Addition Polymers of Aldehydes

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ABSTRACT: The polymerization of aldehydes has played a considerable role in the progress of chain reaction polymerization and has significantly contributed to our knowledge of polymer science. Polyformaldehyde, as homopolymer and copolymer, plays an important role as a significant niche product in engineering plastics use. Higher aldehyde polymerization demonstrates the importance of stereospecificity and the ceiling temperature of polymerization. A discussion of haloacetaldehyde polymers is reserved for an upcoming article. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2293–2299, 2000

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Otto Vogl was born in Traiskirchen, near Vienna, Austria, in 1927. He went to elementary school there and to the middle and high school in Baden, the district seat. He attended the University of Vienna, where he studied organic chemistry. In 1950, he received his Ph.D. with a thesis on steroids. He was appointed an instructor at the II. Chemical Institute of the University of Vienna in 1948, and he subsequently worked on the isolation and synthesis of alkaloids. In 1953, he went to the United States, first to the University of Michigan and then to Princeton University, before joining the Polychemicals Department of DuPont in Wilmington, later moving to the Central Research Department.

Otto Vogl joined DuPont when research in polymer chemistry started to expand rapidly, and he spent his 14 years with DuPont almost entirely on aldehyde polymerization.

In 1970, he received an invitation from the University of Massachusetts to join the newly created Polymer Program as a full professor, and he played a major role in the development of the program. The program soon expanded into the Polymer Science and Engineering Department, now considered by many the leading department of its kind in the United States. In 1983, he accepted the position of the newly created Herman F. Mark Professor at Polytechnic University, the first endowed professorship in polymer science in the United States. In 1995, Otto Vogl retired from Polytechnic University and assumed his position as Emeritus Professor of the Polymer Science and Engineering Department in Amherst.
INTRODUCTION

Aldehydes, like olefins, have a double bond that is susceptible to polymerization. The carbonyl bond of aldehydes, unlike the carbon–carbon double bond of olefins, is highly polarized because of the different electronegativities of the carbon and oxygen atoms of the bond; the dipole moment is about 2.5 D. As a result, aldehydes are susceptible to ionic polymerization, that is, both cationic and anionic polymerizations (eq 1). Cationic polymerization occurs by the addition of an electrophile (or the electrophilic portion of the growing polymer carboxonium ion) to the carbonyl oxygen of the aldehyde or, conversely, by the addition of a suitable anion to the carbonyl carbon, forming an alkoxide. Polymers obtained from aldehydes by either cationic or anionic polymerization have the structure...
of a polyacetal, a polymer chain of alternating carbon and oxygen atoms.  

\[ R \ \overset{\text{anionic}}{\longrightarrow} \ \overset{\text{cationic}}{\longrightarrow} \ \overset{\text{polymer}}{\text{C-O}} \overset{\text{H}}{\text{R}} \]

\( R = \text{H, aliphatic, trihalomethyl} \)  

CARBONYL POLYMERIZATION

The behavior of carbonyl compounds toward protic solvents such as water and methanol allows them to be placed into three categories:

1. **Acetal oligomers**: formaldehyde, glyoxal, and methyl glyoxalate.
2. **Hydrates or hemiacetals**: haloaldehydes (e.g., fluoral, chloral, and bromal).
3. **Unaffected compounds**: acetaldehyde, higher aliphatic aldehydes, and ketones (the degree of hydration is minimal).

POLYFORMALDEHYDE

In 1859, Butlerov first obtained polyformaldehyde as a white solid; the polymer was subsequently the subject of extensive investigations. Staudinger made the polymerization of formaldehyde the center of his efforts on his studies of the structure of long-chain macromolecules, beginning in 1919.

In 1948, it was found that polyformaldehyde could be prepared with a high molecular weight. The polymer had useful mechanical properties suitable for its development as a large-scale polymer and as the first engineering plastic. With these interesting properties, DuPont decided in 1952 to commercialize polyformaldehyde.

