FUNDAMENTAL PRINCIPLES OF CONDENSATION POLYMERIZATION

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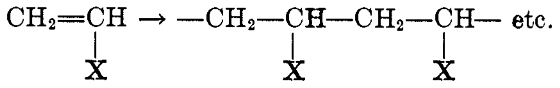
I. INTRODUCTION

In the opening paper (5) of his monumental series of pioneering investigations into the nature of polymeric substances, Carothers introduced a classification of polymer types which has proved to be extremely useful. After suggesting that the characteristic structural feature of high-polymer molecules is the existence of a structural unit —R—, repetition of which describes the entire molecule

$$—R—R—R— \text{ etc.}$$

aside from modification of the terminal units of the chain, he clearly distinguishes two types of polymers: (*1*) *addition polymers*, in which the molecular formula of the structural unit —R— is identical with that of the monomer from which the polymer is formed, and (*2*) *condensation polymers*, in which the structural unit lacks certain atoms present in the monomer from which the polymer is formed or to which it can be degraded by chemical means.

The most important class of addition polymers are formed from unsaturated monomers



$$\mathrm{CH_2{=}}\underset{\overset{|}{\mathrm{X}}}{\mathrm{CH}} \rightarrow \mathrm{{-}CH_2{-}}\underset{\overset{|}{\mathrm{X}}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\overset{|}{\mathrm{X}}}{\mathrm{CH}}\mathrm{{-}} \text{ etc.}$$

where X may be phenyl, halogen, acetoxy, etc. The molecular formula of the polymer is x times the molecular formula of the monomer. Condensation polymers are formed from monomers bearing two or more reactive groups of a character such that they may condense intermolecularly with the elimination of a by-product, usually water. As an example, polyesters are formed from hydroxy acids by intermolecular esterification.

$$x\mathrm{HO{-}R{-}COOH} \rightarrow \mathrm{HO{-}[R{-}COO]}_{x-1}\mathrm{{-}R{-}COOH} + x\mathrm{H_2O}$$

The molecular formula of the polymer in this case is not an integral multiple of the formula of the monomer.

A number of representative condensation polymerizations are shown in table 1. This list is by no means exhaustive, but it indicates the variety of condensation reactions which have been employed in the synthesis of polymers. Cellulose and proteins come within the definition of condensation polymers on the grounds that they can be degraded, hydrolytically, to monomers differing from the structural units by the addition of the elements of a water molecule, although they have not been synthesized as yet by condensation polymerization. This is denoted by the direction of the arrows in the table, indicating depolymerization rather than the reverse.

From the point of view of the scientific investigator, perhaps the most significant feature of condensation polymerization is the commonplace nature of the chemical reactions involved. The knowledge available from the established organic chemistry of most of these reactions provides the basis for accurate predictions concerning the essential structural features of the products obtained. Quoting from the concluding remarks of Carothers' initial paper (5) on the theory of condensation polymerizations:

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

These statements were made when synthesis of high polymers by intermolecular condensation appeared to be little more than a postulated possibility.

Condensation polymerization offers the possibility of constructing high-polymer molecules of accurately known structure. Furthermore, the average molecular weights of condensation polymers can be controlled at will by suitably varying the degree of condensation, and their average molecular weights often can be precisely determined by end-group titration. For these reasons condensation polymers are preferred subjects for fundamental investigations. At the present time, owing in large measure to the work of Carothers and his collaborators, the underlying principles of condensation polymerization are established, and condensation polymers are amenable to exact scientific interpretation. Condensation polymerization has passed beyond the empirical stage.

II. TYPES OF CONDENSATION POLYMERS

From the examples in table 1 it is clear that almost any condensation reaction can be utilized for the production of polymers. The primary requisite is a monomer, or pair of monomers, bearing two or more condensable functional groups. (A monomer such as formaldehyde can be regarded as bifunctional on the grounds that it is capable of forming two bonds with other units.) The products of these reactions are termed polyesters, polyamides, polyethers, etc., depending upon the inter-unit linkage, or upon the reaction involved: esterification, amidation, etc. In other cases it is necessary to use a less concise name, e.g., phenol–aldehyde, or urea–aldehyde, where chemical nomenclature provides no more suitable term.

Cutting across these various chemical types, two classes of condensation polymers are clearly distinguishable: linear polymers formed from reactants which are exclusively bifunctional, and non-linear polymers formed from reactants, some of which are trifunctional or higher (7). Polyesters from hydroxy acids or from glycols and dibasic acids are representative linear condensation polymers; those from glycerol and dibasic acids are three-dimensional. This distinction is warranted both by the structures of the two types of polymers and by their divergent properties.

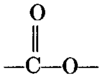
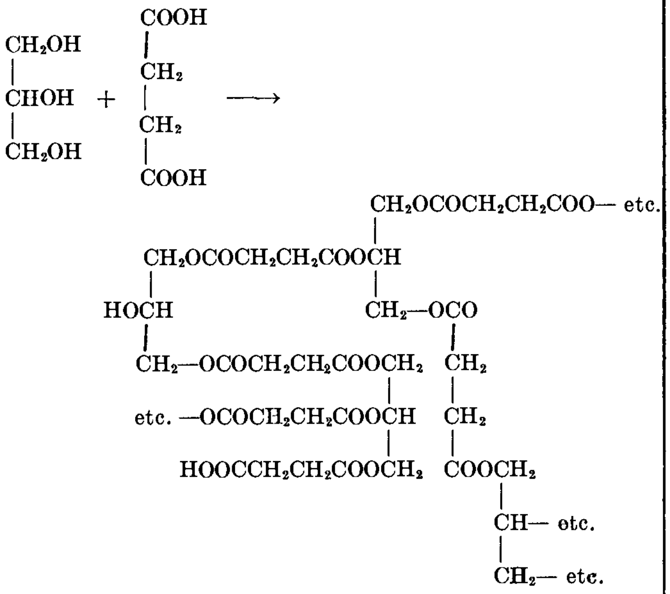
Bifunctional condensation, according to the very nature of the process, necessarily leads to *linear* products of *finite* molecular weight. In view of the impossibility of forcing the condensation reaction to completion, there will always be some few unreacted functional groups. These mark the ends of the linear molecules, which therefore are finite in length.

Linear condensation polymers are soluble in suitable solvents. On account of the regularity of structure, they usually occur in crystalline form. They are fusible, except when the melting point of the crystalline polymer lies above the decomposition temperature.

Non-linear, or three-dimensional, polymerizations are not restricted to growth in two directions only. It is at least conceivable that some of the molecules formed from reactants of functionality greater than two under proper conditions may be indefinitely large. This can be seen from the structure indicated in table 1 for the product from glycerol and succinic acid. As the polymer molecule increases in size its functionality increases, in contrast to the linear polymers prepared from bifunctional monomers, which always carry two functional groups. Although some of these terminal functional groups of the three-dimensional polymer may remain unreacted, others will combine, thus continuing the structure.

TABLE 1

Representative condensation polymers and their properties

TYPE	INTER-UNIT LINKAGE	EXAMPLES	MELTING POINT	CHARACTERISTICS	REFERENCES
			°C.		
Polyester............	 $-\overset{\overset{\displaystyle O}{\Vert}}{C}-O-$	$HO(CH_2)_9COOH \longrightarrow HO-[(CH_2)_9COO]_x-H$	76	Hard; fibers cold draw above M.W. = 9000	(6, 19)
		$HO(CH_2)_2O(CH_2)_2OH + HOOC(CH_2)_4COOH \longrightarrow$ $HO-[(CH_2)_2O(CH_2)_2OCO(CH_2)_4COO]_x-H$	Non-crystalline	Viscous liquid to glass-like; no fibers	(28)
		$HO(CH_2)_{10}OH + HOOC(CH_2)_4COOH \longrightarrow$ $HO-[(CH_2)_{10}OCO(CH_2)_4COO]_x-H$	77	Hard; fibers cold draw above M.W. = 10,000; good strength	(6, 10, 28)
			Non-crystalline	Except at rather low extents of reaction, polymers are insoluble and infusible; no fiber properties; moderate strength	(54)

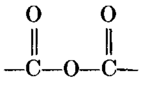
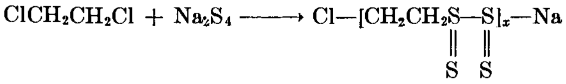
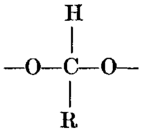
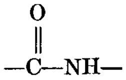
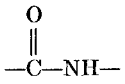
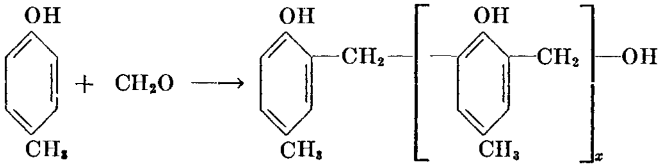
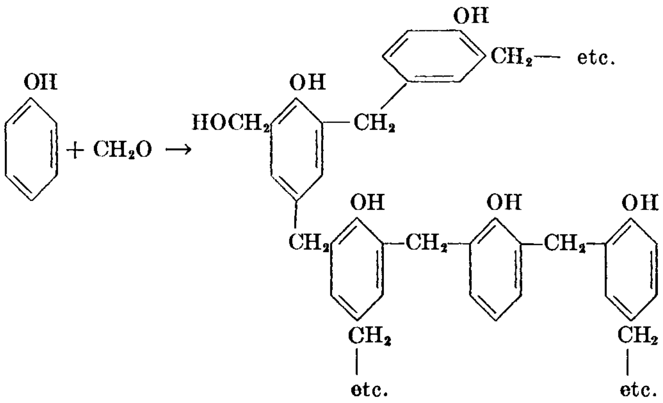
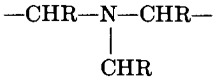
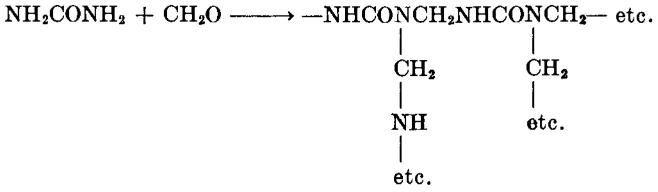
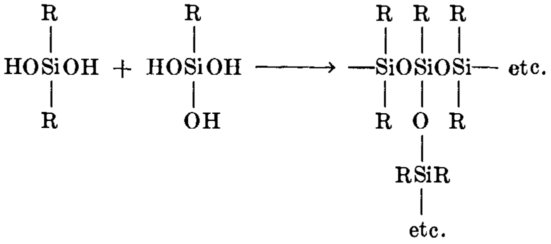
Polyanhydride......	 $-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-$	$HOOC(CH_2)_8COOH \longrightarrow HO-[CO(CH_2)_8COO]_x-H$	83	Similar to crystalline polyesters; fibers cold draw at high molecular weight; very sensitive to water	(48)
Polysulfides.........	$-S-$	$ClCH_2CH_2Cl + Na_2S \longrightarrow Cl-[CH_2CH_2S]_x-Na$	Crystalline		(70)
	$-S-S-$	$HSCH_2CH_2SH + [O] \longrightarrow HS-[CH_2CH_2SS]_x-CH_2CH_2SH$	*ca.* 130	Crystalline	(70)
	 $-\overset{\overset{\displaystyle S}{\|}}{S}-\overset{\overset{\displaystyle S}{\|}}{S}-$	 $ClCH_2CH_2Cl + Na_2S_4 \longrightarrow Cl-[CH_2CH_2\underset{\underset{\displaystyle S}{\|}}{S}-\underset{\underset{\displaystyle S}{\|}}{S}]_x-Na$		Rubber-like; becomes crystalline only on stretching	(70)
Polyacetals..........	 $-O-\overset{\overset{\displaystyle H}{\|}}{\underset{\underset{\displaystyle R}{\|}}{C}}-O-$	$HO(CH_2)_{10}OH + CH_2(OBu)_2 \longrightarrow HO-[(CH_2)_{10}OCH_2O]_x-(CH_2)_{10}OH$	*ca.* 60	Fiber-forming at high molecular weight	(50)
Polyamides.........	 $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$	$NH_2(CH_2)_5COOH \longrightarrow H-[NH(CH_2)_5CO]_x-OH$	205	Fibers cold draw above about M.W. = 8000; high strength	(8, 15, 86)
		$NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow H-[NH(CH_2)_6NHCO(CH_2)_4CO]_x-OH$	260	Similar to the above	(9)

TABLE 1—(*Continued*)

TYPE	INTER-UNIT LINKAGE	EXAMPLES	MELTING POINT °C.	CHARACTERISTICS	REFERENCES
Silk fibroin	 $-\overset{\overset{O}{\Vert}}{C}-NH-$	$NH_2CH_2COOH + NH_2CHRCOOH \longleftarrow -[NHCH_2CONHCHRCO]_x-$	Infusible without decomposition	Crystalline; good strength	
Cellulose	C—O—C	$C_6H_{12}O_6 \longleftarrow -[C_6H_{10}O_4]-O-[C_6H_{10}O_4]-O-$ etc.	Infusible without decomposition	Crystalline; excellent strength when highly oriented	
Phenol-aldehyde	—CHR—		Non-crystalline	Viscous, soluble, thermoplastic	(25)
			Non-crystalline	Sets to an insoluble, infusible resin	(55, 66)

Urea-formaldehyde..	—NH—CHR—NH— and  $\mathrm{-CHR-\underset{\substack{\vert\\CHR}}{N}-CHR-}$	 $\mathrm{NH_2CONH_2 + CH_2O \longrightarrow -NHCO\underset{\substack{\vert\\CH_2\\\vert\\NH\\\vert\\etc.}}{N}CH_2NHCO\underset{\substack{\vert\\CH_2\\\vert\\etc.}}{N}CH_2-\ etc.}$	Non-crystalline	Infusible, insoluble	(52, 67)
Polysilicones........	Si—O—Si	 $\mathrm{HO\overset{\substack{R\\\vert}}{\underset{\substack{\vert\\R}}{Si}}OH + HO\overset{\substack{R\\\vert}}{\underset{\substack{\vert\\OH}}{Si}}OH \longrightarrow -\overset{\substack{R\\\vert}}{\underset{\substack{\vert\\R}}{Si}}O\overset{\substack{R\\\vert}}{\underset{\substack{\vert\\O\\\vert\\RSiR\\\vert\\etc.}}{Si}}O\overset{\substack{R\\\vert}}{\underset{\substack{\vert\\R}}{Si}}-\ etc.}$	Non-crystalline	Oils, greases, to hard thermosetting compositions; resistant to high temperatures	(53, 74)

To look at the situation in another way (7), consider the condensation of 2 moles of glycerol with 3 moles of succinic acid. Each ester group formed decreases by one the number of molecules present, excluding from consideration reactions between two functional groups on the same polymer molecule. Thus, if 5 moles of ester groups are formed intermolecularly, all of the units will be combined into one molecule. But there were initially 6 moles each of hydroxyl and carboxyl groups. Hence, if five-sixths, or 83.4 per cent, of the functional groups were esterified intermolecularly, all units would be combined into a single molecule and, incidentally, any further reaction would of necessity be intramolecular. It would be impossible for the intermolecular reaction to reach this stage without producing structures which assume macroscopic dimensions (7). Macroscopic structures may appear at earlier stages in the condensation. The above argument merely fixes a stoichiometric upper limit.

This calculation is presented to show that condensations of monomers having functionality greater than two should be expected to yield indefinitely large polymer structures at sufficiently advanced stages of the process. These "indefinitely large" or "macro" structures will extend throughout the volume of the polymerized material. Ordinarily their sizes, which will depend on the size of the polymerized sample as well as on the extent of reaction, can conveniently be expressed in grams. On the molecular-weight scale they may be considered as essentially infinite in size.

Among the physical characteristics of three-dimensional condensation polymerizations, the occurrence of a sharp gel point is of foremost significance. At the gel point, which occurs at a well-defined stage in the course of the polymerization, the condensate transforms suddenly from a viscous liquid to an elastic gel. Prior to the gel point all of the polymer is soluble in suitable solvents, and it is fusible as well. Beyond the gel point it is no longer fusible to a liquid nor is it entirely soluble in solvents.

Quite naturally these characteristics have been attributed to the restraining effects of three-dimensional network structures of "infinite" size within the polymer. This is the feature which distinguishes three-dimensional from linear polymers. It could be added that, owing to the greater irregularity of the three-dimensional polymers, generally they are not crystalline. Exceptions are found where the proportion of multifunctional units is small; e.g., in polymers of decamethylene glycol with adipic acid and a very small proportion of tricarballylic acid.

It is possible, of course, to avoid gelation in three-dimensional polymerizations by limiting the extent of esterification or by using proportions of reactants far from the amounts required stoichiometrically. For example, a mixture of 4 molecules of glycerol and 3 of succinic acid will not gel, regardless of the extent of esterification. But the product so obtained bears little resemblance to a linear condensation polymer; its molecular weight is low and its physical properties are inferior. Although these systems containing reactants of higher functionality do not necessarily lead to gelation, their properties nevertheless justify their consideration apart from linear polymers.

III. REACTIONS OF BIFUNCTIONAL COMPOUNDS

A. Characteristics of condensation polymerizations as compared with vinyl-type addition polymerizations

The distinction between condensation and addition polymers, as introduced by Carothers, is based upon the relationship between the compositions of the structural unit and of the monomer. This basis for differentiation is both convenient and appropriate, although whether or not the polymer is of the same empirical composition as the monomer is, in itself, of trivial importance. Justification for this distinction is found in the striking differences between the characteristics of the polymerization *processes*, rather than in the nature of the products.

