Polymerization of higher aldehydes

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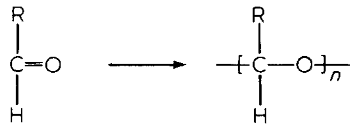
This review concerns the polymerization of substituted aldehydes. Two groups of aldehydes have been subjected to systematic study: (1) higher aliphatic aldehydes containing linear chains with up to 12 carbon atoms; (2) branched hydrocarbon chains, including acetaldehyde; and haloaldehydes, derivatives of acetaldehyde substituted with fluorine, chlorine or bromine in the methyl group. The methods of preparation, purification and characterization of the monomers, the mechanisms of polymerization, their thermodynamics and stereochemistry, and the properties of the resulting polymers are all discussed. In addition it is pointed out that several properties exhibited by the polymers may lend themselves to practical applications in the future.

INTRODUCTION

Polymerization of aldehydes proceeds through opening of the carbon–oxygen double bond (Equation 1)



$$n\,\mathrm{R(H)C{=}O} \longrightarrow \mathrm{-\!\!\left[C(R)(H){-}O\right]\!\!-_{n}} \qquad (1)$$

Thus, there is an analogy between polymerization of carbonyl compounds and polymerization of vinyl monomers (if oxygen is replaced by a methylene group). However, the energy gain resulting from opening of the carbon–oxygen double bond (~ 5 kcal mol^{-1}), is much lower than for opening of the carbon–carbon double bond (~ 20 kcal mol^{-1})[1,2], therefore the equilibrium character of aldehyde polymerization is much pronounced. Nearly all monosubstituted and some disubstituted vinyl monomers are polymerizable (thermodynamically), while only some monosubstituted (aldehydes) and none of the disubstituted (ketones) carbonyl compounds except perfluorobutanone[3] can be polymerized. For polymerizable carbonyl compounds the ceiling temperature is close to or below room temperature.

Present knowledge of aldehyde polymerization is based on the studies of polymerization of formaldehyde. Polymerization of formaldehyde and its cyclic trimer, trioxane (commercially employed to produce thermoplastic polyoxymethylene — trade names: Celcon, Delrin, Hostaform), is a separate subject discussed in numerous reviews[4-9].

This article deals exclusively with polymerization of substituted aldehydes. Systematic studies of polymerization have been carried out only for two groups of substituted aldehydes — (1) higher aliphatic aldehydes containing linear chains with up to 12 carbon atoms; or (2) branched hydrocarbon chains including acetaldehyde, and haloaldehydes, derivatives of acetaldehyde substituted with fluorine, chlorine or bromine in the methyl group. We will discuss the methods for preparation, purification and characterization of monomers, mechanisms of polymerization (including thermodynamics and stereochemistry) and properties of the resulting polymers.

Until now, none of the higher aldehyde polymers have found commercial applications although several properties exhibited by these polymers (especially polymers of haloaldehydes) make them potential candidates for practical application.

MONOMER PREPARATION AND CHARACTERIZATION

Aliphatic aldehydes

Aldehydes with normal alkyl chains and branched aliphatic aldehydes are prepared commercially and used directly or as intermediates for the preparation of the corresponding alcohols or carboxylic acids. The most extensively studied aldehyde is acetaldehyde. A number of these aldehydes have been used as monomers for the preparation of alkyl substituted polyoxymethylenes and copolymers involving these aldehydes.

The preparation, chemistry, and physical properties of these aldehydes are described briefly with special emphasis on the commercial availability and the commercial processes for their preparation.

Acetaldehyde (*ethanal*) is the most important aldehyde of this group. It occurs naturally in some species of fruits which have a tart taste prior to ripening. For many years acetaldehyde was prepared by hydration of acetylene with mercury compounds as the catalyst (Equation 2).

$$\mathrm{CH{\equiv}CH + H_2O \xrightarrow{Cat.} CH_3CHO} \qquad (2)$$

This process was phased out in favour of the more recently developed Wacker process which is the direct oxidation of

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ethylene. This process was developed by Smidt and coworkers[10,11] at the Consortium für Elektrochemie (Equation 3)
and

$$CH_2{=}CH_2 \xrightarrow[\text{[O]}]{PdCl_2/CuCl_2} CH_3CHO \qquad (3)$$

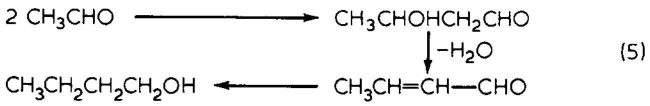
involves the use of a palladium (II) chloride/copper (II) chloride redox catalyst. The palladium-containing component oxidizes the olefin. The copper compound is used for the reoxidation of palladium. High yields (> 85%) and high conversions per pass have been reported and all new acetaldehyde plants are based on this process[12,13].

The aldehyde functional group introduces two reactive sites into the molecule in which it is present. The first is the carbonyl function, but the hydrogen of the α carbon atom to the carbonyl group is also highly reactive. Reactions of acetaldehyde and its homologues are numerous therefore only the significant reactions are discussed with particular emphasis on the technical importance of each reaction or on its potential as a side reaction in the polymerization of the respective aldehydes.

Autoxidation is one of the most important reactions of aliphatic aldehydes, particularly of acetaldehyde, which occurs in the presence of even small amounts of oxygen. This reaction occurs with or without a reagent or catalyst. Catalytic oxidation of acetaldehyde is used for the industrial manufacture of acetic anhydride and acetic acid. This process was also developed by the Wacker Company and consists of a free-radically induced air oxidation of acetaldehyde which, in a radical chain reaction, produces the peroxy acid, its anhydride and ultimately, acetic acid. The two main reactions of acetaldehyde and many of its aliphatic homologues are (i) oxidation to the carboxylic acid and (ii) reduction to the corresponding alcohol (Equation 4). Oxidation of the aldehydes has been studied under a variety of conditions and kinetic expressions have been obtained[14,15].

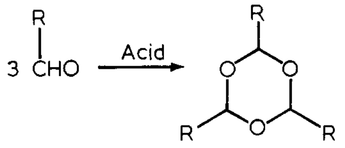
$$CH_3CH_2OH \xleftarrow{\text{Reduction}} CH_3CHO \xrightarrow{\text{Oxidation}} CH_3COOH \qquad (4)$$

The reduction of aldehydes is achieved commercially by hydrogenation. The hydrogenation of acetaldehyde is not a commercially important reaction because the reduction product, ethanol, is prepared commercially by a different method. However, the reduction of higher aldehydes is an important commercial route for some alcohols. In most aliphatic aldehydes there is at least one hydrogen attached to the α carbon atom of the carbonyl group, in the case of non-branched normal aliphatic aldehydes two hydrogen atoms are attached to this α carbon atom. The proton in the α position of the aldehyde functional group is more labile than the protons of a simple hydrocarbon and the α protons are important in a number of reactions of acetaldehyde and its higher homologues. Another important reaction which is used commercially is the aldol condensation (Equation 5). The aldol condensation of acetaldehyde with itself produces aldol which can lose the elements of water to form crotonaldehyde, which in turn can be hydrogenated to form butanol. Acetaldehyde is also used in an aldol condensation reaction with formaldehyde for the preparation of pentaerythritol, which is used in the manufacture of alkyl resins and polyurethanes.



$$\begin{array}{ccc} 2\,CH_3CHO & \longrightarrow & CH_3CHOHCH_2CHO \\ & & \big\downarrow -H_2O \\ CH_3CH_2CH_2CH_2OH & \longleftarrow & CH_3CH{=}CH{-}CHO \end{array} \qquad (5)$$

Other reactions of acetaldehyde and its aliphatic homologues include the cyclotrimerization and cyclotetramerization which are characteristic for many aliphatic aldehydes. For practical purposes, the tetramerization occurs only in the case of acetaldehyde and to limited extent. This cyclization is misleadingly referred to as polymerization and occurs with acid catalysts only. All normal aliphatic aldehydes up to more than 10 carbon atoms and several branched aliphatic aldehydes have been reported to form the cyclic trimer, 2,4,6-trialkyl-1,3,5-trioxane on treatment with acids (Equation 6). In cationic polymerization of acetaldehyde, paraldehyde, the cyclic trimer of acetaldehyde is a frequent by-product of the linear polymer[16].

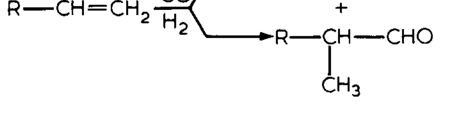


(6)

Metaldehyde, the cyclic tetramer of acetaldehyde, is also observed when the trimerization is carried out at low temperatures. It is used as a fuel and apparently is also effective in the control of garden snails. The most representative values of the physical properties of acetaldehyde and higher aliphatic aldehydes are given in *Table* 1.

n-Propionaldehyde (*propanal*) is less common than acetaldehyde although it has been reported as a constituent of the flavour of certain clams after steaming[17]. A recent commercial route to propionaldehyde is the hydroformylation of ethylene by the 'oxo process' or Roellen reaction[18]. The development of the oxo process stemmed from studies on the Fischer–Tropsch synthesis[19]. The hydroformylation of ethylene to propionaldehyde is not as important commercially as the hydroformylation of higher olefins.