Today, three basic processes are producing about 500,000 metric tons of polyformaldehyde worldwide, both homopolymers and copolymers. Formaldehyde homopolymers are produced from purified formaldehyde. The purification is performed via the hemiacetals of higher water-insoluble alcohols. The purified hemiacetals are thermally cracked, and anhydrous formaldehyde is polymerized with anionic initiators in a hydrocarbon solvent. The polymer must be stabilized by acetate end capping. The copolymerization of formaldehyde is only possible to a limited extent with isocyanates and dimethyketenes. The cationic copolymerization of formaldehyde with BF₃ etherate as the initiator has been achieved with 1,3-dioxolane and butanediol formal.

Anionic formaldehyde polymerization can also be subjected to controlled chain transfer with poly(ethylene oxide glycol), which produces block copolymers of poly-oxymethylene with poly(ethylene oxide) terminal blocks.

Formaldehyde can also be polymerized in protic media, especially in methanol, to high molecular weight polymer. Although this technique is intriguing, it has not been used commercially.

Another way of purifying formaldehyde is the synthesis of trioxane, the cyclic trimer of formaldehyde. Trioxane can readily undergo cationic polymerization in the melt with, for example, BF₃ etherate (eq 2). This homopolymer can readily be acetate-capped (this is done in solution). Trioxane polymerization can also be carried out by trioxane being deposited from the vapor phase onto a cold surface.

\[ n \text{CH}_2\text{O} \overset{\text{cationic}}{\longrightarrow} \overset{\text{anionic}}{\longrightarrow} \overset{\text{polymer}}{\text{CH}_2\text{O}} \overset{\text{R}}{\text{R}} \]

Because trioxane polymerization proceeds by cationic polymerization, trioxane can be readily copolymerized with such cyclic comonomers as ethylene oxide and 1,3-dioxolane. In these cases, random copolymers are produced, and the unstable fraction is removed by thermal degradation.

POLYMERIZABILITY AND CEILING TEMPERATURE (\(T_c\))

Bond-opening polymerizations are, in principle, equilibrium reactions that describe the relative stability (thermodynamics) of the monomer with its polymer. Dainton reported the \(T_c\) of formaldehyde polymerization to be 127 °C. A number of reports claim 125 °C as the \(T_c\); it is believed that the most reliable value is 119 °C. The bond opening of the vinyl double bond is associated with a large negative free enthalpy and a corresponding high \(T_c\) of polymerization (hundreds of degrees).
The gain in energy associated with the formation of two single carbon–oxygen bonds from one carbonyl double bond (aldehyde polymerization) is relatively low (21 kJ \cdot \text{mol}^{-1} \text{)} (Table I). Polyaldehydes often precipitate as crystalline polymers, and the enthalpy of crystallization contributes to the overall enthalpy of the reaction, making it more negative and favoring polymerization. In some cases, the precipitation of the polymer provides the most significant contribution to the driving force for polymerization.

The situation is somewhat different for the ring opening of the cyclic aldehyde trimers. Trioxane, but not higher cyclic aldehyde oligomers, can be further polymerized into a high molecular weight linear polyformaldehyde by a cationic mechanism.

Acetaldehyde can also be viewed as a tautomer of vinyl alcohol that on polymerization could directly yield poly(vinyl alcohol) from the enol form of acetaldehyde, vinyl alcohol, which is not stable. These reactions of acetaldehyde, carried out under anionic (basic) conditions in hydroxylic solvents, led to some aldol condensation. Under more forceful conditions, only polyaldol products of low molecular weights were obtained. Under anhydrous conditions in tetrahydrofuran and lithium aluminum hydride just above the \( T_c \) (230 °C), oligomers were also produced, but with some loss of the elements of water (Table I).

