	142	Sirup	1000	51
Lactone of hydroxyethylglycolic acid	$\left[\underline{\mathrm{O(CH_2)_2OCH_2CO}}\right]$	31	102	62–64, 87–89	460, 1700	73, 51
2,3,4-Trimethyl-arabonolactone	$\left[\underline{\mathrm{OCH_2[CH(OCH_3)]_3CO}}\right]$	45	170	135–138	2000	74
Ethylene oxalate	$\left[\underline{\mathrm{O(CH_2)_2OCOCO}}\right]$	143	116	159, 172	2300, insoluble	35
Propylene oxalate	$\left[\underline{\mathrm{OCH_2CH(CH_3)OCOCO}}\right]$	142	130	176–180	Insoluble	35
Trimethylene carbonate	$\left[\underline{\mathrm{O(CH_2)_3OCO}}\right]$	47	102	Glassy	4000	33
Glycolide	$\left[\underline{\mathrm{OCH_2CO{-}OCH_2CO}}\right]$	86	116	223	Insoluble	75, 76
Lactide	$\left[\underline{\mathrm{OCH(CH_3)CO{-}OCH(CH_3)CO}}\right]$	125	144	Resin	3000	77, 51

since both are dependent upon the conditions under which the polyester is formed.)

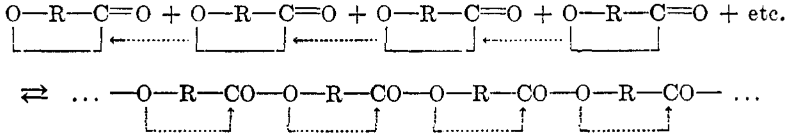
Some of these examples present special features worthy of mention. Monomeric trimethylene carbonate is a very soluble, crystalline solid. If it is heated with a trace of potassium carbonate to 130°C. for a few minutes, the mobile melt suddenly becomes very viscous and evolves a small amount of gas. The colorless sirup on being cooled solidifies to a stiff mass which shows an apparent molecular weight of about 4000. When heated in a vacuum this mass distils almost quantitatively, and the distillate consists of pure monomer.

Ethylene oxalate is a solid crystallizing in transparent, flat diamonds, melting at 143°C. These on standing for a few days in a stoppered container disintegrate to a powder, which consists of a mixture of polymers. By extraction with cold solvents it can be separated into two definite fractions, one melting at 159°C. and having an apparent molecular weight of about 3000, and one melting at 173°C. and having an unknown but probably much higher molecular weight. These fractions on standing for a few days lose their identity; they are partly converted into each other and into monomer. It is interesting to note in connection with the rapidity of these transformations that monomeric ethylene oxalate is exceedingly sensitive to hydrolysis.

Drew and Haworth (74) have obtained the lactone of 2,3,4-trimethyl-*l*-arabonic acid in crystalline form (m.p. 45°C.) and have observed that in the presence of traces of hydrogen chloride it is converted into a crystalline polymeric powder. This has a considerably higher melting point, a lower solubility, and a lower specific rotation than the lactone. Its molecular weight (about 2000) indicates that it is derived from about ten molecules of the latter. At 175°C. it distils completely *in vacuo,* and the distillate consists of pure lactone. Drew and Haworth ascribed a linear polyester structure to this polymer and were inclined to accept its crystallinity as evidence of its absolute homogeneity, but it seems much more probable that it is a polymeric mixture.

The ease of polymerization of the six-membered cyclic esters appears to be related to their susceptibility to hydrolysis. In general, substitution increases the resistance to hydrolysis and diminishes the tendency to polymerize. Thus glycolide polymerizes spontaneously at the ordinary temperature, but lactide only on being heated or exposed to the action of catalysts. Attempts (51) to bring about the polymerization of analogs of glycolide derived from some of the higher α-hydroxy fatty acids have been unsuccessful.

These polyesters are formed from the monomers by a process of ester interchange.

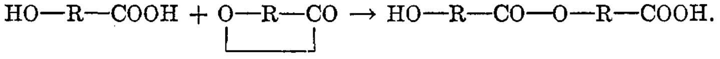


$$O-R-C=O + O-R-C=O + O-R-C=O + O-R-C=O + \text{etc.}$$

$$\rightleftarrows \ldots -O-R-CO-O-R-CO-O-R-CO-O-R-CO- \ldots$$

and the reverse transformation proceeds by a similar mechanism, as indicated by the arrows. Both transformations are catalyzed by acids and bases—typical interchange catalysts.

Direct evidence for this interchange mechanism is found by polymerizing δ-valerolactone in the presence of various amounts of chloroacetic acid (51). This acid actually participates in the reaction, and according to the amount present it regulates the length of the chains produced. The effect of the acid may be compared with that which water might produce. One molecule of water with one molecule of the lactone would simply yield the hydroxy acid. A smaller amount of water would yield some hydroxy acid and this might react with the lactone to form a dimeric ester:



$$HO-R-COOH + O-R-CO \rightarrow HO-R-CO-O-R-COOH.$$

If the amount of water were quite small the polyester molecule would have to be quite large. Apparently chloroacetic acid functions in precisely the same way, and a comparison of the halogen content and neutral equivalent of the polyesters produced under various conditions not only establishes the open chain structure of the polymer, but also clearly indicates the mechanism of the reaction.

It remains to explain why only the six-membered esters are capable of undergoing reversible transformation of this kind. The presence of some strain in such esters is indicated by the great instability of δ-lactones as compared with γ-lactones (78, 79). The Sachse-Mohr theory permits the existence of six-atom rings in two isomeric strainless forms; but in simple rings these two isomeric forms have never been realized, and one is forced to conclude either that such rings are uniplanar and hence highly strained, or that the two isomeric forms are in dynamic equilibrium. Practically this amounts to the same thing, since at each conversion the molecule must pass through the uniplanar position of strain. These strains can be relieved by an ester interchange resulting in the formation of the polyester. The easy depolymerization of the resulting polyester is readily explained by the high degree of probability of the close approach of points six atoms apart in a chain. Polyesters whose structural units are longer than six atoms are not readily depolymerized because of the improbability of close approach of the requisite atoms of the chain. Cyclic esters of five atoms or of more than six atoms are not polymerized because their cyclic systems are free from strain.

In the formation of six-membered cyclic esters from open chain compounds, either the monomer or the polymer may first be isolated according to the experimental conditions, but in either event it is not easy to prove that the form isolated is the primary product and not a polymerization or depolymerization product of the primary product. It seems fairly certain that simple δ-lactones may be formed directly from the corresponding hydroxy acids. On the other hand there is evidence (19) that the self-esterification of lactic acid yields only polylactyllactic acids and that lactide, when it is formed, is produced from these by depolymerization. Since lactide can itself be polymerized to a polylactyllactic acid, the latter furnishes an example of a polymer that can be formed either by addition or by condensation polymerization. In most cases, no doubt, either the cyclic ester or the polymer can be formed first depending upon the conditions.

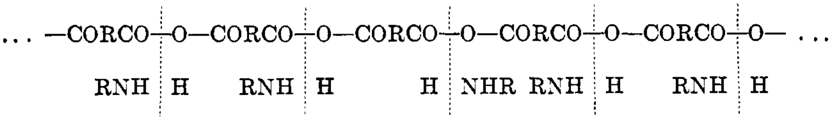
2. Adipic anhydride

The behavior of adipic anhydride (56) illustrates the fact that the property of undergoing reversible polymerization of this type is not peculiar to the polyesters. In this case it is the seven-atom ring that is unstable. Succinic and glutaric anhydrides, the five- and six-atom rings, cannot be induced to polymerize. Sebacic anhydride is polymeric and cannot be depolymerized to a monomer. Adipic anhydride, when it is prepared from the acid, is also polymeric. It is a waxy solid which separates from solvents as a microcrystalline powder. On being heated *in vacuo* it is depolymerized to a considerable extent, and distillation occurs. The distillate is the monomeric adipic anhydride, a liquid freezing at about 21°C. In the presence of traces of moisture this very rapidly reverts to the waxy polymeric form.

A direct chemical proof of the actual structural difference between the two forms of adipic anhydride is possible (56). Both forms react very rapidly with aniline. The monomer, since it contains in its molecule only a single anhydride linkage, can yield only the monoanilide and this is in fact the only product formed.

$$\left\lfloor\underline{\mathrm{CO(CH_2)_4CO{—}O}}\right\rfloor + \mathrm{C_6H_5NH_2} \rightarrow \mathrm{HO{—}CO(CH_2)_4CO{—}NHC_6H_5}.$$

But with the polyanhydride the nature of the final monomeric products will depend upon which side of the anhydride linkage is involved at successive steps:

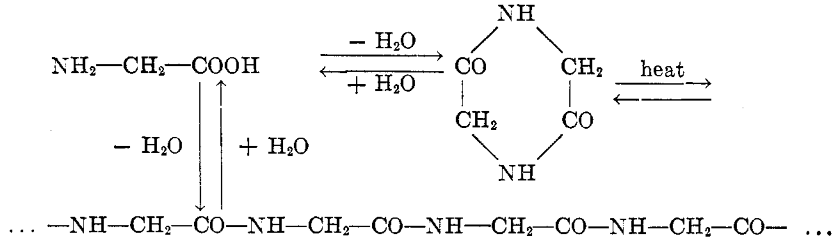


$$\begin{array}{cccccccccc} \ldots\ \mathrm{—CORCO} & \vdots\ \mathrm{—O—CORCO} & \vdots\ \mathrm{—O—CORCO} & \vdots\ \mathrm{—O—CORCO} & \vdots\ \mathrm{—O—CORCO} & \vdots\ \mathrm{—O—}\ \ldots \\ \mathrm{RNH} & \vdots\ \mathrm{H} \quad \mathrm{RNH} & \vdots\ \mathrm{H} \quad \mathrm{H} & \vdots\ \mathrm{NHR} \quad \mathrm{RNH} & \vdots\ \mathrm{H} \quad \mathrm{RNH} & \vdots\ \mathrm{H} \end{array}$$

If the molecule is infinitely long, i.e., if it is so long that the terminal groups can be ignored, considerations of probability indicate that the product will be 50 per cent monoanilide, 25 per cent dianilide, and 25 per cent acid. Within the experimental error these are the yields actually obtained. This indicates that the molecule must be made up of at least ten or fifteen structural units. A cyclic polymer would of course give the same result, but a low molecular weight is excluded by the properties of the material, and a cyclic structure of any kind is made improbable by considerations already discussed.

3. Diketopiperazines and polypeptides

The curious behavior of the α-hydroxy acids is especially interesting in connection with the structure and formation of proteins, since these are for the most part derived from α-amino acids. If glycine were to behave like glycolic acid, the following transformations could be realized.



It appears that diketopiperazine can be polymerized, though with some difficulty (83), and polypeptides are readily obtained by the self-condensation of glycine and its esters.

Balbiano (80) in 1900 showed that when glycine is heated in glycerol solution it loses water and yields as the principal product a horn-like mass, together with a small amount of diketopiperazine. The horn-like material is practically insoluble in all solvents except hot concentrated hydrochloric acid, and by hydrolysis it is converted to glycine. Later this reaction was studied in more detail by Maillard (81), who showed that according to the conditions and time of heating more or less of the dimeric anhydride or the horn-like polymer can be obtained. He also isolated an intermediate individual, triglycylglycine,

$$NH_2—CH_2—CO—NH—CH_2—CO—NH—CH_2—CO—NH—CH_2—COOH.$$

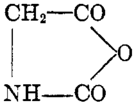
This polypeptide is soluble in water, and Maillard made the curious observation that if its aqueous solutions contain diketopiperazine they deposit on standing an insoluble material. Analytical evidence indicated that this material is a hexapeptide.

