THE POLYMERISATION OF ALDEHYDES

By J. C. BEVINGTON, M.A., PH.D.

(DEPARTMENT OF CHEMISTRY, BIRMINGHAM UNIVERSITY)

THIS Review is concerned primarily with the formation and properties of cyclic and linear polymers of aldehydes. Compounds of the aldol type might be considered in this connection since their molecular formulæ can be written as $(R \cdot CHO)_n$, and similarly the simple carbohydrates which have been prepared from formaldehyde and certain hydroxy-aldehydes might be treated as polymers of the aldehydes since they have the same empirical formulæ ; the aldols and carbohydrates are not true addition polymers, however, and only substances having the repeating unit $\cdot CHR \cdot O \cdot$ are dealt with in this Review. The formation of these polyoxymethylene derivatives can be represented by overall equations which are formally similar to those for the polymerisation of olefinic monomers, but the two types of reaction differ profoundly in many respects.

A chapter was devoted to the polyoxymethylenes in Walker's recent monograph [1] on formaldehyde, but information on polymers of other aldehydes seems never to have been collected and correlated adequately. Polymers of formaldehyde were described by Staudinger [2] in one of the earliest systematic accounts of high polymers ; it appears that in 1932 almost as much was known about the polymers of formaldehyde as about those of olefinic compounds, but the position is very different now since knowledge of the latter type is in a much more advanced state.

High polymers of aldehydes are of no importance as fibres, plastics, or rubbers because they depolymerise readily. Precise work on these polymers is difficult since in only a few cases has it been shown quite unambiguously what catalyst, if any, is responsible for initiating polymerisation. It has not been possible to establish a single set of conditions under which all aldehydes can be converted into high polymers and so a direct comparison of their reactivities cannot be made. Another difficulty in detailed studies of the polymerisations is associated with determinations of molecular weights ; in the case of formaldehyde all but the low polymers are insoluble, and linear polymers of other aldehydes decompose at appreciable rates at room temperature. In some cases the formation of high polymers seems to occur by an ionic mechanism, and this is an added difficulty in the way of a complete understanding of the reactions since even for olefinic monomers much less is known about the ionic type of polymerisation than about the radical type. Aldehydes show a great tendency to form cyclic polymers of low molecular weight.

In one respect the aldehyde polymers are simpler than their olefinic counterparts as they invariably consist of a head-to-tail arrangement of monomer units. This is associated with the fact that the carbonyl bond is
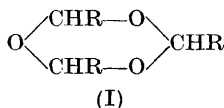
[1] " Formaldehyde ", Reinhold, New York, 1944, Chapter 7.
[2] " Die Hochmolekularen Organischen Verbindungen ", Springer, Berlin, 1932.

strongly polar so that its carbon and oxygen atoms differ markedly in reactivity.

Cyclic Polymers

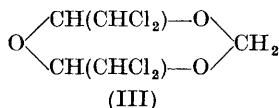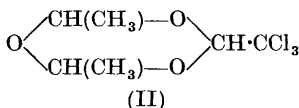**Trimers.**—Many aldehydes form cyclic trimers of general formula (I).

$$O\begin{array}{c} \diagup CHR-O \diagdown \\ \diagdown CHR-O \diagup \end{array}CHR$$

(I)

Among the trimers which have been described are those where $R = H$, CH_3, $CHCl_2$, $CH_3 \cdot CHBr$, and $CH_3 \cdot [CH_2]_9$. The trimer of formaldehyde is usually called trioxan and not trioxymethylene, as the latter name has long been used for a material now known to be a linear polymer of fairly high molecular weight. The best known of the trimers is paraldehyde, derived from acetaldehyde.

The conversion of an aldehyde into its trimer is catalysed by traces of acids and in many cases it proceeds readily at low temperatures. Special conditions are necessary for the preparation of trioxan since formaldehyde forms linear polymers very easily, but the preparations of other trimers present little difficulty. There have been few studies of the kinetics of this type of polymerisation, but the formation of paraldehyde by using phosphoric acid as catalyst has been followed dilatometrically, both for the pure aldehyde and for solutions in benzene.[3] Chloral is polymerised by sulphuric acid to metachloral which is almost certainly a cyclic polymer and may be a trimer ; the reaction can also be promoted by small amounts of the oxidation products of the aldehyde.[4]

The trimers can be depolymerised by acids although they are stable to alkalis ; substances such as ferric chloride which are electron-acceptors and therefore acidic in the broad sense also catalyse the depolymerisation. Mixtures of trioxan and acids can be used as sources of monomeric formaldehyde. The kinetics of the depolymerisations of trioxan and paraldehyde have been studied both in the gas phase and in solution ; [5] both the thermal and the acid-catalysed depolymerisation of paraldehyde proceed at greater rates than those of trioxan under the same conditions.

Mixed Trimers.—A number of mixed trimers of two aldehydes are known, examples being (II) and (III) :

$$O\begin{array}{c} \diagup CH(CH_3)-O \diagdown \\ \diagdown CH(CH_3)-O \diagup \end{array}CH \cdot CCl_3 \qquad O\begin{array}{c} \diagup CH(CHCl_2)-O \diagdown \\ \diagdown CH(CHCl_2)-O \diagup \end{array}CH_2$$

(II)   (III)

It appears that in these mixed trimers one of the aldehydes must be halogenated. These polymers can be made from mixtures of the appropriate monomeric aldehydes with traces of hydrogen chloride as catalyst. Some

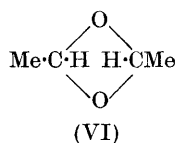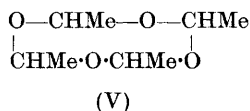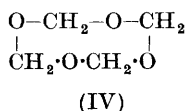[3] Hatcher and Brodie, *Canadian J. Res.*, 1931, **4**, 574.

[4] Moureu, Dufraisse, and Berchet, *Bull. Soc. chim.*, 1928, **43**, 942, 957.

