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Publisher *Taylor & Francis*

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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Rosen, Irving(1967) 'Polymers of Haloaldehydes', Journal of Macromolecular Science, Part A, 1: 2, 267 – 275

**To link to this Article: DOI:** 10.1080/10601326708053970

**URL:** <http://dx.doi.org/10.1080/10601326708053970>

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## Polymers of Haloaldehydes

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### Synopsis

The field of poly(haloaldehydes) is reviewed, with emphasis on recent developments. The poly(chloroaldehydes) described by the early investigators had the common characteristics of being formed "spontaneously" from the monomer, and dissociating on being heated. Characterization of these *meta* polymers by Novak and Whalley showed them to be crystalline and of low molecular weight and to have an OH-ended substituted polyoxymethylene structure.

Recently, high-molecular-weight polymers of chloral, dichloroacetaldehyde (DCA), and chloroacetaldehyde (MCA) have been prepared and characterized. The preferred mechanisms of polymerization of chloral and DCA are quite different, being anionic and cationic, respectively. The two polymers are also end-capped by different techniques for thermal stability. The differences in requirements for both polymerization and end-capping are attributed to differences in structure. Polychloral is intractable, but PDCA is a soluble, amorphous polymer, which readily forms strong films. MCA polymers have been obtained in both amorphous and crystalline forms by the use of cationic and coordination types of catalysts, respectively. The thermal stability of the chloroaldehyde polymer decreases as the chlorine content decreases.

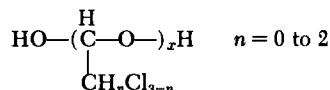
The physical properties of the fluoroaldehyde polymers offer great promise for various applications, but little has been reported on them in the past few years. Considerable potential for further work exists in the area of haloaldehyde copolymers.

Polymers of chloroaldehydes have been known for a long time. Indeed, polychloral, first observed by Liebig in 1832, may be one of the world's oldest known synthetic polymers (1). Two types of polymers were described by the investigators in the early literature. One type consists of the *para* polymers, which are actually cyclic trimers, analogous to paraldehydes. The cyclic trimers

have sharply defined melting points. The other type consists of the *meta* polymers, which are true polymers (Table 1). These polymers are amorphous and do not melt, but rather revert to the monomer on heating.

After the initial observations further investigation of these polymers lay fairly dormant until Novak and Whalley reported their characterization work in 1959 (7,8). In this work the polychloral was prepared by  $H_2SO_4$  and pyridine initiators, while poly(chloroacetaldehyde) (PMCA) and poly(dichloroacetaldehyde) (PDCA) were obtained by spontaneous polymerization. Infrared examination showed the polymers to consist of substituted polyoxymethylene chains with OH groups at the chain ends (see structure below). The infrared spectrum further indicated that the polymers are helical in structure. X-ray diffraction patterns revealed them to be crystalline. With polychloral the degree of crystallinity appeared to depend upon the method of preparation. The PDCA was soluble in acetone (8). The polychloral, on the other hand, was insoluble in all solvents tested, and degradation, rather than solution, occurred in basic solvents (7).

Poly(chloroaldehyde) structure:



## RECENT STUDIES

### Polychloral

Much of the more recent work on polychloral has centered on low-temperature polymerization. Furukawa and co-workers polymerized chloral at  $-78^\circ\text{C}$  with organometallic catalysts, although the yields were low (3 to 45%) (9). An isotactic structure was suggested for the polymer. High yields of polymer were obtained in diethyl ether with a sodium naphthalene complex catalyst (10). Using a polymer prepared in a manner similar to that described by Furukawa, Ilyina and co-workers investigated some of the thermal properties (11). Chloral has also been polymerized at  $-78^\circ\text{C}$  by  $^{60}\text{Co}$  gamma irradiation to a colorless solid (12). Alkali thiocyanate catalysts were found to produce 70% yields of an "amorphous" polymer at  $0^\circ\text{C}$  (13). One patent claims that the aluminum