Except for the solubility effect in aqueous solutions there is no obvious reason why this coupling of the diketopiperazine with the polypeptide should stop at the hexapeptide stage. In glycerol solution one may suppose that it continues progressively and results in the building up of a very long chain. The final horn-like product would then be a polypeptide containing a very large number of structural units—perhaps forty or more. Maillard assigns to this horn-like polymer the structure of a cyclopolyglycylglycine, but no convincing proof of the cyclic formula is presented, and on general grounds an open chain formula seems more probable.

The production of glycine anhydrides in glycerol solution probably involves the formation of glyceryl esters as transitory intermediates, but diketopiperazines and polypeptides can also be obtained by heating amino acids in the absence of a solvent. Curtius and Benrath (82) state that at high temperature the chief product from glycine is a pentapeptide.

The esters of glycine couple with themselves much more readily than the free acid. Curtius (84) showed that glycine ethyl ester loses alcohol even at the ordinary temperature. When water is present the chief product is diketopiperazine, but some polypeptide ester is formed at the same time. Under anhydrous conditions the latter is the chief product. When glycine ethyl ester is dissolved in a little dry ether and allowed to stand at the ordinary temperature, a crystalline precipitate gradually accumulates. This consists almost exclusively of the ethyl ester of triglycylglycine. The esters of such polypeptides are of course capable of coupling with themselves to form still longer molecules. Fischer (85) observed that when the methyl ester of alanylglycylglycine is heated to 100°C. it yields some hexapeptide ester and some less soluble amorphous material. Curtius (84) found that when his triglycylglycine ester was heated to 100°C. *in vacuo* it was converted into an insoluble infusible material having the composition —$NHCH_2CO$—. He assigned to this material the structure of a cyclic octapeptide, but a much more highly polymeric open chain structure seems more probable.

In connection with the polypeptides the behavior of the anhydrides of the N-carboxy amino acids may be mentioned (89). The compound



dissolves readily in water at 0°C. At 15°C. carbon dioxide is evolved and an aqueous solution of glycine results. If, however, the compound is rubbed with a little water at room temperature or is heated, carbon dioxide is lost immediately and an insoluble infusible material is the only other product. This has the composition —$NHCH_2CO$— and on hydrolysis it yields glycine. It appears to be similar to the horn-like product obtained by Balbiano (80). It is quite probably a polypeptide of very high molecular weight. The anhydrides of other N-carboxy α-amino acids behave in a similar fashion (90).

4. Ethylene oxide (14, 15)

Ethylene oxide provides another example of the polymerization of a cyclic compound not involving double bond unsaturation. The polymerization is induced by various catalysts such as alkali metals, tertiary amines, and stannic chloride. Ultraviolet light or Florida earth is not effective. The product is a solid readily soluble in water and in most organic solvents except ether. Its properties vary somewhat according to the method of preparation. By fractional precipitation it can be separated into fractions ranging in apparent molecular weight from about 400 to nearly 5000. The lowest member of this series is liquid and the highest one a solid melting at about 59°C. The polyethylene oxides are not depolymerized by heat; but above 300°C. they decompose and yield a complicated mixture of products containing some acetaldehyde and acrolein. Roithner (15) assigns to polyethylene oxide the following formula,

$$\underline{[O—CH_2—CH_2—O—CH_2—CH_2— \dots —O—CH_2—CH_2]}$$

but the evidence for this structure is largely negative. Unpublished work in this laboratory has led to the detection of terminal hydroxyl groups, indicating that the molecule is an open chain.

Ethylene oxide also polymerizes under certain conditions to yield dioxane (16). Apparently this shows no tendency to polymerize further as the six-membered cyclic esters do.

IV. ADDITION POLYMERIZATION OF UNSATURATED COMPOUNDS

This is the only type of polymerization that is recognized by the usual definitions. Thus Cohen states (91) that "the property of undergoing polymerization is peculiar to unsaturated compounds, from a natural tendency to saturate themselves." So far as the formation of materials of high molecular weight is concerned, such reactions are much less clear-cut than bifunctional condensations, for the latter involve only the application of the known reactions of typical functional groups, and the general structural plan of the product may be inferred directly from the structure of the starting materials. On the other hand, no clue to the intimate details of the mechanism of self-addition can be found in the reactions of the compound concerned with any compounds other than itself. Ethylene oxide and certain cyclic esters and anhydrides already discussed polymerize by self-addition, but these reactions in some respects are radically different from the polymerization of compounds containing multiple linkages.

Under sufficiently drastic conditions almost any compound can be converted into a material of high molecular weight. Thus methane when subjected to the action of alpha particles or to the silent electrical discharge is partly transformed with loss of hydrogen into higher hydrocarbons (165), and benzene in the electrodeless discharge is converted into insoluble, amorphous products (166). The reaction of acetylene with itself illustrates how complicated the polymerization of an unsaturated compound may be. Polymerization at elevated temperature in the presence of active charcoal leads to a complicated mixture of hydrocarbons containing considerable amounts of benzene and naphthalene (167); the use of copper- or magnesium-containing catalysts yields (168) a completely insoluble amorphous powder (cuprene) of unknown structure, and similar products are obtained by the action of ultra-violet light (169), cathode rays (170), or alpha particles (171) on acetylene. On the other hand, the action of the silent electrical discharge (172) at low temperature leads to the formation of considerable amounts of liquid products which contain highly unsaturated open chain compounds.

The brief discussion of addition polymerization contained in the following paragraphs is confined to a few of the simplest and most thoroughly studied cases.

1. *Ethylene and other olefines*

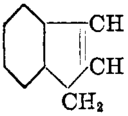
The rather extensive literature on the polymerization of ethylene has recently been reviewed by Stanley (92). Ethylene polymerizes less readily than most of its homologs and derivatives. The polymerization is accelerated by heat, pressure, ultra-violet light, the silent electric discharge, and by certain catalysts such as sulfuric acid (especially in the presence of salts of copper and mercury), zinc chloride, boron trifluoride, and aluminum fluoride. The products are usually oils having a wide boiling range. In general, they are not exclusively of the C_nH_{2n} type; hydrogenation, dehydrogenation, and cyclization may occur at the same time. These products are commercially valuable, but too complicated to furnish any clue as to the mechanism of their formation.

Mignonac and Saint-Aunay (93), however, have succeeded in isolating the first products formed in the action of the silent electrical discharge on ethylene. These products are butene-1 and hexene-1. Pease (94) has found evidence of the presence of butene-1 in the products of the thermal polymerization, and from a study of the kinetics has concluded that this is a chain reaction. In effect at least this reaction involves at the first step the addition of ethylene, as $H + CH{=}CH_2$, to the double bond of another molecule of ethylene, and then a similar addition to butylene.

Lebedev and his collaborators (95) have presented interesting data on the early stages of the polymerization of isobutylene. They used especially Florida earth as a catalyst and obtained mixtures from which a whole series of polymers up through the heptamers was isolated. They found that the trimer was not polymerized under the conditions that lead to higher polymers from either the monomer or the dimer. Hence the higher polymers must be built up by the successive addition of monomer or dimer. As to the precise structure of these polymers very little is known.

2. Vinyl compounds

Substituted ethylenes of the type $CH_2{=}CH{-}R$, in which R is a negative group, polymerize much more readily than does ethylene itself. Examples are:

$CH_2{=}CH{-}C_6H_5$	Styrene (96)
$CH_2{=}CH{-}Cl$ (Br)	Vinyl chloride (bromide) (97)
$CH_2{=}CH{-}O{-}COCH_3$	Vinyl acetate (98, 142)
$CH_2{=}CH{-}COOH$	Acrylic acid (99)
$CH_2{=}CH{-}CHO$	Acrolein (100)
	Indene (101, 105)

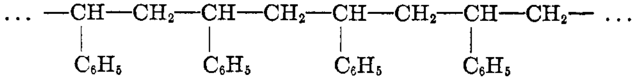
The most extensive and important studies of the polymerization of vinyl compounds are those carried out by Staudinger and his coworkers. The behavior of styrene may be taken as typical. On standing or on being heated, this mobile, volatile liquid first becomes more viscous, then changes to a more or less tough elastic jelly, and finally it may become converted into an exceedingly hard brittle mass. This change is powerfully catalyzed by light and by atmospheric oxygen, and it is inhibited by certain antioxidants such as hydroquinone. Other catalysts that are effective in accelerating the change are organic peroxides and certain metallic halides such as stannic chloride and antimony chloride. If a little stannic chloride is added to an alcohol solution of styrene, the solution becomes warm and the polystyrene quickly separates as an amorphous mass.

Polystyrene is not a definite material having a constant set of properties. By whatever method it is prepared it can be separated by fractional extraction or precipitation into fractions having the same composition but different properties and molecular weights. The lower members are readily soluble in ether and the highest members are quite insoluble. The apparent molecular weights range from 1000 up to 25,000 or more (perhaps as high as 200,000). All these fractions are soluble in benzene, and the viscosity of the solutions increases progressively with increasing molecular weight. The average molecular weight of the crude polymer depends upon the conditions of its formation. Those formed very rapidly, e.g., by the action of heat at high temperature or by the action of stannic chloride at ordinary temperature, have relatively low molecular weights. Those formed more slowly, e.g., by spontaneous polymerization at room temperature, have much higher molecular weights.

The polystyrenes having molecular weights above 10,000 show colloidal behavior; they swell before dissolving, and the viscosity of their solutions is very high. Nevertheless, there is considerable evidence to show that these solutions are true molecular dispersions (102), and that the molecule and the colloidal particle are identical.

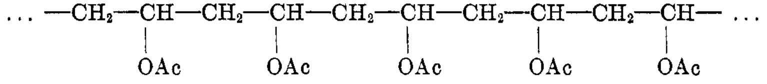
Chemically the polystyrols are completely saturated. They do not decolorize permanganate or absorb bromine. Under sufficiently drastic conditions they can be completely hydrogenated (in the benzene nucleus) without any significant change in molecular weight (103). On being heated to about 320°C. they revert to the monomer, styrene. It is doubtful if this reversion is ever quantitative.

The polymerization of styrene evidently involves the disappearance of the double bond and the formation of very large molecules. The simplest and most probable structure of these large molecules is that suggested by Staudinger.



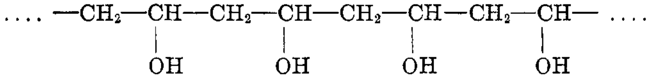
$$\ldots -\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2- \ldots$$

The polymerization of vinyl acetate is similar to that of styrene. In both cases the polymer first formed remains dissolved in the monomer, and the mixture of monomer and polymers can be obtained in the form of more or less tough, transparent, elastic masses. The chemical behavior of the polyvinyl acetate indicates that it is a mixture of molecules of various lengths built up according to the plan indicated in the formula



$$\ldots\ \text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OAc}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OAc}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OAc}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OAc}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OAc}}{\underset{|}{\mathrm{CH}}}\text{—}\ \ldots$$

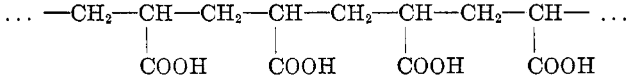
The number of molecules of monomer involved probably ranges between forty and one hundred. By fractional precipitation, samples of different average molecular weights can be obtained, and these naturally differ somewhat in their physical properties. In general the polyvinyl acetates are soluble in organic solvents but not in water. As esters they are readily hydrolyzed. The products are acetic acid and polyvinyl alcohol:



$$\ldots.\ \text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}\text{—}\ \ldots.$$

The latter as a polyhydroxy compound dissolves in water to form rather highly viscous solutions, but does not dissolve in organic solvents.

