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POLYMERS OF CARBONYL COMPOUNDS

M.V.Chistyakova

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I. INTRODUCTION

The synthesis of polymers of carbonyl compounds is a comparatively new branch of macromolecular chemistry and technology, which has attracted much attention from research workers during recent years. Polymers of formaldehyde, which can be used in various industries, are especially important. Great interest attaches also to the synthesis of stable polymers of acetaldehyde, especially as acetaldehyde can be obtained by a simple and cheap method, the oxidation of ethylene[1]. Polymers of several other aldehydes are also known, as well as a polymer of acetone.

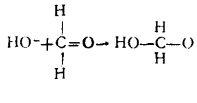
By now a voluminous literature is available on the chemistry and technology of polyformaldehyde, and review papers have been published[2-4], so that in the present survey this polymer will be considered only in relation to other polyaldehydes. The review will be mainly concerned with an examination of published information on the polymerisation of homologues of formaldehyde.

II. PREPARATION AND PROPERTIES OF POLYMERS OF CARBONYL COMPOUNDS

The polymerisation of aldehydes and ketones involves the formation of an acetal chain structure, with alternating carbon and oxygen atoms, independent of the hydrocarbon radical combined with the carbonyl group. Therefore the formation and the properties of these polymers have much in common.

It is believed[3,5,6] that carbonyl compounds polymerise by an ionic mechanism. This is quite likely, since the double bond of the carbonyl group contains a very labile electron pair. Formaldehyde polymerises under the influence of both electrophilic and nucleophilic reagents: *i.e.* polymerisation can take place both by a cationic and an anionic mechanism. This evidently applies also to the polymerisation of acetaldehyde.

The anionic mechanism by which polyformaldehyde is formed is as follows[3]:



Chain propagation:

$$HO-CH_2-O^- + n(CH_2O) \rightarrow HO-(CH_2O)_n-CH_2-O^-.$$

Chain termination:

$$HO-(CH_2O)_n-CH_2O^- + H^+ \rightarrow HO-(CH_2O)_n-CH_2OH.$$

Chain transfer occurs with extraordinary ease during the polymerisation of aldehydes, for example:

$$P-CH_2O-CH_2O^- + H_2O \rightarrow P-CH_2O-CH_2OH + OH^-.$$

The possibility of chain transfer makes extremely severe demands on the purity of the starting materials: even small amounts of chain-transfer agents as impurities may result in the formation of a polymer of low molecular weight.

In order to obtain polymers of high molecular weight, the reaction must be carried out in an anhydrous medium, since the proton produces chain termination, while water molecules are chain-transfer agents[7]. Since aldehydes are readily oxidised, they may contain acids, peracids, and other oxidation products, which are also capable of chain transfer. Thus the molecular weight of polyaldehydes is determined not only by the amount of catalyst but also by the purity of the monomer.

1. Polyformaldehyde

Polymers of formaldehyde have been known since the time of Butlerov, who obtained polyformaldehyde as early as 1859.[8] This history of polyformaldehyde, from the mechanically fragile polymer of low molecular weight to the commercial thermoplastic (Delrin), has been described in detail in the review by Schweitzer *et al.*[3]

The influence of the quantity of monomer, solvent, initiator, stabiliser, temperature, and rate of addition of monomer on the course of the polymerisation of formaldehyde has been described[9]. Since the molecular weight of formaldehyde polymers depends on the amount of impurity in the monomer, great attention has been paid in the literature to the preparation of pure dry formaldehyde[2]. Most of the proposed methods are based on the preparation of formaldehyde by decomposing its polymers of low molecular weight, which are very readily available.

The du Pont Corporation in the USA[10] has suggested a method for obtaining polyformaldehyde of high molecular weight by heating trioxan [paraformaldehyde] with AlF_3, BiF_3, SbF_3, etc.

Physical properties of polyformaldehyde[4,11-16]. Polyformaldehyde is an opaque white material, m.p. 180°, which can easily be dyed any colour. Its physical properties have been described in detail by Gogdall and Hardesty[14], according to whom it possesses great strength, which is virtually unaffected up to 120° and is not diminished by moisture; the modulus of elasticity also possesses great stability.

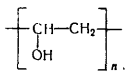
The creep of the material is greater than with amorphous polymers (polystyrene) but less than with crystalline polymers such as polyethylene and polyamides. A distinctive feature of polyformaldehyde is its dimensional stability.

Polyformaldehyde is more durable than ordinary thermoplastics (other than 6,6-nylon). It possesses excellent frictional and electrical properties. Its disadvantage is lack of resistance to acids and alkalis. In spite of this, rigidity and strength, low creep, high tenacity, abrasion resistance, elasticity, dimensional stability, and other properties, make polyformaldehyde one of the most valuable of thermoplastic materials.

2. Polyacetaldehyde

Acetaldehyde is not so readily polymerised as is formaldehyde. Methods of four types are available for polymerisation of acetaldehyde: (*a*) crystallisation polymerisation, (*b*) polymerisation by means of heterogeneous catalysts, (*c*) polymerisation by means of stereospecific catalysts, and (*d*) polymerisation induced by radiation.

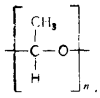
A paper has recently been published[17] on the formation of a polymer of acetaldehyde of the type of poly(vinyl alcohol):



This will be discussed in detail below.

Each type of polymerisation will be examined separately.