TABLE 1  
*Meta* Polymers

Monomer	Catalyst	Description of polymer	Year	Ref.
ClCH <sub>2</sub> -CHO (MCA)	Standing	Amorphous, insol.	1882	2
Cl <sub>2</sub> CH-CHO (DCA)	Standing, or HCl	Amorphous, insol.	1868	3
			1875	4
Cl <sub>3</sub> C-CHO	Standing, or H <sub>2</sub> SO <sub>4</sub> or AlCl <sub>3</sub>	Amorphous, insol.	1913	5
	Pyridine, R <sub>3</sub> N	White powder	1906	6

oxide type of catalyst polymerizes chlorinated aliphatic aldehydes, including chloral at temperatures below  $-40^{\circ}\text{C}$ , although no pertinent examples are given (14).

All of the previously mentioned work was on non-end-capped polychloral. To study the properties of polychloral at elevated temperatures (above the ceiling temperature), an end-capping technique was recently developed (15). The polychloral diol, unlike polyoxymethylene diol, is not readily end-capped in the presence of alkali catalysts. Polychloral is best capped under acid conditions by acid anhydrides and chlorides and does not appear to undergo degradation during the process. Unlike the raw polymer, end-capped polychloral possesses good stability towards hot dimethyl formamide, good stability at elevated temperatures ( $255^{\circ}\text{C}$ ), and an apparently high melting point. The stability toward acids and high melting point is attributed to the rigidity of the polymer chain. From a form of end group analysis, based upon

TABLE 2  
Catalyst Comparison

Catalyst	Concn., mmoles per mole of chloral	Solvent	Time, hr	Temp., $^{\circ}\text{C}$	Convsn., %	Polymer DP
AlBr <sub>3</sub>	6	CH <sub>2</sub> Cl <sub>2</sub>	5	-30	24	190
(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> CH <sub>2</sub> NI	4 <sup>a</sup>	None	0.5	0	55	380
2,6-DPL <sup>b</sup> + Et <sub>2</sub> Zn	29	Propylene	1	-48	59	600

<sup>a</sup> Catalyst dissolved in acetonitrile.

<sup>b</sup> 2,6-Dimethoxyphenyllithium.

the capping technique, metachloral is estimated to have a degree of polymerization ( $\overline{DP}$ ) of about 50.

The availability of a simple means of estimating  $\overline{DP}$  enabled the comparison of polychlorals obtained by means of cationic and anionic initiators (16). Anionic catalysts readily produce high-molecular-weight polymer ( $\overline{DP} \approx 300$  to 600), but a  $\overline{DP}$  of only 200 could be produced with cationic catalysts (Table 2). The anionic system apparently initiates and propagates polymerization much more readily than the cationic system. This is attributed to the inductive effects of the chlorine atoms on the chloral. Little difference was found when products of similar  $\overline{DP}$  were compared as to x-ray diffraction pattern, infrared spectrum, and tractability. This is believed to be due to the single type of structure which is sterically favored.

### Poly(dichloroacetaldehyde)

The earlier DCA polymers mentioned on pages 67 and 68 and also the product described in a more recent report (17) were of low  $\overline{DP}$ . Very recently means of obtaining a high- $\overline{DP}$  polymer were discovered (18). Although DCA has only one chlorine less than chloral, the polymerization and polymer characteristics are quite different. DCA is readily polymerized by Lewis acid catalysts to polymer with terminal OH groups. The polymerization appears to proceed by a conventional cationic mechanism, in which the rate of the termination reaction is much higher than the rate of the transfer reaction. Unlike their action with chloral, basic and neutral catalysts form either very small amounts or no polymer at both 0°C and ambient temperature. The catalyst  $BF_3 \cdot Et_2O$  at 0°C produces very-high-molecular-weight polymer in bulk polymerization. A  $\overline{DP}$  of about 400 is readily attained. Again unlike chloral, the polymer is readily end-capped by acetic anhydride with a pyri-