Addition polymerizations of unsaturated monomers generally proceed by a chain mechanism. Primary activation of a monomer M (or possibly a dimer) is followed by the addition of other monomers in rapid succession until the growing chain eventually is deactivated, with the net result that a polymer molecule, M_x, has been formed from x monomers. The entire synthesis of an individual polymer molecule from unreacted monomers occurs within a brief interval of time—often within a few seconds—whereas the over-all conversion of monomer to a good yield of polymer may require hours. Thus, at any instant during the polymerization process the reaction mixture consists almost entirely of unchanged monomer and of high polymer. Material at intervening stages of growth is virtually absent; the portion consisting of actively growing chains is so small as to be immeasurable by ordinary chemical methods. As the per cent conversion to polymer increases, the average degree of polymerization of the polymerized portion remains approximately the same, or at least does not change commensurately with the extent of conversion to polymer.

$$\mathrm{M} \xrightarrow{\text{activation}} \mathrm{M}^* \xrightarrow{+\mathrm{M}} \mathrm{M}_2^* \xrightarrow{+\mathrm{M}} \mathrm{M}_3^* \longrightarrow \text{etc.}$$

The above characteristics of vinyl addition polymerizations follow naturally from the fact that they are chain reactions in the kinetic sense of the term. As such their reaction mechanisms are complex, and the structures of the polymeric products are sometimes difficult to establish with certainty.

Condensation polymerizations, considered from a general point of view, might appear to be even more complex. To consider the polyesterification of a hydroxy acid, for example, the first step is intermolecular esterification between two monomers, with the production of a dimer.

$$\mathrm{HORCOOH} + \mathrm{HORCOOH} \rightarrow \mathrm{HORCOORCOOH} + \mathrm{H_2O}$$

This step may be followed by reaction of the dimer with another monomer to form a trimer, or the dimer may react with another dimer to form a tetramer, etc. These species in turn may react with monomers, dimers, etc. All of the reactions

$$x\text{-mer} + y\text{-mer} \rightarrow (x + y)\text{-mer}$$

in which x and y assume every possible combination of positive integral values, are to be reckoned with. Whereas in addition polymerization chain growth is ordinarily restricted to the addition of monomers to active chains, in condensation polymerization reactions between two polymer molecules occur as well.

If it were necessary to assign a separate rate constant, k_{xy}, to each of the above reactions occurring in condensation polymerization, kinetic analysis would be extremely difficult if not impossible. However, these various steps need not be differentiated. All involve the same process, e.g., esterification, and, as will be shown later, the rate constants for the various steps are approximately equal. Consequently, the entire polymerization process can be regarded as a reaction between functional groups, e.g., OH and COOH. The individual molecular species and the manifold of steps in which they are involved can be disregarded. This point of view having been adopted, the chemical reaction mechanism of polyintermolecular condensation is no more complex than the condensation of analogous monofunctional compounds. In polyesterification, for example, the rate of esterification is similar to the rate of reaction of ethyl alcohol with acetic acid under similar conditions, it is subject to acid catalysis in a parallel manner, etc. Similarly, the polyamidation reaction parallels closely the rate, temperature coefficient, and reaction order of monoamidations (*cf. seq.*). The essential differences lie only in the functionality of the reactants and the nature of the products produced.

Upon returning to the contrast between the mechanisms of addition and condensation polymerization, it should be noted that the synthesis of any given condensation polymer molecule is accomplished by a series of independent condensations which ordinarily occur at intervals scattered over the period during which the polymerization is carried out, and not during a single comparatively brief interval, as is the case in addition polymerization. Interruption of a linear, or bifunctional, condensation polymerization at an early stage of the process yields a polymer of low average molecular weight. Unless the average degree of polymerization is very low—less than about ten units—it will contain a negligible amount of monomer (less than 1 per cent). As the reaction is continued the low polymers first formed condense further, with the result that the average molecular weight continues to increase. The final molecular weight of a linear-condensation polymer is limited only by the attainable degree of completion of the condensation reaction, or by side reactions which may consume functional groups without producing inter-unit linkages. Thus, in condensation polymerization monomer disappears almost completely during the initial phase of the polymerization process, but in order to attain a high average molecular weight it is necessary to continue the polymerization until the reaction approaches closely to completion. In vinyl addition polymerization, on the other hand, high polymer makes its appearance at the outset, and the duration of the process is determined by the yield of polymer desired, and not by the molecular weight required. Addition-polymer molecules do not respond to further polymerization by inter-reaction with one another (with the exception of some diene polymers).

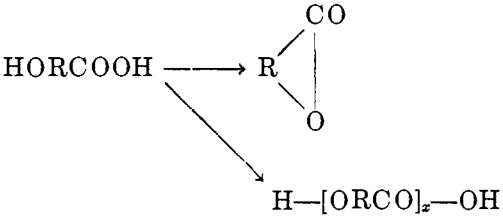
In principle, at least, many vinyl polymers could be synthesized by condensation processes. For example, ethylene can be *addition* polymerized (71) to a product which is essentially —$(CH_2)_n$—. A polymer of the same structure can be obtained by a Wurtz *condensation* of decamethylene dibromide (17):

$$Br(CH_2)_{10}Br + Na \xrightarrow{\text{ether}} H\text{—}[(CH_2)_{10}]_x\text{—}H$$

If other dibromides were used, it is conceivable that the chain structures of other vinyl polymers could be duplicated. However, such methods of synthesis are of no actual importance, and the above example merely emphasizes further that the essential differences between addition and condensation polymerizations occur in the processes of polymerization rather than in the character of the products.

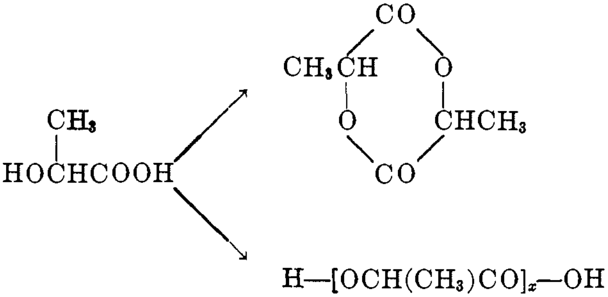
B. Ring formation vs. chain polymerization

Polyfunctionality of the reactants is not sufficient in itself to assure formation of polymer; the reaction may proceed intramolecularly with the formation of cyclic products. For example, hydroxy acids form either (or both) lactone or linear polymer



the direction of the reaction depending on the particular hydroxy acid and, to a lesser extent, on the reaction conditions.

α-Hydroxy acids, such as lactic acid, condense to give both the dimeric cyclic ester, lactide, and a linear polymer:



The condensation of amino acids likewise may produce cyclic and/or linear products; the same is true of virtually all polyfunctional condensation reactions.

The prime factor governing the course followed by a bifunctional reaction is the size of the ring (or rings) which can be obtained through intramolecular condensation. If the ring size is less than five atoms or more than seven, the product will consist almost entirely of open-chain polymer, under ordinary conditions. If a ring containing five annular atoms can be formed, this will be the product exclusively; if of six or seven atoms, either, or both, ring and chain polymer are likely to be formed. Larger rings are formed only under special conditions, e.g., by conducting the condensation at high dilution (75, 89) where opportunities for intermolecular reaction are less favorable, or by heating the polymer in vacuum in the presence of catalysts, the cyclic product being continually removed as it is formed through intramolecular cyclization (49, 50, 83, 84).

The observed dependence of ease of ring formation on ring size for cyclic esters and for cyclic anhydrides is shown in figure 1, taken from a paper by Spanagel and Carothers (83). This type of dependence is quite general, although it will differ in detail from one series to another.

The difficulty with which rings of less than five atoms are formed is readily explained by the strain imposed on the valence angles. Five-atom rings are virtually strainless (in a symmetrical five-atom ring the bond angle is 108°); in all larger rings valence-angle strain can be relieved entirely through the assumption of non-planar forms (Sachse–Mohr theory), except for such obstructions as may arise from steric interferences between substituents. Nevertheless, bifunctional condensations involving units of more than seven atoms do not ordinarily yield rings in appreciable quantity, and, as noted in figure 1, rings of about eight to twelve members are formed with considerable difficulty, even at high dilution or in a vacuum at elevated temperatures in the presence of a catalyst.

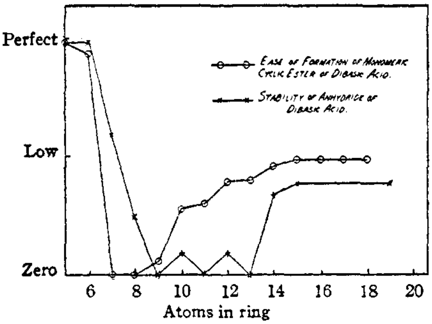


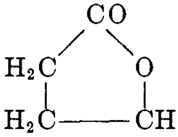
FIG. 1. Ease of formation and stability vs. ring size. (From Spanagel and Carothers (83).)

Carothers and coworkers (6, 16, 83) attributed this minimum in ease of ring formation to two factors: the statistical improbability of the relatively restricted configuration required for the formation of rings in this size range, and the interference, or repulsions, between the hydrogen atoms which necessarily become crowded together within such rings. Scale models of rings composed mainly of —CH_2— groups demonstrate the incidence of these factors. The interferences between the hydrogen atoms leave little freedom of choice in the configuration of the ring. Consequently, the formation of a ring from a bifunctional monomer in this size range will be statistically unfavorable; before such a bifunctional monomer may react intramolecularly, it must coil itself into a specific configuration, in contrast to the numerous other possible configurations available to it in any one of which intermolecular reaction is permissible.

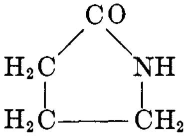
In the scale models of these rings of eight to about twelve members it will be observed further that a number of the hydrogens are forced to occupy positions within the interior of the rings where they are crowded closely together. The domain of the hydrogen atom is ill defined but large. Repulsions between hydrogens extend beyond the kinetic theory radius of about 1.3 Å. Hence, in addition to the statistical improbability of ring configurations for monomers in this size range, they are also energetically unfavorable.

As the ring size is increased above fifteen atoms, the number of permissible ring configurations increases, and it is no longer necessary to crowd hydrogen atoms within the ring. The ease of ring formation increases in this range. However, in ordinary bifunctional condensations (no diluent) the primary product from monomers (or dimers) of fifteen or more members is almost exclusively linear polymer. This results from the statistical improbability that the ends of a long chain of atoms, connected by valence bonds about which there is free rotation, will meet. Although various stable ring configurations are possible for long chains, the total number of other configurations is disproportionately larger; the ring configurations represent but a small fraction of the total of all possible configurations. It can be shown from statistical considerations that the probability that the two ends of a long chain will occupy positions adjacent to each other varies approximately as the inverse three-halves power of the chain length (45, 60), or number of chain atoms. Hence, intramolecular reaction gradually becomes less probable as the length of the bifunctional chain increases. This argument finds further application in supplementing various experimental results which indicate that condensation polymers possess an open-chain rather than a macro-ring structure (6, 10, 12, 62).

The principles set forth above account reasonably well for the course pursued by bifunctional condensations under ordinary conditions and for the relative difficulty of ring formation with units of less than five or more than six or seven members. They do not explain the formation of cyclic monomers from five-atom units to the total exclusion of linear polymers. Thus (6), γ-hydroxy acids condense exclusively to lactones such as I, γ-amino acids give the lactams (II), succinic acid yields the cyclic anhydride (III), and ethylene carbonate and ethylene formal occur only in the cyclic forms IV and V.



I



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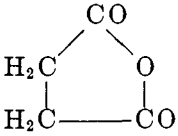
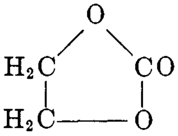


III



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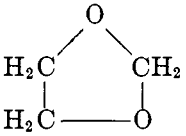


V

Furthermore, formation of these products occurs with much greater ease than linear polymerization of units of six or more chain members, and they are more stable to hydrolysis or other ring-opening reactions.

The steric and configurational factors discussed above would suggest that five-membered rings should form somewhat more readily than rings of six or seven members, but they offer no explanation for the total exclusion of intermolecular condensation, nor do they explain the much greater rate of intramolecular reaction of five-membered units, as compared with the rates of intermolecular reaction of larger units. A possible partial explanation for these peculiarities of five-membered ring closure may be found from further consideration of hydrogen repulsions. In these rings the hydrogen atoms occur around the periphery; hence their mutual interactions are minimized. (In the open-chain planar zig-zag form each hydrogen atom, though slightly farther removed from its nearest neighbors, is surrounded by a greater number of near-neighbor hydrogen atoms than in the planar ring form.) It is doubtful, however, that this factor alone is responsible for the pronounced preference for the ring form which is observed for five-membered units.

Substitution of carbonyl, oxygen, or other atoms or groups for methylene should be expected to modify ring-forming tendencies. Valence angles and bond lengths are altered somewhat, but perhaps of greater importance is the decrease in the number of interfering hydrogens (16) as the methylene members are replaced. According to the present interpretation, a decrease in the proportion of methylene groups should diminish both the overwhelming tendency toward intramolecular reaction of five-membered units and the difficulty of forming rings of eight to twelve members. Other factors doubtless need to be considered as well.

Bifunctional monomers capable of forming six- or seven-membered rings condense variably, depending upon the particular monomer. The products normally obtained in the absence of diluent in various representative bifunctional condensations are listed in table 2 for unit lengths of six and seven members. The term "interconvertibility" refers to the reversible transformation between the ring and the linear polymer. Several of the six-membered units (table 2) prefer the ring form exclusively, but most of them yield both products, or, at least, they are readily interconvertible. Seven-membered units either yield linear polymers exclusively, or, if the cyclic momoner is formed under ordinary conditions, it is convertible to linear polymers.

C. Polymerization of cyclic compounds

The reversible transformation between rings of six members and the corresponding chain polymers occurs with remarkable ease (13). The six-membered cyclic esters, for example, polymerize spontaneously on standing even at room temperature (13). The polymers can be converted readily to the monomeric lactones by distillation. Thus, all of the processes indicated below

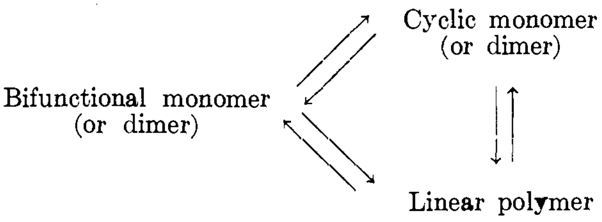
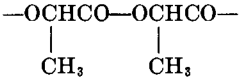
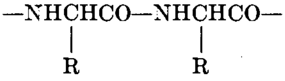


TABLE 2

Ring formation vs. chain polymerization from six- and seven-membered units

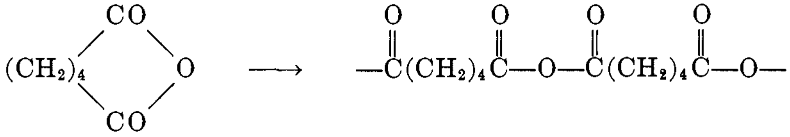
TYPE	STRUCTURAL UNIT	PRODUCTS OF BIFUNCTIONAL CONDENSATION	
		Six-membered unit	Seven-membered unit
ω-Hydroxy acid self ester	$-O(CH_2)_nCO-$	Both ring and polymer spontaneously interconvertible (13)	Chiefly ring; interconvertible (91)
α-Hydroxy acid self ester	 $-O\underset{\substack{\vert\\ CH_3}}{C}HCO-O\underset{\substack{\vert\\ CH_3}}{C}HCO-$	Linear polymer probably is the primary product (13, 22); interconversion is easy	
Alkylene carbonate	$-(CH_2)_nOCOO-$	Both ring and polymer; easily interconvertible (13, 18)	Linear polymer only (18)
Dibasic acid anhydride	$-(CH_2)_nCO-O-CO-$	Ring only	Linear polymer; convertible to ring (47)
Alkylene formal	$-(CH_2)_nOCH_2O-$	Ring only (50)	Both ring and polymer; interconvertible (50)
Self amide of ω-amino acid	$-NH(CH_2)_nCO-$	Ring only (6)	Both ring and polymer (11); interconvertible at high temperatures
Self amide of α-amino acid	 $-NH\underset{\substack{\vert\\ R}}{C}HCO-NH\underset{\substack{\vert\\ R}}{C}HCO-$	Ring usually predominates, but some linear polymer can be formed; interconversion is difficult	
Alkylene sulfide	$-CH_2CH_2S-CH_2CH_2S-$	Linear polymer; converted with some difficulty to ring (63)	
Alkylene ether-sulfide	$-CH_2CH_2O-CH_2CH_2S-$	Linear polymer (70)	

can be realized with most bifunctional monomers of six members and also with some of seven members. Dimers are mentioned in the above scheme in consideration of compounds such as α-amino acids and α-hydroxy acids, the dimers of which are equivalent to six-membered units. The mobility of the above transformation renders difficult a decision as to whether ring or polymer is the primary product of bifunctional condensation in the case of six-membered units (see table 2).

Carothers, Dorough, and Van Natta (13) have drawn attention to the parallelism between the ease of reversible polymerization of six-membered rings and their susceptibility to hydrolysis. No satisfactory explanation for their exceptional reactivity is apparent.

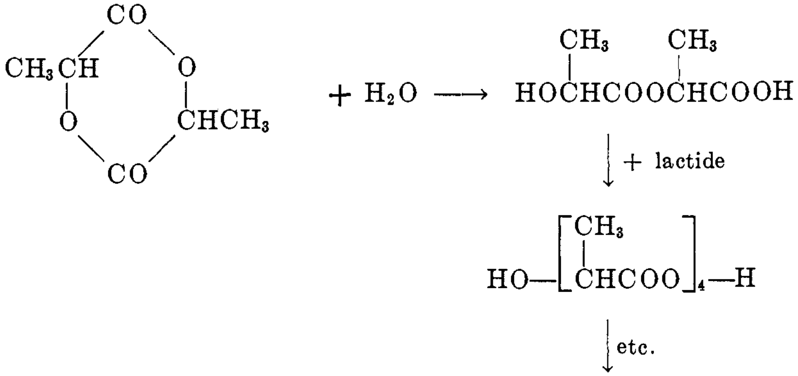
Larger rings, though difficult to form, are relatively stable with respect to polymerization (cyclic anhydrides excepted). However, at elevated temperatures, and preferably in the presence of a catalyst, they can be converted smoothly to linear polymers. Thus, the conversion of cyclic compounds to polymers is quite general (16) except, of course, with the more stable rings of five, and in a few cases six, members where the corresponding polymers are unknown. For example, ε-caprolactam (11, 79), polymethylene carbonates (49), macrocyclic esters (49), macrocyclic amides (44), and cyclic anhydrides such as adipic (47), to mention a few, can be converted to linear polymers under suitable conditions.