(*a*) Crystallisation polymerisation. Polyacetaldehyde was first obtained by this method, applied at the freezing point of the monomer, by Travers[18] and by Letort[19] in 1936. Staudinger suggested for the new polymer a structure based on a methyloxymethylene unit. This suggestion was later confirmed[20,21] by an investigation of the infra-red spectra, and at the present time the following structure is generally accepted for the polymer chain:



According to the most recent work, the molecular weight of the polymer is $(1-2.5)\times 10^6$.

A detailed investigation of the polymerisation of acetaldehyde was begun in 1943, a great contribution having been made by Letort and his coworkers, who worked out a technique for preparing the polymer[22,23]. At first the process seemed very simple: it was sufficient to freeze and unfreeze acetaldehyde several times, when formation of the polymer took place. Polymerisation seemed to be independent of the purity of the acetaldehyde, of the presence of water, air, etc. These workers concluded that the only factor influencing the polymerisation was the rate of crystallisation.

Later[24] they made a more detailed study of this question, and discovered that polymerisation occurs at the interface between the liquid monomer and the crystal. Letort[25] and Rigby and Danby[26] reported that the rate of polymerisation is greatly dependent on the temperature: polymerisation does not occur above the melting point of acetaldehyde (−123.5°), and is very slow below this temperature (see Fig. 1).

Bevington and Norrish[27], in contrast to the above workers, achieved reproducible results by maintaining a high degree of purity during an experiment. They found that the smallest amount of impurity has a great effect on the polymerisation: 0.5 mole % of water, alcohol, or acetone considerably decreases the yield of polymer; the reaction depends on the duration of the experiment, and on water, oxygen, etc. sorbed on the walls of the vessel.

These workers made a more detailed study of the properties of polyacetaldehyde. In contrast to polyformaldehyde, it is soluble in acetone, butyl acetate, ether, acetic acid, carbon tetrachloride, and ethyl alcohol; it swells in benzene, but is insoluble in water and petroleum ether. Polymeric acetaldehyde is a rubber, but it has no great mechanical strength or thermal stability. At room temperature the polymer slowly decomposes, forming acetaldehyde; the process of depolymerisation is accelerated by the presence of acetic acid.

The question of the effect of initiators on the polymerisation of acetaldehyde, left open by these authors, is answered in later papers by Letort *et al.*[28-30] After working with acetaldehyde of the greatest possible purity, they reached a conclusion opposite to that in the earlier work[22,23]. Crystallisation is a necessary but not a sufficient condition for polymer formation, since no polymer is formed in the absence of oxygen. If, however, a measured quantity of air or oxygen is introduced into the reaction mixture, and the latter exposed to ultra-violet radiation, the yield of polymer is markedly increased. Hence these workers reached the quite correct conclusion that the reaction is accelerated by oxidation products of acetaldehyde — acetyl peroxide or peracetic acid.

Special experiments showed the initiator to be peracetic acid formed by the oxidation of acetaldehyde. A more detailed study of the polymerisation established the following facts.

1. The presence of peracetic acid is necessary for the polymer to be formed during crystallisation of the monomer.

2. The duration of polymerisation P affects the yield and molecular weight of the polymer. At high rates of crystallisation ($P \leq 8$ min) the yield increases rapidly with increase in P, reaching a maximum (35%) when $P = 8$ min (Fig. 2). With $13 < P < 38$ min the yield increases linearly with increase in P, but above 38 min it suddenly drops to 6%.

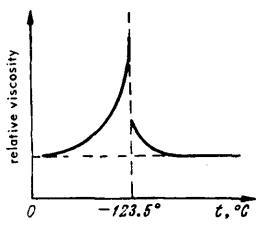


Fig. 1. Dependence of the viscosity of polymer on the temperature of polymerisation.

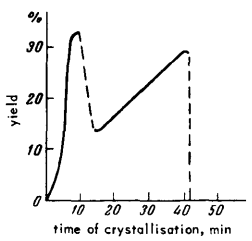


Fig. 2. Dependence of the yield of polymer on the duration of crystallisation.

3. The concentration of peroxide and the number of crystal nuclei also influence the yield and molecular weight of the polymer.

Letort and his collaborators discovered[31,32] a further extremely important fact: the presence of a single initiator is insufficient for the successful polymerisation of acetaldehyde, a cocatalyst — water or ethyl alcohol — being necessary. Fig. 3 gives an idea of the effect of water on the polymerisation: in very small quantities, 15–60 moles per 10^6 moles of acetaldehyde (0.002 wt.%), water exerts an extremely favourable effect on the yield of the polymer; in greater amounts, it begins to act as an inhibitor. It was also found that a mixture of peracetic acid and water produces the maximum effect when equimolar proportions of the components are present.

No exact idea of the mechanism of polymerisation can be obtained from these experimental results. In Letort's view the necessity of introducing a peroxide initiator (peracetic acid) and the inhibiting effect of water indicate a radical mechanism; the phenomenon of cocatalysis provides a weighty argument in support of an ionic mechanism, as does also the fact that several other acids[33], but not acetyl peroxide, can be employed instead of peracetic acid. All the organic acids used and the mineral acids cause polymerisation. In the latter case the yield is considerable, but the degree of polymerisation is low. Lewis acids, especially BF_3, are very active polymerisation catalysts. Ammonium salts of mineral acids also have an initiating effect, but neutral salts (for example NaCl) do not initiate polymerisation.

The method of crystallisation polymerisation is characterised by comparatively low yields of the polymer (of the order of 15%) and very high demands made on the purity of the materials and the experimental technique. The temperature, absence of impurities (air, water, etc.), and the duration and number of crystal nuclei must be controlled most accurately; the method requires exact adjustment of the low temperature (–123.5°, neither above nor below) and regulation of traces of water (up to 0.001%). If the experimental conditions are not adhered to, it is impossible to obtain reproducible results.