[5] Bell and Burnett, *Trans. Faraday Soc.*, 1937, **33**, 355 ; 1938, **34**, 420 ; 1939, **35**, 474.

of the mixed polymers decompose slowly on storage, and all are depoly-merised when warmed with acids ; alkalis have no effect.   Mixed trimers of three aldehydes have not been prepared.[6]

Tetramers and Dimers.—Cyclic tetramers of formaldehyde and acetalde-hyde are known, the accepted structures being (IV) and (V).   Tetra-oxymethylene is rather uncommon and the conditions necessary for its formation have not been closely defined.   Metaldehyde is well known ; it is prepared from acetaldehyde containing traces of acid and the reaction can take place at temperatures only just above the freezing point of the monomer, viz., $- 123°$.   Metaldehyde and paraldehyde are usually formed simultaneously but the yield of the former is increased as the temperature is reduced.
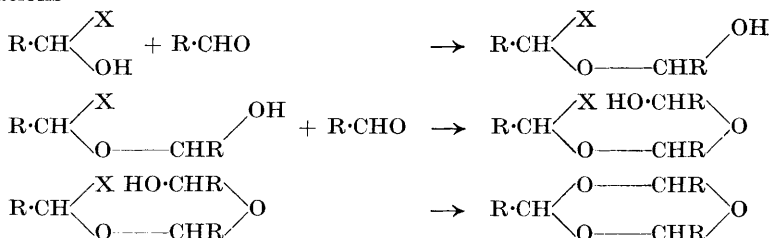
During the formation of metaldehyde at low temperatures by use of alcoholic sulphuric acid as catalyst, another polymer is also formed ; [7] this has a molecular weight corresponding to the formula $(CH_3 \cdot CHO)_2$ and its boiling point is about $74°$, which is intermediate between those of the monomer and the trimer.   This polymer decomposes readily to acetaldehyde and it is possible that it is the dimer (VI).   There have been no reports of similar dimers of other aldehydes.

$$O-CH_2-O-CH_2$$
$$CH_2 \cdot O \cdot CH_2 \cdot O$$
(IV)

$$O-CHMe-O-CHMe$$
$$CHMe \cdot O \cdot CHMe \cdot O$$
(V)

$$Me \cdot CH \quad H \cdot CMe$$
(VI)

The Mechanism of the Formation of Cyclic Polymers.—The alcohol $CH_2Br \cdot CHBr \cdot OH$ loses hydrogen bromide on standing to give the substituted paraldehyde (VII).   This reaction has been cited as evidence for the theory

$$O \begin{cases} CH(CH_2Br)-O \\ CH(CH_2Br)-O \end{cases} H \cdot CH_2Br$$
(VII)
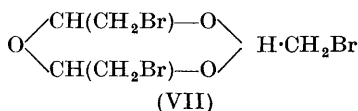
that the formation of cyclic trimers of aldehydes normally involves the compound $R \cdot CHX \cdot OH$ formed by the addition of a molecule of acid HX to the aldehyde.   The polymerisation can then be represented by the set of equations

$$R \cdot CH \begin{cases} X \\ OH \end{cases} + R \cdot CHO \quad \rightarrow \quad R \cdot CH \begin{cases} X \\ O----CHR \end{cases} OH$$

$$R \cdot CH \begin{cases} X \\ O----CHR \end{cases} OH + R \cdot CHO \quad \rightarrow \quad R \cdot CH \begin{cases} X \; HO \cdot CHR \\ O----CHR \end{cases} O$$

$$R \cdot CH \begin{cases} X \; HO \cdot CHR \\ O----CHR \end{cases} O \quad \rightarrow \quad R \cdot CH \begin{cases} O----CHR \\ O----CHR \end{cases} O$$

[6] Hibbert, Gillespie, and Montonna, J. Amer. Chem. Soc., 1928, **50,** 1950.
[7] Travers and Sollers, Trans. Faraday Soc., 1936, **32,** 248.

This scheme involves the addition either of the acid HX or of a hydroxy-compound across a carbonyl bond.   It is known that such additions involve charged bodies as intermediates, so the whole reaction effectively proceeds by an ionic mechanism, and the occurrence of polymerisation at low temperatures is understandable.   It is probable that other cyclic polymers of aldehydes are formed by similar processes.

The polymerisation of chloral in the presence of air is inhibited by small amounts of certain substances, *e.g.*, phenols and aromatic amines,[4] which are effective in stopping free-radical reactions.   This is not evidence for a radical type of polymerisation for this aldehyde because the inhibitors probably prevent the oxidation which furnishes the catalysts for the poly-merisation, and they have only an indirect effect upon the polymerisation.

Depolymerisation of Cyclic Polymers.—The ability of acids to initiate depolymerisation of cyclic polymers of aldehydes suggests that these sub-stances can cause the rupture of carbon–oxygen bonds of the type present in these polymers.   This reaction will be referred to again in the next section.

High Polymers of Formaldehyde

Polymerisation at Low Temperatures.—Liquid formaldehyde polymerises very readily even at temperatures only just above its freezing point ($-118°$), and in the preparation of the monomer stringent precautions are necessary to remove traces of impurities which may initiate reaction.   Even the purest samples of liquid formaldehyde slowly gelatinise at low temperatures ; the gels can be evaporated, giving monomeric gas and only very small amounts of solid,[8] showing that they consist of small quantities of a very high polymer dissolved in the monomer.

No effective stabiliser is known for the aldehyde, although polymerisation may be retarded slightly by quinol.[9]   At low temperatures solutions of the monomer in non-polar solvents are more stable than the pure monomer but they still exhibit a strong tendency to polymerise.   The effect of oxygen is not clear ; Spence and Wild [8] attributed the instability of the monomer, in part, to oxygen adsorbed on the walls of the vessel, but Staudinger [2] stated that the addition of oxygen decreased the tendency of the liquid to poly-merise.   Although effective inhibitors are unknown, a number of substances act as powerful catalysts for the polymerisation of the liquid aldehyde. Traces of hydrogen chloride or boron trifluoride cause almost instantaneous polymerisation of the liquid aldehyde at about $-80°$, and small amounts of normal aliphatic amines cause very rapid polymerisation of solutions of formaldehyde in ether at that temperature.[10]

Staudinger considered that the molecular weight of the polymer formed from the pure aldehyde at low temperatures exceeds 150,000, but confirma-tion is not possible since the polymer is insoluble.   Polymers prepared by using traces of polar catalysts are evidently of much lower molecular weight since they do not possess the plastic properties exhibited by the other polymers at about 160°.