The products formed by polymerization of these rings are not ordinarily distinguishable from the polymers formed by direct condensation polymerization of the bifunctional monomers. Thus, spontaneous polymerization of adipic anhydride (47) gives a product which is identical in composition and in chemical and physical properties with the polymer produced by direct anhydridization of adipic acid. Literal adherence to definition would demand that the one be called an addition polymer and the other a condensation polymer, in spite of their possible identity.



The unequivocal distinction between the two types of *processes*, the one an addition and the other a condensation, by which these various polymers can be prepared cannot, and should not, be disregarded. However, designation of the product as an addition polymer in the one case and as a condensation polymer in the other would lead inevitably to confusion. It is customary to consider polymers of this type as condensation polymers, regardless of their origin. This can be justified on the grounds that the same polymer may be formed by condensation, and it can be degraded, usually hydrolytically, to a monomer(s) differing in composition from the structural unit(s). On this basis the polymer comes within the original definition of condensation polymers.

The mechanism of the addition polymerization of ring compounds bears little resemblance to addition polymerization of vinyl monomers. They are not chain reactions. Usually they proceed by interchange reactions, induced either catalytically (49, 50, 79) or by the presence of small amounts of end-group-producing substances (13, 38). For example, the polymerization of lactide, the cyclic dimer of lactic acid, is accelerated by small amounts of water (3). The water undoubtedly hydrolyzes the lactide to lactyllactic acid, which may then react with other lactide molecules by ester interchange (38). The reaction scheme can be represented as follows:



Similarly, water accelerates the polymerization of ϵ-caprolactam (79), presumably *via* a similar mechanism:

$$\underbrace{NH(CH_2)_5CO} + H_2O \longrightarrow NH_2(CH_2)_5COOH$$

$$\downarrow + \text{cyclic monomer}$$

$$H{-}[NH(CH_2)_5CO]_2{-}OH$$

$$\downarrow \text{etc.}$$

Strong acids or bases, which are sometimes used to catalyze these transformations (31, 38, 49, 50, 91), probably are effective because of their ability to accelerate the interchange reaction between a few end groups and the more abundant inter-unit linkages.

These processes resemble vinyl-type addition polymerizations only in that they proceed exclusively (as here represented) by addition of the monomer (or cyclic dimer) to linear chain molecules. They differ from vinyl polymerization in that the specific rate of the first step, ring opening, is comparable with the specific rate of succeeding monomer additions. Hence, the over-all polymerization process does not assume the characteristics of a chain reaction. Ring-chain polymerizations have not been investigated in detail, but according to the mechanism proposed the various chain molecules (initiated by hydrolysis in the above examples) should undergo more or less simultaneous growth throughout the course of the polymerization. At any intermediate stage of the polymerization the material should be separable into unchanged monomer and polymer. In contrast to vinyl polymerizations, however, as the polymerization is continued not only should the amount of polymer increase, but its average molecular weight should increase also.

IV. KINETICS OF CONDENSATION POLYMERIZATION

The similarities between polyfunctional condensations and the analogous monofunctional reactions were pointed out in the course of the above qualitative discussion of reaction mechanisms. They proceed under similar conditions of temperature and catalysis, their temperature coefficients are similar, etc. It was suggested that the maze of intermolecular reactions, involving molecules of every species in reactions with every other species, may be disregarded, and the entire process can be looked upon merely as a reaction between functional groups. To the extent that this rather sweeping assumption is justified, disappearance of unreacted functional groups must occur in a manner paralleling exactly the course followed by the analogous monofunctional reaction under the same conditions.

In opposition to the unqualified assumption that a polyfunctional reaction and the analogous monofunctional reaction proceed in a quantitatively equivalent manner, it has been held that the rate must necessarily be depressed by the high molecular weight of the intermediate products (which are also reactants) formed in the polyfunctional reaction (2, 6, 14, 23, 46, 64). Various arguments have been advanced in support of the contention that large molecules should be less reactive than smaller ones. The lower mobility of large molecules in the liquid state (23, 64) and the decrease in collision rate (in gases!) with increase in molecular weight are frequently cited as contributing to lower reactivity. The "steric factor" is supposed to be reduced, owing to shielding of the functional group within the coilings of the remainder of the molecule (23, 64). Even statistical mechanics has been invoked to derive (erroneously) a decrease in reactivity with size (2). Furthermore, as polymerization progresses the viscosity of the reaction medium increases rapidly. Dostal and Mark (24) suggest that this rise in viscosity should further depress the reaction rate. It would appear, in the face of the aggregate effects of these alleged obstacles, that the established synthesis of high polymers through condensation polymerization should have been a practical impossibility.

The principles of chemical reactivity as applied to large molecules will be examined first from a theoretical point of view in the paragraphs which follow. Experimental results bearing on the chemical reactivity of polymer molecules will then be presented in the remainder of this section of the paper and in the section which follows.

A. Theory of the reactivity of large molecules

At the outset it should be pointed out that the intrinsic chemical reactivity of a functional group should be essentially independent of the size of the molecule to which it is attached. The intrinsic chemical characteristics of a functional group may, to be sure, be profoundly altered by substitution in the molecule. However, the substituent is effective only when it is introduced near the functional group. If the point of substitution is removed from the functional group by more than five or six atoms, its effect is negligible. The reactivity of the carboxyl group of lactic acid probably is altered somewhat by esterification of its hydroxyl group with another molecule of the hydroxy acid, but addition of a third lactic acid residue scarcely can be expected to affect the reactivity of the terminal carboxyl group appreciably. Consequently, a change in the intrinsic chemical reactivity of the functional groups, if it occurs at all, will be confined to the early stages of the polymerization.

Arguments favoring a decrease in reactivity with molecular size usually have arisen from considerations of the mechanics of interaction of two functional groups attached to large molecules, rather than from any inherent abnormal character of the functional groups themselves. On account of the low mobility of polymer molecules, it has been concluded, for example, that the collision rate is correspondingly diminished. It is well established that large molecules diffuse slowly, but the collision rate of the functional group must not be confused with the diffusion rate for the molecule as a whole. The internal mobility with reference to motions of the terminal functional group will be much greater than the macroscopic viscosity would indicate. While its range of diffusion within an interval of time which is small compared to the period required for displacement of the molecule as a whole will be limited by its attachment to the polymer molecule, the terminal group may diffuse readily over a considerable region through rearrangements in the configurations of nearby segments of the chain. Its actual oscillations against its immediate neighbors may occur at a frequency comparable to, or at any rate not much less than, that prevailing in simple liquids. Thus the actual collision frequency will bear scant relationship to the mobility of the molecule as a whole or to the macroscopic viscosity.

Rabinowitch and Wood (73) have demonstrated in a particularly lucid way that a pair of neighboring molecules, or functional groups, in the liquid state may collide repeatedly before diffusing apart. The lower the diffusion rate the greater the prolongation of this series of encounters between functional groups, but it will be proportionately longer before the functional group diffuses to a new position in which it is again an immediate neighbor of another functional group. Another series of collisions will ensue, and this pair will be separated by diffusion of one of them, unless, of course, that exceedingly rare event, chemical reaction, occurs during one of the collisions. Thus, decreased mobility, due to large molecular size and/or to high viscosity, will alter the time distribution of collisions experienced by a given functional group, but it should not affect to any great extent the collision rate averaged over a period of time long compared with the interval required for diffusion from one partner to the next.

Even if this average collision *frequency* is diminished somewhat by a possible reduction in internal mobility as the polymerization progresses, the *duration* of the collided state will be prolonged proportionately. Hence, the concentration of pairs of functional groups sufficiently close together to permit the condensation reaction to occur (if the necessary energy is available) is independent of mobility. This conclusion can be established more rigorously by following Eyring's (26) theory of reaction rates. The transitory activated complex is defined by Eyring in such a way that its concentration can be expressed as if it were in chemical equilibrium with the reactants. Obviously, mobility within the liquid will not affect the equilibrium: reactants $\rightleftarrows$ activated complex. Since the rate of reaction is proportional to the concentration of activated complex, it will not be affected by the mobility of the molecules, the diffusion rate, or the viscosity.

Exceptions to these conclusions will occur when the molecular mobility is extremely low, i.e., when the molecular weight and the viscosity are extremely high, or when the specific reaction rate is unusually great and the mobility is low (73). If the reaction rate is too fast, or the mobility too low, to allow maintenance of the equilibrium concentration of reactant pairs in positions adjacent to one another in the liquid, then diffusion will become the rate-controlling step. It is unlikely that this will occur in ordinary condensation polymerizations even up to molecular weights and viscosities far in excess of those attained in the experiments described above. For example, in esterification (acid-catalyzed at around 100°C.) less than one collision in 10^8 between functional groups is fruitful in producing ester (51). Within the interval required for this number of collisions, appreciable diffusion of the molecule may easily occur.

In vinyl polymerizations the mobility of the monomer, even in the presence of much polymer, should be adequate to avoid dependence of rate on diffusion in spite of the rapidity of this reaction. The chain-termination step, involving interaction between the termini of two large molecules, occurs at a comparatively high percentage of encounters, i.e., the specific rate constant for this step is large. Here it is not improbable that low mobility may depress the rate of the termination reaction somewhat (thereby producing an acceleration of the polymerization rate in this case) when the viscosity of the system is not reduced through the use of a diluent.

In their recent book dealing with polymerization mechanisms Mark and Raff (64) have suggested further that a long-chain polymer molecule will tend to surround its terminal functional group in such a way as to shield it from contact with other molecules. On the contrary, there is no reason to suppose that a functional group will prefer to imbed itself in its own chain rather than among other similar polymer molecules present in the medium. The inter-twining chains merely act as so much diluent in the same way that ethyl acetate, for instance, acts as a diluent at advanced stages in the esterification of alcohol and acetic acid.

B. Experimental results on linear polyesterification

Experiments on the rates of esterification of polyfunctional and monofunctional reactants demonstrate clearly that, so far as the chemical inter-reaction between functional groups is concerned, mono- and poly-functional reactions are equivalent (28). In these experiments the reaction between precisely equivalent quantities of diethylene glycol and adipic acid, a dibasic acid, was followed by titration of total unreacted carboxyl groups in samples removed from the reaction mixture. The extent of reaction, p, defined as the fraction of the functional groups which have been esterified at the time of removal of the sample, was calculated from the titer. In the same manner diethylene glycol and caproic acid, a monobasic acid, were heated together at the same temperature and the reaction was followed similarly. In figure 2 $1/(1-p)^2$,

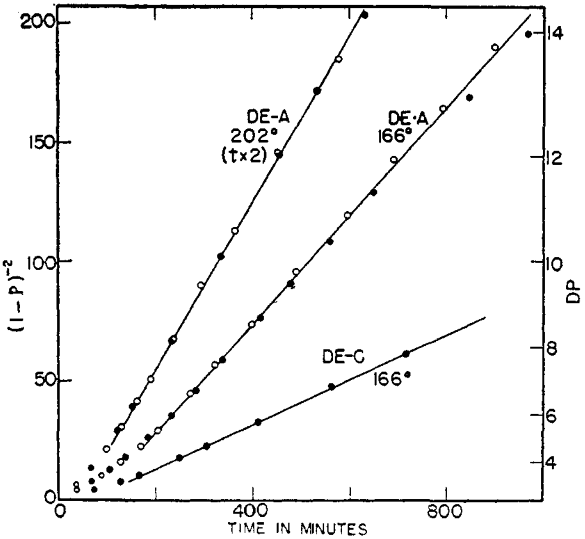


FIG. 2. Diethylene glycol–adipic acid (DE–A) and diethylene glycol–caproic acid (DE–C) reactions. Time values at 202°C. have been multiplied by 2. (From reference 28.)

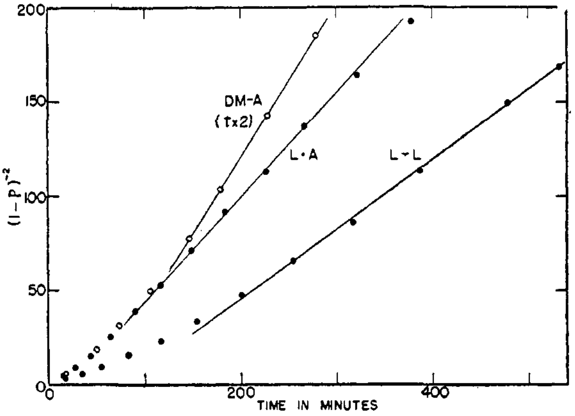


FIG. 3. Reactions of decamethylene glycol with adipic acid (DM–A), lauryl alcohol with adipic acid (L–A), and lauryl alcohol with lauric acid (L–L), all at 202°C. (from reference 28).

which is approximately proportional to the reciprocal of the square of the concentration of functional groups, is plotted against the time in minutes (28). Dots and circles are used to distinguish data from duplicate experiments. Similar results comparing the reactions of decamethylene glycol with adipic acid (bi-, bifunctional), lauryl alcohol with adipic acid (mono-, bifunctional), and lauryl alcohol with lauric acid (mono-, monofunctional) are shown in figure 3

(28). The degree of polymerization, $\overline{DP}_n$, or average number of units per molecule, is equal to $1/(1 - p)$, which is the square root of the ordinates in figures 2 and 3.

The reason for the choice of this particular mode of plotting the results (i.e., as a third-order reaction) will be discussed below. The point of importance here is the similarity of the courses followed by condensations producing polymers and those in which monofunctional reactants are involved. The monofunctional reactions actually are somewhat slower, but this is due principally to the greater equivalent weights of the initial monofunctional reactants, resulting in greater dilution of the functional groups with inert hydrocarbon chains. The curves for the mono- and the poly-functional reactions are superimposable by merely multiplying all time values for one of them by the same factor. If the functional groups in the poly-functional reaction became progressively less reactive as the reaction progressed and the average molecular size increased, this similarity with the monofunctional reaction would not have been observed.

As is well known, esterification reactions are catalyzed by hydrogen ions. In the absence of a strong acid catalyst a second molecule of the carboxylic acid undergoing esterification functions as catalyst. The rate, therefore, should be proportional to the product of the hydroxyl concentration and the square of the carboxyl concentration. When the concentrations, C, of the reacting groups are the same,

$$-\mathrm{d}C/\mathrm{d}t = kC^3$$

where k is the velocity constant. Upon integration this expression becomes:

$$2kt = 1/C^2 - \text{Const.}$$

If the reaction is uniformly third order from the beginning onward, the constant of integration will be $1/C_0^2$, where C_0 is the initial concentration. If the effect on concentration of the decrease in volume due to loss of water during the reaction is neglected, C may be replaced by $C_0(1 - p)$, and

$$2C_0^2kt = 1/(1 - p)^2 - \text{Const.} \tag{1}$$

The velocity coefficient k will be a constant only when the (average) reactivities of unreacted functional groups remain constant throughout the observed course of the reaction. If as the polyfunctional reaction progresses this reactivity is diminished, owing to the increased average size of the reacting species or to the decreased fluidity of the medium, k will not assume a constant value and, consequently, $1/(1 - p)^2$ will not increase linearly with t in accordance with equation 1.

During the initial portion of the esterification reactions shown in figures 2 and 3, equation 1 is not obeyed, as is shown by the curvature in these plots extending as far as about 80 per cent esterification corresponding to a $\overline{DP}_n = 1/(1 - p)$ of 5. This peculiarity has been attributed (28) to the rather pronounced change in characteristics of the reaction medium, particularly its dielectric properties. Whatever the cause of this behavior may be, it is typical of both mono- and poly-esterifications, and is not therefore in any way related to the sizes of the reacting molecules.

Beyond an average degree of polymerization of about 5 and as far as a *DP* of 14, the relationship becomes linear within experimental error. Straight lines have been drawn through the sets of points in figures 2 and 3 in this region. Here the reaction is evidently third order with a velocity coefficient, k, which is unaffected by the increasing average size of the reacting molecules.

Baker, Fuller, and Heiss (1) have published approximate results on the polymerization of ω-hydroxyundecanoic acid at 200°C. Within the experimental error the course of the reaction is third order up to a degree of polymerization of 68. There is no indication of a depression in rate constant with increasing average molecular weight.

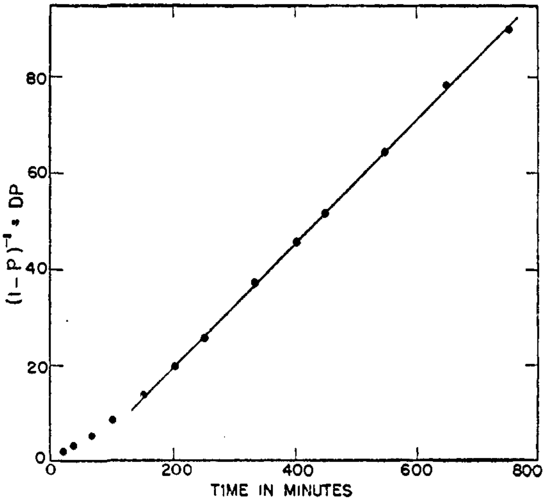


FIG. 4. Reaction of diethylene glycol with adipic acid at 109°C. catalyzed by 0.4 mole per cent of p-toluenesulfonic acid (from reference 28).

These uncatalyzed esterifications become exceedingly slow at high degrees of esterification, owing to the high kinetic order of the reaction. Better success in extending kinetic measurements to higher degrees of polymerization has been achieved with acid-catalyzed polyesterifications (28, 32). The rate then is proportional to the product of the hydroxyl, carboxyl, and acid catalyst concentrations

$$-dC/dt = k'C_{\mathrm{cat}}C^2$$

where C_{cat} represents the catalyst concentration. Since the catalyst concentration is constant, the reaction is second order, and the integrated expression assumes the familiar form

$$C_0C_{\mathrm{cat}}k't = 1/(1-p) - \mathrm{Const.} \tag{2}$$

In figure 4 results for the reaction of diethylene glycol with adipic acid catalyzed by p-toluenesulfonic acid (28) are plotted as a second-order reaction.

Over the early portion of the reaction there is curvature similar to that observed in the uncatalyzed polyesterifications. Thereafter, and at least as far as a degree of polymerization of 90, the disappearance of functional groups is accurately second order. The velocity constant therefore is not affected by molecular size up at least to a molecular weight of 10,000. Concurrently, the viscosity increased over two thousandfold. Similar results have been reported for the polymerization of decamethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid (32).