The hydroformylation reaction is particularly important in the case of propylene to form butyraldehydes but is also important for the hydroformylation of butenes. The oxo process is carried out by reacting the olefin with hydrogen and carbon monoxide in the presence of cobalt carbonyl compounds or cobalt compounds which are capable of forming cobalt carbonyls *in situ* (Equation 7). The hydroformylations of olefins of more than 10 carbon atoms have been studied and some of these are used commercially[20].



$$R{-}CH{=}CH_2 \xrightarrow[H_2]{CO} \begin{cases} R{-}CH_2{-}CH_2CHO \\ + \\ R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CHO \end{cases} \qquad (7)$$

Like acetaldehyde, propionaldehyde can be readily oxidized to propionic acid or propionic anhydride which are used for the preparation of cellulose derivatives. Propionaldehyde can also be reduced to 1-propanol by a number of methods. Like other aliphatic aldehydes, propionaldehyde undergoes the aldol condensation. In

Table 1 Physical properties of some aliphatic aldehydes

Aldehyde	M.p. (°C) and (x)[43]	B.p. (°C at 760 mm)[43]	N_D^{20} [42]	d_4^{20} [44]	M.p. of 2,4-dinitrophenylhydrazone (°C)
Acetaldehyde	−123.5	20.2	1.3316	–	167.5[53]
Propionaldehyde	−81	48–9	1.364	0.8071	155[53]
n-Butyraldehyde	−97.1	74.7	1.3843	0.8048	119[53]
2-Methylpropionaldehyde	−65.9	64	1.3730	0.7938	187[51]
n-Valeraldehyde	−91.5	103.4	1.3947	0.8095	106[53]
2-Methylbutyraldehyde	20 (mixt.)	92–3 (mixt.)			d 135–7 l 135–7[54] dl 129–30
n-Hexaldehyde		131	1.4068	0.8139	105
n-Heptaldehyde	−45	155	1.4125	0.8342	106
n-Octaldehyde		171	1.4217	0.821	105.5
n-Nonaldehyde	−17	62/5			
n-Decaldehyde	−3	44/0.5			
n-Undecaldehyde	+2	55/0.5			
n-Dodecaldehyde	+13	67/0.5			

[x] J. Starr, Ph.D. Thesis, Univ. of Massachusetts, 1977

this way, propionaldehyde and formaldehyde react to form methacrolein[21].

n-Butyraldehyde (*butanal*) occurs in trace amounts in the scent of some Eucalyptus trees and also in tobacco smoke. Commercially, n-butyraldehyde is produced by hydroformylation of propylene. Considering the volume of olefins consumed the hydroformylation of propylene is the most important oxo reaction industrially. Cobalt carbonyls are the usual catalysts although rhodium compounds are also used in this hydroformylation reaction[22]. Both normal and isobutyraldehyde (2-methylpropanal) are obtained. Of these two isomers the n-butyraldehyde is of great commercial importance. The technical efficacy of the hydroformylation of propylene is enhanced by increasing the normal to branched product ratio via the manipulation of the reaction condition or the type and amount of catalysts[23,24] or by regeneration of the oxo starting materials from the unwanted isobutyraldehyde by cracking the isobutyraldehyde back to propylene, carbon monoxide and hydrogen[25]. Cyclic trimers of the isomeric butyraldehydes are formed as by-products in the oxo process especially when acidic conditions develop during the reaction. An excellent review of the oxo process is given by Falbe[25].

The homoaldol condensation of n-butyraldehyde with subsequent dehydration and hydrogenation has a large commercial importance in the production of 2-ethyl-1-hexanol which is used for the production of plasticizers, for example, dioctyl phthalate. n-Butyraldehyde and isobutyraldehyde may be conveniently oxidized to the corresponding acids or reduced to the alcohols. All these reactions have technical importance.

n-Valeraldehyde (pentanal) and 2-methylbutanal are both products of the hydroformylation of 1-butene, and valeraldehyde is the intermediate for the preparation of the corresponding alcohol and acid. The valeraldehydes as well as the butyraldehydes are known for their unpleasant odour.

n-Caproaldehyde (*n-hexaldehyde, hexanal*) is a volatile constituent of the scent glands of a species of coreod[26]. It can be prepared by hydroformylation of n-pentene. Mixed 1- and 2-pentenes reportedly give primarily n-hexanal in the oxo process[27]. n-Hexanol, which can be prepared by hydrogenation of the aldehyde, finds some use for the production of plasticizers. n-Caproaldehyde is capable of undergoing the usual reactions of aliphatic aldehydes.

Aliphatic aldehydes of more than 6 carbon atoms have a more pleasant odour than the lower molecular weight aliphatic aldehydes especially in low concentrations, and are used as additives in the perfume industry. They are much less soluble in water than their lower molecular weight homologues and tend to be of an oily consistency in the liquid state. For comparison, acetaldehyde and propionaldehyde are miscible with water in all proportions and the butyraldehydes and valeraldehydes have substantial solubility in water but they do not have the oily consistency as do the aldehydes with more than 6 carbon atoms in the chain.

Enanthaldehyde (*n-heptaldehyde, heptanal*) occurs in small amounts in some essential oils. Although this aldehyde can and has been prepared by the hydroformylation of 1-hexene[28,29], it is more commonly obtained from the destructive distillation of castor oil[30,31]. Oxidation, reduction, and aldol condensations have been reported with heptaldehyde.

Caprylaldehyde (*n-octaldehyde, octanal*) and the C-9 to C-14 normal aliphatic aldehydes are important in perfume formulation. The C-8 to C-14 aliphatic aldehydes occur in various combinations in the essential or ethereal oils of a variety of botanical species.

Hydroformylation[32,33] and alcohol oxidation[34,35] are technical routes to n-octoaldehyde. n-Octanol, the product of the hydrogenation of octanal, is used technically for the preparation of the corresponding acrylate which is used for copolymerization with methyl methacrylate.

Health and safety factors of aliphatic aldehydes

The pharmacology and toxicology relating to ingestion and inhalation of the aldehydes discussed in the previous sections have been investigated with a variety of mammals. The lower molecular weight aldehydes, particularly acetaldehyde, can have intoxicating and/or narcotic effects in sublethal doses[36,37]. All the aliphatic aldehydes have an irritating effect on the respiratory system of rats and rabbits[37,38]. The aliphatic aldehydes also show definite pressor activity[37,39]. In general, pathological effects decrease with increasing carbon atom number of the aldehyde.

Table 2 Physical properties of some functionally substituted aldehydes

Aldehyde	B.p. (°C mm^{-1})	n_D^{20}	D_4^{20}	M.p. of 2,4-Dinitrophenylhydrazone (°C)
3-Ethoxypropionaldehyde	134/760[56]	1.4038[57]		
3-Methoxypropionaldehyde	121/760[57]	1.4012[57]		
3-Methoxybutyraldehyde	138–40/760[51]	1.4073[51]	0.942[51]	88[51]
3-Methylthiopropionaldehyde	166/750[56]	1.4824[56]	1.036[51]	118.5–119.5[56]
3-Ethylthiopropionaldehyde	185/760[56]	1.4788[56]		100[56]
3-Methylthiobutyraldehyde	78–9/23[59]			
3-Ethylthiobutyraldehyde	92–93/24[58]	1.4720[58]		
3-Cyanopropionaldehyde	85–87/6[51]			
Phenylacetaldehyde	91–2/20[56]	1.5255[51]	1.0319[56]	125–6[56]

Most of the aldehydes discussed in the previous sections have open cup flash points near or below ambient temperatures.

Functionally substituted higher aldehydes

These aldehydes have been prepared in the laboratory and on a larger scale (to a limited extent) but have not been fully exploited commercially. Those aldehydes which have actually been used for polymerization will be discussed.

3-Ethoxypropionaldehyde (4-oxahexanal), and 3-methoxypropionaldehyde (4-oxapentanal) can be prepared by the reaction of acrolein and ethanol or methanol respectively using an alkyl amine[40] as the catalyst or an acid treated anion exchange column[41,42]. 3-Methoxybutyraldehyde (3-methyl-4-oxapentanal) can be prepared from crotonaldehyde and methanol in a manner similar to the preparation of the alkoxypropionaldehydes. Alkylthio substituted aliphatic aldehydes analogous to the previously mentioned alkoxy substituted aliphatic aldehydes have been prepared in a similar manner.