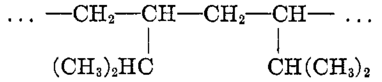
Acrylic acid also polymerizes very readily, yielding a product to which the following formula may be assigned.



$$\ldots\ \text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}\text{—}\mathrm{CH_2}\text{—}\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}\text{—}\ \ldots$$

As a highly polybasic acid it forms a sodium salt which dissolves in water to yield very viscous solutions. The acid itself also dissolves in water (the most highly polymeric varieties swell very strongly and dissolve with difficulty), but does not dissolve in the typical organic solvents. On the other hand, polyacrylic esters prepared by polymerizing acrylic esters are insoluble in water, but soluble in organic solvents.

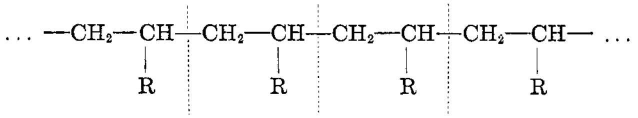
The methyl ester of polyacrylic acid on being treated with methyl magnesium iodide yields a product corresponding approximately in composition to the expected polytertiary alcohol, and this on reduction yields a hydrocarbon. Although the composition of this hydrocarbon does not exactly correspond to that required by the expected structure



$$\ldots -\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{(CH_3)_2HC}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CH(CH_3)_2}}}{\mathrm{CH}}- \ldots$$

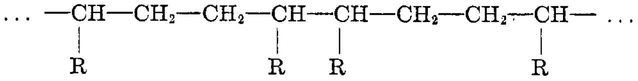
its high molecular weight proves that the ester from which it was derived is also really a material of high molecular weight, and that the units must be joined by carbon-carbon linkages.

The problem of arriving at a definite mechanism for the polymerization of vinyl compounds is complicated by the fact that neither the formation of the polymers nor their chemical behavior furnishes any certain clue to their structure. The general formula



$$\ldots -\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}} \vdots\, \mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}} \vdots\, \mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}} \vdots\, \mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}- \ldots$$

is perhaps more plausible than any other, since, as Staudinger has pointed out, it best accounts for the fact that some polyvinyl compounds (e.g., polystyrene) are smoothly depolymerized by the action of heat: the recurring substituent would weaken the linkages of the chain at the points indicated by the dotted lines. But depolymerization is never quantitative, and it is at least conceivable that a fraction of the units of each chain are arranged in the reverse fashion:



$$\ldots -\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}- \ldots$$

It has already been mentioned that the first step in the polymerization of ethylene is the formation of butene-1 and the second step is the formation of hexene-1. Similar terminal unsaturations have been found by Whitby and Katz in a still longer series of polyindenes, and this suggests that the most plausible mechanism for the polymerization of vinyl compounds is "best represented as proceeding stepwise by the addition regularly of successive molecules of monomer to the double bond present at each stage of the polymerization immediately preceding" (105). This mechanism may be formulated as follows:

$$RCH{=}CH_2 + RCH{=}CH_2 \rightarrow RCH_2CH_2C(R){=}CH_2$$

$$RCH_2CH_2C(R){=}CH_2 + RCH{=}CH_2 \rightarrow RCH_2CH_2CH(R)CH_2C(R){=}CH_2, \text{ etc.}$$

Staudinger disagrees with this view. He claims that the polyindenes do not have any terminal unsaturations, and from analogies based on the behavior of α-methylstyrene (104) he assigns a cyclic formula to polyindene and polystyrene. α-Methylstyrene, $CH_2{=}C(CH_3)C_6H_5$, polymerizes much less readily than styrene, but the reaction may be caused to occur quite rapidly by certain catalysts, e.g., stannic chloride (104). The principal product is the saturated dimer, a substituted cyclobutane. A smaller amount of a saturated trimer is formed at the same time, and in progressively smaller amounts saturated tetramer, pentamer, decamer, hexamer, heptamer, and octamer. On the basis of their physical and chemical properties Staudinger assumes that these higher polymers are respectively six-, eight-, ten-, twelve-, fourteen-, and sixteen-membered rings.

It should be observed however that these products are quite different from those obtained from styrene under similar conditions; moreover, the absence of the α-hydrogen makes it impossible for α-methylstyrene to polymerize by the mechanism suggested above for vinyl compounds generally. It is therefore scarcely permissible to conclude that the high polymers from styrene must be cyclic because the low polymers from α-methylstyrene are cyclic. Other more general grounds for rejecting cyclic formulas for linear high polymers have been presented in previous paragraphs.

The polymerization of vinyl compounds is enormously susceptible to catalytic and anticatalytic effects. Heat also accelerates the polymerization, and in general the more rapidly the polymer is formed, the lower is the average molecular weight of the product. Oxygen and peroxides are catalysts, and antioxidants act as inhibitors. Light, especially the shorter wave lengths of the visible spectrum, accelerates the polymerization. In certain cases the presence of oxygen inhibits this photochemical effect. With the aid of certain specific catalysts, it is possible to convert styrene and certain other vinyl compounds into dimers, but these are stable substances that show no tendency to polymerize further, and they differ structurally from the dimers that have been hypothecated as intermediates in the formation of the high polymers. Under conditions that result in the formation of the latter, no polymers of very low molecular weight can be detected. All these facts indicate that the formation of the high polymer is a chain reaction. The collision of an activated molecule of monomer with another molecule of monomer yields an active dimer capable of coupling with another molecule of monomer, and the activating energy persists in the polymeric chain until it has been built up to a considerable length. Kinetic studies of the polymerization of vinyl acetate (106) and styrene (107) support the idea of a chain mechanism.

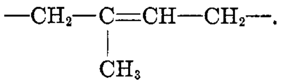
3. Dienes

Butadiene and isoprene are of especial interest in connection with rubber. Nobody knows whether in nature rubber is actually formed from isoprene or not; but it is true that rubber yields some isoprene on thermal decomposition, and that isoprene can be polymerized to a product which more or less resembles natural rubber. Similar products can also be produced from butadiene and from some of its derivatives. Efforts to produce synthetic rubber have led to hundreds of patents and various other publications. This subject is reviewed in a book by Schotz (108). There is space here to mention only two or three points.

Butadiene and isoprene polymerize much less readily than styrene, vinyl acetate, etc., but apparently they are subject to the same kind of accelerating influences. Among the catalysts that have been used are oxygen, peroxides, ozonides, alkali metals, alkali alkyls. When emulsified, especially in the presence of oxygen, they polymerize more rapidly than otherwise.

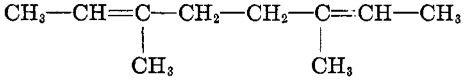
It is claimed in many patents that the presence of proteins, gums, etc., in such emulsions has a favorable effect on the course of the reaction and results in products more nearly resembling natural rubber, but it seems probable that the advantages of such additions are largely imaginary. It is possible to prepare from isoprene and butadiene high polymers that have very little resemblance to natural rubber, and the problem of preparing a synthetic rubber of good quality is enormously complicated and difficult.

The structural unit in the polymeric chain from isoprene appears to be

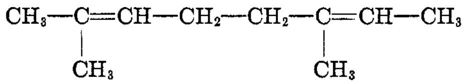


$$-CH_2-\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}=CH-CH_2-.$$

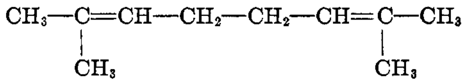
In effect, the polymerization involves the union of a large number of these radicals derived from isoprene by the rearrangement of its bonds. Two such radicals might unite in three ways: 1,1; 1,4; 4,4. Midgley and Henne (109) have captured the first step in the reaction by carrying out the polymerization in the presence of sodium and alcohol so that the terminal valences of the dimer are hydrogenated. The structures of the three products, whose formulas are shown below, prove that all three types of combination occur.



$$CH_3-CH=\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}-CH_2-CH_2-\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}=CH-CH_3$$



$$CH_3-\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}=CH-CH_2-CH_2-\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}=CH-CH_3$$



$$CH_3-\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}=CH-CH_2-CH_2-CH=\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}-CH_3$$

This result indicates that the arrangement of the units in synthetic rubber formed under these conditions is less regular than in natural rubber, but it by no means proves that the actual mechanism of the reaction consists in the direct union of radicals corresponding in formula with the structural unit. The 1,4 addition of H— + —$CH{=}C(CH_3)CH{=}CH_2$ to isoprene, for example, would lead to the same result.

4. Aldehydes

The polymerization of formaldehyde under various conditions leads to polyoxymethylenes. These are microcrystalline powders, which in general cannot be melted or dissolved in organic solvents without decomposition. They have been very elaborately studied by Staudinger and his coworkers (110). These studies have proved that the molecules of the polyoxymethylenes are long chains of the type

$$\ldots\ldots \text{—O—}CH_2\text{—O—}CH_2\text{—O—}CH_2\text{—O—}CH_2\text{—O—}CH_2\text{—} \ldots\ldots$$

The chains contain from forty to at least one hundred structural units. The different varieties of polyoxymethylenes are distinguished by the nature of the terminal groups: in the α-variety the terminal groups are OH; in the β-variety they are OCH_3, and this variety is more inert chemically than the α-variety. By the action of acetic anhydride, the polyoxymethylenes are simultaneously degraded and acetylated. The product consists of a mixture of compounds of the series $CH_3CO\text{—}(O\text{—}CH_2)_x\text{—}O\text{—}COCH_3$. By distillation and crystallization, each individual of this series from x = 1 to x = 20 has been isolated in a fairly pure state. The melting points and boiling points of these individuals increase continuously with increasing molecular weight and their solubilities diminish. The successive members above x = 20 resemble each other so closely and their solubilities are so low, that they cannot be separated into pure fractions.

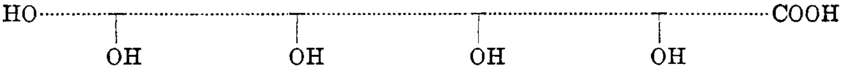
Formaldehyde also polymerizes to yield the cyclic trimer, trioxymethylene, and analogous trimers are the most common forms of the polymers of other aldehydes. It seems possible, however, that some of the metaldehydes are linear polymers of high molecular weight analogous to the polyoxymethylenes. Conant (111) has obtained from butyraldehyde by the action of very high pressure a solid polymer for which he suggests such a structure. This polymer is apparently stable only under pressure. Under the ordinary conditions it rapidly reverts to the monomer.

The thio aldehydes and ketones show more tendency to polymerize than their oxygen analogs (158). Organic silicon compounds of the types $R_2Si{=}O$, $RSi({=}O)OH$, etc., are frequently incapable of being isolated in the monomeric condition, and they invariably polymerize very readily. It is interesting in this connection to compare carbon dioxide and silicon dioxide. The latter is probably a three-dimensional polymer.