The argument presented by Schulz (80) that the rate-controlling step in polyesterification is the removal of water, the esterification process being at or near equilibrium with the water present at advanced stages of the reaction, can be refuted in various ways. The rate constants and temperature coefficients observed in the experiments discussed above are typical of esterifications, the observed rate is accelerated immensely by catalysts, and the rate is not increased by reducing the pressure (28) to accelerate removal of water.

C. Experimental results on other condensation polymerizations

Kienle and coworkers (54) have reported carefully conducted experiments on the course of three-dimensional polyesterifications. They co-reacted glycerol with various dibasic acids: phthalic, succinic, maleic, adipic, and sebacic. In addition to the concentration of free carboxyl groups, they also measured the water evolved as a function of time. Kinetic analysis of their data is complicated by the peculiarity previously discussed of the esterification reaction up to 80 or 90 per cent conversion and by the somewhat lower reactivity of the secondary hydroxyl group of glycerol (77). The reaction progresses smoothly, following a course similar to that observed in the bifunctional polyesterifications discussed above. The data do not support the stepwise reaction mechanism proposed by Kienle. It is interesting to note that water evolution continues smoothly through the gel point, where the macroscopic viscosity reaches infinity.

Satisfactory kinetic data on condensation polymerizations other than polyesterifications are scarce. Polyamidation has been reported (33) to be second order with respect to the functional groups, in conformity with monofunctional amidation (69). Dostal and Raff (25) have investigated the mechanism of the condensation of *p*-cresol with formaldehyde. However, they determined the percentage of polymer rather than the concentration of functional groups as a function of time, and their results are of little value therefore in describing the course of the condensation process in its more important stages.

D. Conclusions

The experimental results discussed above demonstrate that the susceptibility of a functional group to chemical reaction is not affected by the size of the molecule to which it is attached, nor does it depend ordinarily on the viscosity of the reaction medium. Contrary to the contentions of various authors on the subject, this conclusion in no way contradicts the theoretical principles of reactivity and chemical kinetics. It is supported further by investigations on the rates of degradation of polymer molecules, to be discussed in the next section.

In general, therefore, condensation polymerizations can be expected to proceed in a manner paralleling exactly the analogous monofunctional reaction. In drawing this analogy, however, it is necessary to focus attention on the functional groups and not on the percentage of polymer. If, as is most often the case, the monofunctional condensation reaction is second order, then the disappearance of functional groups in the polyfunctional reaction will also be second order. If the rate of the monofunctional reaction is accelerated in proportion to the concentration of a certain catalyst, this catalyst will influence the polyfunctional reaction similarly, etc.

The functional groups of the polymerizing molecules evidently react with one another at random. This conclusion is of foremost importance to the theory of the constitution of condensation polymers, to be discussed in subsequent sections of this review.

V. KINETICS OF DEGRADATION PROCESSES

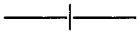
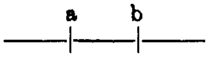
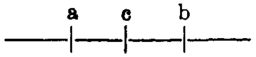
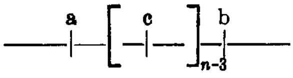
A. Cellulose and cellulose derivatives

When dissolved in strong acids cellulose is degraded through hydrolytic splitting of the β-glucoside linkages between the structural units of the cellulose chain:

$$HO(C_6H_{10}O_4)—[O—(C_6H_{10}O_4)]_{n-2}—O—(C_6H_{10}O_4)OH$$

The process can be followed viscometrically, polarimetrically, or by chemical determination of the aldose end group produced for each bond split. Measurements by Freudenberg and coworkers (41, 42), employing the latter two methods and interpreted according to the theoretical treatments supplied by Kuhn (58, 59), show a continuous increase in the first-order velocity constant for the splitting of the inter-unit linkages over the range from 10 to 100 per cent hydrolysis, corresponding to a change in $\overline{DP}_n$ from 10 to 1. In other words, the linkages remaining near completion of the degradation split with greater ease, on an average, than those initially present.

They also measured rates of hydrolysis, under the same conditions, of several lower polysaccharides: namely, those for which n in the above formula equaled 2, 3, and 4, respectively. Initial concentrations were adjusted to give equal concentrations of glucose at complete hydrolysis. Whereas hydrolysis of the bond in cellobiose progressed in strict accordance with a first-order expression, the calculated first-order rate constants for the disappearance of total β-glucoside bonds for cellotriose and cellotetrose increased as the reaction progressed. Initial rate constants (in 51 per cent sulfuric acid at 18°C.) for hydrolysis of these polysaccharides, expressed as the fraction of inter-unit linkages disappearing per minute, were as follows:

POLYSACCHARIDE	SCHEMATIC STRUCTURE	INITIAL RATE CONSTANTS
		$min.^{-1} \times 10^4$
Cellobiose		1.07
Cellotriose		0.64
Cellotetrose		0.51
Cellulose		0.305

Freudenberg and Kuhn (41, 42) showed that both the velocity constants and the courses followed by the hydrolyses of these various polymers can be accounted for by postulating that one or the other or both of the terminal linkages, a and b, in these various species hydrolyzes more rapidly than internal c linkages. All of the latter can be assumed to hydrolyze at the same rate, or at least their rates are not perceptibly different. If it is assumed, for example, that one of the two terminal linkages, a or b, in an n-mer reacts at a rate equal to cellobiose, 1.07×10^{-4}, and that for each of the other $n - 2$ linkages the rate corresponds to the initial average rate, 0.305×10^{-4}, of hydrolysis of the bonds in cellulose ($n \rightarrow \infty$), then the calculated initial rates for cellotriose and cellotetrose, 0.69×10^{-4} and 0.56×10^{-4}, respectively, are in fair agreement with the observed values. Also, the course of the hydrolysis of cellulose is in good agreement with Kuhn's mathematical analysis (59) of the consecutive reaction problem precipitated by the above postulate.

These results probably can be explained equally well by assuming that the enhanced reactivity is shared jointly by both terminal linkages a and b, neither being as reactive as the linkage in cellobiose (41). Mathematical analysis of the course of the hydrolysis of cellulose in this case is considerably more difficult. However the relative reactivities of the linkages a and b may be related, the results with cellulose indicate that the reactivity of internal c linkages is about constant, independent of molecular weight over the range investigated, i.e., up to $\overline{DP}_n = 10$. The lesser reactivities of the internal linkages can reasonably be ascribed to the short-range substitution effect previously discussed.

The course of the degradation of methylated cellulose in fuming hydrochloric acid at 0°C. was observed by Wolfrom, Sowden, and Lassettre (92) by continuous mercaptalation of the aldose group formed at each bond ruptured. Sulfur analysis gave a direct measure of the number of bonds split. Over the range of their measurements, from $\overline{DP}_n = 150$ to 50, the concentration of unhydrolyzed bonds is almost constant. If the reactivity of the bonds is independent of molecular weight therefore, the number of bonds hydrolyzed should increase linearly with time over this range. That this is the case is shown by the data of Wolfrom and coworkers in figure 5. Had their measurements been extended to greater degrees of hydrolysis, enhanced reactivity of terminal linkages as observed by Freudenberg and Kuhn probably would have been in evidence.

The hydrolysis of cellulose of high molecular weight is best observed viscometrically. The change in the number of end groups over the initial portion of the degradation is too small to be measured accurately by chemical means. The polarimetric method is likewise insufficiently sensitive at high molecular weights. Schulz and Löhmann (82) followed the degradation of celluloses varying from 130 to 1500 units in length dissolved in phosphoric acid by measuring dilute solution viscosity. They originally concluded from their results that the rate of splitting of inter-unit bonds is first order and that the velocity constant is independent of molecular weight. Subsequently (81), they found that the intermediate degraded celluloses were less heterogeneous than would be true if bonds were split strictly at random. Chains of about 500 units were in much greater abundance than would be obtained by random degradation. Schulz and coworkers revised their original conclusions to the extent of postulating that at regular intervals of around 500 units, linkages occur which are much more readily hydrolyzed than the β-glucoside linkages. They suggested that these exceptional linkages are occasioned by the occurrence of xylose units at these intervals.

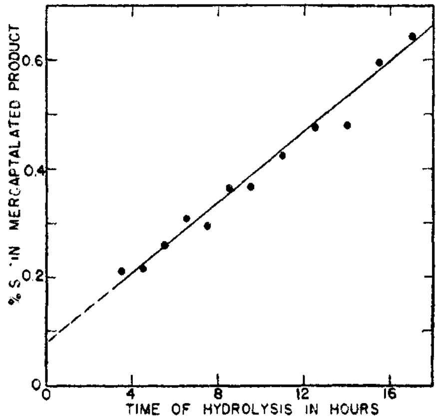


Fig. 5. Hydrolysis of methylated cellulose in fuming hydrochloric acid at 0°C. Reaction followed by mercaptalation method. (Wolfrom, Sowden, and Lassettre (92).)

From a degree of polymerization of about 500 units onward, the hydrolysis of linkages in the cellulose chain is first order. At more advanced stages of the hydrolysis the rate is somewhat more rapid than first order, but this behavior is caused by the greater abundance of more easily hydrolyzed terminal linkages, as found by Freudenberg, Kuhn, and coworkers.

From the various results discussed above it is clear that the *internal* linkages between the units of cellulose and derivatives are equivalent in their reactivity toward hydrolysis regardless of their location in the chain and independent of the length of the chain, at least up to $DP = 500$. At higher molecular weights weaker linkages may be present, owing to specific differences in the chemical character of occasional units of the chain. There is no evidence for an effect of molecular weight *per se* on reactivity up to $DP = 1500$ (molecular weight = 250,000).

B. Hydrolysis of polyamides

Hydrolysis of the polypeptide of glycine

$$NH_2CH_2CO—[NHCH_2CO]_{n-2}—NHCH_2COO^-$$

in alkaline solution (43, 61) follows a pattern similar to that observed for cellulose. In view of the short length of the structural unit and the ionic character of one of the end groups (in alkaline solution), terminal bonds should be expected to possess reactivities differing from internal bonds. In this case the terminal bonds are observed to be less reactive than internal ones. Freudenberg and coworkers (43) showed that the course of the hydrolysis of a synthetic polypeptide of glycine having a $\overline{DP}_n$ of 8 was accurately described by assigning a mean rate for the two terminal bonds a and b (see diagram given above for polysaccharides) equal to the observed initial rate of hydrolysis of the peptide bonds in diglycylglycine ($n = 3$) and a rate for the internal bonds equal to the rate previously deduced (61) for the hydrolysis of the c bond in triglycylglycine ($n = 4$).

Scatchard, Oncley, Williams, and Brown (78) recently presented an interesting interpretation of the hydrolytic degradation of the protein collagen to gelatin and the further degradation of gelatin. They consider that collagen consists of very long polypeptide chains having readily hydrolyzable bonds at regular intervals. In the preparation of gelatin nearly all of these are split, and in addition a small fraction of the less reactive peptide bonds of the resulting fragment (gelatin) molecules are hydrolyzed as well. It is estimated that these easily hydrolyzable bonds of collagen occur at intervals of about 1200 units. In the further degradation of these "fragments" (molecular weight *ca.* 100,000) the rate of splitting of the peptide bonds is observed to be constant for small degrees of reaction. Hence, it is inferred that all linkages in the gelatin molecules are equally susceptible to hydrolysis, and that their reactivity is independent of molecular weight. The degradation of gelatin would appear, therefore, to consist of random splitting of molecules initially uniform in molecular weight. The theoretical treatment of this type of degradation was solved previously by Montroll and Simha (68) and, in a simpler fashion, by Sakurada and Okamura (76). By comparing osmotic-pressure molecular weights of partially degraded gelatin with sedimentation-equilibrium measurements in the ultracentrifuge ("z-average" molecular weight), Scatchard and coworkers were able to show that the molecular-weight heterogeneity is indeed consistent with the view that degradation of gelatin proceeds by random splitting of initially uniform chains. This interpretation of the degradation of the parent collagen chains is strikingly similar to that proposed by Schulz, Husemann, and Löhmann (81) for native cellulose.

Matthes (65) measured the rate of hydrolysis in 40 per cent sulfuric acid at 50°C. of the polyamide

$$NH_3^+\text{—}(CH_2)_5CO\text{—}[NH(CH_2)_5CO]_{n-2}\text{—}NH(CH_2)_5COOH$$

derived from ε-aminocaproic acid. The degree of polymerization decreases strictly in accordance with a first-order splitting of amide linkages over the entire range investigated from $\overline{DP}_n = 220$ to 6.

C. Alcoholysis of polyesters

The kinetics of degradation by alcoholysis of linear polyesters prepared from decamethylene glycol and adipic acid

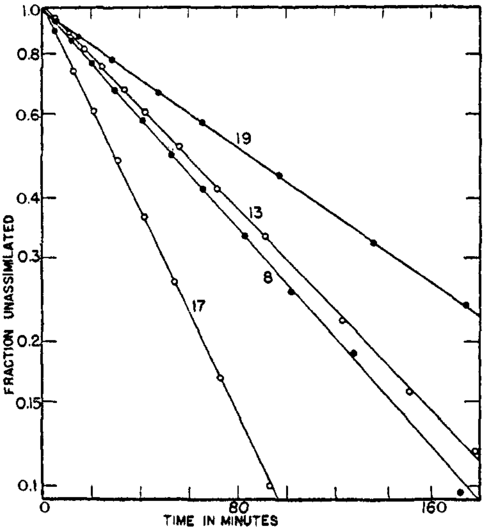
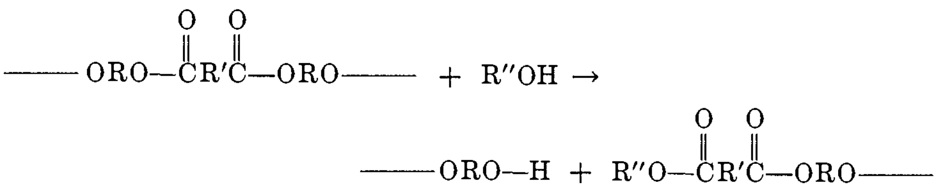


FIG. 6. The partial degradation of decamethylene adipate polyester with small percentages of decamethylene glycol (experiments 8, 13, and 17), or with lauryl alcohol (experiment 19) at 109°C. catalyzed with 0.1 equivalent per cent of *p*-toluenesulfonic acid (31). The fraction of glycol, or alcohol, unassimilated, calculated indirectly from melt viscosity measurements, is plotted on the logarithmic ordinate scale.



$$\text{——ORO—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{—ORO——} + R''OH \rightarrow$$

$$\text{——ORO—H} + R''O\text{—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{—ORO——}$$

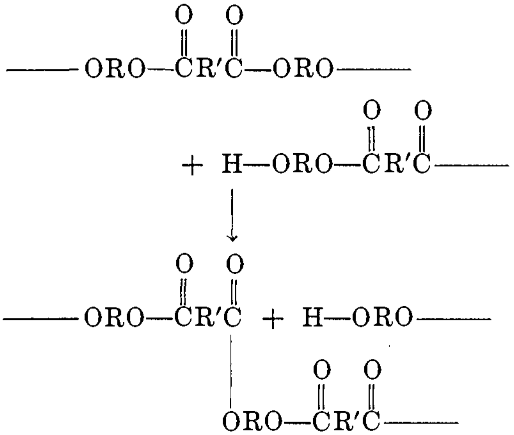
was investigated (31) by a novel method in which the degree of polymerization at various stages of the reaction was computed from the viscosity of the reaction mixture, consisting of polyester plus a small percentage of alcohol, or glycol. The exact empirical relationship (29) between melt viscosity and molecular weight is the basis for this method. Not only is the measurement of the melt viscosity extremely simple; it can be conducted within the reaction vessel without removal of samples or interruption of the reaction.

Esterification is so similar to ester interchange in rate and mechanism as to have obscured the degradation process by simultaneous polymerization had the polyesters employed in these experiments (31) been functionally capable of further esterification. To avoid this difficulty, the polyesters were prepared using a small excess of glycol and the reaction was carried very nearly to completion. The polymers so obtained contained a negligible proportion of free carboxyl groups. Hence, the possibility of further esterification during the interchange experiments was practically eliminated.

In these degradations (31), in contrast to those previously discussed, a small proportion of degrading agent (alcohol or glycol) was employed. The final product of the degradation was a polymer of lower molecular weight than the initial product, rather than the free monomers. From the viscosity at a given stage of the reaction the average molecular weight was calculated, and from this the amount of alcohol (or glycol) assimilated by the polymer through the interchange reaction could be computed. In view of the constancy of the number of ester groups the reaction should be first order with respect to the alcohol, provided, of course, that all ester groups are equally reactive. That this is the case is shown by the linear plots in figure 6 for the reaction at 109°C. catalyzed by *p*-toluenesulfonic acid. In these experiments polymers of initial $\overline{DP}_n$ = 35 to 40 were degraded to $\overline{DP}_n$'s of around 15 to 20.

D. Interchange reactions in condensation polymers

The ready occurrence of the interchange reaction between an alcohol and a polyester suggests at once that polyester molecules bearing terminal hydroxyl groups should be capable of reacting with one another, thus:



$$\text{——ORO—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{—ORO——} + \text{H—ORO—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{——}$$

$$\downarrow$$

$$\text{——ORO—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{—ORO—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{——} + \text{H—ORO——} \qquad \text{(I)}$$

A similar interchange may occur between a carboxy acid end group and an ester, but the rate of this reaction is known to be much slower than the alcoholysis reaction given above. In these interchange reactions between polymer molecules there is no net change in the number of inter-unit linkages, and the number of molecules on either side of the equation is the same. The number-average molecular weight is unaffected therefore. However, these processes can bring about changes in molecular-weight distribution. For example, two average molecules can react to produce one much longer and another correspondingly shorter than the average. Conversely, if a mixture is composed of two species, one very long and the other quite short, they may conceivably interchange with each other to produce polymers intermediate in size.