[8] *J.*, 1935, 338.   [9] Spence, *J.*, 1933, 1193.
[10] Walker, *J. Amer. Chem. Soc.*, 1933, **55**, 2821.

The mechanism of the polymerisation at low temperatures is not certain but a number of points indicate that it is ionic ; these points are : (i) the nature of the catalysts, since substances such as boron trifluoride and hydrogen chloride are unlikely to act as sources of free radicals ; (ii) the extreme rapidity of the reactions at low temperatures ; (iii) the polarity of the carbonyl bond. In the case of catalysis by boron trifluoride, a polar complex is likely to be formed, and growth of the polymer may be represented thus

$$^-BF_3 \leftarrow O{\cdot}CH_2^+ + O{:}CH_2 \rightarrow {}^-BF_3 \leftarrow O{\cdot}CH_2{\cdot}O{\cdot}CH_2^+$$
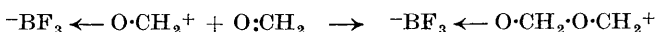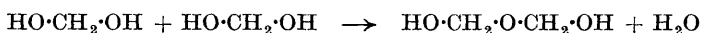
Such a process would require little activation and so could occur readily at low temperatures ; it involves the separation of opposite charges, but as the dielectric constant of liquid formaldehyde is probably quite high, this is not improbable.

Polymerisation in Solution at Normal Temperatures.—Formaldehyde dissolves readily in water, polymerisation occurring to give polyoxymethylene glycols of general formula $HO{\cdot}[CH_2{\cdot}O]_n{\cdot}CH_2{\cdot}OH$ where n probably can have values up to 12 ; if n exceeds this value the polymer is insoluble in water. Cryoscopic measurements have shown that the degree of polymerisation decreases as the concentration of the solution is decreased or as the temperature is raised, and that the process is reversible. The velocities of the polymerisation and depolymerisation reactions have been measured by cryoscopic, interferometric, and dilatometric methods (the results have been summarised by Mark and Raff [11]) and have been found to be comparatively small.
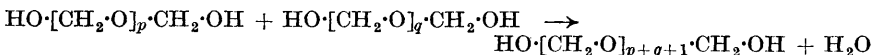
In aqueous solution formaldehyde is believed to form the hydrate $CH_2(OH)_2$ very readily ; evidence for the existence of this hydrate is that the corresponding hydrate of chloral is stable, and that by using the isotope ^{18}O it has been shown that oxygen is exchanged quite readily at 20° between acetaldehyde and water,[12] probably by means of the equilibrium
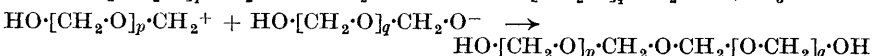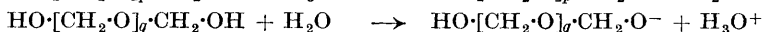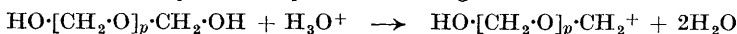
$$CH_3{\cdot}CHO + H_2O \rightleftharpoons CH_3{\cdot}CH(OH)_2$$

The growth of the formaldehyde polymer may result from a polycondensation ; the simplest type of reaction is represented as

$$HO{\cdot}CH_2{\cdot}OH + HO{\cdot}CH_2{\cdot}OH \rightarrow HO{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}OH + H_2O$$

and the general reaction as

$$HO{\cdot}[CH_2{\cdot}O]_p{\cdot}CH_2{\cdot}OH + HO{\cdot}[CH_2{\cdot}O]_q{\cdot}CH_2{\cdot}OH \rightarrow$$
$$HO{\cdot}[CH_2{\cdot}O]_{p+q+1}{\cdot}CH_2{\cdot}OH + H_2O$$

Both polymerisation and depolymerisation are catalysed by hydrogen ions and the former may occur by the following mechanism :

$$HO{\cdot}[CH_2{\cdot}O]_p{\cdot}CH_2{\cdot}OH + H_3O^+ \rightarrow HO{\cdot}[CH_2{\cdot}O]_p{\cdot}CH_2^+ + 2H_2O$$
$$HO{\cdot}[CH_2{\cdot}O]_q{\cdot}CH_2{\cdot}OH + H_2O \rightarrow HO{\cdot}[CH_2{\cdot}O]_q{\cdot}CH_2{\cdot}O^- + H_3O^+$$
$$HO{\cdot}[CH_2{\cdot}O]_p{\cdot}CH_2^+ + HO{\cdot}[CH_2{\cdot}O]_q{\cdot}CH_2{\cdot}O^- \rightarrow$$
$$HO{\cdot}[CH_2{\cdot}O]_p{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_q{\cdot}OH$$

[11] " High Polymeric Reactions ", Interscience, New York, 1941, pp. 374 *et seq.*
[12] Herbert and Lauder, *Trans. Faraday Soc.*, 1938, **34**, 432.

The net reaction clearly can be represented by the general equation above. The mechanism of the depolymerisation is discussed in a later section.

The common polymer, paraformaldehyde, consists of a mixture of polyoxymethylene glycols, the average degree of polymerisation being about 30.