In 1959 Letort[34] published yet another paper on the synthesis of polyacetaldehyde, in the presence of ammonium persulphate and BF_3. Contrary to the earlier hypothesis of the necessity for crystallisation, it was discovered that the reaction can also take place above the melting point of acetaldehyde, at -80° or -65°; the presence of traces of water as cocatalyst is still necessary. The yield of the polymer is 30–50%.

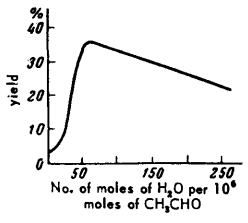


Fig. 3. Effect of water on the yield of polymer.

The main requirement of the method is the very exact measurement of small quantities (of the order of 10^{-4}%) of the catalyst and cocatalyst.

(*b*) Polymerisation of acetaldehyde using heterogeneous catalysts. The work of Furukawa *et al.*[35,36] provided a more practicable and cheaper method for obtaining acetaldehyde polymers at a higher temperature (-70° instead of -123.5°). The reaction was carried out in the presence of aluminium oxide, prepared by hydrolysis of the isopropoxide; before the experimental the aluminium oxide was heated in a current of dry air at 600° for 15 h (see Table 1).

Table 1 shows that the degree of dehydration of the aluminium oxide has a great effect on the reaction: ignition at 200° and at 1150° yields an inactive oxide, the best results being obtained with the oxide heated at 500°–600°. The reaction is also influenced by the temperature of polymerisation: at -10° or 15° no polymer is formed; at -184° a polymer is formed with a high molecular weight, but in low yield.

The resulting polymer is a non-sticky, highly elastic material which is soluble in most solvents — acetone, ether, butyl acetate, carbon tetrachloride, ethyl alcohol, and benzene — and insoluble in water, petroleum ether, and carbon disulphide. The infra-red spectrum indicates that the polymer obtained by means of aluminium oxide consists of the same structural units as Letort's polymer.

Experiment showed that basic substances (KOH, triethylamine, ammonia) inhibit the polymerisation.

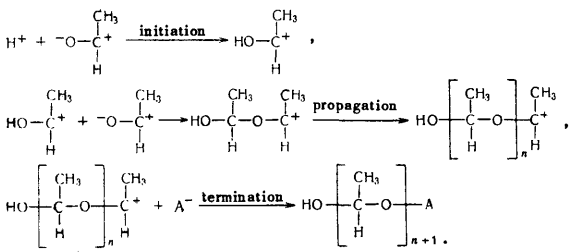
TABLE 1. Synthesis of polyacetaldehyde on aluminium oxide.

Aluminium oxide			Polymerisation		Polymer		
origin	ignited at, °C	water content, %	temp., °C	time, h	yield, %	η [d]	degree of polymerisation
Aluminium isopropoxide	—	—	— 70	43	0		
A[a]	200	20.3	— 70	43	0		
A	400	3.6	— 70	43	49	7.07	50 000
A	600	1.4	— 70	43	55	7.17	52 000
A	800	0.5	— 70	43	91	5.40	33 000
A	1000	0.2	— 70	43	76	6.65	40 000
A	1150[c]	0.0	— 70	43	8	0.03	
B[a]	not ignited[b]	13.5	— 70	65	23	3.88	17 500
B	600	1.6	— 70	65	66	2.40	9 400
B	1000	0.2	— 70	43	57	4.30	23 000
B	600[e]	1.6	— 70	55	63	4.07	21 000
B	600	1.6	— 70	20	0		
B	600[f]	1.6	—184	1.5	34	4.35	23 500
C			—184	1.5	9	5.60	35 000

Note. A[a] — oxide prepared by decomposition of aluminium isopropoxide; B[a] — commercial aluminium oxide (8–14 mesh); [b] commercial aluminium oxide used without being ignited; [c] no water present at 1150°; [d] in ethyl methyl ketone at 27.6°; [e] the monomer was distilled onto aluminium oxide under nitrogen at 1 atm; [f] aluminium oxide cooled with liquid air, and acetaldehyde distilled into it for 1½ h, the reaction mixture then being heated to room temperature and the polymer separated in the usual way; C in absence of aluminium oxide (acetaldehyde was condensed in liquid air in a tube for 1½ h).

Oxides other than alumina were tested, and it was found that CrO_3 and MoO_3 give high polymers in low yields; Be_2O_3, P_2O_5, MgO, ThO_2, and aluminosilicates form some polymer of low molecular weight; and SiO_2, CuO, TiO_2, ZrO_2, V_2O_5, ZnO, Fe_2O_3, MnO, CaO, BaO, PtO_2, PdO, and Ni_2O_3 yield no polymer. Hence it was concluded that aluminium oxide is exceptionally active in the polymerisation of acetaldehyde.

The reaction mechanism suggested by Furukawa for the polymerisation of acetaldehyde on aluminium oxide is as follows:



Later the polymerisation of acetaldehyde on Al_2O_3–SiO_2, ThO_2 [37] was reported, as well as polymerisation in the presence of aluminium oxide activated with diethylzinc,[38] which will be discussed in detail below.

In 1959 the production of a stable elastic polymer of acetaldehyde was described[39]; the new polymer was quite cheap, being half the price of acrylonitrile and butadiene–styrene rubbers; it was better than the latter in thermal stability. There was also a report[39] of the synthesis of a rubberlike polymer of acetaldehyde by the du Pont Corporation. This rubber could be vulcanised by irradiation and other methods without the use of sulphur.