### Table I

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>bp (°C)</th>
<th>Ceiling Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCHO</td>
<td>−19</td>
<td>119</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>21</td>
<td>−39</td>
</tr>
<tr>
<td>CH₂OOCOCHO</td>
<td>44 (35 torr)</td>
<td>26</td>
</tr>
<tr>
<td>CF₃CHO</td>
<td>−19</td>
<td>85</td>
</tr>
<tr>
<td>CCl₃CHO</td>
<td>98</td>
<td>17</td>
</tr>
<tr>
<td>CBr₃CHO</td>
<td>174</td>
<td>−75</td>
</tr>
<tr>
<td>CFOBrCHO</td>
<td>56</td>
<td>41</td>
</tr>
</tbody>
</table>
containing aliphatic side chains attached to the backbone of methacrylate polymers or polyesters.

STEREOCHEMISTRY OF POLYALDEHYDES

Polymers of aldehydes substituted with an aliphatic side chain, such as the methyl group in acetaldehyde, are subject, just as olefin polymers, to stereochemistry at the addition of each monomer unit. As a result, when no preferred stereochemistry is involved during the polymerization, the polymers obtained are atactic. Stereospecific meso-addition results in the formation of isotactic polymers; racemo-addition results in the formation of syndiotactic polymers. Syndiotactic polyaldehydes have never been synthesized. It has been speculated that the monomer addition that leads to isotactic polymers proceeds by the direct formation of the isotactic helix (3).

DIALDEHYDE POLYMERS

The simplest dialdehyde, glyoxal, polymerizes easily into solid polymers under anhydrous conditions; these polymers are insoluble, infusible, and apparently highly crosslinked. According to the IR spectra evidence, the polymers contain only C—O—C linkages.

Glutaraldehyde, succinaldehyde, and phthalaldehyde have been cyclopolymerized into relatively low molecular weight amorphous polymers with acid initiators. These polymers are actually copolymers; the repeat monomer units undergo normal carbonyl polymerization but also have a considerable number of cyclopolymerized units (five- and six-membered ring sizes) in the polymer chain.

POLYMERS FROM FUNCTIONALLY SUBSTITUTED ALDEHYDES

Functionally substituted higher aldehydes, 3-methoxy(3-ethoxy)propionaldehyde, 3-methoxybutyraldehyde, and 3-cyanopropionaldehyde, have been polymerized. Glycidaldehyde has been claimed to have been polymerized into two types of polymers, polyacetals at low temperatures and polyethers at higher temperatures. Propiolaldehyde gives low molecular weight amorphous polymers for which the polyacetal structure seems to have been established.

Polymerizations of methacrolein and benzaldehyde have been attempted a number of times; acrolein and methacrolein have been polymerized through the carbon–carbon double bond but never into a polymer with a pure polyacetal structure.

Methyl Glyoxalate

Methyl glyoxalate is now prepared in commercial quantities as a pharmaceutical intermediate by ozonolysis from methyl maleate or methyl fumerate and becomes a colorless glass on standing. Methyl glyoxalate has a structure similar to that of methyl acrylate, the carbonyl oxygen having replaced the methylene group of methyl acrylate. We investigated the glassy oligomer of methyl glyoxalate briefly. Acetate capping with acetic anhydride was unsuccessful because it caused transesterification. End capping could be achieved with phenyl isocyanate. The stabilized polymer (oligomer) had a degree of polymerization of 10–20. Poly(methyl glyoxalate) is a most attractive aldehyde polymer and should be reinvestigated in the future.

Optically Active Aldehydes

Optically active polyaldehydes have been prepared from aliphatic aldehydes possessing chiral centers in the side chains. Citronellal has specifically been studied. The optical activity of the polyaldehyde is higher than expected from the optical activities of the corresponding monomers. This effect is based on the conformational rigidity or helicity of the chain near the asymmetric cen-
ters of the side chains. Degradation of the optically active polymers leads to monomers with the same optical activity as that of the monomer before polymerization; thus, no racemization of the chiral center in the monomer unit occurred during polymerization and depolymerization.