The terminal hydroxyl groups of the polyoxymethylene glycols can be replaced by other groups. Monomeric formaldehyde is freely soluble in the lower alcohols and polymers can be recovered from the solutions ; if an alcohol $R \cdot OH$ is used, polymers of the series $R \cdot O \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot OH$ are formed. Polymers of this type can also be prepared by controlled treatment of the glycols with alcohols, $e.g.$,

$$HO \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot OH + CH_3 \cdot OH \longrightarrow HO \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot O \cdot CH_3 + H_2O$$
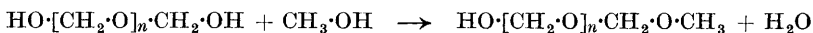
The heat of polymerisation of formaldehyde, calculated from the heats of combustion of the monomer and its polymer, is approximately equal to the heat of solution of the aldehyde in water and alcohols ; Walker [10] related the heats of polymerisation and solution with saturation of the aldehyde molecule. Dimethyl ethers of general formula $CH_3 \cdot O \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot O \cdot CH_3$ can be prepared by the action of methyl alcohol on the glycols in the presence of traces of sulphuric or hydrochloric acid. Treatment of the glycols with acetic anhydride yields diacetates of general formula $Ac \cdot O \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot OAc$. The diacetates and the dimethyl ethers are more stable than the glycols from which they are derived. Individual members of the diacetate series having values of n up to about 20 have been isolated, and fractionation of the dimethyl ethers has also been achieved. The physical properties change progressively with the molecular weight. The molecular weights of fairly low polymers can be determined satisfactorily by the cryoscopic method, and those of higher polymers by end-group assay ; in the latter method the polymer is hydrolysed and the liberated acetic acid or methyl alcohol is determined. Polyoxymethylene diethyl and dipropyl ethers have also been prepared.

Polymerisation in the Gas Phase.—If gaseous formaldehyde is in contact with a surface at a temperature below about 90°, deposition of polymer occurs at an appreciable rate. The reaction was studied by Spence [9] and by Carruthers and Norrish,[13] the latter workers making a detailed kinetic study. They used an apparatus the whole of which was heated to about 100° while mixtures of formaldehyde and other substances were made ; then part of the surface was cooled to about 20° and the ensuing polymerisation was followed manometrically. It was found that formic and acetic acids are powerful catalysts, and that the catalysed polymerisations have the characteristics of a branching-chain reaction. The rate of polymerisation could be expressed by an equation of the form

$$\text{Rate} = \frac{[\text{aldehyde}][\text{catalyst}]}{k'[\text{aldehyde}] - k''[\text{catalyst}]}$$

so that the rate increased markedly with rising catalyst concentration. A set of chemical equations consistent with the observed kinetics was constructed. The reactive centres are assumed to be present on the cold surface

and to grow by the successive addition of aldehyde molecules from the gas phase. The formation of primary centres is believed to occur thus when formic acid is present
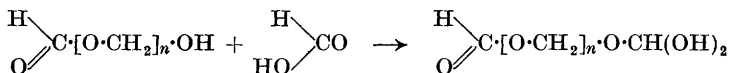
$$\underset{O}{\overset{H}{\diagdown}}C \cdot OH + CH_2O \longrightarrow \underset{O}{\overset{H}{\diagdown}}C \cdot O \cdot CH_2 \cdot OH$$
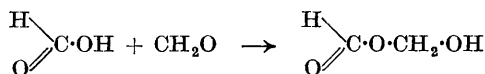
The growth of polymer is believed to involve the hydroxyl group according to the equation

$$H \cdot CO \cdot O \cdot CH_2 \cdot OH + CH_2O \longrightarrow H \cdot CO \cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot OH$$
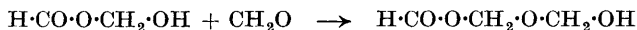
The kinetics indicate that deactivation of a centre occurs by reaction with an aldehyde molecule, the suggested equation being

$$H \cdot CO \cdot [O \cdot CH_2]_n \cdot OH + CH_2O \longrightarrow H \cdot CO \cdot [O \cdot CH_2]_n \cdot CHO + H_2O$$
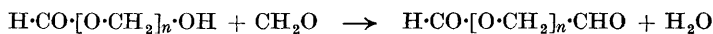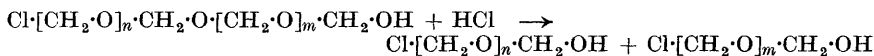
the polymer molecule losing its hydroxyl group and therefore its capacity for growth. According to the kinetics, branching occurs by the reaction of a centre with a molecule of formic acid, the process being represented thus :

$$\underset{O}{\overset{H}{\diagdown}}C \cdot [O \cdot CH_2]_n \cdot OH + \underset{HO}{\overset{H}{\diagdown}}CO \longrightarrow \underset{O}{\overset{H}{\diagdown}}C \cdot [O \cdot CH_2]_n \cdot O \cdot CH(OH)_2$$

The two hydroxyl groups can engage in growth reactions so that both structural and kinetic branching develop. A similar set of equations can be written for catalysis by acetic acid.

Hydrogen chloride, stannic chloride, and boron trifluoride are even more powerful than formic and acetic acids as catalysts for the gas-phase polymerisation, and they promote reactions which appear to be branching-chain processes.[14] It is believed that the polymerisation catalysed by hydrogen chloride involves the formation of the compound $Cl \cdot CH_2 \cdot OH$, and that growth and deactivation of centres occur in the same way as in the case of catalysis by formic acid. A branching reaction of the type envisaged for formic acid cannot apply for hydrogen chloride since that substance does not contain an unsaturated group and cannot be incorporated in a growing chain. There is good evidence that hydrogen chloride can cause the rupture of carbon–oxygen bonds in polyoxymethylene polymers, and it is believed that such a reaction occurs during polymerisation. The catalyst is thought to split the polymer chain into fragments each of which possesses a hydroxyl group and is therefore able to act as a centre for polymerisation, the suggested equation being

$$Cl \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot O \cdot [CH_2 \cdot O]_m \cdot CH_2 \cdot OH + HCl \longrightarrow$$
$$Cl \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot OH + Cl \cdot [CH_2 \cdot O]_m \cdot CH_2 \cdot OH$$

As a result of this reaction, kinetic branching occurs but only straight-chain polymers are produced. The suggested equations indicate that in each polymer molecule there is one molecule of hydrogen chloride combined,

[14] Bevington and Norrish, *Proc. Roy. Soc.*, 1951, *A*, **205,** 517.

and this relationship can be used to determine the average chain-length of the polymer.