3-Cyanopropanal has been prepared by the hydroformylation of acrylonitrile[43,44]. The physical properties of these aldehydes are listed in *Table* 2.

Dialdehydes

These aldehydes are capable of polymerizing to linear polymers with complicated structures, including cyclic structures, in the repeat unit. They usually are not stable for any length of time in the monomeric state and are handled either as aqueous solutions of oligomers or as unstable intermediates which can be transformed readily into the aldehyde when needed.

Glyoxal(biformyl, oxaldehyde) is prepared on a commercial scale by the dehydrogenation of ethylene glycol[45,46]. Pure anhydrous glyoxal is unstable as such and polymerizes readily to a complex structure. Glyoxal reacts with water in a highly exothermic reaction, similar to formaldehyde. Aqueous solutions of glyoxal consists of a complex mixture of monomeric linear and cyclic oligomeric water soluble reaction products which are hydroxy terminated. Glyoxal, as an aqueous solution of the oligomers, finds use in the textile and paper industry for dimensional stabilization and for improving wet strength. Glyoxal has recently found use also in some bacteriocidal formulations.

Succinaldehyde (butanedial) can be prepared by a variety of routes; for example, by reaction of chlorine and tetrahydrofuran with subsequent acid hydrolysis[47]. Pure anhydrous succinaldehyde polymerizes readily, however, it can be stored as the cyclic acetal, 2,5-dimethoxytetrohydrofuran.

Table 3 Physical properties of some dialdehydes

Aldehyde	B.p. (°C mm^{-1})	D_4^{20}	M.p. of 2,4-dinitrophenylhydrazone (°C)
Glyoxal	50/760[56]	1.3826[56]	328[51]
Succinaldehyde	169–70/760[60]	1.4262(18°C)[60]	280[51]
Glutaraldehyde	187–9/760[60]		182–3[61]
Malealdehyde	54–61/10[56]	1.4575[56]	270–80[62]
Phthalaldehyde	83–4/0.8[56]		

Aqueous solutions of succinaldehyde consist mainly of the cyclic monohydrate, 2,5-dihydroxytetrahydrofuran, according to proton magnetic resonance studies[48]. Succinaldehyde in its aqueous solution reacts readily with protein and polyhydroxyl compounds.

Glutaraldehyde (pentanedial) is an important dialdehyde. Glutaraldehyde is a useful bacteriocide and its ability to crosslink protein makes it a useful fixative in biological sciences. A review of its use in histochemistry has been published recently[49]. Glutaraldehyde is also important in textile chemistry for the improvement of dimensional stability of cotton fibres. Glutaraldehyde is used mainly in aqueous solutions and its behaviour parallels that of succinaldehyde[48,50]. The corresponding cyclic methyl acetal is hydrolyzed rapidly to the dialdehyde.

Malealdehyde (butenedial) is a highly reactive α, β-unsaturated dialdehyde. The chief route to malealdehyde is via 2,5-dialkoxydihydrofurans. Malealdehyde in its stable form has been used for crosslinking of polyamide fibres.

Phthalaldehyde (1,2-benzenedicarbonal) is obtained by ozonolysis of naphthalene[51]. Phthalaldehyde is an exception to the general rule of reluctance of aromatic aldehydes to polymerize through the carbonyl group perhaps because of the spatial proximity and the mutual electronic effects of the two aldehyde functional groups.

The health and safety factors of the aldehydes of the previous two sections vary and the safety literature should be consulted before any work with these aldehydes is undertaken[52].

Haloaldehydes

Haloaldehydes are compounds where one or more hydrogen atoms of an aliphatic aldehyde are replaced by halogen atoms. For practical purposes, especially for the

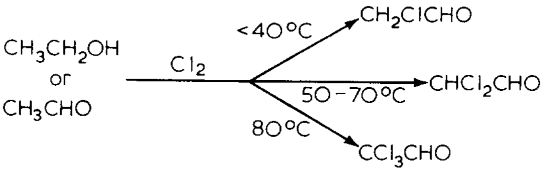
Table 4 Physical properties of some haloaldehyde polymers

Aldehyde –CHO	B.p. (°C at 760 mm)	C=O stretching frequency (cm^{-1} xx)[55]	Density ($g\ cm^{-1}$)	2,4 DNP m.p (°C)	Ceiling temperature (°C)
CH_2F	64	–	–	147	–
CHF_2	27	–	–	–	–
CF_3	–19	1780	1.47	150	85
CH_2Cl	85	1738	–	–	–
$CHCl_2$	89	1748	–	–	–
CCl_3*	98	1760	1.50	–	11
CBr_3	174	1742	2.73	–	–75
CF_2Cl	18	–	1.45	135	63
$CFCl_2$	56	1770	1.43	–	41
CF_2Br	43	1755	1.80	–	48
$CFBr_2$	116	1751	2.25	–	–7
CCl_2Br	127	1754	1.87	–	–15
$CClBr_2$	148	1750	2.27	–	–40

* M.p.–57°C
xx–bulk

purpose of this review article, compounds of fluorine, chlorine or bromine are the only haloaldehydes which are discussed here with special emphasis on those aldehydes which have been polymerized.

Chlorinated aldehydes: Chloraldehydes are generally prepared by chlorination of the corresponding alcohol or aldehyde. Chlorination of ethanol gives primarily trichloroacetaldehyde (chloral). Chlorine acts as the chlorinating and oxidizing agent in this process and a good yield of chloral is obtained[63]. Chloral, in addition to mono- and dichloroacetaldehyde, can also be obtained by chlorination of acetaldehyde; the reaction is catalysed by metal halides such as $AlCl_3$, $FeCl_3$, $SbCl_3$ [64,65] (Equation 8).

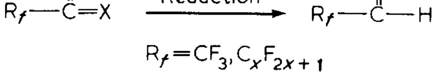


(8)

Low temperatures (<40°C) and low catalyst concentrations are needed for the formation of monochloroacetaldehyde. In the temperature range 30–70°C the main product is dichloroacetaldehyde while chloral is formed in this reaction when the reaction temperature exceeds 80°C. In all cases, aldehyde yields of up to 80–90% have been reported[66]. This method has also been used for the preparation of chlorinated aldehydes with more than two carbon atoms in the chain, for example, the chlorination of *n*-butyraldehyde[67]. Dichloroacetaldehyde can also be prepared in 70–80% yield by the reaction of acetylene, chlorine and water at 80°C [68]. Reports indicate that the best potential method for the preparation of chloral is the oxidative chlorination of ethylene in the presence of $FeCl_3$. The physical properties of the halogenated acetaldehydes including the three chloroacetaldehydes are listed in *Table* 4.

Brominated aldehydes: Bromal has been prepared by bromination of ethanol or acetaldehyde.

Fluoroaldehydes: The best known fluoroaldehyde is the perfluorinated acetaldehyde, fluoral, which was prepared first by Henne[69]. It was synthesized by reduction of trifluoroacetamide with lithium aluminium hydride. Several additional methods have been used for the fluoral synthesis and these seem to be typical for preparative methods for perfluoroaldehydes in general. In addition to the reduction of the amide, the reduction of trifluoroacetic acid with lithium aluminium hydride[70–73], especially by inverse addition in ether, gave good yields of fluoral. It was also obtained by hydrogenation of trifluoroacetyl chloride over Pd catalysts at 250°C [74,75] (Equation 9).



$$R_f-\overset{\overset{O}{\|}}{C}=X \xrightarrow{\text{Reduction}} R_f-\overset{\overset{O}{\|}}{C}-H \qquad (9)$$

$$R_f=CF_3, C_xF_{2x+1}$$

Fluoral has also been prepared by fluorination of liquid vinyl acetate with fluorine gas at –50°C [76]. The most important fluorination method having the greatest commercial potential is the vapour phase treatment of chloral with HF over activated CoF_2–AlO_3, Cr_2O_3 or chromium oxyfluoride at 200–400°C [77–79]. The physical properties of fluoral and higher fluoroaldehydes are described in *Table* 4.

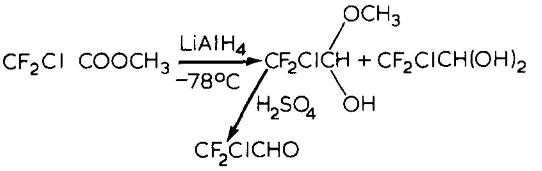
Higher fluoraldehydes: Complete substitution with fluorine in higher aldehydes is similar to that for fluoral. An additional method is the oxidation of fluoroalcohols with chlorine gas[80] or the reaction of Grignard reagent with perfluoronitriles[81].

α-Fluoroaldehydes: This class of aldehydes includes those with one or two fluorine atoms, α- to the CHO group. Specific placement of the fluorine atoms in this position is more difficult[82]. Monofluoro and difluoroacetaldehyde are included in this category for convenience and are described in *Table* 4. Two examples of cyclic fluoraldehydes are known. Both are produced by the addition of an unsaturated aldehyde (acrolein or methacrolein) to tetrafluoroethylene[83].