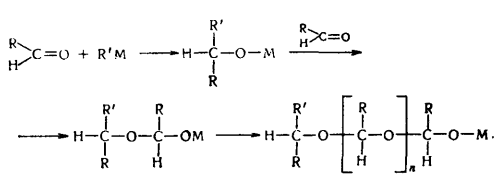
This practically exhausts the information available on the synthesis of elastic polyacetaldehyde.

(*c*) Stereospecific polymerisation of acetaldehyde. Until recently only elastic acetaldehyde polymers of irregular structure were known, although the possibility of obtaining polymers of regular structure is suggested by the molecular structure of the monomer.

In 1960 Natta[40] and Furukawa[41] and their collaborators discovered that acetaldehyde and its homologues form insoluble solid polymers in the presence of organometallic catalysts (metals of Groups II and III) at low temperatures. The polyacetaldehyde obtained in this way is a white thermoplastic resin. It is a solid, and, in contrast to the amorphous polymer, is insoluble in the usual organic solvents at their boiling points.

Apart from this information, which appeared in 1960, no other data have been published on the properties of plastic polyacetaldehyde, although work on these lines is evidently continuing.

The suggested reaction mechanism is



A crystalline, isotactic chain structure was suggested for these polymers on the basis of the infra-red spectra and X-ray data.

Recently Furukawa *et al.*[38] have synthesised polyacetaldehyde by the method described previously[41], using aluminium oxide activated with diethylzinc as catalyst. A block polymer was obtained, differing from ordinary polyacetaldehyde. It is a solid, sparingly soluble in methanol and soluble in chloroform. It was concluded from an examination of the infra-red spectra that it consisted of polymeric chains of acetaldehyde which were partly amorphous and partly crystalline.

From a detailed X-ray structure analysis of isotactic polyacetaldehyde, Natta *et al.*[42] concluded that the unit cell contains 16 monomeric units. It is similar in structure, not to polypropylene as was to be expected, but to polyvinylcyclohexane. The oxygen atoms in the polymer are shielded by the methyl groups, resulting in complete insolubility of isotactic polyacetaldehyde in the usual organic solvents.

(*d*) Polymerisation of acetaldehyde under the influence of ionising radiation. The possibility of obtaining polyacetaldehyde by this method was reported in 1960 by Chachaty[43]. Polymerisation was carried out in liquid and solid phases exposed to γ-radiation. With polymerisation in the liquid phase (-80°) an induction period is observed, and then reaction proceeds at a constant rate up to 20% conversion, after which the velocity of polymerisation increases rapidly. The polymer obtained is amorphous and rubberlike, similar to that of Letort and Furukawa, soluble in organic solvents, and unstable to heat; the molecular weight of the polymers lies between 5×10^5 and 1.5×10^6.

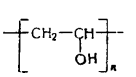
A radical mechanism for the polymerisation of acetaldehyde under the conditions investigated was suggested on the basis of the data obtained, although no final conclusion was reached.

In this way the range of catalysts for the polymerisation of acetaldehyde was extended, and it was established that acetaldehyde, like formaldehyde, can be polymerised by both anionic and cationic mechanisms. A radical method is also possible.

Copolymers of acetaldehyde with other aldehydes and monomers have been little discussed in the literature. At the plenary session of the International Symposium on Macromolecular Chemistry held in Moscow in 1960, Mark[7] mentioned that work was being carried out on the copolymerisation of acetaldehyde with formaldehyde and with acetone; great interest is aroused by work on the copolymerisation of acetaldehyde with acrolein at the carbonyl double bond. The resulting copolymers, owing to the presence of double bonds in the side-chains, would be capable of vulcanisation by the usual methods.

Chachaty[43] describes an acetaldehyde–formaldehyde copolymer obtained by γ-irradiation. It contains 20–50% of formaldehyde, and is a rubberlike elastic material which is more stable than polyacetaldehyde. The other properties of the copolymer are not described.

Polymers obtained by the above methods have a polyoxymethylene structure. The probability of the existence of an enol form of acetaldehyde, $CH_2:CHOH$, under certain conditions would make it possible for polymerisation to occur at the vinyl bond with formation of a poly(vinyl alcohol) type of polymer:



Imoto[17] obtained a polymer having the structure (according to its infra-red spectrum) of partly dehydrated poly(vinyl alcohol):

$$CH_3-(CH-CH_2)_n-CH=CH-(CH-CH_2)_m-(CH=CH)_k-CHO$$
$$\quad\quad\quad

chloroform. When heated above 120° the polymer decomposes to the monomer. The polymer of dichloroacetaldehyde is also formed spontaneously[58] as a block of soft, transparent material; the polymer is insoluble in water and alcohol, but soluble in acetone, from which it can be precipitated by methanol as a white solid which decomposes on being heated. The X-ray diffraction patterns showed both polymers to be crystalline. Their properties have not been described.

Polymers of trichloroacetaldehyde are known too[59-65]. They are formed when an amine — pyridine, trimethylamine, or quinoline — is added to anhydrous[63,64] chloral; polymeric chloral can also be obtained by the action of sulphuric acid on anhydrous chloral or chloral hydrate[61,62].

The polymer is a white solid, insoluble in all the organic solvents used other than pyridine and dimethylformamide. Later work by Novak and Whalley[65] showed that addition of the latter solvents to polychloral is accompanied not by dissolution but by degradation of the polymer. They showed by a detailed investigation of the infra-red spectra and X-ray diffraction patterns of polymeric chloral obtained in different ways — in the presence of sulphuric acid, pyridine, etc. — that, like other polyaldehydes, it is analogous to polyformaldehyde with hydroxyl groups at the ends of the chain.