The nature of the catalysts indicates that the mechanism of the catalysed polymerisation of formaldehyde in the gas phase may be essentially ionic. The suggested scheme involves the addition of hydroxy-compounds across the polar carbonyl bond, and such processes normally involve charged intermediates.

The conflicting reports on the effect of oxygen on the polymerisation of the liquid monomer at low temperatures were mentioned on p. 144 ; in the gas phase it appears that oxygen exerts no specific effect on the reaction and behaves only as an inert diluent like nitrogen.[14] This is evidence against a free-radical mechanism since polymerisations of that type are usually affected by oxygen.

Depolymerisation of Formaldehyde Polymers.—The fact that the de-polymerisation of the cyclic polymer trioxan is catalysed by acids indicates that carbon–oxygen bonds of the type present in aldehyde polymers can be broken by acids, and further that in the acid-catalysed depolymerisation of linear polymers of formaldehyde the bonds which are broken are not necessarily near the ends of the polymer chains.

The depolymerisation of polyoxymethylene glycols and diacetates is catalysed both by acids and by alkalis, but with the dimethyl ethers and trioxan only acids are effective. Staudinger suggested that there are two distinct mechanisms for depolymerisation of linear polymers. Under alkaline conditions a step-wise degradation is believed to occur, units containing only one formaldehyde molecule being split off ; it is thought that polymers with methoxy end-groups are stable under these conditions because these groups resist the initial attack. Acidic catalysts are thought to be able to cause any carbon–oxygen bond in the chain to break, and as this process is independent of the nature of the end-group, the glycols, diacetates, and dimethyl ethers behave similarly.

Step-wise degradation is thought to occur during the thermal depoly-merisation of polyoxymethylene polymers ; it is believed that the first bond to break is one very near the end of the polymer chain, since the stability of a polymer depends to a considerable extent upon the nature of the end-groups.

If traces of hydrogen chloride or boron trifluoride are added to formalde-hyde polymers in a vacuum at about 100°, the depolymerisation is acceler-ated.[14] It is thought that the polymer chains are split into reactive frag-ments by the same type of process as that suggested for the branching process during polymerisation, and that the increase in the rate of depoly-merisation results from the increase in the number of points from which monomer molecules can be shed. The mechanism of the depolymerisation of poly(methyl methacrylate) has been elucidated by determining the molecular weight of the polymer at stages during the reaction, but a similar method cannot be used for formaldehyde polymer owing to the impossibility of determining molecular weights.

Polyoxymethylene glycols have definite dissociation pressures of formal-

dehyde and these pressures have been measured at various temperatures. These results have been used [15] to calculate the changes in heat content and entropy accompanying the reaction

$$CH_2O_{\text{gas at 1 atm.}} \longrightarrow \text{solid polymer}$$
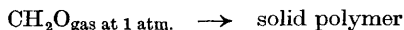
at 25°. The calculated values for ΔH and ΔS are $- 13 \cdot 3 \pm 1 \cdot 5$ kcal./mole and $- 32 \cdot 5 \pm 4$ cal./deg. mole respectively ; from the equation

$$\Delta G = \Delta H - T . \Delta S$$

it is calculated that ΔG is equal to zero at 137°. According to these calculations gaseous formaldehyde at 1 atmosphere should not polymerise at temperatures above 137° ; this predicted " ceiling temperature " is in fair agreement with observed values.

Properties of Linear Polyoxymethylene Polymers.—The lower polyoxymethylene glycols are soluble in water, acetone, and ether, but the solubility decreases as the molecular weight rises, and the compound $HO \cdot [CH_2 \cdot O]_{12} \cdot H$ is only very sparingly soluble in acetone. Separation of the lower members of this series of polymers has been effected by fractional precipitation from acetone solution by light petroleum. The higher glycols appear to dissolve slowly in water but the process involves partial depolymerisation and so is not true solution. The lower diacetate and dimethyl ether polymers are soluble in a number of liquids but the solubility falls off with increasing chain-lengths. The melting points of some of the lower members of the series of polymers have been measured, and as expected the melting point rises with chain-length.

The linear polymers of formaldehyde are shown by X-ray diagrams to be fairly crystalline.[1] The degree of crystallinity of a polymer prepared at low temperatures can be increased by warming it to the softening point and then cooling it.

The magnetic susceptibilities of various high polymers of formaldehyde have been measured. Farquharson [16] reasoned that for a linear polymer with repeating unit $\cdot CH_2 \cdot O \cdot$ the magnetic susceptibility should approach the value of $- 0 \cdot 496 \times 10^{-6}$ as the chain-length increases. A marked discrepancy was observed for a material known as δ-polyoxymethylene formed by prolonged treatment of polyoxymethylene dimethyl ether of high molecular weight with boiling water. It appears that this material is not a simple polyoxymethylene ; from the nature of its degradation products Staudinger had concluded previously that δ-polyoxymethylene contains a few $\cdot CH(OH) \cdot$ groups in its chain, formed by rearrangement of $\cdot CH_2 \cdot O \cdot$ groups.

High Polymers of Acetaldehyde

Preparation and Structure.—A high polymer of acetaldehyde was first described by Letort [17] and Travers [18] independently. If a sample of liquid aldehyde is frozen, or if the vapour is condensed on a glass surface cooled in liquid air, and then the solid is warmed to room temperature, a viscous

[15] Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 331.   [16] *Ibid.*, 1937, **33**, 824.
[17] *Compt. rend.*, 1936, **202**, 767.   [18] *Trans. Faraday Soc.*, 1936, **32**, 246.

liquid or even a gel is sometimes produced. Unchanged aldehyde can be removed under reduced pressure, leaving a rubber-like solid which can also be recovered by precipitation with water. Osmotic measurements on solutions in ethyl methyl ketone gave a value of 510,000 for the average molecular weight of a sample of the polymer ; [19] the material had undergone partial depolymerisation before the measurements were made, however. The course of the polymerisation is influenced profoundly by many factors, for example, the purity of the aldehyde, the state of the surface upon which condensation occurs, and the rate of solidification or condensation.