V. POLYFUNCTIONAL REACTIONS AND NON-LINEAR POLYMERS

The polymers discussed thus far, whether formed by condensation or by self-addition, are of a type that may be symbolized by the formula . . . . $-A-A-A-A-A-A-A-$. . . . Reactions of condensation are not limited to bifunctional compounds, however. If one of two reactants contains two functional groups and the other contains more than two, the product will be not a simple chain but a more complicated structure. Such reactions may be called bi-trifunctional, bi-tetrafunctional, tri-trifunctional, etc. (18). Reactions of this class are especially important technically in connection with the formation of synthetic resins. Two examples may be considered.

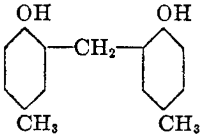
The glyptal resins are formed by the action of phthalic acid on glycerol. The reaction first leads to the formation of a fairly soft, soluble, thermoplastic resin, and this on being heated further yields a hard, insoluble resin which is completely lacking in thermoplasticity. The only reaction involved in the process is esterification (112), and the resin can be saponified completely to yield phthalic acid and glycerol (51). Analysis of the resin just before the infusible stage is reached shows that the glycerol and the phthalic acid are far from having reacted completely with each other, that is, free carboxyl and presumably free hydroxyl groups are still present. The behavior of a dihydric alcohol such as ethylene glycol in this reaction presents quite a different picture from glycerol. With the glycol it is possible to obtain complete esterification, but however far the reaction is carried the product does not become infusible or insoluble. The reason for this difference is obvious. The polyester formed from the dibasic acid and the glycol is linear; as the reaction progresses the molecules grow, but the growth takes place only in one dimension. Similar chains formed in the reaction of glycerol with phthalic acid would bear hydroxyl groups



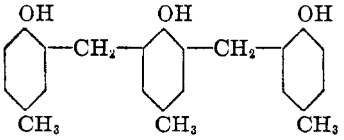
$$\mathrm{HO}\cdots\cdots\underset{\mathrm{OH}}{\top}\cdots\cdots\underset{\mathrm{OH}}{\top}\cdots\cdots\underset{\mathrm{OH}}{\top}\cdots\cdots\underset{\mathrm{OH}}{\top}\cdots\cdots\mathrm{COOH}$$

By reaction of these groups with phthalic acid the chains would be linked together, and thus a very complicated three-dimensional molecule would be built up. After a certain degree of complexity is reached, the possibility of molecular mobility no longer exists. It is conceivable that this cross-linking of the chains finally results in a mass that is essentially a single molecule. In any event it is easy to see how the possibility of further reaction disappears long before all the carboxyl and hydroxyl groups have a chance to participate. It is easy to see also why the action of any dibasic acid on glycerol always yields an amorphous resin, whereas the polyesters from dibasic acids and dihydric alcohols are frequently crystalline.

The formation of Bakelite from phenol and formaldehyde may also be classified as a tri-bifunctional reaction. The formaldehyde behaves as though it were HO—CH_2—OH, and it reacts no doubt largely at the *o*- and *p*-hydrogens of the benzene nucleus. With phenol itself the number of possible products even of quite low molecular weight is so great that no intermediate polymeric individuals can be isolated. On the other hand *p*-cresol has only two readily reactive positions. Thus it is possible as Koebner has shown (113) to isolate the compounds indicated below



and



as crystalline individuals, by causing formaldehyde and *p*-cresol to react in the appropriate ratios, and these can be used to build up still longer chains of the same series. The progressive hydrolysis of silicic esters to silicon dioxide, already discussed in a previous paragraph, furnishes another example of the formation of a three-dimensional polymer.

Addition polymerization may also lead to the formation of three-dimensional structures. Thus acetylene reacts with itself under the influence of certain catalysts (not necessarily copper) with the formation of cuprene, an infusible and insoluble powder, and Staudinger suggests (2) that in this reaction the first step is the formation of unsaturated chains . . . . —CH═CH—CH═CH—CH═CH— . . . . which subsequently combine with one another. The vulcanization of rubber probably also involves the cross-linking of the long chains through the agency of the unsaturated linkages present (39).

VI. NATURAL POLYMERS

1. *The association theory versus the structural theory*

The peculiar and difficult physical and chemical behavior of polymers has occasionally led to the suggestion that forces of a peculiar kind are involved in their formation. Thus Thiele in 1899 (132) suggested that perhaps in such materials as polystyrene the molecules of monomer are bound together merely by partial valences. Röhm in 1901 (115) concluded that the transformation of monomeric acrylic esters into the highly polymeric form is not chemical reaction but a kind of allotropic change. Later Schroeter (116, 117) suggested that the formation of dimeric ketene and of tetrasalicylide is due to the manifestation of an excess of peripheral external force about the monomeric molecules, and that the actual chemical structures of the monomeric molecules are not changed in the process. These particular suggestions are not tenable in the light of chemical evidence now available, but the association theory of polymeric structure reappeared about 1924 and was widely accepted as an explanation of the peculiarities of natural high polymers (118). According to one form of this theory, cellulose, for example, might be an anhydroglucose having the molecular formula $C_6H_{10}O_5$. This molecule, because of the unusual strain of its cyclic structure or for some other reason, is supposed to exhibit enormously exaggerated forces of association or residual valence, and hence to behave physically as though it were a material of very high molecular weight. In the same way proteins might be built up by the mutual association of various small units, e.g., diketopiperazines.

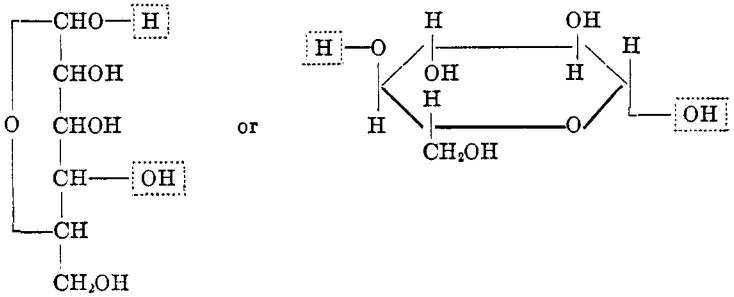
In support of this theory various investigators showed that it was possible by freezing and boiling point methods to obtain small and rapidly shifting values for the molecular weights of polysaccharides, proteins, and rubber. Repetition of these determinations by other investigators proved, however, that the low results were due in most cases to errors in technic. Other support came from x-ray studies, which indicated that the unit cell of the crystal lattice of some high polymers is too small to contain a very large molecule. It was assumed at the time that a unit cell could not contain less than one molecule, but studies of known substances of high molecular weight proved that this assumption was incorrect. Meanwhile Staudinger's studies of synthetic materials repeatedly demonstrated that polymerization may lead to the formation of very long chains built up by real chemical forces in a regular fashion, and that such synthetic materials often resemble natural high polymers in many significant physical and chemical properties. Studies made in this laboratory on high polymers formed by condensation reactions led to the same conclusion. The idea that natural high polymers involve some principles of molecular structure peculiar to themselves and not capable of being simulated by synthetic materials is too strongly suggestive of the vital hypothesis, which preceded the dawn of organic chemistry, to be seriously considered.

It should be emphasized in this connection that polymerization is not peculiar to unsaturated compounds, and that a very high degree of mobility in the relation between a monomer and its polymer does not preclude the intervention of real primary valence forces in the process or the presence of a definite macromolecular structure in the polymer. This fact is illustrated especially by adipic anhydride and the six-membered cyclic esters discussed in previous sections of this paper. These materials appear to exhibit all the supposedly diagnostic features of association polymerization; nevertheless their transformation into polymers is a real chemical process, and the polymers are actually made up of large molecules. No example is yet known in which a small molecule of known structure simulates a material of high molecular weight without undergoing any change in structure.

A return to the simple structural theory of organic chemistry and the application of modern tools have been responsible, during the past five years, for very rapid progress in the interpretation of the structure and properties of some of the simpler, naturally occurring high polymers. It appears that many naturally occurring macromolecular materials have a linear polymeric structure. The present status of this subject has been reviewed by Meyer and Mark (3), and in the following paragraphs only cellulose and rubber are briefly discussed.

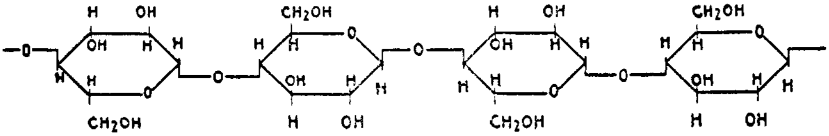
2. Cellulose

Chemical evidence for a linear polymeric structure in the cellulose molecule has long been available (125). More recently, Haworth's proof of the structure of cellobiose (120) and certain studies of the relation of glucose and cellobiose to cellulose (122) furnished the basis for tentative efforts to determine the nature of the units in the molecular chain (121). Sponsler and Dore (123) on the basis of x-ray evidence first put the linear polymeric structure in explicit form. This formula was further developed by Meyer and Mark (119), and it can now be said that the structure of cellulose, at least in its essential outlines, is definitely known. In its simplest chemical form the structural unit of cellulose may be represented by the bivalent radical derived by the removal of water from glucose (glucopyranose)



Glucose

A large number of these units are united chemically to form a long chain which constitutes the cellulose molecule.



Cellulose

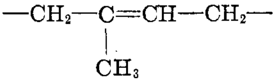
(For a more detailed picture of the spatial arrangements in this chain, including the atomic distances, see reference 3.) In the cellulose fiber (cotton, ramie, etc.) these long molecules are lined up parallel with each other along the fiber axis.

To complete this formula it is necessary to specify the nature of the terminal groups and the length of the chain. The most reasonable assumption is that the chains are open and terminated by hydroxyl groups (alcoholic at one end and semi-acetal at the other), but no very definite experimental evidence on this point is available. Meyer and Mark estimate that the molecular chains are made up of from sixty to one hundred glucose units (molecular weight, 10,000 to 16,000), and they assume that the molecules are segregated into compact bundles (crystallites or micelles) from which the gross structure of the cellulose fiber is built up. Staudinger, however, has presented evidence (124) that the crystallites do not persist in dispersions of cellulose and its derivatives, and that the molecules have a weight much higher than 16,000. Stamm (126) has made direct measurements of particle size in ammoniacal copper dispersions of cellulose by the Svedberg ultracentrifugal method and obtained a value (on the copper-free basis) of 40,000 ± 5 per cent. The molecules in a given sample of cellulose are probably not all of the same length, but Stamm's data indicate a much higher degree of homogeneity than one might expect.

According to this picture cellulose, like other high polymers, is not a chemical individual in the sense of being composed of identical molecules, and its structure cannot be completely specified by a single exactly defined formula. On the other hand, this picture accounts for the physical and chemical behavior of cellulose just as completely and satisfactorily as the formulas of simple compounds account for their properties. Cellulose fibers are very strong because of the parallel arrangement of the long molecular chains along the fiber axis. These chains adhere firmly to one another because of the cumulative force of association of the numerous hydroxyl groups. Strong aqueous alkali is able to penetrate this structure, and the resulting spreading apart of the chains causes lateral swelling. Other reagents (e.g., nitric acid) can penetrate the structure and esterify the hydroxyls without completely changing the apparent physical structure of the fiber. Cellulose is degraded much more rapidly by acids than by alkalies because the units are joined together by acetal linkages. The great length of the molecules accounts for the high viscosity of dispersions of cellulose and its derivatives. The very first stages of degradation greatly reduce the viscosity (124) because, for example, the hydrolytic absorption of 1 part of water in 2000 is capable of reducing by half the average size of the molecules. Undegraded cellulose has little or no reducing power (130) because it contains only one reducing group in an exceedingly large molecule, but reducing power is manifested and increases progressively with hydrolysis (124, 127). Complete hydrolysis finally gives a quantitative yield of glucose (125); cellobiose, a triose, a tetrose (128) and higher polysaccharides are formed as intermediate products. The hydrolysis agrees in its kinetics with the theoretical requirements for the chain structure (129). This structure also accounts for the presence of three esterifiable hydroxyl groups for each C_6 unit, and for the fact that completely methylated cellulose yields 2,3,6-trimethylglucose on hydrolysis (121).