Also like other polyaldehydes, polychloral is depolymerised at 140°–200° with formation of the monomer. The rate of thermal degradation is greatly dependent on the method of preparation. This effect is believed to be associated with the presence of traces of the acid or basic catalyst. X-Ray diffraction data showed that the crystallinity of the polymers also depends on the method of polymerisation.

Recently Furukawa *et al.*[41,59] have obtained a resinlike crystalline polymer from chloral (in the presence of an organometallic catalyst at a low temperature), which they suppose to have an isotactic structure, although they do not describes its properties. The literature contains no data on polymers of other chlorinated aldehydes.

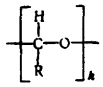
The polymerisation of fluorinated aldehydes of the aliphatic series has also been investigated during the past decade. This is a new field in the chemistry of polyaldehydes, since monomeric fluoroaldehydes were first obtained only in 1950[66].

Very scanty data are available in the literature on the preparation and properties of polymers of fluorinated aldehydes. In 1950 Schechter[66] first prepared a polymer of the first representative of this series — trifluoroacetaldehyde — and since then papers have been published[67-69] on polymers of pentafluoropropionaldehyde and heptafluorobutyraldehyde.

The polymers are obtained as a result of spontaneous[66,67,70] radical or ionic polymerisation. It is possible that the spontaneous polymerisation is caused by traces of some impurity. Acetyl peroxide, benzoyl peroxide, cumene hydroperoxide, and sodium persulphate can be employed as initators for the radical polymeristion of perfluoroaldehydes[70]. Radical polymerisation can be carried out at room temperature, being slowed down by a fall in temperature and accelerated by a rise. Polymerisation takes place also in the air, but is faster in its absence. All fluoroaldehydes readily form hydrates in the presence of water, so that polymerisation should be carried out in anhydrous media.

The higher fluoroaldehydes polymerise more slowly than trifluoroacetaldehyde, and the order of effectiveness of the catalysts is different. Heptafluorobutyraldehyde polymerises rapidly by an ionic mechanism, in the presence of sulphuric acid or acetic anhydride. A peroxide initiator is less effective. The opposite holds for the polymerisation of trifluoroacetaldehyde.

The usual polyaldehyde structure, *i.e.* a substituted polyoxymethylene chain, has been suggested for the polymeric fluoroaldehydes:



where R = C_nF_{2n+1} and k = 1–3.

Properties of polymeric fluoroaldehydes[70]. Polymeric fluoroaldehydes are transparent resinous materials which are insoluble in the usual organic solvents. They possess a unique and valuable combination of properties: they contain more than 50% of fluorine, and hence do not burn, they possess exceptional resistance to the action of various corrosive agents, and are resistant both to hydrocarbon and to aqueous solvents.

The resistance of these polymers to the action of fuming nitric acid even at elevated temperatures is of especial interest. Thus the polymer of trifluoroacetaldehyde lost only 0.8% of its weight after being boiled in fuming nitric acid for 6 h. The polymers are resistant to cold concentrated sulphuric acid, but are dissolved on boiling. Those of trifluoroacetaldehyde are also very resistant to the action of alkalis at room and elevated temperatures. Fluoroaldehyde polymers neither melt nor soften on being heated without the application of pressure; at high temperatures they, like other polyaldehydes, decompose to the monomers.

It can be seen from these facts how extensive and important are the practical potentialities for the employment of these polymers, especially under corrosive conditions at high temperatures.

5. Polyacroleins

Among polymers of unsaturated aldehydes, only polymeric acrolein has been described in detail in the literature, and this has already been known for more than a century. It was first mentioned in 1843, when Redtenbacher[71] found that acrolein passes spontaneously into an insoluble white solid. He suggested that the acrolein had polymerised, and termed the product "bisacryl".

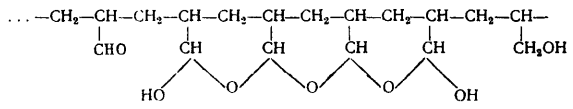
Subsequently Moureu and Dufraisse[72] discovered that the process is accelerated by light and by oxygen; quinol, catechol, and organometallic compounds inhibit the polymerisation of acrolein. It can take place by anionic, cationic, and radical mechanisms, and also in the presence of redox systems[73]. In many cases polymerisation is very rapid, even at low temperatures[74]. Techniques for the polymerisation of acrolein have been described in detail[75-80].

Physicochemical properties. Polyacroleins exist as powders, which are sparingly soluble in organic solvents, and which at 200°–220° sinter to a yellow or

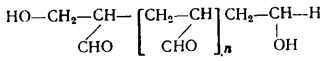
brown mass. The physicochemical properties of polyacrolein are greatly dependent on the mode of polymerisation. Polymer samples obtained in different ways differ in solubility, thermal stability, viscosity, etc., but no explanation of these differences is given in the literature.

The structure of the polyacroleins is not sufficiently understood, although a considerable number of papers have been published on this problem[74,76,77,81]. It has been established (by oxime formation) that these polymers contain carbonyl groups. The formation of hemiacetals, bisulphite derivatives, hydrazones, and phenylhydrazones has been described, as well as the Cannizzaro reaction. The spectra show the presence of an ether link. Although polyacroleins obtained in different ways differ in properties, their spectra show no substantial differences.