Staudinger [20] suggested that the polymer has a long-chain structure with repeating unit ·CHMe·O· ; this structure has been confirmed by consideration of the properties of the polymer,[21] X-ray diffraction data,[22] and infrared spectra.[23]

A technique in which acetaldehyde vapour is condensed on a cold surface under carefully controlled conditions has been used in a detailed study of the polymerisation.[24] The variations in the yield of polymer with changing conditions can be explained readily if centres for polymerisation are assumed to be formed on the cold surface as the aldehyde condenses, and if an aldehyde molecule can either be incorporated in a growing polymer molecule or condense on the cold surface without reaction. It appears that the active centres have fairly long lives and that they can be deactivated in three ways, viz., by a process involving a centre and a molecule of aldehyde, by one involving a centre and a molecule of a foreign substance, and spontaneously. Since condensation without reaction is possible, yields of polymer less than 100% are to be expected ; reductions in the yield may be due either to decreases in the number of primary centres or to premature termination of the growing chains.

Although there are no effective inhibitors for the low-temperature polymerisation of formaldehyde, small amounts of certain substances, e.g., water, ethyl alcohol, and paraldehyde, suppress the polymerisation of acetaldehyde at its freezing point. Acetic acid has a marked effect upon the reaction, increasing the yield of polymer but decreasing its molecular weight ; it also catalyses the depolymerisation. The effects of acetic acid are believed to be similar to those of hydrogen chloride on the polymerisation of formaldehyde ; the acid is thought to cause the rupture of carbon-oxygen bonds to give reactive points which either take up or shed monomer molecules according to the prevailing conditions. If the break occurs during polymerisation, the chance of an aldehyde molecule condensing without reacting is reduced, and consequently the yield of polymer is increased, and at the same time the average molecular weight is reduced.

There have been conflicting reports on the necessity for some substance

[19] Muthana and Mark, *J. Polymer Sci.*, 1949, **4**, 91.
[20] *Trans. Faraday Soc.*, 1936, **32**, 249.
[21] Rigby, Danby, and Hinshelwood, *J.*, 1948, 234.
[22] Powell, quoted in ref. (21).
[23] Sutherland, Philpotts, and Twigg, *Nature*, 1946, **157**, 267.
[24] Bevington and Norrish, *Proc. Roy. Soc.*, 1949, *A*, **196**, 363.

other than acetaldehyde to be present in order to initiate the polymerisation. Recent careful work by Letort and Pétry [25] indicates that traces of a peroxide in the aldehyde are essential for polymerisation.

It has been shown conclusively [21, 24, 26] that solidification is essential if polymerisation is to occur ; if liquid aldehyde is supercooled below its freezing point no reaction takes place. Letort and Pétry [25] have shown that there is a connection between the number of centres for the crystallisation of liquid acetaldehyde and the yield of polymer. The polymer is formed while solidification is proceeding, and the yield is unaffected by the length of time for which the aldehyde is frozen ; inhibitors can be added to frozen aldehyde without influencing the amount of polymer which can be recovered. There have been suggestions [21, 26] that the latent heat of fusion can in some way be used for activation. An alternative explanation for the need for solidification is that the growing centres are thereby fixed and ring-closure is made impossible ; further, in liquid systems a reactive point might be effectively screened by a " cage " of molecules. No information about the crystal structure of acetaldehyde is available, but it would be interesting to know whether in the crystal the carbon and oxygen atoms of the carbonyl groups lie in positions corresponding approximately to their positions in the polymer chains ; if this were so and a polymer once began to grow, propagation of the chain during growth of the crystal might proceed quite easily. An ionic mechanism for the polymerisation would be in accord with the following facts : (i) reaction occurs readily at low temperatures ; (ii) the formation of cyclic polymers of acetaldehyde is catalysed by acidic substances ; (iii) the carbonyl bond is strongly polar. Letort and Pétry [25] favour a mechanism involving free radicals, in view of their conclusion that a peroxide is an essential catalyst for the reaction.

High polymers of acetaldehyde have been the subject of a patent.[27] It was claimed that boron trifluoride, or other active halide catalyst, converts acetaldehyde into the polymer $CH_3 \cdot CH(OH) \cdot [CH_2 \cdot CH(OH)]_n \cdot CHO$, n having values up to about 5000. The suggested formula is probably incorrect, since it corresponds essentially to polyvinyl alcohol which is insoluble in acetone and other liquids claimed to dissolve the polymer. Formaldehyde, propaldehyde, and methyl ketones were reported to polymerise similarly but in all cases the conditions for reaction were not defined closely. The polymerisation of formaldehyde can certainly be catalysed by boron trifluoride and similar substances, but attempts to make polymers of other aldehydes and of acetone with these catalysts have failed.

Comparison of the Properties of the High Polymers of Formaldehyde and Acetaldehyde.—The high polymer of acetaldehyde is more soluble than those of formaldehyde, dissolving in acetone, diethyl ether, carbon tetrachloride, butyl acetate, and other liquids. At room temperature the methyl-substituted polyoxymethylene is more rubbery than the unsubstituted material. The differences in solubility and mechanical properties can be related to

[25] Compt. rend., 1950, **231**, 519, 545.
[26] Letort, Duval, and Rollin, ibid., 1947, **224**, 50.
[27] U.S.P. 2,274,749, March 3, 1942.

differences in crystallinity; the presence of the methyl groups in the acetaldehyde polymer must make it more difficult to fit the chains into a lattice, and consequently the acetaldehyde polymer would be less crystalline than the formaldehyde polymer under similar conditions. The replacement of hydrogen atoms by methyl groups affects the properties of other polymers in a similar way; for example, the polymers of acrylic acid and acrylonitrile are much less soluble than those of methacrylic acid and methacrylonitrile, and polyethylene is much less rubbery than polyisobutene.