3. *Rubber*

It is well known that rubber hydrocarbon has the same empirical composition as isoprene (C_5H_8); that isoprene can be polymerized to yield a material resembling natural rubber; and that the behavior of rubber toward halogens, hydrobromic acid, and hydrogen indicates the presence of one double bond for each five atoms of carbon. Harries many years ago (131) showed that the degradation of rubber by ozone yields chiefly levulinic acid and aldehyde, and this fact indicates that the rubber molecules must be largely built up by the repetition of the unit



$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-$$

in a regular manner as indicated below.

$$\text{(II)}\quad \ldots -CH_2CMe=CHCH_2-CH_2CMe=CHCH_2-CH_2CMe=CHCH_2- \ldots$$

$$\ldots -CMe=CHCH_2CH_2CMe=CH- \ldots \xrightarrow{\text{ozonization}} CHOCH_2CH_2COMe$$

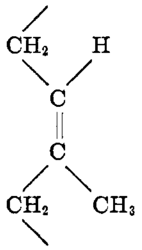
Rubber Levulinic aldehyde

Harries first assumed that the rubber molecule is an eight-membered ring. Later the discovery of larger fragments in the products of degradation by ozone led him to suggest a larger cyclic structure. The physical properties of rubber clearly indicate however that it is macromolecular. Pickles (133) suggested the more plausible linear polymeric structure indicated above, and Staudinger (134) has brought forward a large mass of evidence in favor of this structure. The best evidence available indicates that the average weight of the rubber molecule is exceedingly large—perhaps in the neighborhood of 70,000 (135). It appears, moreover, that molecules having widely different sizes must be present in a given sample of rubber. Raw rubber is not homogeneous in its behavior toward solvents. When placed in contact with ether it swells and part of it diffuses into solution fairly rapidly. The action of fresh ether on the residue is much slower, and it is possible to carry the process of extraction so far as to obtain ultimately a residue that shows scarcely any tendency to dissolve. On the basis of such experiments it has been assumed that rubber is made up of two phases, sol and gel, and that the properties of rubber are due to the colloidal relationships of these two phases. In support of this idea there is the fact that colloidal dispersions of the jelly type frequently exhibit striking elasticity. This is true, for example, of polystyrene when it is swollen with unpolymerized styrene or with other hydrocarbon solvents. Whitby (137), however, has shown that sol-rubber (diffused) alone shows all the characteristic physical properties of raw rubber and differs from the latter only in degree. Moreover, it appears that sol- and gel-rubber are not distinct species and that neither of them is homogeneous. Rubber probably consists of a long continuous series of molecules of differing lengths. The smallest molecules dissolve quite readily and the largest ones only with difficulty.

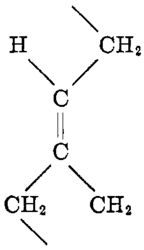
If the rubber molecule is built up uniformly according to the regular plan indicated in formula II it should yield levulinic acid and aldehyde as the exclusive products of degradation by ozone. The yields of these products obtained by Harries accounted for only about 70 per cent of the rubber. Pummerer (136) has recently undertaken a reëxamination of the Harries method, using carefully purified rubber, and has been able to account for 90 per cent of the rubber. He finds significant amounts of succinic acid, acetic acid, and acetone among the products. If the rubber molecule is an open chain, it might have an extra double bond at one end, and according to the disposition of this bond any of the above named by-products might be produced by ozonization. These products might also result from occasional irregularities in the arrangement of the units along the chain. The various possibilities have been outlined by Whitby (137).

Although the examination of unstretched rubber by x-rays gives only an amorphous ring, stretched rubber gives a sharp fiber diffraction pattern (138). When unstretched rubber is cooled in liquid air and then fractured by impact, it breaks up into irregular fragments; stretched rubber treated in the same way breaks up into thin fibers along the axis of stretch (139). These facts show that stretched rubber is much more highly oriented than unstretched rubber.

The structural unit of rubber contains a double bond and this brings about the possibility of stereoisomerism. The units may be in the *cis* or the *trans* form (or both).



cis form



trans form

The x-ray data are said to favor the *cis* orientation (140). A spatial model of a long chain of such *cis* units is capable of being coiled up into a cylindrical spiral, and this spiral can be stretched out into a long chain. Various writers have suggested that the spiral model is capable of explaining the reversible stretching of rubber. This model has recently been discussed in detail by Fikentscher and Mark (140). It is assumed that the residual valence forces at the double bonds are responsible for holding the spiral in its compressed form. When the rubber is stretched, work is done against these forces, and the molecules assume the chain-like form, where they are much more highly oriented with respect to one another. Vulcanization is assumed to involve the chemical linking of these spiral chains at occasional points through sulfur atoms. A very small amount of combined sulfur does not interfere with the stretching of the spirals, but it prevents the chains from slipping past one another or being torn apart; consequently vulcanized rubber is not plastic, and it is not dissolved but only swelled by rubber solvents. As the amount of combined sulfur increases, the entire structure becomes more rigidly linked together, the plastic properties are completely suppressed, and the ability to imbibe solvent is lost. This picture is useful but it can hardly be said to account completely for the remarkable properties of rubber.

VII. THE PHYSICAL PROPERTIES OF HIGH POLYMERS

Perhaps the most important result of the study of synthetic high polymers has been to establish the fact that such materials are actually made up of exceedingly large molecules in the sense of the ordinary structural theory of organic chemistry. This is a point on which considerable scepticism has prevailed in the past, and the attempt to evade or ignore the idea of the molecules in dealing with high polymers has led to much speculative confusion.

It is true that synthetic linear high polymers are invariably mixtures whose molecules are chains of slightly differing lengths, and it is difficult to obtain reliable estimates of the average size of these molecules. Nevertheless it must be admitted that a molecule does not lose any of its definiteness as an entity either through the fact that it is exceedingly large or through the fact that it cannot be completely separated from other similar but slightly different molecules, and the properties of high polymers must ultimately be conditioned by the kinds of molecules which they contain.

It would be beyond the intended scope of this paper to attempt a detailed discussion of the relation between the molecular structure and the physical properties of high polymers, but there are two or three points that deserve some mention.

It is evident that in some respects the physical behavior of a molecule whose length is 100 times as great as its other dimensions must be profoundly different from that of a small compact molecule. Enormously long, flexible, and clumsy molecules must be very sluggish in their kinetic behavior, and it is not surprising that high polymers cannot be distilled or that they are never obtained in the form of thin mobile liquids.

The cohesive forces which resist the separation of molecules from one another (as measured, for example, by the heat of vaporization) increase continuously with increasing molecular weight in a given series, and in high polymers they reach values greatly in excess of the energy required to rupture a primary valence linkage in a chain (141). For this reason high polymers cannot be distilled without decomposition; indeed it appears that the upper limit of distillability may lie at as low a molecular weight as 1200 to 1500 (44).

1. Solubility and colloidal properties

High polymers are subject to the same rough qualitative solubility rules that apply to simple compounds: like dissolves like; polar compounds dissolve in polar solvents and non-polar compounds in non-polar solvents; solubility in a given series diminishes with increasing molecular weight. Thus, rubber and polystyrenes are soluble in benzene, but not in acetone; polyamides are not dissolved by the usual organic solvents, but are dissolved by hot formamide; polyacrylic acid is soluble in water, while its esters dissolve in organic solvents but not in water; polystyrenes of low molecular weight (about 1000) are soluble in ether while polystyrenes of high molecular weight (about 20,000) are only slightly soluble in ether but are still dissolved by benzene.

The solubility of high polymers is sometimes surprisingly great compared with that of analogous simple compounds of much lower molecular weight. The higher normal paraffin hydrocarbons (e.g., heptacontane) are practically insoluble in any solvents at the ordinary temperature, while polystyrene and hydrorubber, which are essentially very long paraffin chains substituted at intervals by phenyl and methyl groups, dissolve readily in benzene. One reason for this no doubt lies in the fact that most high polymers are mixtures of molecules of different lengths, and these are capable to a certain extent of behaving independently in their solubility behavior. Moreover, the crystal lattices of high polymers are not so well ordered and rigidly constructed as those of low molecular weight materials and they may, for this reason, be more susceptible to attack by solvents.

The fact that the cohesive forces operating between large molecules are exceedingly high does not mean that polymers are incapable of forming molecular dispersions. Solubility depends upon specific affinities. Soluble linear polymers of relatively low molecular weight (e.g., 1000 to 5000) dissolve spontaneously and very rapidly in appropriate solvents and yield solutions which are not highly viscous. The osmotic unit in these solutions is the molecule, not an aggregate of molecules. For various polyesters this has been proved (32, 34) by the fact that the same molecular weight values are obtained in a variety of solvents and by both freezing point and boiling point methods. Moreover, as the data of table 2 show, direct chemical determinations of molecular weight give the same values as the osmotic methods. Polyesters having molecular weights considerably above 5000 dissolve in the same solvents as the lower polyesters, but the process of solution is slower and the solutions are more viscous (51). The same behavior is observed in other polymeric series. Polystyrenes having molecular weights of about 1000 dissolve instantly in benzene, and the viscosity of the solutions is low; polystyrenes having molecular weights above 10,000 swell before dissolving, and the solutions are highly viscous (102). These evidences of colloidal behavior are due simply to the fact that the molecules are exceedingly long. The probable mechanism of solution of certain polymers is best illustrated by a specific example.

Rubber is made up of enormously long hydrocarbon chains ranging perhaps from 1000 to 10,000Å. in length. These chains have a high specific affinity for certain non-polar solvents such as benzene. In a mass of rubber, adjacent chains are firmly bound to one another by cohesive forces. The structure is not an entirely regular one and there is no doubt a considerable amount of purely mechanical entanglement. Benzene, by virtue of its specific affinity for the chains, is capable of penetrating into the mass, solvating the chains, and spreading them apart. The structure thus becomes swollen and more tenuous, and finally individual fragments are carried away into solution. The fragments may be single molecules or only incompletely disrupted aggregates, but finally, if sufficient solvent is present, the latter are broken down and what amounts to an actual molecular dispersion results. This dispersion has a very high viscosity even when quite dilute, for the molecules are not only very large, but, owing to the fact that they are solvated and extended in only one dimension, they have an effective radius of action quite out of proportion to their size.