A fully satisfactory account of the rôle and importance of these interchange processes in condensation polymers would necessitate detailed consideration of the subject of molecular-weight distribution, to be covered in the next section. For the purposes of the present qualitative discussion it will be sufficient to point out the rather obvious fact that, regardless of the initial distribution of molecular weights at commencement of interchange, ultimately the interchange processes will lead to a state of (dynamic) equilibrium in which the concentration of each species remains constant. These concentrations define the "equilibrium molecular weight distribution" (38, 39, 90) for a given (fixed) extent of polymerization, or number of inter-unit linkages. Incidentally, this distribution happens to be identical with that which is obtained directly from random intermolecular condensation without simultaneous, or subsequent, occurrence of interchange reactions (38). Thus, interchange, though it may occur freely, ordinarily will have no effect on the molecular-weight distribution of a condensation polymer. (Important exceptions will be noted later.) The current discussion will be confined to linear polymers, but similar conclusions obviously may be applied to three-dimensional polymers as well.

For the purpose of experimentally observing the occurrence of interchange between polymer molecules, two polydecamethylene adipates, one of low and another of high average molecular weight, were mixed (38). These polymers were so prepared that their end groups were predominantly hydroxyl, in order to minimize simultaneous occurrence of esterification. *p*-Toluenesulfonic acid catalyst was used, and the mixture was fused and heated at 109°C. Ordinary chemical methods would be useless for observing the interchange, owing to the constancy of the concentrations of ester linkages and terminal hydroxyls. The melt viscosity, however, depends not on the number-average molecular weight $\overline{M}_n$, which is constant, but on the weight average $\overline{M}_w$, which shifts as the molecular-weight distribution is altered (at constant $\overline{M}_n$). The empirical relationship between melt viscosity and weight-average molecular weight (29) being known, it was possible to observe the change in distribution due to interchange by simple melt viscosity measurements on the reaction mixture.

One set of results is shown in figure 7. The viscosity dropped rapidly at first, and then approached a limiting value asymptotically. This decrease in viscosity of nearly 60 per cent was produced entirely by alteration of the molecular-weight distribution. The total number of molecules, and $\overline{M}_n$ as well, necessarily remained constant, owing to the nature of the reactants, but the numbers of the larger molecular species were drastically decreased through interchange. These larger molecules exerted a greater influence on the viscosity than the smaller ones; hence, a decrease in viscosity accompanied equilibration of the size distribution. The observed final viscosity is close to that calculated for the equilibrium distribution (38) having the number-average molecular weight dictated by the molecular weights and proportions of the initial ingredients. The agreement lies within the limits of accuracy of the empirical viscosity relationship as applied to these particular polymers.

Interchange also may occur in other condensation polymers. Brubaker, Coffman, and McGrew (4) have shown that when two polyamides formed from different monomers (e.g., one formed from triglycol diamine and adipic acid and the other from hexamethylenediamine and adipic acid) are heated together for about 30 min. at 285°C., they combine to give a product differing from both initial polymers. This product is not merely a mixture of molecules of the two original components, as is shown by their inseparability by the action of a selective solvent. The product differs, also, from the copolymer of the same composition prepared directly from the monomers.

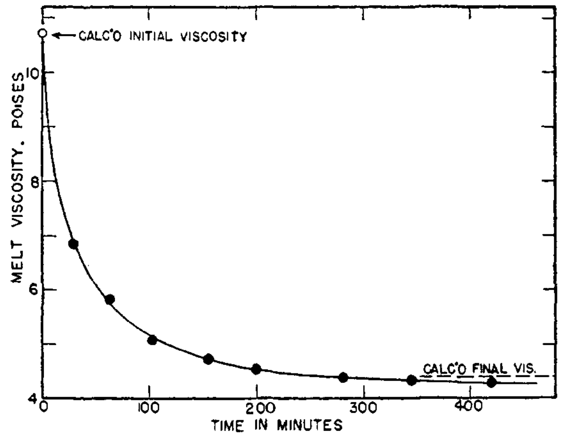
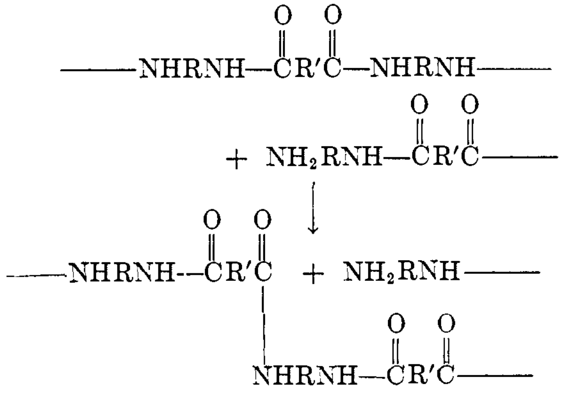


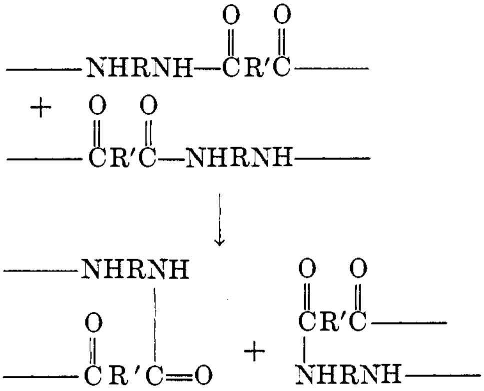
FIG. 7. Interchange reaction between two polydecamethylene adipate polymers at 109°C catalyzed by *p*-toluenesulfonic acid. Melt viscosity vs. time of reaction. Initial mixture: 42.4 per cent of polymer for which $\bar{M}_n = 6200$, and 57.6 per cent of polymer having $\bar{M}_n = 1860$. The horizontal broken line indicates the viscosity calculated for the theoretical equilibrium molecular-weight distribution. From data given in table II of reference 38.

There is ample evidence in the literature on polyamides, and on monomeric amides as well, for the occurrence of the amine-amide interchange reaction



$$\begin{array}{l} \text{———NHRNH—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{—NHRNH———} \\ \qquad\qquad + \; NH_2RNH\text{—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{———} \\ \qquad\qquad\qquad \downarrow \\ \text{———NHRNH—}\overset{\overset{O}{\|}}{C}R'\underset{\underset{\text{NHRNH—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{———}}{|}}{\overset{\overset{O}{\|}}{C}} \; + \; NH_2RNH\text{———} \end{array} \qquad \text{(II)}$$

which is analogous to the polyester interchange (I) given above. It is likely, furthermore, that another type of interchange—namely, interchange between two amide linkages—can occur in polyamides:



$$\begin{array}{l} \text{——NHRNH—}\overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}\text{——} \\ +\ \text{——}\overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}\text{—NHRNH——} \end{array} \Big\downarrow \begin{array}{l} \text{——NHRNH} \\ \quad\quad\quad | \\ \text{——}\overset{O}{\overset{\|}{C}}R'C{=}O \end{array} + \begin{array}{l} \overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}\text{——} \\ | \\ \text{NHRNH——} \end{array} \qquad \text{(III)}$$

In the experiments reported by Brubaker *et al.*, evidently interchange occurred by way of either, or both, of these processes (II and III) to the extent that few of the initial polymer molecules remained intact. The reaction was not, however, allowed to continue until interchange reactions had brought about the state of equilibrium in which the units would be combined purely at random, as in copolymers prepared directly from the same monomers.

The counterpart of reaction III in polyesters, i.e., ester–ester interchange, proceeds at an extremely slow rate, if indeed it occurs at all. Little is known concerning interchange reactions in other polymers, aside from what can be inferred from the known chemical characteristics of the linkage. As has already been mentioned, ring–chain interconversions undoubtedly proceed by interchange reactions. Hence, the occurrence of this interconversion in a given case would indicate that interchange between polymers can also occur, although the rates may differ considerably (particularly if the ring is one of six members). Polyanhydrides certainly interchange readily with carboxylic acid end groups, in analogy with I and II above. Whether or not anhydride–anhydride interchange, like III, occurs is not known, but the acceleration of the conversion of cyclic anhydrides to linear polymers by traces of water favors the former mechanism.

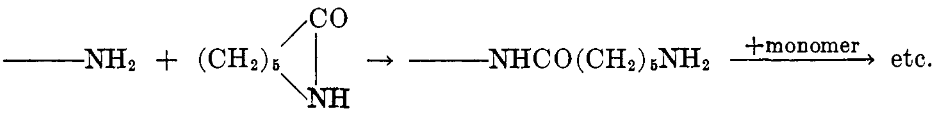
In some cases the linkage is too stable to enter readily into interchange reactions, e.g., in the hydrocarbon polymers prepared from decamethylene dibromide and sodium, in polyethylene oxide

$$HO{-}[CH_2CH_2O]_{x-1}{-}CH_2CH_2OH$$

(although classification of this as a condensation polymer is questionable), to a considerable degree in polymeric sulfides, and in cellulose and its derivatives.

The concept of mobile reshuffling of sections of high-polymer molecules, and the consequent transitory existence of individual molecules, at temperatures far below their decomposition points is interesting in itself. As pointed out above, the process is of importance in altering the distribution of an artificial mixture of two polymers from the same monomers but differing in average molecular weight, and in cross-blending the molecules of two polymers prepared from different monomers and subsequently heated together. It should also be mentioned that Carothers (6, 12) employed polymer interchange in producing high-molecular-weight polyesters from a substantial stoichiometric excess of ethylene glycol over dibasic acid. The initial products were of low molecular weight, owing to the excess of glycol, but on further heating in vacuum excess glycol was removed and the molecular weight was advanced. Now the amount of free glycol remaining at completion of the esterification of 5 mole per cent excess of glycol over dibasic acid (without loss of glycol) is extremely small—about 0.25 per cent of the initial amount of glycol. However, as this is removed by vaporization, interchange between hydroxyl terminal groups and, in this case, the ester linkages nearest the ends of chains will tend to restore the equilibrium concentration of free glycol. Hence, more glycol can be removed and the average degree of polymerization advances gradually.

Interchange may be of importance (38) also in altering the distribution of molecular weights in polymers prepared from cyclic compounds. In the case of ϵ-caprolactam, for example, if polymerization is brought about by relatively few free amino groups, possibly belonging to ϵ-aminocaproic acid molecules introduced at the start, and the reaction proceeds according to the following mechanism:



$$\text{——}NH_2 + (CH_2)_5\begin{matrix}CO\\ |\\ NH\end{matrix} \rightarrow \text{——}NHCO(CH_2)_5NH_2 \xrightarrow{+\text{monomer}} \text{etc.}$$

then the final molecular-weight distribution will be unusually sharp (30) (Poisson distribution); its homogeneity with respect to molecular size will be better than is attainable by a very careful fractionation of a polymer of the usual degree of heterogeneity. This is a direct consequence of the above mechanism: successive addition of monomers to a fixed number of equivalent terminal groups (30). If the reaction conditions are such that interchange reactions also occur, and in the above example this is likely to be the case, the molecular-weight distribution will shift to the much broader equilibrium distribution (see figure 9).

VI. CONSTITUTION OF LINEAR CONDENSATION POLYMERS

A. Molecular weights of linear polymers

In a straightforward condensation of bifunctional units of the hydroxy acid or amino acid type, which for the sake of generality can be represented as

$$A—B \rightarrow A—BA—BA—\text{etc.} \qquad \text{(type i)}$$

where A and B are the complementary functional groups and AB is the linkage formed by their condensation with one another, the number of molecules necessarily will equal the number of unreacted A or B groups. The average molecular weight (number average), $\bar{M}_n$, will be given by the reciprocal of the number of moles of unreacted A or B groups per gram. The same will be true of a glycol–dibasic acid condensation

$$\text{A—A} + \text{B—B} \rightarrow \text{A—AB—BA—etc.} \qquad \text{(type ii)}$$

provided that precisely equivalent quantities of the two reactants are employed and that no loss of either reactant occurs by volatilization. The condensations are assumed to occur without interference from side reactions. The degree of polymerization, $\overline{DP}_n$, for either type will be given by the quotient of the total number of units, N_0, divided by the total number of molecules. The latter, being equal to the number of unreacted A or B groups, is given by $N_0(1 - p)$, where p is the extent of reaction previously employed. Hence, for linear polymerization of bifunctional units (exclusively) in which equimolar quantities of A and B groups are present:

$$\overline{DP}_n = 1/(1 - p) \tag{3}$$

At 95 per cent reaction ($p = 0.95$) there will be an average of twenty units per molecule; at 99 per cent reaction, one hundred units; etc. The problem of attaining high molecular weight reduces to the problem of forcing the condensation reaction as nearly as possible to completion. At the same time, side reactions which otherwise consume functional groups must be reduced to a very low minimum (29).

If the reaction is second order, then according to equation 2:

$$\overline{DP}_n = \text{Const.} \times t + 1 \tag{4}$$

In accordance with this relationship, the average molecular weight in acid-catalyzed polyesterifications increases linearly with time (figure 4).

If the reaction is third order, then according to equation 1:

$$\overline{DP}_n = (\text{Const.} \times t + 1)^{1/2} \tag{5}$$

Except at very low $\overline{DP}_n$'s

$$\overline{DP}_n = \text{Const.} \times t^{1/2} \tag{5'}$$

Thus, in third-order polyesterifications (uncatalyzed) and in uncatalyzed polyanilidation (33), high molecular weights are reached only by continuing the reaction for a long time. This is not the result of inherent sluggishness of the reaction owing to high viscosity, nor is it due to the difficulty with which water formed in the reaction is removed from the polymer, as was once supposed (14). The third-order reaction between functional groups permits the average molecular weight to increase only in proportion to the square root of the time; hence the apparent falling off in the rate of polymerization as the molecular weight increases (28).

Molecular weights of linear condensation polymers can be controlled by discontinuing the reaction at the desired stage. However, the polymers produced in this way may undergo further condensation if heated subsequently, as, for example, in the course of processing and fabricating operations. The resultant change in properties frequently is undesirable.

This susceptibility to further polymerization can be avoided and the molecular weight can be controlled by the application of the "molecular weight stabilization" method for controlling molecular weight (12, 72). This is accomplished by displacing the precise stoichiometric balance between the primary bifunctional reactants through the addition of a small amount of a so-called "molecular weight stabilizer", which is nothing more than a monofunctional or bifunctional reactant incorporated in small proportion with the primary monomers.

For example, lauric acid has been used in the stabilization of polyamides (72). If the reactant is an amino acid, at completion of the reaction the lauric acid-stabilized molecules will have the structure

$$\mathrm{RCO{-}[NHR'CO]_{x-2}{-}NHR'COOH}$$

If lauric acid is added to a stoichiometric mixture of a dibasic acid and a diamine, the molecules produced at complete amidation will be of three types:

$$\mathrm{RCO{-}[NHR'NHCOR''CO]_{(x-1)/2}{-}OH}$$

$$\mathrm{RCO{-}[NHR'NHCOR''CO]_{(x-3)/2}{-}NHR'NH{-}COR}$$

$$\mathrm{HOCOR''CO{-}[NHR'NHCOR''CO]_{(x-1)/2}{-}OH}$$

Similarly, an excess of one or the other reactant in a type ii linear condensation may perform the function of a molecular-weight stabilizer. For example, an excess of dibasic acid in a glycol–dibasic acid condensation causes the product of complete esterification to have the formula

$$\mathrm{HOCOR'CO{-}[OROCOR'CO]_{(x-1)/2}{-}OH}$$

The relationship of the molecular weight, or degree of polymerization, to the proportion of stabilizer employed and the extent of completion of the condensation can be computed in various ways. One which is quite general (27, 29) is given here. Consider a condensation either of type i or of type ii, in which first of all the reactants are present in stoichiometric quantities. To either of these is added a stabilizer B—B, which may or may not be identical with one of the co-reactants in the type ii reaction. Let

N_A = total number of A groups initially present
N_B = total number of B groups initially present
$r = N_\mathrm{A}/N_\mathrm{B}$
p = fraction of A groups which have reacted at a given stage of the reaction.

The total number of units is given by

$$(N_\mathrm{A} + N_\mathrm{B})/2 = N_\mathrm{A}(1 + 1/r)/2$$

The total number of ends of chains can be expressed as

$$2N_\mathrm{A}(1 - p) + (N_\mathrm{B} - N_\mathrm{A}) = N_\mathrm{A}[2(1 - p) + (1 - r)/r]$$

and this must equal twice the total number of molecules, since each linear molecule has two ends. The number-average degree of polymerization is given by

$$\overline{DP}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{1 + r}{2r(1 - p) + 1 - r} \tag{6}$$

At completion of the reaction ($p = 1$)

$$\overline{DP}_n = (1 + r)/(1 - r) \tag{7}$$

$$= \frac{\begin{pmatrix}\text{Moles bifunctional units} \\ \text{exclusive of stabilizer}\end{pmatrix}}{(\text{Moles stabilizer units})} + 1 \tag{7'}$$

The same equations are applicable to stabilization with monofunctional units B—, provided that r is redefined as follows:

$$r = N_A/(N_A + 2N_{B—})$$

Equation 7′ requires no revision. Other special cases can be similarly treated, as, for example, when two or more types of stabilizers are employed simultaneously.

Equations 7 and 7′ emphasize the marked effect of a small amount of stabilizer in limiting the ultimately attainable molecular weight. One mole per cent of stabilizer units limits the average degree of polymerization to about one hundred units, for example. It emphasizes further the precision with which the stoichiometric balance must be maintained in linear condensation in order for high molecular weights to be reached. Loss of a fraction of a per cent of one or the other ingredient in a type ii condensation through volatilization from the reaction mixture, or loss of functional groups through side reactions in either type of condensation, may appreciably limit the molecular weight attainable.

The effects of loss of ingredient, of side reactions, and of monofunctional impurities in vitiating molecular weights derived from chemical determination of one or the other end group have been discussed previously (29) in some detail. This source of error, though small at low degrees of polymerization, increases approximately as the square of $\overline{DP}_n$. The percentage error increases directly with the molecular weight and to a close approximation is given by

$$(\text{Per cent excess of one unit}) \times \overline{DP}_n/2$$

Thus, at $\overline{DP}_n = 200$, a loss of 0.1 per cent of one or the other of the bifunctional reactants A—A or B—B introduces a 10 per cent error in the value of the molecular weight calculated directly from the number of terminal A or B groups.