TABLE 3  
Relative Thermal Decomposition Rates

	PDCA	Polychloral
Capped polymer	$k_{220} = 3.47\%/min$	$k_{220} = 0.04\%/min$
Uncapped polymer	$k_{190} = 1.83\%/min$	$k_{280} = 1.48\%/min$

**TABLE 4**  
Physical Properties of End-Capped PDCA

Tensile strength, psi	3,300
Tensile modulus, psi	112,000
Elongation, %	30
Hardness of disk, Shore A	94
Flammability	Self-extinguishing
Crystallinity	Amorphous
Melting point	Decomposes at 230°C

dine catalyst to increase its thermal stability. The thermal stability of PDCA is much lower than that of polychloral (Table 3).

Melting point, infrared, and x-ray diffraction measurements confirm that the polymer produced with the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is amorphous. The polymer is soluble in many common organic solvents, such as tetrahydrofuran and methyl ethyl ketone, and can be cast into films and be compression-molded. Cast films of the polymer are only partially orientable. Table 4 summarizes some of the basic physical properties of cast films of the high-molecular-weight PDCA.

An attempt was made to improve the tractability and solubility of polychloral by copolymerization with DCA (19). Zinc alkyl catalysts at temperatures less than about  $-40^\circ\text{C}$  in toluene produce high-molecular-weight copolymers in satisfactory yields. The reactivity ratios show that the comonomers tend to be randomly arranged along the chain. Copolymers were obtained with substantial amounts of DCA, but these remained insoluble and infusible. To determine the physical properties of the copolymers, test samples were prepared by an "in place" monomer casting polymerization technique. Table 5 summarizes the results of this

**TABLE 5**  
Mechanical Properties of Chloral/Dichloroacetaldehyde Copolymers

Mole-% DCA in polymer	Tens. strength, psi	Tens. modulus, psi $\times 10^2$	Elong., %	Deflection temp., $^\circ\text{C}$ (264 psi)
28	6000	1600	12	124
45	6100	2100	12	132

**TABLE 6**  
MCA Polymerization

Catalyst	Yield, %	Amorphousness, %	Crystallinity, %
ZnEt <sub>2</sub>	19	0	1000
Al(OEt) <sub>3</sub>	28	0	100
AlEt <sub>2</sub> Cl	31	47	53
AlEtCl <sub>2</sub>	28	43	57
BF <sub>3</sub> ·Et <sub>2</sub> O	38	100	0

evaluation. The physical properties of the copolymers were independent of the DCA content over the range tested. This may be attributed to isomorphism in the two polymers, which would be consistent with their structural similarity (20).

### Poly(chloroacetaldehyde)

Two types of polymer have been obtained in the homopolymerization of MCA, depending upon the catalyst used (Table 6) (21). No statement is made in Ref. 21 about the molecular weights of the polymers, but the absence of COH absorption in the infrared spectra indicates they are probably high. The results are consistent with those in a recent patent, which describes a BF<sub>3</sub>-catalyzed polymerization of MCA at -10 to -50°C to an elastic amorphous thermoplastic (22).

From data on the thermal decomposition of the uncapped polymer one can estimate a thermal decomposition rate in air,  $k_{100} = 0.096\%/min$ . From this value one obtains  $k_{190} \geq 2\%/min$ . Although this estimate is made for the stability in air, it probably would be of the same order of magnitude in an inert atmosphere. With this estimation it is interesting to note that the relative stabilities of the chloroaldehyde polymer series are  $Cl_3CCHO > Cl_2HCCHO >$

**TABLE 7**  
Decomposition Rates of Uncapped Polymers

Monomer unit	Measurement temp., °C	$k$ , %/min.
Cl <sub>3</sub> CCHO	280	1.48
Cl <sub>2</sub> HCCHO	190	1.83
ClH <sub>2</sub> CCHO	190	$\geq 2$
H <sub>3</sub> CCHO	190	>MCA

$\text{ClH}_2\text{CCHO} > \text{H}_3\text{CCHO}$  (Table 7). The decomposition rates increase as the number of chlorine atoms on the monomer unit decreases. The apparent order of stabilities may be due to a combination of steric and inductive effects. The steric effect of the chlorines hinders the attack on the  $\text{C}-\text{O}-\text{C}$  bond, whereas the inductive effect reduces the instability of that bond.