Toxicity of fluorine containing aldehydes: The highly toxic nature of many fluorine containing organic compounds, particularly fluoroacetic acid, is well known[84]. Such compounds were considered as chemical warfare agents and fluoroacetic acid and its derivatives, fluoroacetate, fluoroethanol, fluoroacetamide and others including fluoroacetaldehyde, have been reported as having equal toxicity[85]. Any compound which can be oxidized or hydrolysed *in vivo* to fluoroacetic acid will exhibit toxic properties and toxicities related directly to the presence of the FCH_2CO-group. The mechanism of the toxic action is well established; it involves the Krebs tricarboxylic acid cycle, where citric acid is produced by enzymic action. The fluoro acid forms fluorocitrate which competes in this reaction, thus blocking the enzyme in the cycle and causing an accumulation of citric acid. Two FCH_2CO-group precursors on a molecule enhance toxicity as with 2-fluoroethyl fluoroacetate.

Fluoroacetaldehyde must therefore be considered toxic. L.D.$_{50}$ has been measured at 6 mg /kg[84,86]. The difluoro and trifluoroacetaldehydes were reported as nontoxic[84,85] but recent work has shown that fluoral hydrate causes hepatitis and accumulation of fat in the liver[87]. The mechanism is similar to the blocking of thiol or amino groups of peptides and proteins[88].

The symptoms of fluoroacetate poisoning are loss of coordination, convulsions and respiratory depression with lethal dosage leading to death by cardiac failure[85,89].



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Mixed perhaloacetaldehydes

Fluorochloracetaldehydes: Difluorochloroacetaldehyde was prepared by dehydration of the mixed hemiacetal-hydrate of difluorochloroacetaldehyde with sulphuric acid and again with P_2O_5 (Equation 10)[90,91]. The hydrate was obtained from the reverse $LiAlH_4$ reduction of $CClF_2COOCH_3$ which was commercially available. Fluorodichloroacetaldehyde was also prepared by $LiAlH_4$ reduction at −78°C of methyl fluorodichloroacetate which in turn was made from methyl trichloroacetate and SbF_3 [90,92]. The physical characteristics of the aldehydes are shown in *Table* 4.

Fluorobromoacetaldehydes: Difluorobromoacetaldehyde and fluorodibromoacetaldehyde were prepared by two different methods[93,94]. Firstly, 1,1-difluoro-2,2-dibromethylene was oxidized with oxygen at 0°C and gave a mixture of difluorobromoacetyl bromide and fluorodibromoacetyl fluoride. This mixture of the difluorobromoacetyl bromide and fluorodibromoacetyl fluoride was treated with methanol to give the methyl esters. Methyldifluorobromoacetate was readily separated from methylfluorodibromoacetate by distillation.

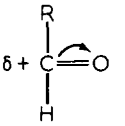
The individual methyl esters were reduced with $LiAlH_4$ at 0°C and gave the corresponding aldehyde hydrates which were dehydrated in the usual way. This route is the preferred method for the preparation of fluorodibromoacetaldehyde.

Chlorobromoacetaldehydes: Dichlorobromoacetaldehyde and chlorodibromoacetaldehyde were also prepared by two synthetic methods[95,96]. The reaction product of chloral and Ph_3P was brominated to give 1,1-dichloro-1,2-dibromoethoxy triphenylphosphonium chloride. This compound could be hydrolysed to the hydrate of dichlorobromoacetaldehyde which was then dehydrated with sulphuric acid to the free aldehyde. A better way for the preparation of chlorodibromoacetaldehyde was the bromination of chloroacetaldehyde diethyl acetal followed by decomposition of the bromination product with sulphuric acid.

Toxicity of perhaloaldehydes: The toxicity of perhaloaldehydes other than specific fluorinated compounds have not been studied extensively. In view of the new developments and the concern of chlorinated compounds in general, the compounds should be treated with care and assumed to be toxic until otherwise proven. When burned in an excess of oxygen, they generate such highly toxic gases as phosgene and carbonyl fluoride, a reaction which chloral, for example, undergoes even at room temperature.

POLYMERIZATION

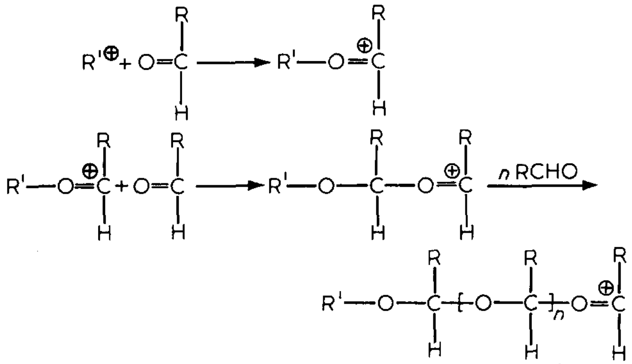
The carbonyl bond, unlike the carbon–carbon double bond, is highly polarized (a dipole moment about 2.5 *D*)[97,98] because of the different electronegativities of the carbon and oxygen atoms (Equation 11).



(11)

Consequently, aldehydes are susceptible to ionic but not radical polymerization (the only possible exception being fluoral for which radical polymerization has been claimed[99]). Many aldehydes can be polymerized by cationic and anionic mechanisms (Equation 12).

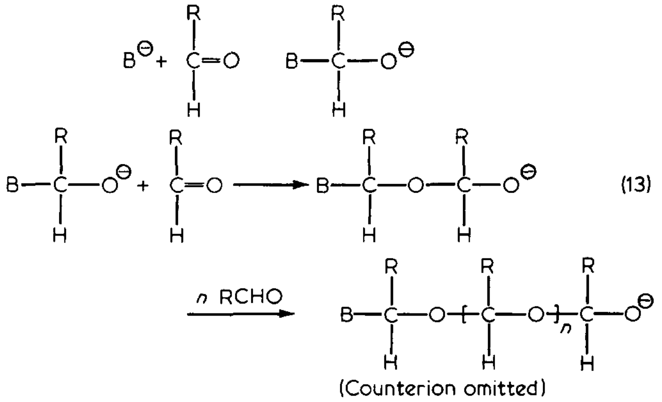
Initiation and propagation in cationic polymerization can be visualized as the nucleophilic attack of the carbonyl oxygen to an electrophile with the formation of carboxonium ion (Equation 12):



(12)

(Counterion omitted)

In anionic aldehyde polymerization, addition of the electrophilic carbonyl carbon to a suitable nucleophile results in the formation of an alkoxide ion as the propagating species (Equation 13).



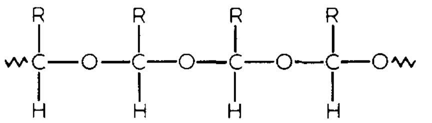
(13)

(Counterion omitted)

Table 5 Enthalpies, entropies and ceiling temperatures of polymerization of aldehydes

Aldehyde	Standard state	Solvent	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} (deg)	T_c (°C)	Ref.
CH_3CHO	lc		0			100
	lc					102
"	lc′		27.6	119	−39	103
n−C_3H_7CHO	lc		20.5			104
"	sc	n-hexane	35.5	122		104
	sc	n-hexane	21.5			104
i−C_3H_7	gc		46			105
	lc		16			105
	ss	THF	15.5	74		106
n−C_4H_9CHO	sc		22.2	108		107
	lc		22.6	97	−42	107
$CH_3OCH_2CH_2CHO$	ss		20.1	94		108
	lc		19.7	82	−35	108
CCl_3CHO	gc′		71 ± 8	190 ± 30		109
	gc′		65.5			105
	gc		51			105
	lc′		38 ± 8	95 ± 30		109
	lc′		34.5			105
	lc		20			105
	ss	THF	14.6	52	11	106
	sc′	toluene	37.8	134	9	110
	sc′	pyridine	33.5	117		109
	sc′	n-heptane	39	142		106
$(CH_3)ClCCHO$	ss	THF	19.7	90	−54	105
$(CH_3)ClCCHO$	ss	THF	17.2	69	−24	105
CF_3CHO	gc		64.5	187		111
"	sc′	toluene	54.9	155	81	110
CBr_3CHO	sc′	toluene	19.1	100	−77	110
CF_2ClCHO	sc′	"	51.0	152	63	110
$CFCl_2CHO$	sc′	"	56.2	179	41	110
CF_2BrCHO	sc′	"	43.4	135	48	110
$CFBr_2CHO$	sc′	"	29.0	114	−19	110
CCl_2BrCHO	sc′	"	31.2	122	−17	110
$CClBr_2CHO$	sc′	"	26.0	116	−40	110

The mechanism preferred for a particular aldehyde monomer depends on the nature of the substituent *R*. Polymers obtained from aldehydes by either cationic or anionic polymerization have the structure of a polyacetal. The main chain consists of alternate carbon and oxygen atoms (Equation 14).



$$\sim\overset{R}{\underset{H}{C}}-O-\overset{R}{\underset{H}{C}}-O-\overset{R}{\underset{H}{C}}-O-\overset{R}{\underset{H}{C}}-O\sim \qquad (14)$$

The enthalpy of polymerization of aldehydes is much lower than the enthalpy of polymerization of vinyl monomers of similar structure, therefore the ceiling temperature of polymerization is relatively low (often below room temperature).