The following formula agrees well with the spectroscopic data and the chemical properties of the polyacroleins:

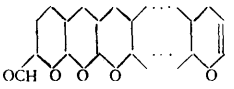


The formula below has been suggested[82,83] for acrolein polymers obtained by the use of organic bases:



where $n = 0-5$.

Scherlin[84] and his collaborators propose a polycyclic structure, formed by a process of continuous diene synthesis, for the polyacrolein (bisacryl) obtained by heating:



Other structures have also been suggested to represent polymeric acrolein[85], but none can be regarded as having been rigorously proved.

It is evident from this brief survey that the polymerisation of acrolein has not been investigated in detail, although several workers (for example Schulz and his collaborators) are carrying out intensive research in this field. The conditions under which the polymerisation of acrolein could be made to occur solely at the vinyl or solely at the carbonyl double bond, which would be of the greatest interest, are unknown.

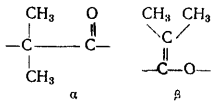
Mark[7] reported that work was being done on the preparation of rubberlike copolymers of acrolein and acetaldehyde. Owing to the presence of a double bond, such copolymers would be capable of vulcanisation with sulphur. No other data have been published on the polymerisation of acrolein at the carbonyl bond.

Polymers of methacryldehyde have also been described[86]. No polymers of other unsaturated aldehydes have been reported.

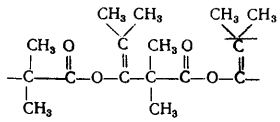
6. Polymers of Ketones

Kargin *et al.*[87] have recently described the preparation of polymers of acetone. Polymerisation was carried out by the simultaneous condensation of molecular beams of the monomer and the initiator (metallic magnesium) on a strongly cooled wall. A layer of condensate consisting of a vitrified molecular mixture of acetone and magnesium was deposited on the wall. If the temperature of the latter was allowed to rise, conditions were created, at the instant of the phase transition, which were kinetically favourable to polymerisation. This resulted in the formation of a polymer of acetone as an elastic white mass soluble in acetone (specific viscosity 0.6 at a concentration of 0.5 g per 100 ml of acetone). At room temperature this polymer is depolymerised; even the most stable specimens in the absence of oxygen and moisture can exist for at most 10–12 h.

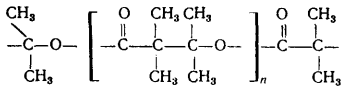
In 1960 Natta *et al.* reported the preparation of a polymer of dimethylketen[88] and of its copolymers with acetone and with acetophenone[89]. In the presence of aluminium bromide or triethylaluminium, dimethylketen gives a regular polymer or, more precisely, a copolymer derived from the two double bonds in the monomer:



Thus, the polymer has the following structure:



The dimethylketen–acetone copolymer is formed by polymerisation of the former at the C=C double bond, and of the latter at the carbonyl double bond:



A similar product is obtained by the copolymeristion of dimethylketen with acetophenone.

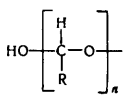
No other information on the polymerisation of ketones is available in the literature.

III. MOLECULAR STRUCTURE OF CARBONYL POLYMERS

A quite large literature exists on this question, concerned mainly with polyformaldehyde[4,12,90,91]. Koch and Lindvig[4] made a detailed study of the structure of this compound, and found that the molecules have a linear chain structure, no branching being detected. The molecular weight distribution is similar to that of polymers having a narrow distribution (for example 6,6-nylon).

Novak and Whalley[21,47,58,65,90] have published a series of papers on the infra-red spectra of polymeric aldehydes. They studied the spectra of polymers of formaldehyde, acetaldehyde, propionaldehyde, n- and iso-butyraldehyde

and -valeraldehyde, n-heptanal, and mono-, di-, and tri--chloroacetaldehyde. The spectra of polymers prepared in different ways were found to have an identical structure (Furukawa[36] reached a similar conclusion on comparing the spectra of polyacetaldehyde obtained by different methods). The band around 3440 cm^{-1} forms an exception, having different intensities in different specimens, and being completely absent in some of them. This frequency was assigned to stretching vibrations of the terminal OH group. The variation in its intensity is obviously associated with the different molecular weights of the polymer specimens. On the basis of their investigations, Novak and Whalley ascribe to polyaldehydes a substituted polyoxymethylene structure:



where R is a radical containing 0–7 carbon atoms or a halogenated radical.

The exact molecular structure of polymeric acrolein has not been established; there is evidence that polymerisation involves rupture of both double bonds, resulting in a cross--linked structure.

IV. DEGRADATION AND STABILISATION OF POLYALDEHYDES

A characteristic property of polyaldehydes is their degradation by heat, acids, bases, etc. The causes of and the laws governing the degradation and stabilisation of polyaldehydes are considered individually, since this problem is of great importance for the practical application of these polymers.

Whereas with carbon-chain and many heterochain polymers an increase in thermal stability merely extends their possible fields of application, polymers of carbonyl compounds cannot be of any practical use without being stabilised. Polyformaldehyde, first obtained as long as a century ago, has begun to be employed as a constructional material only during recent years, when it has proved possible to increase its thermal stability considerably.

With the high polymers of other carbonyl compounds which have been obtained the problem of stabilisation still remains unsolved, so that they cannot yet be utilised. Therefore a solution to the problem of the stabilisation of such polymers is important not only from the theoretical but also from the practical point of view.

We shall examine the published data available on the degradation and stabilisation of polymers of carbonyl compounds.