Molecular weights of synthetic condensation polymers almost invariably have been determined by end-group methods. The viscosity methods (solution or melt) which may be employed have been established on the basis of end-group determinations. Cryoscopic and ebullioscopic methods may be sufficiently accurate below about 5000 molecular weight, and in this region agreement with end-group methods has been confirmed (12, 85). Kraemer and Van Natta (57) reported an ultracentrifuge sedimentation value for a polyhydroxydecanoic acid of about 25,000 molecular weight which was in good agreement with the end-group titration value (19). However, this agreement is of dubious significance in view of the ambiguity in the type of average obtained from the ultracentrifuge data, as well as the probability of sufficient pyrolytic loss of functional groups at the high temperature used in synthesis (40) to vitiate the end-group molecular weight.

B. Molecular-weight distribution in linear condensation polymers

The principle of equal reactivity of all functional groups during condensation polymerization is the foundation for the theoretical derivation of molecular size distribution relationships (27). No other postulates or assumptions are required. At every stage of the polymerization equal opportunities for reaction are available to all unreacted functional groups. At conclusion of the condensation the probability that a given functional group has reacted (when $r = 1$) is invariably equal to p, the fraction of all functional groups which have reacted. The significance of this statement lies in the fact that if a given unit is known to be attached through one reacted functional group to a sequence of n consecutive units, the probability that the other functional group of the unit has reacted is still equal to p, and independent of the length of the chain as indicated by n.

Consider, for example, the polyester produced from an ω-hydroxy acid. Suppose that a terminal hydroxyl group of one of the molecules has been located at random and we wish to know the probability that this molecule is composed of exactly x units.

$$\mathrm{H{-}\underset{1}{ORCO}{-}\underset{2}{ORCO}{-}\underset{x-1}{\cdots\cdots}{-}\underset{x}{ORCO}{-}OH}$$

The probability that the carboxyl group of the first unit is esterified is equal to p. The probability that the carboxyl of the second unit is esterified, this probability being independent of whether or not linkage 1 has been formed, is likewise equal to p. The probability that this sequence continues for $x - 1$ linkages is the product of these separate probabilities, or p^{x-1}. This is the probability that the molecule contains at least $x - 1$ ester groups, or at least x units. The probability that the x^{th} carboxyl group is unreacted, thus limiting the chain to exactly x units, is $1 - p$. Hence, the probability that the molecule in question is composed of exactly x units is given (27) by

$$P_x = p^{x-1}(1 - p) \tag{8}$$

Obviously, the probability, P_x, that any molecule selected at random is composed of x units must equal the mole fraction of x-mers.

The total number of x-mers is given by

$$N_x = N(1 - p)p^{x-1}$$

where N is the total number of molecules of all sizes. Letting N_0 represent the total number of units

$$N = N_0(1 - p)$$
$$N_x = N_0(1 - p)^2p^{x-1} \tag{9}$$

If the added weight of the end groups (equal to H + OH for each molecule) is neglected, the molecular weight of each species is directly proportional to x. Hence the weight fraction can be written

$$w_x = xN_x/N_0$$

The error introduced by this approximation will be significant only at very low molecular weights. Substituting from equation 9:

$$w_x = x(1 - p)^2p^{x-1} \tag{10}$$

The same derivation holds for type ii polymers from equivalents of A—A and B—B reactants. It also applies to polymers stabilized with small amounts of monofunctional units, although here it becomes necessary to replace the extent of reaction p with another quantity, the probability that a given functional group has reacted with a *bifunctional* monomer. Type ii polymers stabilized with an excess of one or the other ingredient will be discussed later.

If interchange reactions occur subsequent to the formation of the inter-unit linkages, the above distribution will not be altered. The basis for this statement can be indicated briefly as follows: (For more rigorous treatments of this problem see references 38, 39, and 90.) If interchange reactions occur freely, ultimately a state of dynamic equilibrium will be attained in which each species is formed at a rate equal to its destruction. The concentrations of the various species (i.e., the size distribution) will then be constant. The above size-distribution relationships were derived from the principle of equal reactivity in the *kinetic* sense that all unreacted functional groups are equally susceptible to condensation. Here it is necessary to postulate equal reactivity in the *thermodynamic* sense that all functional groups share an equal probability of existing at any instant in the reacted condition, regardless of the sizes of the molecules involved. This probability again can be designated by p, the fraction of all groups which are reacted, and the previous derivations and results apply without alteration. Hence the same size distribution is obtained by interchange equilibration as is produced initially by random condensation. Polymers produced by random condensation will not be altered by interchange processes; regardless of whether the linkages are irreversibly or reversibly formed, the same molecular-weight distribution will prevail. The same distribution also is obtained by random degradation of infinitely long molecules (58).

Mole-fraction (or number) distribution curves calculated from equation 8 are shown in figure 8 for polymers having average $\overline{DP}_n$'s of 20, 50, and 100, respectively. The corresponding weight-fraction distributions calculated from equation 10 are shown in figure 9. As is also evident from the equations, monomers are present in greater numbers than any other single species, and this is true at all stages of the condensation. The number curves exhibit monotonic decreases as the number of units is increased. On a weight basis, however, the proportion of very low polymers is small, and is diminished as the average molecular weight is increased. Maxima in the weight-distribution curves occur very near the number-average value of x, i.e., very near $x = \overline{DP}_n$.

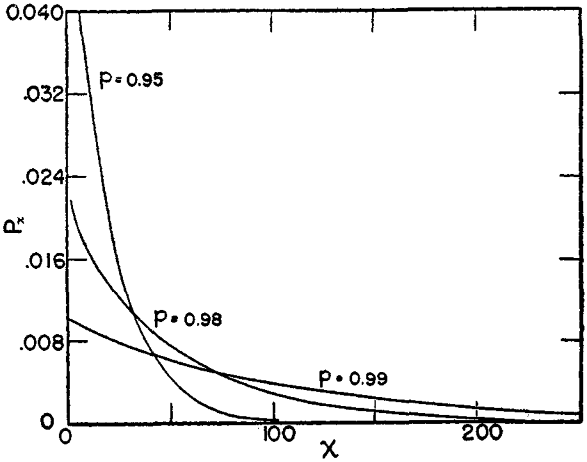


FIG. 8. Molecular-weight distributions for linear condensation polymers on a number or molar, basis for several extents of reaction p. Mole fractions P_x vs. number of structural units x, as calculated from equation 8. See reference 27.

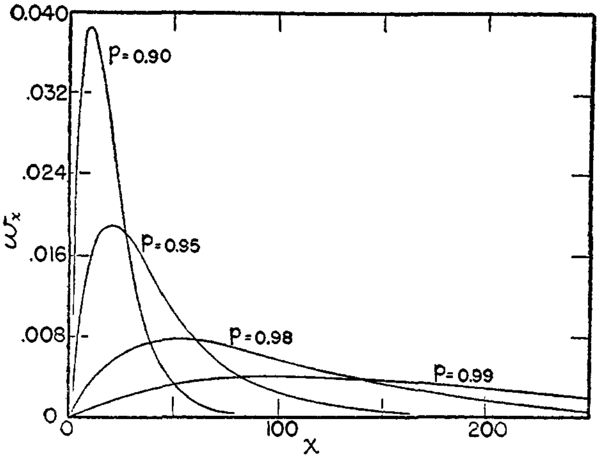


FIG. 9. Molecular-weight distributions for linear condensation polymers on a weight basis for several values of the extent of reaction p. Weight fractions w_x vs. number of structural units, x, as calculated from equation 10. See reference 27.

In type ii condensations three types of molecular species are present (27):

$(A—AB—B)_{x/2}$ Type iiAB

$(A—AB—B)_{(x-1)/2}A—A$ Type iiAA

and

$B—B(A—AB—B)_{(x-1)/2}$ Type iiBB

All molecules containing an even number of units necessarily will be of type iiAB, while those containing an odd number of units will be of type iiAA or iiBB. If the numbers of A—A and B—B units in the reaction mixture are exactly equal, there will be as many *even* as *odd* molecules, and the odd molecules will be equally divided between types iiAA and iiBB. The molecular-weight distribution given above applies here also; only this alternation in end groups will occur between successive even and odd values of x.

If an excess of one component is employed in the reaction, the relative numbers of these three types of species will be altered. Taking the B—B unit to be the one present in excess, there will be more type iiBB than type iiAA molecules. Furthermore, there will be more of these *odd* x molecules (including both sub-types together) than *even* molecules. This is readily evident from the fact that there are more B than A end groups. At completion of the reaction only type iiBB molecules will remain.

Mathematical expression of the distribution of sizes for these three types is rather complex (see reference 27). If the distribution for a type ii polymer containing an excess of one reactant is plotted graphically, all three types being included on a single curve, an alternation will be observed in the weight, or number, fraction from one x value to the next; there is less x-mer, where x is an even integer, than of $(x - 1)$-mer or of $(x + 1)$-mer. However, the separately considered distributions for each of the three types of molecules are virtually identical in character with the curves shown in figures 8 and 9. If an "average" distribution curve is drawn from which the alternation in abundance from one species to the next is smoothed out, the curve so obtained is virtually identical with the curve for the linear polymer formed from equal numbers of the two reactants. In conclusion, all of these variously modified bifunctional condensations yield closely similar molecular-weight distributions.

In addition to the ordinary number-average molecular weight obtained by chemical end-group methods, or by the classical thermodynamic methods (freezing-point lowering, boiling-point elevation, or osmotic pressure) for molecular-weight determination, various other average molecular weights frequently are required for the interpretation of polymer properties. The melt viscosity, for example, depends directly on the *weight-average* molecular weight (28) rather than on the *number average*. Solution viscosities usually depend on an intermediate type of average.

The number average is given by

$$\bar{M}_n = \Sigma M_x N_x / \Sigma N_x \tag{11}$$

where M_x is the molecular weight of an x-mer, and the summations are over all species from $x = 1$ to infinity. The weight-average molecular weight is defined (56) as

$$\bar{M}_w = \Sigma \bar{M}_x w_x / \Sigma w_x \tag{12}$$

Setting $M_x = xM_0$, where M_0 is the molecular weight of a structural unit, or the mean of the molecular weights of the structural units in a type ii polymer, and substituting from equations 9 and 10:

$$\bar{M}_n = M_0\Sigma[xp^{x-1}(1 - p)^2]/\Sigma[p^{x-1}(1 - p)^2]$$

The summations in this equation are equal, respectively, to 1 and to $(1 - p)$. Hence

$$\bar{M}_n = M_0/(1 - p)$$

which is the result previously obtained as expressed in equation 3. The weight average becomes

$$\bar{M}_w = M_0\Sigma[x^2p^{x-1}(1 - p)^2]/\Sigma[xp^{x-1}(1 - p)^2]$$

which reduces to

$$\bar{M}_w = M_0(1 + p)/(1 - p) \tag{13}$$

In a similar manner the root-mean-square molecular weight can be shown to be

$$\bar{M}_{rms} = M_0(1 + p)^{1/2}/(1 - p) \tag{14}$$

These various averages, or modes of the distribution, stand in the ratio (29):

$$\bar{M}_n:\bar{M}_{rms}:\bar{M}_w::1:(1 + p)^{1/2}:(1 + p)$$

When the molecular weight is large, p can be replaced by unity, and the above ratio becomes approximately $1:\sqrt{2}:2$, i.e., the various averages or modes of the distribution stand in the same ratio to one another independent of the degree of polymerization.

Direct experimental verification of the theoretical size distribution in linear condensation polymers, as expressed by equations 8 and 10, has not been reported. Determination of the molecular-weight distribution by fractionation of the polymer, followed by construction of the distribution curve from the molecular weights of the fractions, would be of little value on account of the crudity of separation which can be achieved by any known methods. Ultracentrifuge measurements have not proved satisfactory for this purpose. The recent light-scattering method for molecular-weight determination established by Debye (20, 21) is, in principle at least, applicable to this problem, but the molecular weights of condensation polymers are rather too low for best results from this method.

On the other hand, the size-distribution theory receives strong confirmation from the success with which it has been applied to various problems, including the melt viscosities of mixtures of linear polymers (29), the viscometric measurement of the rates of alcoholysis of polyesters (31), and the equilibration between low- and high-molecular-weight polyesters (38). The theory has been applied successfully to the quantitative treatment of each of these problems. If the actual distribution curve deviates appreciably from the theoretical, it must certainly be assumed that this departure will vary with the average degree of polymerization, the deviation presumably becoming greater the greater the degree of polymerization. Even a slight deviation of this character would have vitiated the agreement obtained between theory and experiment in the investigations referred to.

Logically, there is no necessity for experimental verification of the theoretical size-distribution functions. They are derived solely from the principle of equal reactivity of all functional groups, which is abundantly confirmed by experiment, not to mention the support which it receives from the theory of reactivity of large molecules. Although most of the experimental results have been obtained on polyesters, there is no reason to doubt that the equations also describe accurately the size distributions in other linear condensation polymers.

VII. CONSTITUTION OF THREE-DIMENSIONAL CONDENSATION POLYMERS

Analysis of the constitution and molecular-weight distribution of three-dimensional condensation polymers is much more difficult, as would be expected from their structures as compared with linear polymers (see table 1). Likewise, polymerization of multifunctional reactants is complicated experimentally by the occurrence of gelation, as previously discussed early in this review. The sudden transformation of the reaction mixture from a viscous liquid to an elastic material of infinite viscosity, which transformation characterizes the gel point, has been attributed to the formation of infinite network structures, i.e., molecular structures which assume macroscopic size and which extend throughout the medium. The suddenness with which gelation occurs is significant. Immediately following the gel point a small fraction of the material is insoluble in all solvents which do not react chemically in such a way as to degrade the polymer; the remainder is soluble and can be extracted from the former. Thus, two portions of the polymer can be differentiated: the soluble "sol" and the insoluble "gel", which constitutes the infinite network structures. As condensation polymerization proceeds beyond the gel point, the percentage of gel increases at the expense of sol. Simultaneously, the polymer becomes more tough and less extensible.

Another feature of three-dimensional polymerization which deserves mention is the low "molecular weight", or more accurately the low number-average molecular weight, of the polymerizing mixture at the gel point. This has been shown most clearly by Kienle and coworkers (54) in the case of glycerol–dibasic acid condensations. However, their conclusions from these observations that infinite networks are not formed at gelation, and consequently that gelation is the result of other causes, arise from a misinterpretation of the average molecular weight (34) (*cf. seq.*).

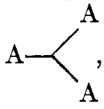
These characteristics of three-dimensional polymerizations can be shown to be necessary consequences of the polyfunctional nature of the reactants. The theory goes even further in providing quantitative relationships governing the location of the gel point, the transformation of sol to gel, and in depicting the molecular-weight distribution. The method again is a statistical one. The following assumptions are employed.

All functional groups are assumed to be equally reactive, independent of the degree of polymerization and viscosity. This assumption is amply verified in the case of linear condensations, as previously discussed. Some qualification is required, however, in the case of certain multifunctional reactants such as glycerol. Here the middle (secondary) hydroxyl group is less reactive (77) than the two primary hydroxyl groups. This circumstance complicates application of the theory. If the relative reactivities of primary and secondary hydroxyl groups are known, the theory can be applied by merely employing different extent of reaction values, p' and p'', for them. In principle, then, this is no obstacle to prevent application of the statistical treatment to glycerol–dibasic (or polybasic) acid condensations. A more serious distortion could result from the possible effect of esterification of one hydroxyl on the reactivities of its neighbors, owing to their close proximity in the glycerol molecule. As already pointed out for linear polymers, this effect is likely to modify only the very low degree of polymerization portion of the molecular-weight distribution.

Condensation reactions are assumed to occur only between functional groups on different molecules, except in the case of infinite networks. This assumption that condensations involving finite species are exclusively intermolecular is the most serious source of error. The work of Kienle and coworkers (54) shows that in glycerol–dibasic acid condensations the decrease in number of molecules is perceptibly less than the number of inter-unit linkages formed. (If the reactions were exclusively intermolecular, the formation of each linkage would combine two molecules into one.) Consequently, a small part of the reaction must occur intramolecularly. This same assumption, or approximation, is inherent in the treatment of linear polymers. However, there the opportunities for intramolecular reactions were relatively much smaller.

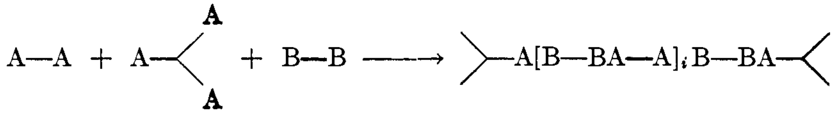
In this section the location of the gel point, the molecular-weight distribution, and the nature of the sol-to-gel conversion in three-dimensional polymers will be discussed.

A. The gel point: criteria for incipient formation of infinite networks

Consider, for example, the polymerization of a bifunctional unit A—A, a trifunctional unit , and a bifunctional unit of opposite character B—B. Structures such as that shown in figure 10 will be formed. It is the purpose of the following treatment to determine the conditions which will make possible the existence of an infinitely large, branched structure (34). In order to simplify the problem, any given molecule such as the one represented in figure 10 can be regarded as an assembly of chains connected together through trifunctional units. Each portion of a molecule between two branch units (in this case trifunctional units), or between a branch unit and a terminal unreacted functional group (e.g., OH or COOH), will be called a chain. The lengths of the chains will vary, but for the present this variation is unimportant.

First of all it is necessary to determine the branching coefficient α, which is defined as the probability that a given functional group of a branch unit leads *via* a chain of bifunctional units to another branch unit. In a polymer of the type shown in figure 10, α is the probability that an A group selected at random from one of the trifunctional units is connected to a chain the far end of which connects to another trifunctional unit. As will be shown later, both the location of the gel point and the course of the conversion of sol to gel are directly related to α.