In early studies of polymerization of aldehydes, the increasing polymerizability of these monomers at very low temperatures (crystallization polymerization) or under very high pressure (high pressure polymerization) was noticed. When thermodynamic aspects of the polymerization became fully understood it was possible to interpret both polymerization and degradation of aldehyde polymers correctly in terms of monomer–polymer equilibria.

The thermodynamics of aldehyde polymerization will be characterized briefly before discussing in detail mechanisms of polymerization and polymer properties.

THERMODYNAMICS OF ALDEHYDE POLYMERIZATION

The ceiling temperature (T_c) of polymerization is defined as a temperature at which the free energy of polymerization is equal to zero (for a given standard state) and is determined by the magnitude of enthalpy and entropy of the polymerization (Equation 15).

$$\Delta G_{\text{polym.}} = \Delta H_{\text{polym.}} - T\Delta S_{\text{polym.}} = 0$$

$$T_c = \Delta H_{\text{polym}}/\Delta S_{\text{polym.}} \qquad (15)$$

For bond opening polymerizations, the $\Delta S_{\text{polym.}}$ depends only slightly on the nature of the monomer; $\Delta H_{\text{polym.}}$ is a measure of difference in bond energies between monomer and polymer and depends strongly on such factors as the nature of the bond opened upon polymerization, and possible steric repulsions between substituents in the polymer[1,2].

The gain in energy associated with the formation of two single carbon–carbon bonds from one double carbonyl bond is relatively low ($\sim$5 kcal mol^{-1})[100]. $\Delta H_{\text{polym.}}$ depends on the nature of the substituent, but for aldehyde polymerization the ΔH_{1c} (enthalpy from liquid monomer to crystalline polymer state) value does not exceed -13 kcal mol^{-1}. Because ΔS_{1c} of polymerization is usually close to -30 cal mol^{-1}, T_c's of aldehyde polymerizations are close to, and often below, room temperature (298 K). Known values of ceiling temperatures, $\Delta H_{\text{polym.}}$ and $\Delta S_{\text{polym.}}$ are collected in *Table* 5. Polyaldehydes are often

Table 6 Thermodynamic parameters for cyclotrimerization

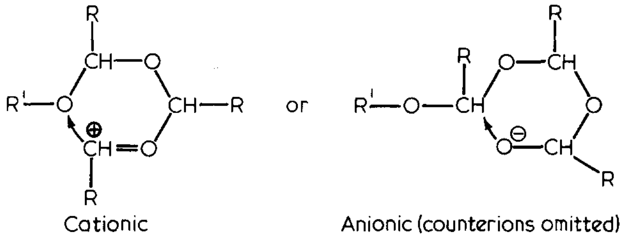
Aldehyde	Standard state	$-\Delta H$ kJ mol^{-1}	$-\Delta S$/deg mol	T_c (°C)	Ref.
CH_2O	gc′	64.9	134	96	112
CH_3CHO	"	32.7	99	55	103
n–C_3H_7CHO	"	12.6	42	22	113
"	ss(CH_2Cl_2, 1 mol l^{-1})	26.0	97	−9	113
"	ss(toluene, 1 mol l^{-1})	32.6	111	17	113

obtained as insoluble crystalline materials in the polymerization media. In such cases the enthalpy of crystallization contributes to the overall enthalpy of reaction making it more negative, favouring polymerization; in some cases precipitation of polymer provides the main driving force for polymerization[101]. A typical example of such a system is the polymerization of formaldehyde in protic media[101].

The equilibrium character of the aldehyde polymerization is also seen in the degradation behaviour. Thermal degradation of polyaldehydes leads to quantitative formation of monomers and it was concluded that the degradation of polyacetals proceeds as a reverse reaction to propagation (by so-called unzipping), due to the thermodynamic instability of the polymer with respect to its monomer above the T_c. This depropagation reaction is initiated by breaking the weakest bond within the polymer chain (thermally or otherwise), usually at the chain ends. All polyaldehydes are relatively unstable thermally; their stability, however, may be improved considerably by introducing stable endgroups (endcapping).

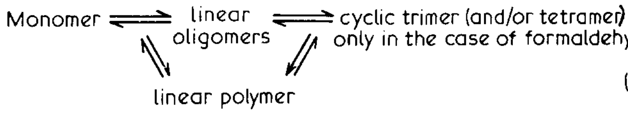
Cyclic oligomers

Formation of cyclic oligomers (mainly trimers) in the presence of acids (but not bases) is a characteristic feature of many aldehydes including formaldehyde. Linear polyaldehydes may be formed in the presence of both acidic and basic initiators. Equation 16 indicates that cyclic trimers could be formed by cyclization of a corresponding linear polymer:



(16)

Linear chains containing three monomer units and an active chain end may easily assume conformations suitable for the formation of trioxane rings, as indicated by the scheme, because six membered rings are practically unstrained. Whether such a conformational arrangement results in the formation of cyclic trimers (or tetramers) or not, depends on the ability of the growing ion to break the acetal bond (back-biting reaction). It is well established that the acetal bond is fairly reactive towards cationic species but practically unreactive towards anions. This explains why, under favourable conditions, cyclic trimers are formed under cationic conditions but not under anionic conditions for the polymerization of aldehydes. Cyclic trimers of formaldehyde, trioxane, can be further polymerized to linear polymer by a cationic mechanism. Cyclic trimers of higher aldehydes, regardless of the substituted R, cannot polymerize under any conditions. Cyclotrimerization is a reversible reaction although precipitation of trimer from the reaction medium may affect the position of equilibrium. The same is true for the polymerization to linear polymer. Thus, the full scheme of polymerization may be visualized as follows (Equation 17):



(17)

The ceiling temperature for cyclotrimerization is higher than that for polymerization. The relevant quantitative data are only available for a limited number of systems.

At temperature regions between T_c for cyclotrimerization and T_c for polymerization, the only possible reaction is cyclotrimerization. At lower temperatures (below T_c for polymerization), formation of a linear polymer becomes possible and at these conditions the relative concentrations of monomer, cyclic trimer and linear polymer should be governed by the corresponding equilibrium constants, provided that rates of both processes are comparable and the system is homogeneous. Usually, however, polymerization of aldehydes proceeds as a heterogeneous process and polymer precipitates from the reaction medium. Under such conditions the relative concentrations of cyclic trimer and linear polymer may be governed by other factors such as solubility and thermodynamic parameters of phase transitions. Because cyclic oligomers are formed through the cyclization of short linear polymeric chains, their stereochemistry should be related to the stereochemistry of linear polymers. All cyclic oligomers which have been isolated as side products of cationic aldehyde polymerizations (except for chloral trimers) have an all *cis* structure as determined by n.m.r. studies[110]. This means that before cyclization occurs a polymeric chain must contain at least three (in the case of cyclic trimer formation) subsequent *cis* placements. In other words, it must contain an isotactic sequence. In the polymerization of aldehydes, formation of isotactic diads is strongly preferential to the formation of syndiotactic diads; crystalline polyaldehydes are always isotactic and even amorphous polyacetaldehyde obtained by cationic polymerization contains 65–70% of isotactic diads.

If cyclization occurred randomly, this would lead to formation of all *cis* isomers and also some amount of *cis–cis–trans* isomers. The absence of this isomer indicates that additional mechanisms of selection exist which permit cyclization of linear oligomers containing three subsequent *cis* placements (isotactic diads) and prevent cyclization of oligomers containing syndiotactic diads. This is due to the fact that the conformation shown in Equation 16 may be much more easily assumed in the case of longer isotactic sequences because all bulky side groups may occupy, in this case, preferred equatorial positions.