1. Polyformaldehyde

This polymer is formed from the monomer at temperatures not exceeding 110°. The maximum temperature of polymerisation is considerably lower with solutions of formaldehyde in organic solvents. In methylene chloride it is 30° for a 0.06 M concentration and 0° at 0.04 M.[92]

The rate of degradation of polyformaldehyde depends on many factors. According to results obtained by Schweitzer *et al.*[3], polymers of improved thermal stability can be obtained by using special methods of polymerisation. This is explained by a smaller number of weak links in the polymer, but no convincing arguments in support of this explanation are given.

Such special methods for the polymerisation of formaldehyde are described in a series of patents[2]. The resulting polyformaldehyde possesses a high molecular weight, which, however, does not explain its increased thermal stability, since the product of the spontaneous polymerisation of liquid formaldehyde has low thermal stability in spite of a high molecular weight[3].

The patent literature lists several compounds which have been proposed as stabilisers for polyformaldehyde. They can be divided into four groups: (1) substituted hydrazines and hydrazides; (2) secondary and tertiary aromatic amines; (3) substituted phenols and naphthols; and (4) urea, thiourea, and their derivatives.

These substances were used before to increase the resistance to "aging" of other polymers, since they are antioxidants, *i.e.* they retard chain oxidations which take place by a radical mechanism.

Polyamides[94] and sulphonamides[95] have recently been suggested for the stabilisation of polyformaldehyde. Polymers possessing basic properties also act as stabilisers[96]. Considerably greater stabilisation is achieved by replacing the terminal OH groups of the polyoxymethylene glycol by $OCOCH_3$ or OCH_3 groups. Staudinger himself observed a considerable increase in the heat resistance of the diacetates and the dimethyl ethers compared with the original glycols[97], but the products which he investigated were not of very high molecular weight.

The acetylation of polyformaldehyde has been described in detail in the patent literature[23]. The acetylated polymer is considerably more stable (by a factor of about 10) than the original. It can be worked by the usual methods employed with thermoplastic materials, in particular by pressure casting.

Polyformaldehyde is degraded also by exposure to ultra--violet radiation. The usual additives, which strongly absorb short-wave radiation, such as hydroxybenzophenone derivatives[98], have been proposed to retard the photodegradation of polyformaldehyde.

Staudinger suggested a mechanism for the degradation of polyformaldehyde in acid and alkaline media. Rupture of the main chain takes place in the presence of acids, whereas alkalis react with the terminal OH groups, after which monomeric formaldehyde molecules are split off one by one from the polymer chain[97]. Later, several suggestions were made in the patent literature concerning the mechanism of the thermal degradation of polyformaldehyde. However, these are in the nature of hypotheses, since they are not supported by experimental data. The subject was greatly clarified by a paper by Kern and Cherdron[99], showing that five reactions leading to the separation of monomer occur during thermal degradation: (1) depolymerisation, starting at the end-groups of the macromolecule; (2) oxidative cleavage; (3) cleavage by secondary oxidation products; (4) thermal decomposition; and (5) hydrolysis and acid catalysed hydrolysis.

Depolymerisation, beginning at the terminal groups, occurs according to the scheme:

$$—O—CH_2—O—CH_2—OH \rightarrow —O—CH_2—OH + CH_2O \rightarrow \text{etc.}$$

The reaction is of first order with respect to the polymer. The low thermal stability of polyoxymethylene glycols is due mainly to the occurrence of this reaction. Above 160° it is accompanied by cleavage of the polymer chain by oxygen, which also forms compounds which accelerate the decomposition (probably HCOOH).

The inherent strength of the macromolecular chain is characterised by the temperature of purely thermal decomposition, which with the dimethyl ethers of polyoxymethylene glycols is above 270°, the decomposition being a first-order reaction. Addition of acidic substances considerably accelerates the decomposition of polyformaldehyde.

Kern and Cherdron feel that a combination of methods should be used to increase the thermal stability of the oxymethylene polymer: (*a*) protection of the end-groups; (*b*) addition of antioxidants which are not acidic in nature; and (*c*) addition of substances to combine chemically with the formaldehyde evolved during degradation. They consider protection of the end-groups to be the most important. This is reasonable, since it is this type of degradation which determines the thermal stability of polyformaldehyde.

2. Polyacetaldehyde

Right at the start of work on the synthesis of polyacetaldehyde it became evident that this polymer decomposes at room temperature and above, forming the monomer[18]. The first semiquantitative estimate of its rate of degradation was given by Letort[23]: after 40 days at room temperature in air the polymer had lost 9% of its weight.

Later Rigby and Danby[26] reported that the most stable specimens of polyacetaldehyde rubber which they had synthesised were converted to a liquid after two weeks at room temperature. According to their results, depolymerisation does not take place below -9° with the most stable specimens, or below -20° with the least stable. They were unable to determine the temperature coefficient of the rate of decomposition because of the poor reproducibility of the results.

All papers on the synthesis of polyacetaldehyde indicate that the polymer is formed only below -30°. Comparison of these results with those of Rigby and Danby[26] yields a rough estimate of the limiting temperature for the polymerisation of acetaldehyde, *i.e.* between -20° and +30°.

Like Rigby, Bevington and Norrish[27] were unable to obtain reproducible results for the kinetics of the decomposition of polyacetaldehyde. In their view its stability is intermediate between those of polyformaldehyde and of polymers of the higher aldehydes obtained under high pressures. Investigating depolymerisation in air from loss in weight, they were the first to note the autocatalytic character of the reaction. They were also the first to point out the catalytic action of acetic acid, which has been demonstrated by direct experiment. In view of this, Bevington and Norrish explain the difference in stability between different specimens of polyacetaldehyde by the presence of different amounts of acetic acid, formed when acetaldehyde is oxidised by the air.