The view that lyophilic dispersions of linear high polymers are usually true molecular dispersions, although it has not yet been generally accepted by colloid chemists (see 174), has been supported by Staudinger with a large mass of evidence (146, 102, 124, 135), which in its cumulative force seems to the writer fairly conclusive. Reference may be made also to Stamm's determination with Svedberg's ultracentrifuge of the particle size of cellulose dispersions in copper-ammonia solutions (126). He obtained the value 40,000 ±5 per cent. It is quite certain on various grounds that the average molecular weight of cellulose cannot be less than about 16,000, so that if Stamm's particle is an aggregate it cannot contain more than two or three molecules. It seems highly arbitrary to assume that the solvent action of the dispersing agent, which depends upon a specific affinity for the cellulose molecules, should be capable of carrying off the molecules only as pairs or triplets and never as single molecules.

It is of course not contended that association never occurs in lyophilic solutions of high polymers, but merely that association occurs only as the result of some appropriate peculiarity in the molecular structure of the polymer, e.g., through the presence of recurring amide or carboxyl groups.

2. Crystallinity

Linear polymers, in spite of their lack of complete homogeneity and their high molecular weight, are by no means always amorphous. As indicated in table 1, all the polyesters derived from glycols of the series $HO(CH_2)_xOH$ and acids of the series carbonic, oxalic, succinic, etc., separate from solvents in the form of powders which show quite definite melting points. On the other hand, similar esters derived from phthalic acid are invariably transparent, amorphous resins. The ability to crystallize appears to require a high degree of linear symmetry in the structural unit. The presence of side chains such as methyl or phenyl groups on the units, and the random mixing of structural units, which occurs, for example, when polymers are prepared from a single glycol and two different acids, diminish the tendency toward crystallinity. Thus, polyesters and polyamides derived from unsubstituted aliphatic compounds are crystalline, and so also are the polyoxymethylenes and polyethylene oxide, while polymers derived from vinyl compounds of the type $XCH{=}CH_2$ are usually amorphous. In these vinyl polymers the X group diminishes the linear symmetry of the chain; moreover in the formation of such polymers occasional inversions of the order of the units probably occur.

The behavior of ethylene succinate (molecular weight, 3000) on crystallization appears to be typical of many high molecular weight materials. It separates from a melt or from concentrated solutions in chloroform as doubly refracting microscopic spherulites which grow to what appear to be star-like clusters of needles. Further growth leads to frost-like patterns. The melt finally solidifies to an opaque porcelain-like mass. From dilute alcohol solutions ethylene succinate separates in very thin, discrete needles, but these lose their identity as soon as the solvent has evaporated. This behavior is highly characteristic of very long chains. It is reproduced in all its details by such diverse materials as triacetylinulin (150), *n*-heptacontane (51), and trimethylcellulose. The photomicrographs of crystalline trimethylcellulose presented by Hess (149) would serve equally well to represent ethylene succinate. Linear polymers in the form of microcrystalline powders have a pronounced tendency to become electrified, and they strongly adsorb considerable amounts of water vapor even when they show scarcely any tendency to dissolve in water.

The crystallization of linear polymers probably involves the parallel arrangement of the long chains into compact bundles, since this arrangement enables the molecules to exert their maximum cohesive force (151). Loose parallel swarms of molecules may also exist in melts or solutions of the polymers. Molecules of identical length might be arranged in bundles as shown in figure 1 (a), but especially with very long molecules, a less regular type of structure such as that shown in (b) might be produced. The arrangement shown in (b) has no sharp boundaries and this defect would be exaggerated if the molecules were not all of the same length. Since the molecules of a specimen of high polymer are very long and have not all the same length the lattice bundles first formed must more nearly resemble (b) than (a). In the presence of solvent, such crystals might persist as discrete particles, but in the absence of a solvent they would tend to coalesce and lose their identity, owing to the absence of sharp boundaries and the incomplete neutralization of the residual forces of the projecting molecules. Thus, it is never possible to isolate large discrete (unsolvated) crystals of high polymers. Moreover, though solid masses of crystalline high polymers may be either hard and brittle or very tough, or soft and wax-like, they never show any definite planes of cleavage. The coalescence of the initial crystallites, which occurs as a molten mass of polyester finally solidifies, must occur in a random and rather disordered fashion, and it is probable also that the crystallites are cemented together by molecules that have not succeeded in completely identifying themselves with any particular crystallite.

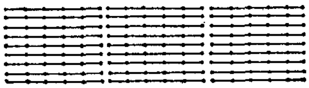


FIG. 1a

FIG. 1b

The melting points of crystalline linear polymers show certain regularities. For a given molecular weight the melting points increase with the cohesive force (polarity) of the structural units. Polyamides have much higher melting points than analogous polyesters. Polyesters derived from short chain dibasic acids melt higher than those derived from the longer chain acids; mixed polyesters melt lower than simple ones. For a given polyester the melting point usually increases with increasing molecular weight up to a certain point, and after that it remains unchanged even though the molecular weight be increased many fold. Melting points are sometimes rather vague, but more frequently they are surprisingly sharp even when the molecular weight is so high that the molten polymer shows no sign of flowing and the only indication of melting is the disappearance of opacity.

The question of the meaning of the term crystallinity in connection with high polymers is rather confused. Linear polyesters whose molecular weights lie below 5000 are definitely crystalline; they have sharp melting points and the crystals can actually be seen under the microscope. The evidences of crystallinity in polyesters whose molecular weights lie above 10,000 are somewhat more vague, but even these materials furnish sharp x-ray powder diffraction patterns. Similar though less sharply defined patterns are obtained from a transparent sheet of regenerated cellulose. These patterns indicate that part at least of the molecules of such materials must be definitely ordered with respect to one another. On the other hand, certain linear polymers, e.g., polystyrene, can be obtained in the form of white powders which show no microscopic or x-ray evidence of crystallinity. In these cases apparently the molecules tend to collect into discrete aggregates of some kind, but not in a sufficiently orderly fashion to exhibit any of the usual properties associated with crystals.

3. Mechanical properties

High polymers are very extensively used as structural materials in the construction of artifacts. One has only to mention cellulose, silk, and rubber to indicate the great economic importance of these non-chemical uses of organic materials. These uses depend upon such properties as mechanical strength, toughness, pliability, and elasticity. Such properties are found to a useful degree only among polymers of very high molecular weight. The synthetic materials of this class that have been most successfully used are three-dimensional polymers such as Bakelite and the glyptals. These materials have considerable strength, rigidity and toughness, but they are completely amorphous, and they are greatly inferior to natural fibers in breaking strength and pliability. The breaking strength of a flax fiber (100 kg. per sq. mm.) is of the same order as that of a good grade of steel (152). The qualities necessary for a useful fiber appear to be associated with a very high molecular weight linear polymeric structure and a certain degree of crystallinity or definite order in the arrangement of the molecules. The relation between molecular structure and arrangement and the physical properties of fibers has been most clearly recognized and discussed by Meyer and Mark (3). In a natural cellulose or silk fiber the long molecular chains are arranged in an ordered fashion parallel with the fiber axis. This state of affairs is symbolized in figure 2. This arrangement provides the maximum possible strength in the direction of the fiber axis since the mutual cohesive force of the long chains is fully utilized. To rupture the fiber it is necessary to cause the chains to slip past one another against this cohesive force as indicated in the dotted line. A transparent sheet of regenerated cellulose shows (by x-ray patterns) a certain degree of order in the arrangement of its molecules, but there is no general orientation. This state of affairs is symbolized in figure 3. This more or less random arrangement of ordered molecular aggregates can be brought into the more highly ordered state symbolized in figure 2 merely by the action of mechanical stress. Thus the strength of a sheet of Cellophane that initially has approximately the same strength in all directions can be so changed, merely by careful stretching, that its strength along the axis of stretch is increased several fold (153). At the same time its strength along the axis normal to its stretch is considerably diminished. The strength of a rayon filament can be increased several fold by the action of stress while it is in the spinning bath, and a comparison of the x-ray patterns shows a much higher degree of orientation along the fiber axis in the filament formed under stress. For a rough mechanical analogy of the mechanism of this process one may picture a disordered mass of long straws (molecules) coated

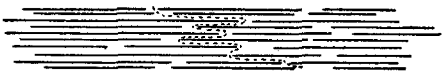


FIG. 2

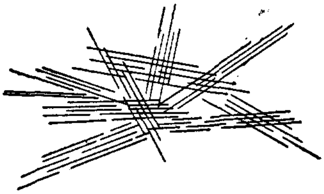


FIG. 3

with a semi-fluid adhesive (cohesive force). The gradual application of stress to such a mass would finally bring the straws into parallel alignment where they would more strongly cohere and resist the further action of stress.

The peculiarities of high polymers are nowhere more strikingly exemplified than in this curious ability to accept permanent orientations through the action of mechanical stress. The properties of simple organic compounds are, generally speaking, independent of their physical history; they are completely determined by the nature of the molecules. Very large molecules, however, are not capable of adjusting themselves instantly to any changes in physical environment, and the properties of a very high molecular weight material may vary over a wide range depending upon the physical treatment it has received.

REFERENCES

(1) STAUDINGER, H.: Helv. Chim. Acta **12**, 1183 (1929).

(2) STAUDINGER, H.: Z. angew. Chem. **42**, 37, 67 (1929).

(3) MEYER, K., AND H. MARK: Der Aufbau der hochpolymeren organischen Naturstoffe. Akademische Verlagsgesellschaft, Leipzig (1930).

(4) STAUDINGER, H.: Ber. **59**, 3019 (1926).

(5) SCHEIBER, J., AND K. SANDIG: Die künstlichen Harze. Wissenschaftliche Verlagsgesellschaft, Stuttgart (1929).

(6) MEERWEIN, H.: Houben's Die Methoden der organischen Chemie, 3rd edition, Volume II, p. 593. Georg Thieme, Leipzig (1925).

(7) MEYER, K.: Naturwissenschaften **16**, 781 (1928); Z. angew. Chem. **41**, 935 (1928).

(8a) HILL, H. S., AND H. HIBBERT: J. Am. Chem. Soc. **45**, 3124 (1923).

(8b) FRANKE, A., AND E. GIGERL: Monatsh. **49**, 8 (1928).

(9) HESS, K.: Die Chemie der Cellulose, p. 574. Akademische Verlagsgesellschaft, Leipzig (1928).

(10) USHAKOV, S. N., AND A. V. KON: C. A. **24**, 3796 (1930).

(11) INGOLD, C. K., AND E. H. INGOLD: J. Chem. Soc. **1928**, 2249.

(12) BERZELIUS, J. J.: Jahresbericht **12**, 63 (1833).

(13) Reference 3, p. 47.

(14) STAUDINGER, H., AND O. SCHWEITZER: Ber. **62**, 2395 (1929).

(15) ROITHNER, E.: Monatsh. **15**, 665 (1894).

(16) FAWORSKI, A.: Chem. Zentr. **1907**, I, 16.

(17) LOURENÇO: Ann. chim. phys. **67**, 293 (1863).

(18) CAROTHERS, W. H.: J. Am. Chem. Soc. **51**, 2548 (1929).

(19) DIETZEL, R., AND R. KRUG: Ber. **58**, 1307 (1925).

(20) WILLSTÄTTER, R., AND C. CRAMER: Ber. **43**, 2976 (1910).

(21) GOLDSCHMIDT, S., E. SCHULZ, AND H. BERNARD: Ann. **478**, 1 (1930).

(22) BUSCH, M., AND W. SCHMIDT: Ber. **62**, 2612 (1929).