Table 7

Temperature (°C)	Tensile strength (p.s.i.g.)	Ultimate elongation (%)
23	25–27	580
−10	120	15
−40	990	11

POLYMERIZATION OF ACETALDEHYDE

Cationic polymerization

Polyacetaldehyde was first obtained independently by Travers and Letort in 1936 by cooling acetaldehyde vapour to liquid air temperature and allowing it to melt[115–117]. This observation led to the concept of so-called 'crystallization polymerization'[118,119]. It was believed that the phase transition alone was sufficient to bring about polymerization. 'Crystallization polymerization' produced in a highly irreproducible manner and with a poor yield a rubber-like, elastomeric, high molecular weight polyacetaldehyde. Further studies carried out in the late fifties revealed that the same elastomeric polymer can be obtained if acetaldehyde is polymerized at low temperature in the presence of typical cationic initiators such as Brönsted and Lewis acids (H_2SO_4, $BF_3 \cdot Et_2O$, P_2O_5, PCl_3, $SnCl_4$ and $FeCl_3$ were listed as most active[16,120] or insoluble initiators including metal oxides (e.g. Al_2O_3)[121,122] or salts (e.g. sulphates)[16]. It was established that all those polymerizations proceeded by cationic mechanism and it was concluded that 'crystallization polymerization' was initiated by traces of acidic impurities[117].

Elastomeric polyacetaldehyde was also prepared by γ-ray[123] and X-ray[124] initiated polymerization.

Polymerization of acetaldehyde must be carried out at low temperatures because the ceiling temperature of acetaldehyde polymerization is −40°C[1]. At higher temperatures cyclization to cyclic trimer–paraldehyde (and to a lesser extent cyclic tetramer–metaldehyde) dominates and paraldehyde is the sole reaction product if acetaldehyde is treated at room temperature with a strong acid[125].

Molecular weights of elastomeric polyacetaldehyde are high. Intrinsic viscosities as high as 8 were reported and the equation $[\eta] = 1.68 \times 10^{-3}\ \bar{M}_n\ 0.65$ was derived from studies of the relationship between viscosity and number average molecular weight of fractionated samples measured by membrane osmometry[125].

The thermal stability of elastomeric polyacetaldehyde is rather poor. It may be, however, considerably improved by endcapping with acetic anhydride or by addition of stabilizers or antioxidants[125,127].

Stabilized elastomeric polyacetaldehyde decomposes at 0.01% min^{-1} at 111°C under nitrogen[117]. Some typical mechanical properties of elastomeric polyacetaldehyde are given in *Table* 7.

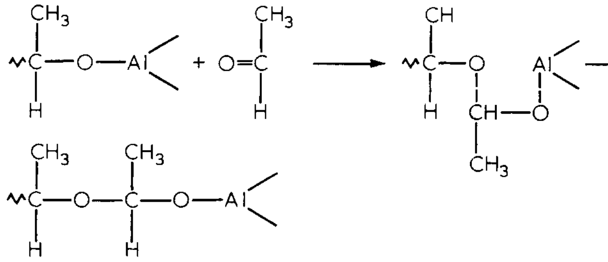
Anionic polymerization

In a Belgian Patent[128] the anionic polymerization of acetaldehyde and higher aldehydes to crystalline polymer in the presence of alkali metal alkoxides was described. This polymer had entirely different properties from those of elastomeric polyacetaldehyde, and it was recognized that this was due to the stereoregular structure of the polymer[128,129]. Furukawa and Natta also reported the preparation of crystalline polyacetaldehyde in the presence of aluminium and zinc alkyls and established that crystalline polyacetaldehyde is exclusively isotactic[129,130].

Since then the stereospecific anionic polymerization of acetaldehyde in the presence of various classes of initiators including aluminium and zinc alkyls, alkali metal alkyls, alkoxides and hydrides has been studied extensively[131–139]. It was established that low temperature (−60 to −80°C) and a solvent with low dielectric constant are essential conditions for stereospecific polymerization[140], and that stereospecific polymerization of acetaldehyde (and also higher aldehydes) leads exclusively to isotactic polymer. No syndiotactic polyaldehydes have ever been obtained.

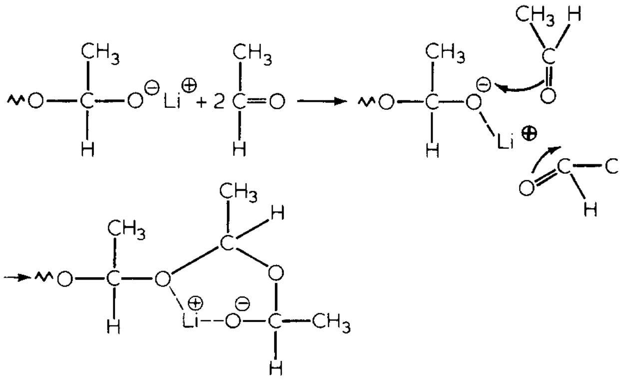
Considerable effort has been undertaken in order to clarify the mechanism of stereospecific aldehyde polymerization, especially by Vogl, Furukawa and Natta. It was found that metal alkyls are not true initiators. In the first step aluminium (or zinc) alkyls react with aldehyde, water or specific additives (hydroxides, acetates, ketones) to form alkoxide species which initiate stereospecific polymerization. Several mechanisms were suggested to explain the mechanism of stereospecific addition.

Natta suggested a mechanism according to which metal (aluminium) atoms form a complex with oxygen that precedes the terminal oxygen[141] (Equation 18).



(18)

Vogl and Bryant proposed a mechanism in which the metal atom is coordinated by four oxygens[100] (Equation 19). This kind of coordination would account for the formation of isotactic diads. Isotactic polyacetaldehyde was a 4_1 helical structure with an identity period of 4.8 Å and a melting point (with decomposition) of ~165°C; the isotactic polymer is insoluble in all solvents including hydrocarbons, ethers, alcohols and acetone and upon heating it degrades to monomer.



(19)

Molecular weights of crystalline polyacetaldehyde are lower by about two orders of magnitude than molecular weights of amorphous elastomeric polymers[131].

Table 8 Transition temperatures of polyaldehydes

Aldehyde	Side chain melting (°C)	Main chain melting (°C)
CH_3CHO	–	165–180
C_2H_5CHO	–	185
n–C_3H_7CHO	–	245
n–C_4H_9CHO	85	140–145
n–$C_5H_{11}CHO$	90–92	138–150
n–$C_6H_{13}CHO$	77–100	148–157
n–$C_7H_{15}CHO$	39–49	137–152
n–$C_8H_{17}CHO$	45–77	120–150
n–$C_9H_{19}CHO$	35–65	110–130
n–$C_{10}H_{21}CHO$	30–68	95–110
n–$C_{11}H_{23}CHO$	59–69	–

Higher aldehydes. Polymers of higher aldehydes (n- and isobutyraldehyde) were first prepared by Bridgman and Conant in 1929 by prolonged action of high pressure (~ 1000 atm) on the monomers[142]. More detailed studies carried out later independently by Novak and Whalley[143], Vogl[120], Furukawa[131], Natta[144] and Sumimoto[113] provided experimental basis for better understanding of polymerization of higher aldehydes.

It is now believed that 'spontaneous high-pressure' polymerization proceeded by a cationic mechanism and was initiated by traces of acidic impurities[145] (also an incorrect radical mechanism was suggested)[146,147]. Formation of polymers under those conditions and at room temperature is attributed to the effect of pressure on the ceiling temperature[148].

High pressure polymerization usually gives waxy or solid amorphous polymers (e.g. of n-butyr- or n-valeraldehyde). When the size of side groups increases, the tendency to form crystalline polymer is pronounced for high pressure polymerization of higher aliphatic aldehydes and crystalline polymers of iso-, butyr- and n-heptylaldehyde were obtained by this polymerization technique[143]. Conventional cationic polymerization carried out at low temperature in the presence of Lewis acids ($BF_3 \cdot Et_2O$, $SnCl_4$, $SnBr_4$) leads to formation of partly crystalline polymers of aldehydes with long linear or branched side chains[117]. It is concluded that stereospecificity of higher aldehyde polymerization is induced by steric requirements stemming from monomer structure rather than by nature of initiator or mechanism of propagation, although under otherwise equal reaction conditions, the anionic mechanism tends to favour more isotactic polymers.

This conclusion was confirmed by more detailed studies of anionic aldehyde polymerization. The degree of crystallinity of polyaldehydes obtained in the presence of anionic catalysts increases with increasing bulkiness of side chains[100]. Anionic polymerization was initiated with typical anionic initiators including alkali metals, alkali metal alkoxides, Grignard reagents and Ziegler–Natta type catalysts at -78°C in nonpolar solvents (e.g. n-pentane). (For n-hexaldehyde and higher homologues the initial temperature should be higher (~ -60°C) to avoid crystallization of monomer, the temperature is lowered to -78°C as polymerization proceeds[149–150]).

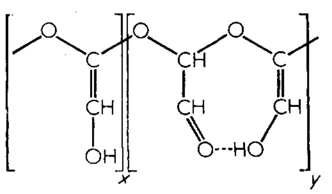
All crystalline higher aliphatic polyaldehydes are isotactic[129,151,152] and crystallize in a fourfold helix with an identity period ranging from 4.8 to 5.2 Å. Most isotactic polyaldehydes are insoluble at room temperature but are soluble at elevated temperatures in some aromatic solvents, cyclic hydrocarbons and higher boiling halogenated olefins. Copolymers of acetaldehyde with higher aldehydes, which are crystalline over the entire range of compositions, show the phenomenon of isomorphism, that is, different monomeric units are incorporated statistically into the chain without disturbing the crystallinity. Isomorphism was observed for copolymers of acetaldehyde with propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-heptaldehyde and n-octaldehyde[153].