The Stability of the Acetaldehyde Polymer.—The high polymer of acetaldehyde is less stable than the linear polymers of formaldehyde, the rate of depolymerisation of the former being appreciable at room temperature; as stated already, the cyclic trimer of acetaldehyde is less stable than the corresponding polymer of formaldehyde. The differences between the stabilities of the polymers of the two aldehydes is ascribed to a weakening of the carbon–oxygen bonds caused by the methyl groups. The replacement of hydrogen atoms by methyl groups affects similarly the stabilities of polymers of certain olefinic monomers; for example, poly*iso*butene is considerably less stable thermally than polyethylene. As will be shown later, replacement of the methyl groups in polyacetaldehyde by larger alkyl groups reduces the stability of the polymer still further.

Polymerisation under Other Conditions.—Acetaldehyde polymerises to a certain extent when subjected to very high pressures;[28] for example, treatment for 30 mins. at 300° under 5000 atmospheres gives a viscous liquid from which a rubbery material can be isolated. Water is formed during the treatment and crotonaldehyde can be detected easily. It appears that the polymer is derived from the unsaturated aldehyde and not directly from acetaldehyde, and there is no evidence that the polymer is a polyoxymethylene derivative.

Ultrasonic waves have been used to induce polymerisation in acetaldehyde,[29] but it is clear that the polymer was of the aldol type. The action of high-speed cathode rays on acetaldehyde vapour produces solid compounds which have been referred to rather loosely as polymers.[30] They cannot be true polymers of the aldehyde since their production is accompanied by the appearance of decomposition products, and acetaldehyde and acetone seem to give the same solid material.

High Polymers of Butaldehyde

Formation of the Polymer at High Pressures.—Butaldehyde has been converted into a high polymer by the application of a pressure of 12,000 atmospheres for 24 hours at 30°.[31] It was shown that very careful purification of the aldehyde reduced the tendency for reaction, and that oxidation products of the aldehyde are probably essential catalysts. It was concluded

[28] Leĭpunskiĭ and Rienov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 624.
[29] Demann and Asbach, *Tech. Mitt. Krupp Forschungsber.*, 1940, **3**, 12; see *Chem. Abs.*, 1940, **34**, 3972.
[30] McLennan and Patrick, *Canadian J. Res.*, 1931, **5**, 470.
[31] *J. Amer. Chem. Soc.*, 1932, **54**, 628.

that a peroxide derived from the aldehyde, and not butyric acid, was the active substance. The peroxide decomposes slowly under normal conditions, and it was suggested that the initiation of polymerisation is associated with this decomposition.

Benzoyl peroxide could be used as a catalyst for the polymerisation, and certain substances such as ethyl alcohol acted as inhibitors.

Depolymerisation of the Polymer.—The polymer of butaldehyde reverted to the monomer quite readily, the rate rising with temperature. The process resembled the depolymerisation of other aldehyde polymers, both linear and cyclic, in that it was accelerated by acids ; alkalis also acted catalytically. The ease of depolymerisation and the high yield of monomeric aldehyde indicate that the polymer was most probably of the polyoxymethylene type with repeating unit $\cdot CH(C_4H_9)\cdot O\cdot$.

An attempt was made to study the depolymerisation more closely. The polymer was suspended in 1 : 4-dioxan and the freezing point of the liquid gradually fell ; on the assumption that the depression was due entirely to liberated monomer, the rate of depolymerisation was calculated. From the rates of depolymerisation at a series of temperatures, it is estimated that the overall activation energy for the process is very roughly 15 kcal. per mole of monomer. It appears that the polymer of butaldehyde is less stable than the high polymers of formaldehyde and acetaldehyde.

Linear polymers of formaldehyde can be stabilised to a certain extent by replacement of the terminal hydroxyl groups by other groups such as $\cdot O\cdot CH_3$ and $\cdot O\cdot CO\cdot CH_3$. Attempts to stabilise the butaldehyde polymer similarly were unsuccessful, for the necessary reagents themselves accelerated the depolymerisation.

The Mechanism of Polymerisation.—Conant and Peterson [31] pointed out that the decomposition of the peroxide believed to be the essential catalyst for the polymerisation occurs at normal pressures and that the need for high pressures during the polymerisation is not associated with that decomposition. The high pressures cause the molecules in the liquid to be packed tightly and perhaps also to be orientated in a way favourable for the propagation of a reaction chain ; the polymer is denser than the monomer and so high pressures should favour the production of polymer.

It was suggested that polymerisation proceeds by an energy chain reaction but this seems improbable. Peroxide-catalysed reactions involve free radicals, and since this polymerisation is catalysed by peroxides, there is evidence for a radical mechanism. The overall activation energy for the polymerisation can be estimated by comparing the activation energy for depolymerisation and the heat of polymerisation. As indicated already, the activation energy for depolymerisation is roughly 15 kcal. per mole ; the heat of polymerisation of butaldehyde is probably a little less than that of formaldehyde which is in the range of 12—15 kcal. per mole. If the polymerisation and depolymerisation proceed *via* the same reactive intermediates, it is probable that the polymerisation requires an activation energy of roughly 3 kcal. per mole.
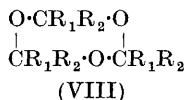
A direct comparison of the polymerisations of formaldehyde, acetalde-

hyde, and butaldehyde is not possible because the high polymers are formed under such widely different conditions. Qualitatively, it is clear that the ease with which polymerisation occurs and the stability of the polymer both decrease as the size of the alkyl group is increased. Certain observations on the polymerisation of thioaldehydes confirm that the size of the group attached to the carbonyl group may influence the polymerisation. Thioformaldehyde and other thioaldehydes of low molecular weight polymerise extremely readily, and only thioaldehydes with high molecular weights are at all stable in the monomeric form. Most thioaldehydes form cyclic polymers, but a few having very large molecular weights tend to form linear polymers.[32]

Polymerisation of Other Aldehydes at High Pressures.—*iso*Butaldehyde, *n*-valeraldehyde, and *n*-heptanaldehyde resemble *n*-butaldehyde in giving substituted polyoxymethylenes when subjected to very high pressures.[31] Evidence was obtained that the two butaldehydes can form co-polymers.