(23) Wagner-Jauregg, T.: Ber. **63,** 3213 (1930).
(24) Blaise, E., and A. Koehler: Compt. rend. **148,** 1773 (1909).
(25) Ruzicka, L., and M. Stoll: Helv. Chim. Acta **11,** 1159 (1928).
(26) Johansson, H.: Lunds Universitets Ärsskrift, II (2) **12,** 3 (1916).
(27) Johansson, H.: Ber. **48,** 1262 (1915).
(28) Blaise, E. E., and L. Marcilly: Bull. soc. chim. [3] **31,** 308 (1904).
(29) Chuit, P., and J. Hausser: Helv. Chim. Acta **12,** 463 (1929).
(30) Lycan, W. H., and Roger Adams: J. Am. Chem. Soc. **51,** 625, 3450 (1929).
(31) Bougalt, J., and L. Bourdier: Compt. rend. **147,** 1311 (1908).
(32) Carothers, W. H., and J. A. Arvin: J. Am. Chem. Soc. **51,** 2560 (1929).
(33) Carothers, W. H., and F. J. Van Natta: J. Am. Chem. Soc. **52,** 314 (1930).
(34) Carothers, W. H., and G. L. Dorough: J. Am. Chem. Soc. **52,** 711 (1930).
(35) Carothers, W. H., J. A. Arvin, and G. L. Dorough: J. Am. Chem. Soc. **52,** 3292 (1930).
(36) Kerschbaum, M.: Ber. **60,** 902 (1927).
(37) Marvel, C. S., and E. R. Birkhimer: J. Am. Chem. Soc. **51,** 260 (1929).
(38) Staudinger, H.: Ber. **53,** 1073 (1920).
(39) Meyer, K., and H. Mark: Ber. **61,** 1948 (1928).
(40) Davidoff: Ber. **19,** 406 (1886).
(41) Vorländer, D.: Ann. **280,** 167 (1894).
(42) Tilitschejew, M.: J. Russ. Phys. Chem. Soc. **57,** 143 (1925); Chem. Zentr. **1926,** I, 2667.
(43) Kienle, R. H., and G. Hovey: J. Am. Chem. Soc. **52,** 3636 (1930).
(44) Carothers, W. H., J. W. Hill, J. E. Kirby, and R. A. Jacobson: J. Am. Chem. Soc. **52,** 5279 (1930).
(45) Franke, A., and O. Kienberger: Monatsh. **33,** 1189 (1912).
(46a) Schlubach, H. H., and E. C. Goes: Ber. **55,** 2889 (1922).
(46b) Ziegler, K., and H. Colonius: Ann. **135,** 474 (1930).
(47) Schorigen, P.: Ber. **43,** 1931 (1910).
(48a) Gabriel, S.: Ber. **22,** 3338 (1889).
(48b) Schotten, C.: Ber. **21,** 2240 (1888).
(49a) Carothers, W. H., and G. J. Berchet: J. Am. Chem. Soc. **52,** 5289 (1930).
(49b) Gabriel, S., and T. A. Maass: Ber. **32,** 1266 (1899).
(50a) v. Braun, J.: Ber. **40,** 1835 (1907).
(50b) Manasse, A.: Ber. **35,** 1367 (1902).
(50c) Diehl, L., and A. Einhorn: Ber. **20,** 377 (1887).
(51) Unpublished results.
(52a) v. Braun, J., and A. Steindorff: Ber. **38,** 3083 (1905).
(52b) v. Braun, J.: Ber. **43,** 2853 (1910).
(52c) v. Braun, J., and C. Müller: Ber. **39,** 4110 (1906).
(53a) Littmann, E. R., and C. S. Marvel: J. Am. Chem. Soc. **52,** 288 (1930).
(53b) Knorr, L., and P. Roth: Ber. **39,** 1420 (1906).
(54) Staudinger, H., and E. Ott: Ber. **41,** 2214 (1908).
(55) Voerman, G. L.: Rec. trav. chim. **23,** 265 (1904).
(56) Hill, J. W.: J. Am. Chem. Soc. **52,** 4110 (1930).
(57) Grignard, V., and G. Vignon: Compt. rend. **144,** 1358 (1907).
(58) Hückel, W.: Fortschritte Chem., Physik. physik. Chem. **19,** No. 4, 7 (1927).

(59) LONSDALE, K.: Proc. Roy. Soc. (London) **123**, 494 (1929).
(60) KING, G.: J. Oil Colour Chem. Assocn. **13**, 28 (1930).
(61) LE FEVRE, J. W.:. J. Chem. Soc. **1929**, 733.
(62) FERBER, E.: Ber. **62**, 183 (1929).
(63) SMYTH, C. P., AND W. S. WALLS: J. Am. Chem. Soc. **53**, 527 (1931).
(64) TILITSCHEJEW, M.: J. Russ. Phys. Chem. Soc. **58**, 447 (1926); C. A. **21**, 3358 (1927).
(65a) GANE, R., AND C. K. INGOLD: J. Chem. Soc. **1928**, 1594.
(65b) GANE, R., AND C. K. INGOLD: J. Chem. Soc. **1928**, 2267.
(66) MOHR, E.: J. prakt. Chem. **98**, 315 (1918).
(67) STOLL, M., AND G. STOLL-COMTE: Helv. Chim. Acta **13**, 1185 (1930).
(68) v. BRAUN, J., AND B. BARTSCH: Ber. **45**, 3376 (1912).
(69) STANLEY, W. M., AND R. ADAMS: J. Am. Chem. Soc. **52**, 1200 (1930).
(70) RUGGLI, P.: Ann. **392**, 92 (1912).
(71a) RUZICKA, L., M. STOLL, H. W. HUYSER, AND H. A. BOEKENOOGEN: Helv. Chim. Acta **13**, 1153 (1930).
(71b) RUZICKA AND COWORKERS: Helv. Chim. Acta **9**, 230, 249, 339, 389, 399, 499, 715, 1008 (1926); **10**, 695 (1927); **11**, 496, 670, 686, 1174 (1928).
(72) FICHTER, F., AND A. BEISSWENGER: Ber. **36**, 1200 (1903).
(73) HOLLO, E.: Ber. **61**, 895 (1928).
(74) DREW, H. D. K., AND W. N. HAWORTH: J. Chem. Soc. **1927**, 775.
(75) BISCHOFF, C. A., AND P. WALDEN: Ann. **279**, 45 (1893).
(76) BISCHOFF, C. A., AND P. WALDEN: Ber. **26**, 262 (1893).
(77) BISCHOFF, C. A., AND P. WALDEN: Ann. **279**, 71 (1893).
(78) CARTER, S. R., W. N. HAWORTH, AND R. A. ROBINSON: J. Chem. Soc. **1930**, 2125.
(79) JOHANNSON, H., AND H. SIBELIUS: Ber. **52**, 745 (1919).
(80a) BALBIANO, L.: Ber. **34**, 1501 (1901).
(80b) BALBIANO, L., AND D. TRASCIATTI: Ber. **33**, 2323 (1900).
(81a) MAILLARD, L. C.: Ann. chim. **1**, 519 (1914).
(81b) MAILLARD, L. C.: Ann. chim. **2**, 210 (1914).
(82) CURTIUS, T., AND A. BENRATH: Ber. **37**, 1279 (1904).
(83) SHIBATA, K.: Acta. Phytochim. **2**, 39 (1925); **2**, 194 (1926).
(84a) CURTIUS, T.: Ber. **37**, 1284 (1904).
(84b) CURTIUS, T.: Ber. **16**, 753 (1883).
(85) FISCHER, E.: Ber. **39**, 2924 (1906).
(86) DELEPINE, M.: Bull. soc. chim. [4] **27**, 740 (1920).
(87) GRICHKEVITCH-TROKHIMOVSKY, E.: Bull. soc. chim. [4] **24**, 541, 543, 546, 548, 549, 551 (1918).
(88) KATZ, J. R.: Z. angew. Chem. **41**, 329 (1928).
(89a) LEUCHS, H., AND W. GEIGER: Ber. **41**, 1721 (1908).
(89b) LEUCHS, H.: Ber. **39**, 857 (1906).
(90) CURTIUS, T., AND W. SIEBER: Ber. **55**, 1543 (1922).
(91) COHEN, J. B.: Organic Chemistry, Part I, p. 193. Edward Arnold and Company, London (1928).
(92) STANLEY, H. M.: J. Soc. Chem. Ind. **49**, 349T (1930).
(93) MIGNONAC, G., AND R. V. DE SAINT-AUNAY: Bull. soc. chim. **47**, 522 (1930).
(94) PEASE, R. H.: J. Am. Chem. Soc. **52**, 1158 (1930).

(95) Lebedev, S. V., and G. G. Koblyanskii: Ber. **63**, 1432 (1930).

(96a) Staudinger, H., M. Brunner, K. Frey, P. Garbsch, R. Signer, and S. Wehrli: Ber. **62**, 241 (1929).

(96b) Staudinger, H., K. Frey, P. Garbsch, and S. Wehrli: Ber. **62**, 2912 (1929).

(96c) Staudinger, H., and M. Brunner: Helv. Chim. Acta **12**, 972 (1929).

(96d) Milas, N. A.: Proc. Natl. Acad. Sci. **14**, 844 (1928).

(97a) Staudinger, H., M. Brunner, and W. Feist: Helv. Chim. Acta **13**, 805 (1930).

(97b) Flumiani, G.: Z. Elektrochem. **32**, 221 (1926).

(98a) Staudinger, H., K. Frey, and W. Starck: Ber. **60**, 1782 (1927).

(98b) Whitby, G. S., J. C. McNally, and W. Gallay: Trans. Roy Soc. Can. **22**, 27 (1928).

(98c) Hermann, W. O., and W. Haehnel: Ber. **60**, 1658 (1927).

(99) Staudinger, H., and E. Urech: Helv. Chim. Acta **12**, 1107 (1929).

(100) Moureu, C., and C. Dufraisse: Ann. chim. **15**, 158 (1921).

(101a) Staudinger, H., A. A. Ashdown, M. Brunner, H. A. Bruson, and S. Wehrli: Helv. Chim. Acta **12**, 934 (1929).

(101b) Staudinger, H., H. Johner, and V. Wiedersheim: Helv. Chim. Acta **12**, 958 (1929).

(101c) Staudinger, H., H. Johner, G. Schiemann, and V. Wiedersheim: Helv. Chim. Acta **12**, 962 (1929).

(102a) Staudinger, H., and W. Heuer: Ber. **63**, 222 (1930).

(102b) Staudinger, H., and K. Frey: Ber. **62**, 2909 (1929).

(102c) Staudinger, H., and R. Machemer: Ber. **62**, 2921 (1929).

(102d) Staudinger, H.: Kolloid-Z. **51**, 71 (1930).

(103a) Staudinger, H., E. Geiger, and E. Huber: Ber. **62**, 263 (1929).

(103b) Staudinger, H., and V. Wiedersheim: Ber. **62**, 2406 (1929).

(104) Staudinger, H., and F. Breusch: Ber. **62**, 442 (1929).

(105) Whitby, G. S., and M. Katz: J. Am. Chem. Soc. **50**, 1160 (1928).

(106) Starkweather, H. W., and G. B. Taylor: J. Am. Chem. Soc. **52**, 4708 (1930).

(107) Taylor, H. S.: Private communication.

(108a) Schotz, S. P.: Synthetic Rubber. E. Benn, London (1926).

(108b) Pankow, M.: Kunststoffe **20**, 219, 248 (1930).

(109) Midgley, T., Jr., and A. L. Henne: J. Am. Chem. Soc. **52**, 2077 (1930).