Isotactic polyaldehydes melt, with some decomposition, at a higher temperature than the corresponding olefin polymers. The notable characteristic feature of melting behaviour of higher polyaldehydes is the double melting point which is attributed to the separate melting of polyoxymethylene backbone chains and the separately crystallized phase of aliphatic side chains[154–159]. A similar phenomenon was observed earlier for polymers containing aliphatic side chains attached to the hydrocarbon backbone but a side chain length of at least 10 carbon atoms was necessary to induce side chain crystallization[160]. For polyaldehydes this effect is noticeable already for poly(n-valeraldehyde) and is especially pronounced for poly(n-heptaldehyde) and aldehydes with even higher aliphatic chain lengths. The melting behaviour of polyaldehydes was studied in detail by Vogl and coworkers[149,150,154–159]. This is the first case of side chain crystallization of polymers where both the helical isotactic polyacetal main chain and the aliphatic normal side chain take part in separate crystallization in different phases. The crystallization of the main chain does not occur when the side chain is longer than 10 carbon atoms and the crystalline phase exists entirely of the crystallites of the paraffinic side chain. The transition which can be ascribed to crystallization of side chain occurs at 40–100°C (*Table* 8). The transition due to the melting of the main chain is above 120°C and in some cases overlaps with the endothermic peak of the polyaldehyde degradation.

Acetaldehyde copolymers. Acetaldehyde has been copolymerized with a number of comonomers including formaldehyde[161], higher aldehydes[162,163], ketenes[164] and isocyanates[165]. Preparation of block copolymers of acetaldehyde and olefins has also been claimed[166–169]. Copolymers of acetaldehyde with isocyanates show improved thermal stability due to the presence of stable urethane linkages which serve as 'zipper jammers'[165].

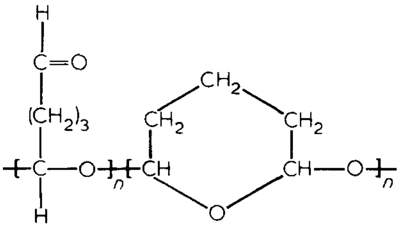
CYCLOPOLYMERIZATION OF DIALDEHYDES

The simplest dialdehyde, glyoxal, polymerizes easily under anhydrous conditions to solid polymer. Polymers prepared by X-ray irradiation of pure monomer (obtained by the thermal decomposition of crude polyglyoxal) were insoluble and infusible and, according to i.r. spectra, contained only C–O–C linkages[170]. More detailed structural studies were carried out for polymers prepared at -78°C in THF solution with Na/naphthalene as initiator[171]. It was established that polyglyoxal contains two types of repeating units: (Equation 20)



$x > y$ (20)

Glutaraldehyde[172–174], succinaldehyde[175] and phthalaldehyde[176] were polymerized with Lewis acid initiators to relatively low molecular weight amorphous polymers. Investigation of polymer structure revealed that these products are actually copolymers containing repeating units formed by 'normal' carbonyl polymerization and by cyclopolymerization (Equation 21). The relative concentration of individual comonomer units depends on the experimental conditions of polymerization (as shown for glutaraldehyde):

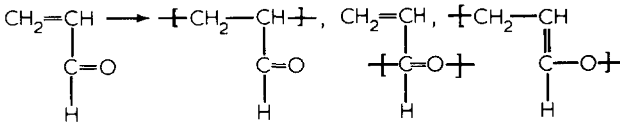

(21)

OPTICALLY ACTIVE POLYALDEHYDES

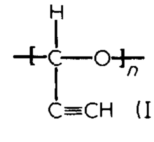
Optically active polyaldehydes were prepared from aldehydes possessing optically active side chains[177,178]. The optical activity of polymers is higher than that of corresponding monomers due to the conformational rigidity around the asymmetric centre in the side chains of polymers and does not depend on the degree of crystallinity. Degradation of optically active polymers led to monomers with the same optical activity as before polymerization; thus, no racemization had occurred during polymerization.

Polymerization of unsaturated aldehydes

The only unsaturated aldehyde which has been studied in some detail is acrolein[179–181]. Acrolein may be polymerized by radical or ionic mechanisms. The properties of the polymer depend to a large extent on the polymerization method used. This is due to the fact that acrolein can form three different repeating units depending on the reaction mechanism (Equation 22).


$$CH_2{=}CH(CHO) \longrightarrow [CH_2{-}CH(CHO)]_n,\ [CH(CH{=}CH_2){-}O]_n,\ [CH_2{-}CH{=}CH{-}O]_n \quad (22)$$

Polymers obtained under different polymerization conditions differ in solubility, thermal stability, viscosity, etc.; they are generally powders with low solubility in organic solvents. Although polymers with high degrees of acetal structure seem to have been prepared and the polymers have been hydrogenated to what seems to be polypropionaldehyde, additional work is needed to establish the existence of pure homopolymers Methacrolein and benzaldehyde. Sumitomo polymerized propiolaldehyde $CH{\equiv}C{-}CHO$(I) in the presence of $BF_3 \cdot Et_2O$ at low temperatures to low molecular weight amorphous polymers for which the polyacetal structure was established[182].


$$[CH(C{\equiv}CH){-}O]_n$$
(I)

HALOALDEHYDES

Studies of polymerization of haloaldehydes have contributed greatly to our present understanding of aldehyde polymerization. The most thoroughly studied systems were halogenated derivatives of acetaldehyde but polymerization of higher haloaldehydes has been described. Chloral (trichloroacetaldehyde) occupies a special position because of the availability of monomer and potential practical application of polychloral and consequently polymerization of this monomer and the properties of the polymer were studied in detail[183–192].

Polymerization of chloral

Chloral can be polymerized by both anionic and cationic mechanisms. Anionic polymerization may be initiated even with relatively weak bases. The most widely used initiators were alkali metal alkoxides, tertiary amines, tertiary phosphines, quaternary ammonium and phosphonium salts and organometallic compounds. Anionic polymerization even with rather weak nucleophiles proceeds with a high rate and gives polychloral with high yield. For example, bulk polymerization of chloral with 0.2 mol % of lithium tertiary butoxide gives 85% conversion after 3 min at a bath temperature of 0°C[193–194]. On the contrary, cationic polymerization can be initiated only by strong Lewis or Brönsted acids (BF_3, CF_3SO_3H, H_2SO_4). The rates of polymerizations are normally lower (for example, 40% conversion with 2 mol% of CF_3SO_3H at −5° after 300 h)[195]. The notable exception is a high rate observed for $AlCl_3$ and $SbCl_3$ initiated chloral polymerization. There is some doubt as to whether this polymerization is a pure cationic process as there is no information about the initiation of chloral polymerization with Lewis bases, but reactions of chloral with BCl_3 [196] have been described (Equation 23).

$$CCl_3CHO + BCl_3 \longrightarrow (CCl_3CHCl{-}O)_3B \quad (23)$$

Polymers of chloral are completely insoluble in any organic solvent including chloral monomer (reported solubility in pyridine is in fact caused by degradation[189]) and are presumably isotactic showing the same configuration as isotactic polyacetaldehyde with an identity period of 5.1 Å. Polychloral is infusible and a hypothetical melting point was extrapolated on the basis of melting points of copolymers of chloral with formaldehyde as 460°C, which is far above composition temperature[190].

Insoluble and fusible polymer of chloral, once formed and precipitated, could not be fabricated by any known method which excluded any practical application and limited the scope of methods which could be used to study polymerization of chloral.

Significant progress was achieved when Vogl found that if chloral was mixed with anionic initiator above the polymerization threshold temperature (58°C for bulk polymerization) and the mixture was subsequently cooled below this temperature (usually to 0°C) under quiescent conditions, the self-supporting 'homogeneous' gel was formed already at low conversion (3%) and further polymerization proceeds to high conversion (85–90%) as a 'pseudohomogeneous' process. This polymerization technique was called 'cryotachensic polymerization'. In this way polychloral pieces of desired shape, including films or sheets, can be prepared directly by this monomer casting polymerization[192,193].

Thermal stability of polychloral, like other polacetals, is limited because it is dependent on the method of preparation and post-treatment procedures. Mechanism of thermal degradation and methods of improving thermal stability of polychloral have been studied in detail[196-202]. Relatively poor thermal stability of unstabilized polychloral is due to depropagation (unzipping) which starts from the weak spots (usually the endgroups) the only product of degradation being chloral monomer. Therefore, the nature of polymeric endgroups determines the thermal stability of polychloral samples.