The formation of chains, as defined above, from the reactants can be represented by the equation



$$\mathrm{A{-}A} + \mathrm{A{-}}\!\!<^{\mathrm{A}}_{\mathrm{A}} + \mathrm{B{-}B} \longrightarrow\ >\!\!\mathrm{{-}A[B{-}BA{-}A]_{\mathit{i}}B{-}BA{-}}\!\!<$$

where i may have any value from 0 to ∞. Other chains will be formed, one end, or both ends, of which consist of unreacted terminal groups. Under the assumption of equal reactivities of all A and of all B functional groups, the probability that the first A group on the left has reacted is given by p_A, the fraction of all A groups which have reacted; similarly, the probability that the B group on the right of the first B—B unit has reacted is given by p_B. Let ρ represent the ratio of A's (reacted and unreacted) belonging to branch units to the total number of A's in the mixture. Then, the probability that a B group has reacted with a branch unit is $p_B\rho$; the probability that it is connected to a bifunctional A—A unit is $p_B(1 - \rho)$. The probability that the A group of a branch unit is connected to the sequence of units shown in the above formula is given by

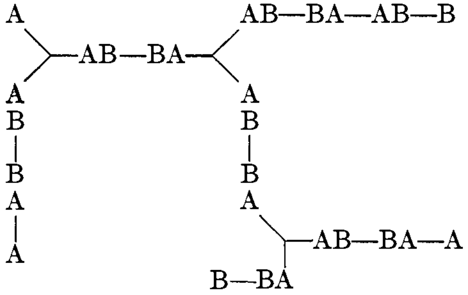


FIG. 10. Trifunctionally branched polymer composed of A—A and B—B bifunctional units, and of $\mathrm{A{-}}\!\!<^{\mathrm{A}}_{\mathrm{A}}$ trifunctional units. AB or BA is the product of the condensation of two functional groups.

$$p_A[p_B(1 - \rho)p_A]^i p_B\rho$$

The probability, α, that the chain ends in a branch unit regardless of the number, i, of bifunctional units is given by the sum of such expressions having $i = 0$, 1, 2 . . . etc., respectively. That is,

$$\alpha = \sum_{i=0}^{\infty} [p_A p_B(1 - \rho)]^i p_A p_B \rho$$

Upon evaluating this summation:

$$\alpha = p_A p_B \rho/[1 - p_A p_B(1 - \rho)] \tag{15}$$

Letting the ratio of A to B groups initially present be represented by r, as in the case of type ii linear polymers:

$$p_B = r p_A$$

Substituting in equation 15 to eliminate either p_B or p_A:

$$\alpha = r p_A^2 \rho/[1 - r p_A^2(1 - \rho] \tag{15'}$$

or

$$\alpha = p_B^2 \rho/[r - p_B^2(1 - \rho)] \tag{15''}$$

In the application of these equations, ordinarily r and ρ will be determined by the proportions of the initial ingredients employed, and either the unreacted A or B group will be determined analytically at various stages of the reaction. α can then be calculated employing either equation 15′ or equation 15″, depending on which group is determined directly. Hence, α is readily calculable from experimentally observed and controlled quantities.

Several special cases are of interest. When there are no A—A units, $\rho = 1$ and

$$\alpha = r p_A^2 = p_B^2/r \tag{16}$$

when A and B groups are present in equivalent quantities, $r = 1$, $p_A = p_B = p$, and

$$\alpha = p^2 \rho/[1 - p^2(1 - \rho)] \tag{17}$$

If the branch unit is other than trifunctional, e.g., if it is tetrafunctional, the same equations for the calculation of α can be employed; r and ρ have been so defined as to preserve these equations independent of the functionality of the branching unit. The above scheme is not completely general, however. For example, two multifunctional units, one bearing A and the other B groups, may be present. Or, a multifunctional unit bearing both A and B groups may occur. Other variations could be added. In general, an α can be calculated from the proportions of reactants and the extent of reaction by a procedure resembling that given above (34), but adapted to the particular type of reaction involved. A somewhat more difficult case is encountered when functional groups of differing reactivities are present, as in the glycerol–dibasic acid condensations already mentioned. But even here the calculation of α is feasible (34), if the necessary experimental measurements are provided.

The critical value of α at which the formation of infinite network becomes possible can be deduced as follows: If the branching unit is trifunctional, as in figure 10, each chain which terminates in a branch unit is succeeded by two more chains. If both of these terminate in branch units, four more chains are reproduced, etc. If $\alpha < 1/2$, there is less than an even chance that each chain will lead to a branch unit and thus to two more chains; there is a greater than even chance that it will end at an unreacted functional group. Under these circumstances the network cannot possibly continue indefinitely. Eventually termination of chains must outweigh continuation of the network through branching. Consequently, when $\alpha < 1/2$ all molecular structures must be limited, i.e., finite, in size.

When $\alpha > 1/2$, each chain has better than an even chance of reproducing two new chains. Two such chains will on the average reproduce 4α new chains, etc.; n chains can be expected to lead to $2n\alpha$ new chains, which is greater than n when $\alpha > 1/2$. The expected-number of chains in each succeeding generation of chains is greater than the number of chains in the preceding generation. Under these circumstances, branching of successive chains *may* continue the network indefinitely. Indefinitely large structures, or what we have called infinite networks, are then possible. Hence, $\alpha = 1/2$ represents the critical condition for the incipient formation of infinite networks.

It is important to note, however, that beyond $\alpha = 1/2$ by no means all of the material will be combined into infinite molecules. For example, in spite of the favorable probability of branching, a chain selected at random may be terminated at both ends by unreacted functional groups. Or, it may possess a branch at only one end, and both of the succeeding two chains may lead to unreacted "dead ends". These and other finite species will co-exist with infinite networks so long as $1/2 < \alpha < 1$. The relative amounts of sol and gel portions will be discussed later.

The above treatment can be generalized to include polymerizations in which the branched unit is of higher functionality than three, or in which more than one type of branched unit is present. A general statement of the critical condition for formation of infinite networks is the following: Infinite network formation becomes possible when the expected number of chains (or elements) which will succeed n chains (or elements), through branching of some of them, exceeds n (34). That is, if f is the functionality of the branching units (i.e., units having a functionality greater than two), gelation will occur when $\alpha(f - 1)$ exceeds unity. The critical value of α is, therefore,

$$\alpha_c = 1/(f - 1) \tag{18}$$

If more than one type of branching unit is present, $(f - 1)$ must be replaced by the appropriate average, weighted according to the numbers of functional groups attached to the various branched units. The critical condition can be expressed in various ways, but the above is a convenient form for application to condensation polymers.

A close analogy exists between these three-dimensional polymerizations and gas-phase chain reactions which may undergo branching. If the probability of termination of the kinetic chain $(1 - \alpha)$ in the gas-phase reaction exceeds the probability of branching (α) with reproduction of two chain carriers, the chains are of finite length, and the rate of reaction attains a finite steady-state value. If the probability of branching exceeds the probability of termination, the reaction accelerates without limit and an explosion is observed. The formation of infinite networks, which as will be shown is concomitant with gelation, is analogous to explosion in chain reactions. A very slight alteration of temperature or pressure is sufficient to cause a gas-phase chain reaction accompanied by branching to accelerate from a moderate (or even negligible) rate to explosion. Similarly, a very small change, brought about by one means or another, in the total number of intermolecular linkages may change a three-dimensional polymer from a moderately viscous liquid to a gel having infinite viscosity.

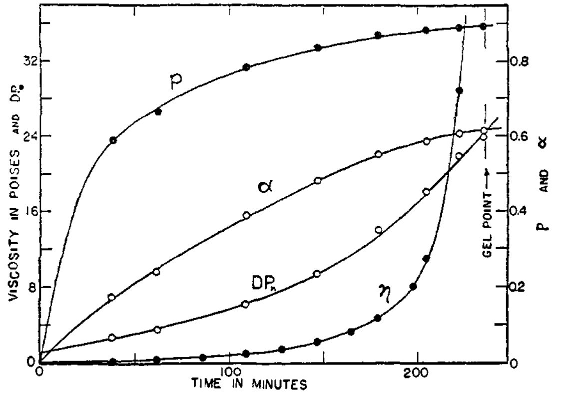


FIG. 11. The course of a typical three-dimensional polyesterification (34). The results shown are those for the third experiment reported in table 3. Reaction conducted at 109°C. catalyzed with 0.20 equivalent per cent p-toluenesulfonic acid.

B. The gel point: experimental results

If gelation in three-dimensional polymers occurs as a result of the formation of infinite networks, the observed gel point should be located at the point at which α reaches its critical value, as defined by equation 18, except to the extent that theory is vitiated by neglecting intramolecular linkages. Experimental results on several three-dimensional condensation polymerizations confirm this postulate.

Kienle and Petke (54) observed that in the reaction of glycerol with an equivalent amount of succinic, adipic, or sebacic acid, gelation occurred at 76.5 ± 1 per cent esterification, i.e., at $p = 76.5$. If the differing reactivities of the hydroxyl groups of glycerol are neglected, equation 15 can be applied with $r = 1$ and $\rho = 1$. Hence, $\alpha_c = p^2 = 0.58$. Correction for the lower reactivity of the secondary hydroxyl would lower α_c somewhat. The theoretical value of α_c according to equation 18 is 0.50.

The writer (34) observed the gel point in reactions of diethylene glycol with succinic or adipic acid and varying proportions of the tribasic acid, tricarballylic. Samples were removed from the reaction mixture at various intervals and titrated for unreacted carboxyl groups. The extent of reaction values (p) plotted against time, as in figure 11, were accurately extrapolated to the gel point, which was precisely observed by the sudden loss in fluidity as demonstrated by the failure of bubbles to rise in the mixture. Samples removed just prior to gelation were completely soluble in chloroform. Just after gelation they contained a small amount of gelatinous insoluble matter (gel) which remained suspended in the solvent. The viscosity of the mixture was also measured (figure 11). α was calculated from the proportions of ingredients (r and ρ) and from the extent of esterification of the carboxyl groups, p_A, using equation 15′. The number-average degree of polymerization $\overline{DP}_n$, calculated from the relationship (34)

$$\overline{DP}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{f(1 - \rho + 1/r) + 2\rho}{f(1 - \rho + 1/r - 2p_A) + 2\rho} \tag{19}$$

is not very large nor is it increasing rapidly at the gel point. This merely means that at the gel point many molecules are still present; it does not preclude the formation of a fractional amount of indefinitely large structures at or beyond the gel point.

TABLE 3

Gel points for polymers containing tricarballylic acid

ADDITIONAL INGREDIENTS, DIETHYLENE GLYCOL AND	$r = \frac{\text{COOH}}{\text{OH}}$	ρ*	p AT GEL POINT		$\alpha_{\text{obsd.}}$ AT GEL POINT
			Observed	Calculated†	
Adipic acid	1.000	0.293	0.911	0.879	0.59
Succinic acid	1.000	0.194	0.939	0.916	0.59
Succinic acid	1.002	0.404	0.894	0.843	0.62
Adipic acid	0.800	0.375	0.9907	0.955	0.58

*ρ = 3 × [tricarballylic acid]/[total carboxyl groups].

† Calculated from equation 15′ when $\alpha = 1/2$.

Other similarly obtained results are summarized in table 3. In every case the observed gel point is reached at higher than the theoretical extent of reaction. In the polymerization of pentaerythritol ($f = 4$) with an equivalent quantity of adipic acid gelation occurs at $\alpha = p^2 = 0.366$, compared with the theoretical $\alpha_c = 0.333$. The discrepancies are believed to be due to the failure of the theory to take into account a minor degree of intramolecular condensation. In effect, some of the inter-unit linkages are wasted in forming these intramolecular connections. Hence, the reaction must be carried somewhat farther to reach the critical point. Nevertheless, there is sufficient correlation between the approximate theory and experiment to confirm the hypothesis that gelation is caused by infinite networks.

C. *Molecular-weight distribution in three-dimensional polymers*

Three-dimensional polymers can be obtained from numerous combinations of bi- and multi-functional units of various types. A completely general treatment of the size-distribution problem is impractical, therefore. Rather, separate size-distribution expressions have been derived for various more or less general types of three-dimensional polymers. The fact that these possess a number of characteristics in common facilitates a unified discussion of the constitution of three-dimensional polymers.

The writer (35, 36) derived size-distribution relationships for tri- and tetrafunctional types, employing as assumptions those given above. Guided somewhat by the form of these size-distribution expressions, Stockmayer (87) succeeded in deriving more general distribution equations for various polymers in which the branching unit is f-functional. The statistical-mathematical derivations of these equations will not be repeated here. We shall be concerned solely with their physical interpretation.

The simplest possible type of three-dimensional polymer is that in which all units are of the same functionality f and in which all functional groups possess the same reaction probability p. (That is, if A groups of one monomer condense with B groups of another monomer, these are to be present in equivalent quantities in order that p_A shall equal p_B.) An example would be the condensation of a trihydric alcohol with an equimolar proportion of a tribasic acid, the hydroxyl groups of the former and the carboxyl groups of the latter being equally reactive. Or, both reactants might be tetrafunctional. Another example, a somewhat hypothetical addition type, would be provided by a pure triglyceride of a drying oil acid, each acid radical of which is capable of undergoing dimerization with another acid radical, to the total exclusion of other polymerization reactions. Still another example may be found in phenol–formaldehyde condensations in which the phenol is exclusively trireactive, as shown in table 1. Here it is necessary to regard the phenol as the structural unit, the formaldehyde merely supplying the inter-unit linkage. To obtain the weight distribution it then becomes necessary to assume that the molecular weight of a given species is proportional to the number of phenol residues which it contains. This approximation may distort the low-molecular-weight portion of the distribution curve.

For polymers of the above type Stockmayer (87) has derived the weight-distribution function

$$w_x = \frac{(1-\alpha)^2}{\alpha}\left[\frac{(fx-x)!f}{(x-1)!(fx-2x+2)!}\right]\beta^x \tag{20}$$

where f is the functionality of the unit(s), x is the number of units in the molecule, and β is defined by

$$\beta = \alpha(1-\alpha)^{f-2} \tag{21}$$

In accordance with the previous definition, α is the probability that one "leg" of a branch unit connects to another branch unit. In the present case $\alpha = p$, the extent of reaction, or the probability of reaction for any given functional group. An x-mer molecule with $x > 3$ can be constructed in various ways from x f-functional units ($f > 2$). Equation 20 combines all of these into a single w_x, regardless of the particular way in which the x units are connected.

The weight distribution prescribed by Stockmayer's equation (equation 20) for the trifunctional case ($f = 3$) is plotted in figure 12 for several stages of the condensation as indicated by α. In contrast to the weight-fraction distribution for linear condensation polymers, the curve shows a monotonic decrease with increase in size x. In other words, monomers always are present in greater amount, even on a weight basis, than species of any other (finite) size; x-mers are more abundant than ($x + 1$)-mers, etc. As the reaction progresses, i.e., as α increases, the distribution curve falls less steeply with increasing x; w_x's for the larger species increase with α. Even at the gel point, which according to equation 18 should occur at $\alpha = 1/2$, the curve displays a continuous decrease approaching zero as x proceeds toward infinity, and most of the material is present in polymers of rather low degree of polymerization. The distribution becomes increasingly broad as the gel point is approached.

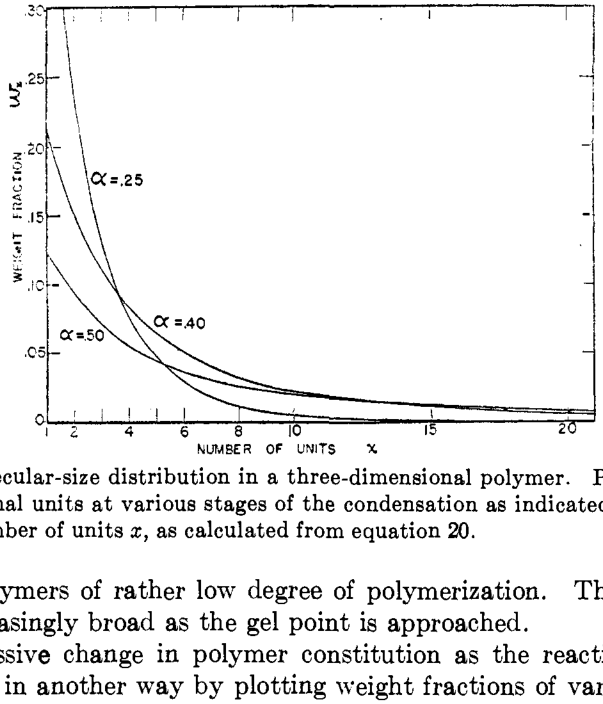


FIG. 12. Molecular-size distribution in a three-dimensional polymer. Polymers formed from trifunctional units at various stages of the condensation as indicated by α. Weight fraction vs. number of units x, as calculated from equation 20.

The progressive change in polymer constitution as the reaction progresses can be shown in another way by plotting weight fractions of various polymers against the extent of reaction $p = \alpha$. Plots of this type are shown in figure 13, calculated again from equation 20 with $f = 3$. Obviously, the amount of monomer must decrease continuously as the condensation progresses. Dimer begins to form at once, reaches a maximum amount near $\alpha = 0.2$, and then decreases as the condensation continues. Trimer formation does not set in at once, owing to the fact that it is a secondary product formed from dimer. Its curve reaches a maximum somewhat later—near $\alpha = 0.3$—and then decreases. Curves for tetramers (two tetramer structures are possible, but both are included in w_4 from equation 20) are similar; the maximum comes later. In no case, however, does the maximum occur beyond the gel point $\alpha = 1/2$.

The region beyond the gel point also is included in figure 13. The per cent gel curve and other features of polymer constitution in this region will be discussed later. It is sufficient to note here that the curves representing weight fractions of various species continue through the gel point without discontinuity.

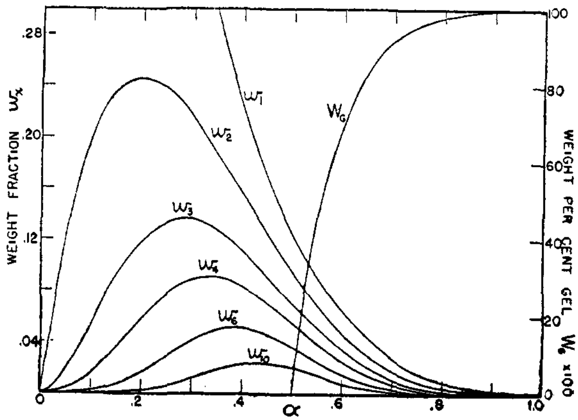


Fig. 13. Weight fractions of various species in a simple trifunctional condensation as a function of α, which in this case equals the extent of reaction p. The weight fraction of gel, W_g, is calculated from equation 29′.