TABLE 2.

Weight loss of polymer after 3 min		Dependence of weight loss and viscosity on time of pyrolysis at 110°		
temp., °C	weight loss, %	time, h	weight loss, %	η
40	0.23	0	0	3.9
60	0.18	0.5	3.75	1.4
80	0.64	1.0	8.43	1.1
100	1.60	1.75	16.9	0.9
110	3.76	2.0	25.5	0.7
120	8.38			

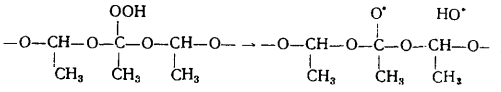
The degradation of polyacetaldehyde was studied subsequently by Bovey and Wands[45], who used specimens of polyacetaldehyde rubber, stabilised with 2-naphthylamine, which they had obtained from Letort. Their results are summarised below (see Table 2).

The data in Table 2 indicate that degradation of polyacetaldehyde is markedly accelerated with rise in temperature above 100°, and that during degradation the molecular weight drops sharply even when the loss in weight is small. Furthermore, infra-red spectroscopy has shown only acetaldehyde to be present among the degradation products. Application of Grassie and Melville's method[100] to the results indicated that, at the start of decomposition, every cleavage of the polymer chain was accompanied by 159 eliminations of a monomer unit. This quantity increases as the process continues, reaching a steady value of about 400.

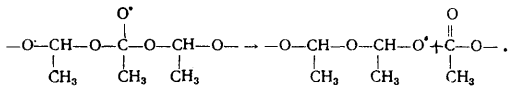
Smets and Delzenn reported during 1956–1957 [101,102] that the polyacetaldehyde chain cleaves in two ways, by heterolytic and by homolytic cleavage. In both cases this is followed by rapid depolymerisation to acetaldehyde.

The instability of polyacetaldehyde in neutral solutions is explained by homolytic decomposition of hydroperoxide side-groups (one group per 1000–4000 acetaldehyde units) with subsequent chain cleavage and depolymerisation[101].

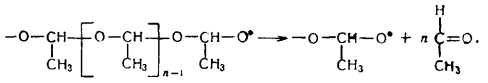
1. Decomposition of the hydroperoxide group:



2. Homolytic cleavage of the chain:



3. Depolymerisation:

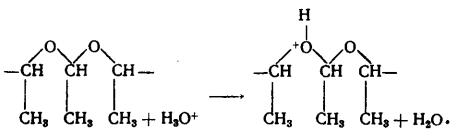


The usual activation energy for processes 1 and 2 is 29 kcal mole^{-1}, and the total activation energy for depolymerisation 18.8 kcal mole^{-1}. The process is inhibited by quinol and by dinitrobenzene.

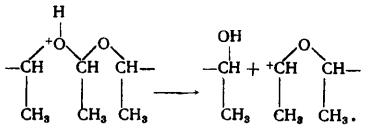
In the presence of acetic acid the rate of decomposition of polyacetaldehyde is increased by a factor of about 700 compared with the spontaneous process. By analogy with

acetals of low molecular weight, Smets and Delzenn suggested the following mechanism for the acid hydrolysis of polyacetaldehyde[102].

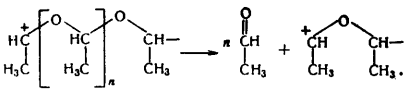
1. Addition of a proton to the acetal:



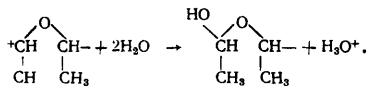
2. Heterolytic fission:



3. Depolymerisation of the carbonium ion:



4. Nucleophilic substitution of the carbonium ion:



An important point is that the H_3O^+ ion can break the polymer chain at any position. The activation energy for the acid hydrolysis of polyacetaldehyde is 20.4 kcal mole^{-1}, which agrees well with the value of 20.5 kcal mole^{-1} for diethylacetal. The small activation energy for depolymerisation, only 2.4 kcal mole^{-1}, is characteristic of ionic processes. The ionic character of depolymerisation follows also from its insensitivity to the presence of inhibitors of radical processes. Kinetic measurements made by these workers support their hypothetical mechanism for the decomposition. Thus the rate of cleavage and the rate of depolymerisation vary linearly with the concentration of acid in the solution, while the rate of formation of acetaldehyde in each experiment remains constant even when the extent of reaction is considerable.

No papers have been published recently on the degradation and stabilisation of polyacetaldehyde. There is only an isolated report that a polyacetaldehyde has been prepared in the University of Kyoto which is more heat resistant† than butadiene–styrene rubber[39]. The same report states that a similar polymer has been obtained by the du Pont Corporation.

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Research on the polymers of carbonyl compounds, which was only started comparatively recently (the main literature has appeared during 1955–1960), is being intensively pursued at the present time. Previously known polymers are being studied more thoroughly, and the preparation of polymers of several new carbonyl compounds is being investigated. Thus during 1959–1960 three new methods have been found for the polymerisation of acetaldehyde, the possibility of obtaining stereoregular polymers of aldehydes has been discovered, and polymers of acetone, dimethylketen, etc. have been obtained.

All this suggests that polymers of carbonyl compounds will, in the not very distant future, be of practical as well as academic interest. This will necessitate the solution of the most important problem of the chemistry of the aldehyde polymers — to find sufficiently reliable methods for their stabilisation.

† The report does not make it clear whether this refers to heat resistance or to thermal stability.

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ROTATORY DISPERSION AND ITS APPLICATION IN ORGANIC CHEMISTRY

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