### Poly(fluoroaldehydes)

There was a flurry of activity concerning poly(fluoroaldehydes) a number of years ago, after the first preparation of polyfluoral in 1950 (23). More recently there have been only scant reports on polyfluoral, possibly because of fluoral's tendency to spontaneous polymerization (23,24). The dearth of information on polyfluoroaldehydes is somewhat surprising in the light of the outstanding properties claimed for this class of materials (Table 8).

TABLE 8  
Polymers of Fluoroaldehydes

Monomer	Catalysts	Properties
$\text{CF}_3\text{CHO}$	Spontaneous, perox., acid	Nonflammable, chemically resist., insol., high decompn. point (24)
$\text{C}_2\text{F}_3\text{CHO}$	Spontaneous, perox., acid	
$\text{C}_3\text{F}_7\text{CHO}$	Acid	
$\text{CClF}_2\text{CHO}$	Spontaneous	(25)
$\text{CF}_2\text{HCHO}$	$\text{P}(\text{OEt})_3$ at $-80^\circ\text{C}$	(26)

The structure of polyfluoral is probably that of the typical OH-terminated substituted polyoxymethylene. The surprising resistance to alkali vis à vis polychloral is probably due to the hydrophobic nature of the polymer. There have been reports of polyfluorals with lower thermal stabilities than those observed by Husted and Ahlbrecht (24), but the discrepancies may be due to molecular-weight differences in the polymers. To improve further the stability of the polyfluoroacetals the terminal OH groups have been replaced by means of a reaction with halides, such as  $\text{PCl}_5$  and  $\text{SOCl}_2$ , at  $200^\circ\text{C}$  (26).

### FUTURE PROSPECTS

A classical approach to the modification of the properties of homopolymers is copolymerization. Copolymerization may serve to depress the melting point, increase solubility, and increase ther-



mal stability. There are only a few reports of investigations into this potentially fruitful area, all of which have appeared recently (Table 9). Most have been limited to copolymers of a haloaldehyde and another aldehyde, especially with the aim of modifying polyformaldehyde. There remain many ways in which the flame resistance of the chloroaldehydes and the lubricity of the fluoroaldehydes may be utilized by copolymerization. Hopefully, additional studies will be made, which could lead to the preparation of new compositions of matter with useful properties.

TABLE 9  
Copolymers of Haloaldehydes

Haloaldehyde	Comonomer	Conditions	Areas investigated	Ref.
Cl <sub>3</sub> CCHO	Cl <sub>2</sub> HCCCHO	ZnR <sub>2</sub> , -40°C	Wide range of compns., react. ratios, "in-place" polymeri- zation	19 27
Cl <sub>3</sub> CCHO	CH <sub>2</sub> O	Ø <sub>3</sub> P, -72°C	Wide range of compns.	28
		R <sub>3</sub> N, 0 to -40°C	Wide range of compns.	29
		AlEt <sub>3</sub> , -70°C	Reactivities, structure	30
Cl <sub>3</sub> CCHO	ethylene oxide	AlEt <sub>3</sub> , -78 to 0°C	Wide range of compns.	31
Cl <sub>3</sub> CCHO	ØNCO	Anionic cats., low temp.	Improved thermal stability	32
ClH <sub>2</sub> CCHO	CH <sub>3</sub> CHO	AlEt <sub>3</sub> , -78°C	Wide range of compns., react. ratios.	21
F <sub>3</sub> CCHO	CH <sub>2</sub> O	R <sub>3</sub> P, R <sub>4</sub> NX, -35°C	Modified polyoxy- methylene	33
Higher fluoro- aldehydes	CH <sub>2</sub> O	R <sub>3</sub> P, R <sub>4</sub> NX, -35°C	Modified polyoxy- methylene	33

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Received by editor September 9, 1966

Submitted for publication September 9, 1966