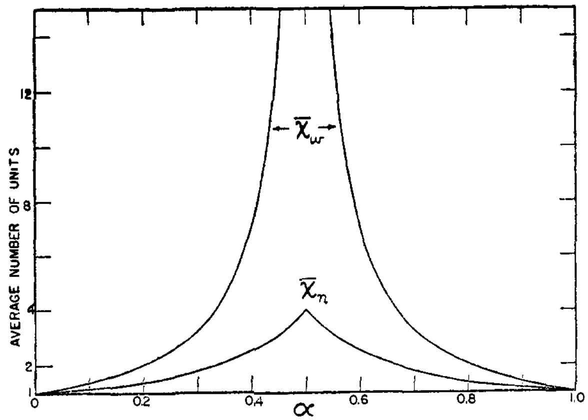


Fig. 14. Number-average, $\bar{x}_n$, and weight-average, $\bar{x}_w$, number of units per molecule in a simple trifunctional condensation as a function of α. Calculated from equations 22 and 23 with $f = 3$.

It can readily be shown that the number-average value of x is given by

$$\bar{x}_n \equiv \overline{DP}_n = 1/(1 - \alpha f/2) \tag{22}$$

for the simple f-functional case presently under consideration. The weight average of x, found by summing over equation 20, is

$$\bar{x}_w = \Sigma x w_x = (1 + \alpha)/[1 - (f - 1)\alpha] \tag{23}$$

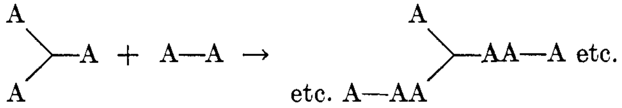
These averages are plotted against α in figure 14 for $f = 3$. As the reaction progresses the number average increases, but more slowly than does the weight average. At the gel point the number-average molecular weight has increased only fourfold; i.e., there are one-fourth as many molecules as were present initially. This is in accordance with the comparatively low molecular weights which have been observed (54) for three-dimensional polymers at their gel points.

The weight-average degree of polymerization increases more rapidly as the reaction progresses, running to infinity at the gel point. This is true in spite of the fact that precisely at the gel point only finite species are present, according to the distribution equation. (Only when α exceeds the critical value by a finite amount does the theory permit the existence of infinite networks.) The progression of the melt viscosity to infinity (see figure 11) as the gel point is approached is readily explained, inasmuch as melt viscosity generally depends on weight-average molecular weight (29).

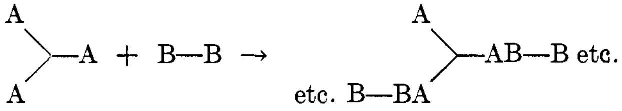
The ratio of $\bar{x}_w$ to x_n frequently has been proposed as an index of the heterogeneity of polymers. At the gel point this ratio becomes infinite, which is further indication of the extreme heterogeneity of three-dimensional polymers at the gel point.

The portion of figure 14 beyond the gel point will be discussed later.

For the condensation of f-functional units with bifunctional units, e.g.,



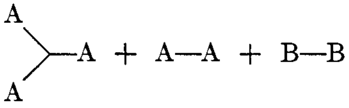
or



where A and B are present in equivalent amounts, Stockmayer (87) has derived the number-distribution equation

$$N_{n,l} = fN_0\rho^{n-1}(1-\rho)^l p^{n+l-1}(1-p)^{fn-2n+2} \times \frac{(fn-n+l)!}{n!\,l!\,(fn-2n+2)!} \qquad (24)$$

where $N_{n,l}$ is the number of molecules in the polymer which contain n f-functional and l bifunctional units, N_0 is the number of f-functional units in the entire polymeric mixture, ρ is the ratio of the functional groups on branch units to the total number of functional units, and p again is the extent of reaction. Stockmayer (87) similarly has derived an expression for the distribution of "n, l, s-mers" formed from three reactants, one of them f-functional, the others bifunctional, e.g.,



This type includes the polyesters, such as were employed in the gelation experiments previously discussed (see table 3). These equations are difficult to apply, inasmuch as they contain more than one size variable; e.g., the molecular weight depends on *both* n and l in equation 24.

When the chains between the f-functional branch units are long—for example, when the proportion of branch units is small and, hence, the average number of A—A and B—B units between branch units is large—the above equations can be replaced approximately by a more tractable distribution function (87):

$$W_n = 2(1 - \alpha)^2 \frac{(fn - n + 1)!\beta^n}{n!(fn - 2n + 2)!} \tag{25}$$

where W_n is the weight fraction of molecules composed of n branch units, regardless of individual lengths of chains between branch units. Hence, equation 25 gives a "complexity" distribution rather than the actual size distribution. β is defined as in equation 21, and α again is the branching expectancy calculable from equations such as 15, 16, or 17.

When $f = 3$, equation 25 reduces to the equation previously derived by the writer (35)

$$W_n = (1 - \alpha)^2 \frac{(2n + 2)!}{(n + 1)!(n + 2)!} \beta^n \tag{26}$$

or

$$W'_z = (1 - \alpha)^2 \frac{(z + 1)!}{[(z + 1)/2]![(z + 3)/2]!} \beta^{(z-1)/2} \tag{26'}$$

where z, the number of chains per molecule, is related to n by the equation:

$$z = 2n + 1$$

(z is necessarily an odd integer.)

The similarity between these complexity distribution equations (equations 25, 26, and 26′) and the size-distribution equation (equation 20) for the simple f-functional case is apparent. If the weight fractions of polymers containing 0, 1, 2 . . . n, etc. branch units, or the corresponding weight fractions W'_z of polymers composed of 1, 3, 5 . . . z, etc. chains, are plotted against n, or z, the complexity curves so obtained are very similar in character to the *size* distribution for the simple f-functional case in figure 12.

To obtain the actual molecular-weight distribution in the present case it is necessary to take into consideration the variation in the lengths of the individual chains. These will vary according to the distribution previously derived for linear polymers (see equation 10). Thus, with reference to the "z" distribution of equation 26′, single chains, present in weight fraction W'_1, will cover a broad range of sizes. Similarly, W'_3 includes polymers varying considerably in total size, although the size distribution for $z = 3$ polymers is less than for the $z = 1$ polymer; etc. To obtain the weight fraction w_x of species composed of x units, regardless of the number of chains z, it is necessary to add together the weight fraction of $z = 1$ molecules having x units, the weight fraction of $z = 3$ molecules having a combined total of x units in their three chains (including the branch unit), etc. This operation can be simplified mathematically to the extent that calculation of the actual size distribution becomes feasible (35).

Figure 15 has been constructed for the purpose of showing the effect of $f = 3$ branching units on the distribution. The calculations have been made for chains having an average length of fifty units. The $\alpha = 0$ curve, for linear chains in the total absence of branch units, has been calculated from equation 10 with $p = 0.98$. The other curves represent bifunctional condensations to which have been added small amounts of trifunctional units such that $\alpha = 0.25$ and 0.50, respectively, when the reaction has been carried to the point where each contains an average of fifty units per chain. These curves do not represent successive stages of a given polymerization; *both* α and the average chain length increase as the condensation of given proportions of bi- and tri-functional units progresses. They are merely intended to show the dependence of the shape of the distribution curve on the degree of branching, α.

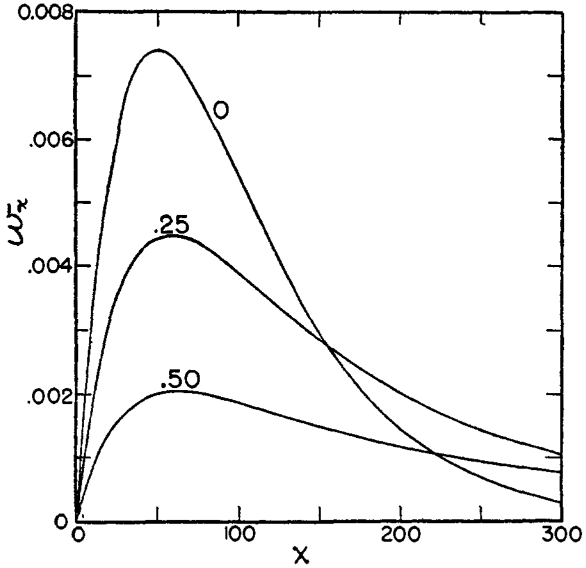


FIG. 15. Weight-fraction distributions vs. number of units for various degrees of trifunctional branching at constant average chain lengths of fifty units in each case. The curves represent $\alpha = 0$ (no branching), $\alpha = 0.25$, and $\alpha = 0.50$ (critical point).

The area under each of these curves extended to infinite x is the same. The position of the maximum is shifted comparatively little by increase in α (i.e., by increasing the proportions of trifunctional units), but the height is decreased. The quantity of high-molecular-weight material increases at the expense of lower polymers in such a way that the distribution curve is broadened as α increases. The weight-average degree of polymerization $\bar{x}_w$ at the gel point ($\alpha = 1/2$) again is infinite. The number-average molecular weight at the gel point is only three times the average molecular weight per chain.

These general principles apply similarly to three-dimensional addition polymers (36, 37, 88), such as those formed in the copolymerization of vinyl and divinyl reactants. They are also applicable to cross-linking of long polymer chains, such as occurs in the vulcanization of rubber, and to the phenomenon of protein gelation (37) under certain conditions.

D. Conversion of sol to gel

There is nothing in the derivations of the various distribution equations which limits them to the region up to the gel point. In a simple f-functional condensation, for example, it is obvious that the weight fraction of monomer is always equal to the probability that all of the f-functional groups of a given monomer unit are unreacted, i.e.,

$$w_1 = (1 - p)^f = (1 - \alpha)^f$$

which can also be obtained by setting $x = 1$ in equation 20. The weight fraction of dimers can be deduced directly as the probability that one, and only one, functional group of the unit has reacted, multiplied by the probability that the remaining $f - 1$ functional groups of the attached unit are unreacted.

$$w_2 = f\alpha(1 - \alpha)^{f-1}(1 - \alpha)^{f-1} = f\alpha(1 - \alpha)^{2f-2}$$

Clearly, these derivations place no restrictions on α, except that it be in the physically real range from zero to unity. Hence, these weight fractions, as well as those for higher species obtained from equation 20, should apply equally well before and after the gel point. The same reasoning can be applied in the case of branched polymers with long chains.

It is true that these expressions are somewhat inaccurate, owing to the disregard of intramolecular reactions. This approximation will be more serious the larger the molecule. There is relatively little likelihood of intramolecular reaction in monomers, dimers, and other lower species (except, of course, where formation of a ring of five, six, or sometimes seven members is possible). Thus, as α increases toward the gel point and larger species are formed, this approximation becomes increasingly important. Obviously, the infinite network will contain intramolecular linkages (which, in fact, are responsible for the many circuitous connections and, hence, net-like structure of the gel fraction), and these will become more abundant in the gel fraction as α increases. If it were necessary to make the approximation that intramolecular reactions are totally excluded, the theoretical treatments would be of little value much beyond the gel point. This is not the case. The distribution equations actually include only the species of finite size. They are essentially oblivious of infinite networks. This is inherent in their derivation (35, 36). Hence, in deducing these distribution equations it was necessary merely to assume, or rather to make the approximation, that no intramolecular reactions occur *within finite species*. No reservations for infinite networks were necessary.[1]

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[1] The interpretation given here follows closely the one originally presented by the writer (35, 36, 37). Stockmayer (87) originally questioned the validity of this literal application of the distribution equations beyond the gel point. In the present discussion the writer has attempted to express the fundamental logic of the procedure more clearly, employing for the most part Stockmayer's more general distribution equations to illustrate the conclusions.

Upon examining the various distribution equations for three-dimensional polymers (see equations 20, 25, and 26) each is found to consist of three factors: a function of α, a function of f and the size variable x or n, and β^x, or β^n. If the sum of the weight fractions of all finite species (infinite species are not included in the equations, as already mentioned) is taken, the first of these factors can be placed outside the summation. If, for example, the simple f-functional case is considered, then upon introducing equation 20:

$$\sum_{\text{all finite } x} w_x = \frac{(1-\alpha)^2}{\alpha} \sum_{x=1}^{\infty} \left[\frac{f(fx-x)!\beta^x}{(x-1)!(fx-2x+2)!} \right] \tag{27}$$

β is a function of α (see equation 21) such that it possesses a maximum at $\alpha = \alpha_c$, the critical value of α (see equation 18). For all other permissible values of β there are two values of α which satisfy equation 21, one of them less and the other greater than α_c. The above summation on the right is equal to $\alpha'/(1-\alpha')^2$, where α' is the lower root of equation 21 for the given value of β; that is, where $\alpha' < \alpha_c$. Hence, the sum of all w_x's is equal to unity when $\alpha = \alpha' < \alpha_c$.

If, on the other hand, the reaction has progressed beyond the gel point so that $\alpha > \alpha_c$, then Σw_x will be less than unity. The summation on the right of equation 27, since it does not contain α explicitly, again will equal $\alpha'/(1-\alpha')^2$, where α' is the lower root of equation 21 for the given value of β. In other words, this summation is the same for either value of α, namely $\alpha > \alpha_c$ or $\alpha' < \alpha_c$, since both α and α' give the same value of β. But the function of α occurring before the summation is different for α and α'. Hence, when $\alpha > \alpha_c$ the sum of all weight fractions of finite species is given by

$$W_s = \Sigma w_x = \frac{(1-\alpha)^2\alpha'}{(1-\alpha')^2\alpha} \tag{28}$$

which is less than unity. This is the weight fraction of sol, or soluble species in the polymer. The summation is less than unity, owing to the presence of infinite networks not included in the distribution equation. The weight fraction, W_g, of these infinite networks, or gel, can be obtained by difference:

$$W_g = 1 - (1-\alpha)^2\alpha'/(1-\alpha')^2\alpha \tag{29}$$

When the units are trifunctional, according to equation 21 $\alpha' = (1-\alpha)$. Hence (87),

$$W_g = 1 - (1-\alpha)^3/\alpha^3 \tag{29'}$$

where $\alpha > \alpha_c = 1/2$. The weight percentage of gel calculated from this equation is plotted in figure 13. Its formation commences abruptly at the critical point, rises rapidly, and proceeds to 100 per cent as α goes to unity, i.e., as the reaction proceeds to completion.

It follows similarly from the form of the distribution function (25) for the complexity distribution in polymers composed of long chains joined by f-functional units that in this case

$$W_g = 1 - (1-\alpha)^2/(1-\alpha')^2 \tag{30}$$

where α and α' are roots of equation 21 with $\alpha > \alpha_c$ and $\alpha' < \alpha_c$. In the trifunctional case this reduces to

$$W_g = 1 - (1 - \alpha)^2/\alpha^2 = (2\alpha - 1)/\alpha^2 \tag{30'}$$

where $\alpha \geqslant 1/2$. The weight fraction of gel proceeds to unity somewhat less rapidly with increase in α than in the previous case, but otherwise the sol-to-gel conversion is similar.

It is interesting to examine the molecular-weight distribution in the sol fraction beyond the gel point. As is evident from the above discussion, the distribution function at some value $\alpha > \alpha_c$ is the same as for the conjugate value $\alpha' < \alpha_c$, except for the previously mentioned factor in the distribution function, which is an explicit function of α. This factor, which in the distribution function (20) occurs as $(1 - \alpha)^2/\alpha$, is less for α than for α', but it is the same for species of all sizes, or complexities. In a simple f-functional condensation, therefore, the same size distribution prevails *within the sol fraction* at $\alpha > \alpha_c$ as occurred for the entire polymer earlier in the condensation when the extent of reaction corresponded to α', where α' and α are roots of equation 21 for the same value of β. Only the absolute amounts of each species are smaller, and these are all reduced by the same factor W_s. Consequently, the distribution curves in figure 12 apply also to the sol after gelation at the respective α values 0.60 and 0.75.

Inasmuch as the molecular-weight distribution always approaches zero as x becomes very large, it is clear that the demarcation between sol and gel is by no means an arbitrary distinction. Extremely large ("almost infinite") molecular species, which might be regarded as intermediate between sol and gel, are never present in more than infinitesimal quantity. The structural distinction between sol and gel is as well defined as that between a liquid and its vapor, notwithstanding the physical interspersion of sol in gel.

In the course of a simple f-functional condensation polymerization larger species gradually are formed at the expense of smaller molecules. The distribution broadens, as shown in figure 12, reaching a maximum degree of heterogeneity at the critical point. Here infinite networks suddenly make their appearance (see figure 13). Gel increases at the expense of sol as the condensation continues. The sol which remains decreases in average molecular weight, owing to the preferential conversion of the larger, more complex, species to the infinite network fraction. The molecular-weight distribution of the sol retraces in the reverse direction the exact course followed by the polymer up to the gel point. Weight and number averages of the sol exhibit a corresponding retroversion, as is shown in figure 14.

Other types of three-dimensional polymers (35, 36) behave similarly as they pass beyond the gel point. In the case of occasionally branched long chains formed by condensation of bifunctional and f-functional units, the complexity distribution of the sol after gelation reverts over the same course traversed up to the gel point (35), as can be shown from equation 25. Thus for $f = 3$, the *complexity* distribution of the sol is the same at $\alpha = 0.7$ as prevailed for the polymer as a whole when $\alpha = 0.3$. However, as the condensation progresses in this case there is an increase in the average chain length as well as in α. Consequently the molecular weight averages for the sol at $\alpha = 0.7$ will be greater than those at $\alpha = 0.3$ in proportion to the increase in the average chain length.

So far, experiments to determine the actual course of the conversion of sol to gel in a quantitatively observed condensation polymerization have not been reported, nor has the predicted decrease in complexity of the sol with increase in α been verified. It is to be expected that results of this nature will differ somewhat from the theoretical predictions, owing to the occurrence of intramolecular condensations within finite species. The observed gel points, as was shown above, occur somewhat beyond the calculated critical values on this account. The greatest departure from the approximate theory should, in fact, occur at the critical point. It is to be expected that in order to depict actual condensations it will be necessary to distort the α scales of diagrams such as figures 13 and 14. The gel point will have to be shifted to slightly larger α's (as here calculated), the curves on the left (prior to gelation) being expanded and those on the right compressed in such a way that the greatest distortion occurs near the critical α.

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