Copolymerizations

Crystalline, apparently isotactic copolymers of acetaldehyde with higher aldehydes, which are crystalline over the entire range of composition, show the phenomenon of isomorphism, indicating that different comonomer units are incorporated statistically into the chain without disturbing the crystallinity. Isomorphism has been described for copolymers of acetaldehyde with propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-heptaldehyde, and n-octaldehyde.48

Acetaldehyde has also been copolymerized with a number of other comonomers, including formaldehyde, ketenes, and isocyanates.52

Cyclic oligomers of aldehydes

Formaldehyde, acetaldehyde, and higher aliphatic aldehydes readily form cyclic trimers and tetramers.53

Cyclic trimers of higher aldehydes cannot be polymerized by ring opening into linear polymers because the $T_c$ for cyclotrimerization is higher than that for polymerization. Between the $T_c$ for polymerization and the $T_c$ for trimerization, the only possible reaction is cyclotrimerization. At lower temperatures, that is, below the $T_c$ for polymerization, the formation of a linear polymer becomes possible and usually is exclusive. For higher aliphatic aldehydes, this means that with acid catalysis, the $T_c$ of cyclotrimerizations (and even of the much less favored tetramerization) is much higher than that of the formation of linear polymers. Acetaldehyde also forms tetramers.56 Higher cyclic oligomers of formaldehyde have also been isolated.57–59

Trichloroacetaldehyde (chloral)54 forms the trimer only under special conditions with concentrated sulfuric acid from chloral hydrate.55

These aldehyde oligomers have the structure of cyclic acetals, with the six-membered trimers (trioxane and paraldehyde) being particularly stable; interestingly enough, the normal paraldehyde is the “isotactic,” equatorial trimer. The eight-membered tetramer of formaldehyde, tetroxane, as well as the tetramer of acetaldehyde, was also found to be stable.

Trioxyane, discovered in 1886,60 was found in 1922 to form linear high molecular weight polymers of formaldehyde,61 (see also ref. 62), polyoxymethylene, which has the same structure as the polyoxymethylene prepared from formaldehyde.

Linear Aldehyde Oligomers

Linear formaldehyde oligomers have been studied and characterized by Staudinger. More recently, the oligomers were synthesized and isolated as individual molecules of uniform oligomers, and their crystal structure was determined.63

Fabrication of polyaldehydes

Commercial polyformaldehydes, including homopolymers (mp = 178 °C) and copolymers (~165 °C) are melt-fabricated by extrusion or injection molding at 200–230 °C. For certain applications, parts may be machined from a larger stock.

Elastomeric polyacetaldehyde or polyfluoral, as well as the relatively low molecular weight poly(methyl glyoxalate), is soluble and can be handled in solution. Poly(n-heptaldehyde) can be fabricated by solid-state compaction, but no other polyaldehyde has been fabricated.

Stability and stabilization of polyaldehydes

Polyformaldehyde (pure and optimally stabilized) is thermally stable up to 300 °C. The polyformaldehyde backbone is sensitive to acid-catalyzed degradation and sometimes has a small amount of thermally unstable (usually hemiacetal) end groups. Polyformaldehyde requires a thermal stabilizer, usually a polyamide, or other acid scavengers.

Polymers of higher aliphatic polyaldehydes as secondary hemiacetals are very difficult to stabilize by end capping because of the steric hindrance surrounding the hemiacetal end groups.

Polyformaldehyde is also sensitive to autoxidation because the hydrogen of the methylene group attached to two oxygen atoms is readily abstracted from the polymer chain by radicals during the autoxidation scheme. Phenolic antioxidants are used for stabilization. The autoxidative instability of polymers of higher aliphatic aldehydes is much greater, and no effective stabilizer system has yet been found.

For outdoor use, polyformaldehyde must also be stabilized with ultraviolet stabilizers against solar radiation to minimize photo-oxidation.
REFERENCES AND NOTES