(110a) Staudinger, H., R. Signer, H. Johner, M. Lüthy, W. Kern, D. Russidis, and O. Schweitzer: Ann. **474**, 145 (1929).

(110b) Staudinger, H., and M. Lüthy: Helv. Chim. Acta **8**, 41, 65, 67 (1925).

(110c) Staudinger, H., H. Johner, R. Signer, G. Mie, and G. Hengstenberg: Z. physik. Chem. **126**, 425 (1927).

(110d) Staudinger, H., and R. Signer: Helv. Chim. Acta **11**, 1047 (1928).

(110e) Mie, G., and J. Hengstenberg: Helv. Chim. Acta **11**, 1052 (1928).

(110f) Staudinger, H., and R. Signer: Z. Krist. **70**, 193 (1929).

(110g) Kohlschütter, H. W.: Ann. **482**, 75 (1930).

(110h) Ott, E.: Z. physik. Chem., Abt. B, **9**, 378 (1930).

(111a) Conant, J. B., and C. C. Tongberg: J. Am. Chem. Soc. **52**, 1659 (1930).

(111b) Bridgman, P. W., and J. B. Conant: Proc. Natl. Acad. Sci. **15**, 680 (1929).
(112) Kienle, R. H., and A. G. Hovey: J. Am. Chem. Soc. **51**, 509 (1929).
(113a) Koebner, M.: Chem.-Ztg. **54**, 619 (1930).
(113b) Pollak, F., and F. Riesenfeld: Z. angew. Chem. **43**, 1129 (1930).
(114) Tschugaeff, L.: Ber. **39**, 3199 (1906).
(115) Röhm: Dissertation, Tübingen, 1901. Cited in reference 99.
(116) Schroeter, G.: Ber. **49**, 2697 (1916).
(117) Schroeter, G.: Ber. **52**, 2224 (1919).
(118a) Abderhalden, E.: Naturwissenschaften **12**, 716 (1924).
(118b) Bergmann, M.: Naturwissenschaften **13**, 1045 (1925).
(118c) Pringsheim, H.: Naturwissenschaften **13**, 1084 (1925).
(118d) Bergmann, M.: Ber. **59**, 2973 (1926).
(118e) Hess, K.: Ann. **435**, 1 (1924).
(119a) Meyer, K. H., and H. Mark: Ber. **61**, 593 (1928).
(119b) Mark, H., and K. H. Meyer: Z. physik. Chem., Abt. B, **2**, 115 (1929).
(119c) Mark, H., and G. v. Susich: Z. physik. Chem., Abt. B, **4**, 431 (1929).
(120) Haworth, W. N., C. W. Long, and J. H. G. Plant: J. Chem. Soc. **1927**, 2809.
(121a) Freudenberg, K., and E. Braun: Ann. **460**, 288 (1928).
(121b) Freudenberg, K.: Ann. **461**, 130 (1928).
(122a) Irvine, J. C.: Chem. Reviews **1**, 41 (1924).
(122b) Freudenberg, K.: Ber. **54**, 767 (1921).
(123a) Sponsler, O. L., and W. H. Dore: Colloid Symposium Monograph **4**, 174 (1926). Chemical Catalog Company, New York.
(123b) Sponsler, O. L.: Nature **125**, 633 (1930).
(124a) Staudinger, H., and O. Schweitzer: Ber. **63**, 3122 (1930).
(124b) Staudinger, H., and O. Schweitzer: Ber. **63**, 2317 (1930).
(124c) Staudinger, H., and H. Freudenberger: Ber. **63**, 2331 (1930).
(125) Willstätter, R., and L. Zechmeister: Ber. **46**, 2401 (1913).
(126) Stamm, A. J.: J. Am. Chem. Soc. **52**, 3047 (1930).
(127) Bergmann, M., and H. Machemer: Ber. **63**, 316 (1930).
(128) Willstätter, R., and L. Zechmeister: Ber. **62**, 722 (1929).
(129a) Kuhn, W.: Ber. **63**, 1503 (1930).
(129b) Freudenberg, K., W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn: Ber. **63**, 1528 (1930).
(130) Bergmann, M., and H. Machemer: Ber. **63**, 2304 (1930).
(131) Harries, C.: Ber. **37**, 2708 (1904); **38**, 3985 (1905).
(132) Thiele, J.: Ann. **306**, 92 (1899).
(133) Pickles, S. S.: J. Chem. Soc. **98**, 1085 (1910).
(134a) Staudinger, H., and J. Fritschi: Helv. Chim. Acta **5**, 785 (1922).
(134b) Staudinger, H.: Ber. **57**, 1203 (1924).
(134c) Staudinger, H., and W. Widmer: Helv. Chim. Acta **7**, 842 (1924).
(134d) Staudinger, H.: Z. angew. Chem. **38**, 226 (1925).
(134e) Staudinger, H., and E. Geiger: Helv. Chim. Acta **9**, 549 (1926).
(134f) Staudinger, H.: Kautschuk **1925**, 5.
(134g) Staudinger, H.: Kautschuk **1927**, 63.
(134h) Staudinger, H., M. Asano, H. F. Bondy, and R. Signer: Ber. **61**, 2575 (1928).

(134i) Staudinger, H., H. F. Bondy, and E. Geiger: Ann. **468**, 1 (1929).
(134j) Staudinger, H., and H. F. Bondy: Ann. **468**, 1 (1929).
(134k) Staudinger, H.: Kautschuk **5**, 94, 126 (1929).
(134l) Staudinger, H., and H. F. Bondy: Ber. **62**, 2411 (1929).
(134m) Staudinger, H., and H. F. Bondy: Ber. **63**, 724 (1930).
(134n) Staudinger, H., and E. O. Leupold: Ber. **63**, 730 (1930).
(135a) Staudinger, H., and H. F. Bondy: Ber. **63**, 734 (1930).
(135b) Staudinger, H.: Ber. **63**, 921 (1930).
(135c) Staudinger, H., and H. Joseph: Ber. **63**, 2888 (1930).
(135d) Staudinger, H.: Kautschuk **6**, 153 (1930).
(135e) Staudinger, H., and H. F. Bondy: Ber. **63**, 2900 (1930).
(136) Pummerer, R.: Z. angew. Chem. **43**, 757 (1930); Pummerer, R., G. Ebermayer, and K. Gerlack: Ber. **64**, 809 (1931).
(137) Whitby, G. S.: Trans. Inst. Rubber Ind. **5**, 184 (1929); **6**, 40 (1930).
(138a) Katz, J. R.: Chem.-Ztg. **49**, 353 (1925).
(138b) Meyer, K. H., and H. Mark: Ber. **61**, 1939 (1928).
(139) Hock, L.: Gummi-Ztg. **39**, 1740 (1925).
(140) Fikentscher, H., and H. Mark: Kautschuk **6**, 2 (1930); Rubber Chemistry and Technology **3**, 201 (1930).
(141) Dunkel, M.: Z. physik. Chem., Abt. A, **138**, 42 (1928).
(142) Whitby, G. S., J. C. McNally, and W. Gallay: Trans. Roy. Soc. Can. **22**, 27 (1928).
(143) Lee, W. B., and P. J. Van Rysselberge: J. Phys. Chem. **33**, 1543 (1929).
(144) Katz, J. R.: Z. angew, Chem. **42**, 828 (1929).
(145) Ruzicka, L., M. Stoll, H. W. Huyser, and H. A. Boekenoogen: Helv. Chem. Acta **13**, 1152 (1930).
(146a) Staudinger, H.: Kolloid-Z. **53**, 19 (1930).
(146b) Signer, R.: Z. physik. Chem., Abt. A, **150**, 257 (1930).
(147) Meyer, V., and P. Jacobson: Lehrbuch der organischen Chemie, zweiter Band, dritter Teil. Walther de Gruyter and Company, Berlin and Leipzig (1920).
(148) Wittig, G.: Stereochemie, p. 277. Akademische Verlagsgesellschaft, Leipzig (1930).
(149) Reference 9, p. 432.
(150) Pringsheim, H., and W. G. Hensel: Ber. **63**, 1096 (1930).
(151) Reference 3, p. 50.
(152) Reference 3, p. 153.
(153) Mark, H.: Melliands' Textilber. **10**, 695 (1929).
(154a) Zappi, E. V.: Bull. soc. chim. **19**, 249 (1916).
(154b) v. Braun, J., and W. Sobecki: Ber. **44**, 1918 (1911).
(155) Grignard, V., and Tcheoufaki: Compt. rend. **188**, 357 (1929).
(156) Konrad, E., O. Bächle, and R. Signer: Ann. **474**, 276 (1929).
(157) Kipping, F. S., A. G. Murray, and J. G. Maltby: J. Chem. Soc. **1929**, 1180.
(158) Schönberg, A.: Ber. **62**, 195 (1929).
(159) Brit. patents, 279,406 and 314,524.
(160) Morgan, G. T., and F. H. Burstall: J. Chem. Soc. **1930**, 1497.
(161) Mansfield, W.: Ber. **19**, 696 (1886).

(162) v. Braun, J., and A. Trümpler: Ber. **43,** 547 (1910).
(163) v. Braun, J.: Ber. **43,** 3220 (1910).
(164) Wallach, O.: Ann. **312,** 205 (1900).
(165) Lind, S. C., and G. Glockler: J. Am. Chem. Soc. **51,** 2811 (1929).
(166a) Harkins, W. D., and D. M. Gans: J. Am. Chem. Soc. **52,** 5165 (1930).
(166b) Austin, J. B., and I. A. Black: J. Am. Chem. Soc. **52,** 4552 (1930).
(167a) Zelinsky, N.: Ber. **57,** 264 (1924).
(167b) Fischer, F., F. Baugert, and H. Pichler: Brennstoff-Chem. **10,** 279 (1929).
(167c) Pease, R. N.: J. Am. Chem. Soc. **51,** 3470 (1929).
(167d) Schläpfer, P., and M. Brunner: Helv. Chim. Acta **13,** 1125 (1930).
(168a) Sabatier, P., and J. B. Senderens: Bull. soc. chim. **25,** 683 (1901).
(168b) Brit. patent, 303,797.
(168c) Schläpfer, P., and O. Stadler: Helv. Chim. Acta **9,** 185 (1926).
(169a) Lind, S. C., and R. S. Livingston: J. Am. Chem. Soc. **52,** 4613 (1930).
(169b) Bates, J. R., and H. S. Taylor: J. Am. Chem. Soc. **49,** 2438 (1927).
(170a) McLennon, J. C., M. A. Perrin, and J. C. Ireton: Proc. Roy. Soc. (London) **125A,** 246 (1929).
(170b) Coolidge, W. D.: Science **62,** 441 (1925).
(171) Lind, S. C., D. C. Bardwell, and J. H. Perry: J. Am. Chem. Soc. **48,** 1556 (1926).
(172) Mignonac, G., and R. V. de Saint-Aunay: Compt. rend. **188,** 959 (1929); Bull. soc. chim. **47,** 14 (1930).
(173) Hunter, W. H., and G. H. Woolett: J. Am. Chem. Soc. **43,** 135 (1921).
(174a) Reference 3, p. 173.
(174b) Kraemer, E. O., and G. R. Sears: J. Rheology, in press.
(174c) Loewen, H.: Kautschuk **7,** 12 (1931).
(174d) Mark, H.: Kolloid-Z. **53,** 32 (1930).