Polymers of Ketones

Apart from the patent claim in respect of methyl ketones (see p. 151), there are no records of ketones polymerising to compounds with repeating unit $\cdot C(R_1R_2)\cdot O\cdot$. Thioketones readily form cyclic trimers of general formula (VIII). This difference between ketones and their sulphur analogues may occur because the sulphur atom is larger than the oxygen atom. The reason for acetone, for example, not forming a cyclic trimer may be that the methyl groups on one carbon atom interfere with those on another ; in thioacetone the carbon atoms are further apart and so the chance of interference between the methyl groups is reduced.

$$
\begin{array}{c}
\text{O·CR}_1\text{R}_2\text{·O} \\
| \qquad\qquad | \\
\text{CR}_1\text{R}_2\text{·O·CR}_1\text{R}_2 \\
\text{(VIII)}
\end{array}
$$

The Polymerisation of Dialdehydes

Pure glyoxal polymerises only slowly and the process is accelerated by traces of water, but very little is known about the polymerisation of compounds of this type. Glyoxal might give rise to two distinct types of polymers with repeating units $\cdot O\cdot CH : CH\cdot O\cdot$ and $\cdot O\cdot CH(CH : O)\cdot$ and so be compared with butadiene which also contains conjugated double bonds and for which both 1 : 2- and 1 : 4-addition are possible. It should be noted that a polymer with the first of the repeating units above would not be a polyoxymethylene derivative, since the chain would consist of alternate pairs of carbon and oxygen atoms, and also that if such a polymer existed it could be produced only by a reaction of the free-radical type and not by one of the ionic type. A polymer having the second repeating unit could have a branched or cross-linked structure.
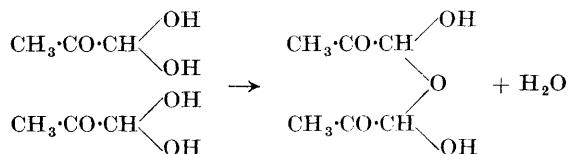
The polymerisation of methylglyoxal $CH_3\cdot CO\cdot CHO$ was studied by

[32] See *e.g.*, " Organic Chemistry ", edited by Gilman, Wiley, New York, 2nd edn., 1942, p. 923.

Moulds and Riley,[33] who found that the rate was affected by the purity of the material and that traces of water catalysed the reaction. The polymer was sometimes produced as a hard glass, and it could be decomposed to monomer quite easily, indicating that it was probably of the polyoxymethylene type. It was suggested that the first stage in the reaction is the addition

$$CH_3 \cdot CO \cdot CHO + H_2O \longrightarrow CH_3 \cdot CO \cdot CH(OH)_2$$

and that then two molecules of the product reacted thus

$$CH_3 \cdot CO \cdot CH {\Large\diagup}^{OH}_{\diagdown OH} \qquad CH_3 \cdot CO \cdot CH {\Large\diagup}^{OH}_{\diagdown O}$$
$$\longrightarrow \qquad\qquad {\Large\diagup}O \quad + H_2O$$
$$CH_3 \cdot CO \cdot CH {\Large\diagup}^{OH}_{\diagdown OH} \qquad CH_3 \cdot CO \cdot CH {\diagdown OH}$$

Further similar condensations would lead to the building of large molecules. This mechanism is essentially the same as those discussed already in connection with the polymerisation of aldehydes to cyclic trimers and the polymerisation of formaldehyde in aqueous solution. It was argued that the polymerisation of methylglyoxal did not involve the carbonyl group having a methyl group attached to it, since diacetyl $CH_3 \cdot CO \cdot CO \cdot CH_3$ does not polymerise under these conditions. The second carbonyl group of methylglyoxal is essentially ketonic and therefore would not be expected to enter into polymerisation reactions.

Polymers of Unsaturated Aldehydes

Keten, $CH_2 : C : O$, polymerises readily and the reaction shows characteristics of an ionic process ; for example, the speed of reaction varies with the dielectric constant of the medium and it may be appreciable at temperatures as low as $- 80°$.[34] A dimer of uncertain structure [35] is produced but it is clearly not of the polyoxymethylene type.

Certain substituted ketens polymerise more readily than keten itself. Solutions of dimethylketen, $C(CH_3)_2 : C : O$, in ether undergo vigorous polymerisation if treated with traces of trimethylamine at $- 80°$.[36] Hard glassy products of quite high molecular weight are produced. These polymers revert to the monomer at temperatures in the range 100—200°, and this ready depolymerisation may indicate that the main chain of the polymer

$$\begin{array}{cc} \cdot C \cdot O \cdot & \cdot CMe_2 \cdot C \cdot \\ \| & \| \\ CMe_2 & O \\ (IX) & (X) \end{array}$$

consists of alternate carbon and oxygen atoms, i.e., the repeating unit is (IX) and not (X). There is also some chemical evidence that the polymer

[33] J., 1938, 621.
[34] Rice and Greenberg, J. Amer. Chem. Soc., 1934, **56,** 2132.
[35] Whiffen and Thompson, J., 1946, 1005.
[36] Staudinger, Helv. Chim. Acta, 1925, **8,** 306.

is a substituted polyoxymethylene, *viz.*, (i) the polymer readily absorbs bromine, indicating the presence of olefinic bonds : (ii) ozonolysis yields acetone and non-volatile products, suggesting that the polymer contains : CMe_2 groups. On the other hand, when the polymer is treated with alcoholic potash at 100°, the chief product is $CHMe_2 \cdot CO \cdot CHMe_2$ indicating that it may contain the unit $\cdot CMe_2 \cdot CO \cdot CMe_2 \cdot$ which would be the case if the olefinic and not the carbonyl bond opened during polymerisation. Infrared measurements would most probably distinguish between the two possible repeating units since the one contains the $C=C$ bond and the other the $C=O$ bond.

Acraldehyde and α-methylacraldehyde give products of high molecular weight in the presence of dilute aqueous alkali,[37] but they are not polyoxymethylene derivatives.

[37] Gilbert and Donleavey, *J. Amer. Chem. Soc.*, 1938, **60**, 1737, 1911.