Anionic polymerization of chloral proceeds as a living process. At high conversion living alkoxide anions become entrapped within the polychloral gel matrix which leads to their deactivation. Reaction with adventitious water may, however, lead to formation of fractions of polymer terminated with hydroxyl groups[196,197].

Thermal stability of polychloral was studied by thermogravimetric analysis and it was found that indeed unstabilized polychloral decomposes at relatively low temperature. Bimodal character of differential thermogravimetric (d.t.g.) curves indicate the presence of two fractions containing 'deactivated' alkoxide and hydroxyl endgroups.

Different methods of incorporating more stable endgroups during and after the polymerization were studied including application of suitable chain transfer agents or decomposable (alkylating) counterions and various post-treatment procedures. It was concluded that if polymerization is initiated with Ph_3P (the true initiator is phosphonium salt $Ph_3P^+{-}O{-}CH{=}CCl_2Cl^-$ formed in reaction of Ph_3P with CCl_3CHO) and polymer is subjected to post-treatment using the solution of PCl_5 in CCl_4, degradation starts at 250°C and reaches a maximum rate at 340°C (heating rate 20° min^{-1}, nitrogen atmosphere). Thus, properly stabilized polychloral has a thermal stability comparable with that of commercial polyoxymethylene (Delrin).

Mechanical and electrical properties of polychloral are also comparable with properties of commercial engineering plastics. The polymer is, however, completely nonflammable[191,200].

CHLORAL COPOLYMERS

Copolymerization of chloral with a number of comonomers was described in the patent literature; only the copolymerization of chloral with mono- (MCA) and dichloroacetaldehyde (DCA)[203] and isocyanates (both aliphatic and aromatic)[204-211], ketenes and formaldehyde and trioxane is well established. Copolymers of chloral with MCA are soluble in $CHCl_3$, while copolymers with DCA are insoluble. Both do not melt below decomposition temperature and their thermal stability is intermediate with respect to the corresponding homopolymers. The most thoroughly studied system was the copolymerization of chloral with isocyanates. For this system reactivity ratios were determined and it was concluded that $r_2 = 0$. An independent kinetic study under cryotachensic conditions revealed that isocyanate is incorporated into the copolymers mainly in the last stage of copolymerization. The resulting chloral copolymers are not uniform in structure and the average macromolecule can be visualized initially as an almost pure acetal polymer with gradually increasing numbers of urethane linkages at the end of the macromolecules, formed at the end of the copolymerization. The total amount of isocyanate comonomers which can be incorporated into a chloral copolymer depends on the isocyanate structure; aromatic isocyanates are more reactive than aliphatic isocyanates in copolymerization with chloral and probably near the end of polymerization form alternating copolymers.

The thermal stability of chloral copolymers is greatly improved with respect to that of unstabilized chloral homopolymer. This is due to the fact that terminal fragments of the chain, from which degradation starts, are considerably enriched in urethane linkages. Copolymerization with 5–10 mol% of aliphatic or aromatic isocyanates provides an alternate route for preparation of thermally stable chloral polymers; the mechanical properties of chloralisocyanate copolymers are similar to those of homopolymers.

POLYMERIZATION OF FLUORAL

Fluoral can be polymerized by both anionic and cationic mechanisms[212]. Anionic initiators which, according to patent literature, polymerize fluoral involve alkali metal cyanides and halides, carboxylates, ammonium and sulphonium salts, phosphines and phosphates[213,214]. Cationic polymerization can be initiated by strong Lewis acids (PF_5, $SbCl_5$, BF_3, $AlCl_3$, $SnCl_4$); strong protonic acids are less effective[214-216]. As in the case of chloral polymerization, the overall rate of polymerization of fluoral is higher for anionic mechanism. According to Busfield, cationic polymerization initiated by BF_3 has a living character. This, however, was not recognized for anionic polymerization probably because of precipitation of polymer and formation of living but occluded alkoxide anions.

Fluoral is the only aldehyde which has been described to polymerize via opening of the carbonyl double bond by a free radical mechanism. Polymerization initiated by AIBN seems to proceed at the early stages of polymerization similar to conventional vinyl polymerization, with second order termination[99] but the rate of polymerization increases at low conversion probably due to precipitation of polymer.

It is interesting that polymer morphology depends very little on the type of initiator used, while temperature has a considerable effect. Anionically polymerized polyfluoral was soluble and amorphous when polymerized at −78°C but insoluble and crystalline if polymerized at room temperature[217]. It was suggested from i.r. studies that crystalline polyfluoral has a helical isotactic structure[218].

Thermal stability of endcapped polyfluoral is similar to that of polychloral but oxidative stability is rather poor. The polymer degrades much more rapidly in oxygen than in nitrogen atmosphere[216].

BROMAL

Polymerization of bromal was successfully achieved recently[219]. The large size of the CBr_3 group of bromal causes considerable steric crowding in the polymer and $\Delta H_{polym.}$ and the T_c are consequently low (−77°C for 1 mol solution in toluene). Because of this and difficulties with monomer purification, all previous attempts to polymerize bromal failed. After the suitable method of purification was developed and thermodynamic limitations were considered, it was found that bromal could be polymerized at −78°C by both anionic (with pyridine as initiators) or by cationic (with triflic acid) mechanisms. Again, as in the case of other aldehydes, anionic polymerization proceeds with higher overall rate and gives higher yields. The resulting polymer is crystalline (insoluble) and infusible. Thermal stability of unstabilized polybromal is limited (maximum on d.t.g. curve at 146°C) but is considerably improved by endcapping with PCl_5 (maxima at 230°C and 280°C).

OTHER HALOGENATED DERIVATIVES OF ACETALDEHYDE

More detailed information is available on the polymerization of partly chlorinated acetaldehyde (MCA and DCA)[91,220] and aldehydes of the general formula $X'_n X''_m X'''_{3-(n+m)}$CHO where $X_1 = f$, $X_2 = \text{Cl}$ and $X_3 = \text{Br}$. All mixed perhalogenated acetaldehydes (with the exception of FClBr CHO) were recently prepared and polymerized[91–93,95–98].

The behaviour of MCA and DCA in polymerization is intermediate between acetaldehyde and chloral. Replacing chlorine atoms in the CCl_3 group by hydrogen results in an increased reactivity of the monomers in cationic polymerization. Cationic initiators which are effective to polymerize DCA include $SnCl_4$, $SbCl_5$ and BF_3Et_2O. Some bases (phosphines, amines or quaternary ammonium salts) which are excellent initiators of chloral polymerization do not initiate polymerization of MCA and DCA. Organometallic compounds, however, are good initiators (AlR_3, ZnR_2, $Al(OR)_3$). Cationic initiators polymerize MCA to amorphous soluble polymers while in the presence of Et_2Zn or Et_2Mg crystalline polymer insoluble in $CHCl_3$ is formed. In AlR_3 initiated polymerizations both soluble and insoluble polymer fractions are formed

Thermal stability of polymers of partially chlorinated acetaldehydes is rather poor even after endcapping. Poly-DCA decomposes fairly rapidly at 220°C and poly-MCA when heated at 100°C in air loses 20% of weight in 4 h. As in the case of polychloral, no softening or melting was observed below the decomposition temperature.

As may be expected, perhaloacetaldehydes containing two different halogen substituents are polymerized by anionic as well as cationic mechanisms. Thermodynamic polymerizability decreases when fluorine is replaced by chlorine and chlorine by bromine as indicated by the corresponding T_c listed in *Table* 4.

The increasing size of the CX_3 group favours the formation of insoluble, crystalline, presumably isotactic polymers. In the case of the smallest CF_3 substituent (fluoral), both amorphous and crystalline polymer may be obtained depending on the reaction conditions and initiations. If one fluorine is replaced by chlorine, amorphous polymer can still be obtained. If, however, two fluorine atoms are replaced by two chlorine atoms only insoluble crystalline polymer is formed independently of the reaction conditions. If the CX_3 group contains even one bulky bromine atom as in the case of CF_2Br substituents, the formation of low molecular weight amorphous soluble polymers is still possible but typically insoluble crystalline polymers are produced by both cationic and anionic mechanisms. All other perhaloacetaldehydes produce polymers which are completely insoluble and presumably isotactic.

OTHER HALOALDEHYDES

Information on the polymerizability of halogenated derivatives of aldehydes other than acetaldehyde are scarce. Tetrafluoropropionaldehyde was polymerized to crystalline polymer[140] and some other examples of polymerization of perfluoroaldehydes are described in the patent literature.

Aldehydes of general formula $(CH_3)_nCl_{3-n}CCHO$ were polymerized by an anionic mechanism. It was concluded that in THF solvent, polymerization proceeds as a living system; the polymerizability in this series decreases when Cl substituents are replaced by CH_3 groups[105].

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