

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

### Polyaldehydes: Introduction and Brief History

O. Vogl<sup>a</sup>

<sup>a</sup> CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

**To cite this Article** Vogl, O.(1967) 'Polyaldehydes: Introduction and Brief History', Journal of Macromolecular Science, Part A, 1: 2, 203 – 207

**To link to this Article: DOI:** 10.1080/10601326708053966

**URL:** <http://dx.doi.org/10.1080/10601326708053966>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Polyaldehydes: Introduction and Brief History

---

O. VOGL

CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,  
E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE

Aldehyde polymers were prepared long before the true nature of a macromolecule was recognized. Polyaldehydes made important contributions in crucial phases of the development of our knowledge of polymers. They have the distinction of providing several first discoveries that added to the understanding of addition polymerization and to the determination of the structure of polymers.

It was not until the commercialization of a polyaldehyde, polyformaldehyde, that polyaldehydes received general recognition on their own merits.

Polyaldehydes are addition polymers of aldehydes of high molecular weight and polyacetal structure. The word "polyaldehyde" has, unfortunately, been used in the past very indiscriminately for any polymeric product of an aldehyde. The term "aldehyde polymerization" should, however, be used only for the addition polymerization of an aldehyde that yields a polyacetal of reasonable molecular weight. The oligomerization of aldehydes to cyclic trimers or tetramers should be described respectively as trimerization and tetramerization. Aldehyde polycondensations should also be differentiated clearly from the addition polymerizations. Polyaldehydes are polyacetals and should be distinguished from polyethers, although they have some formal similarities to them.

Polyaldehydes may be conveniently classified as polymers of formaldehyde and polymers of higher aldehydes. Polymers of formaldehyde or polyoxymethylenes may be classified again as those made from formaldehyde and those made from trioxane.

The higher polyaldehydes, on the other hand, may be classified as polyoxymethylenes with aliphatic side chains and those with haloaliphatic side chains.

The historic development of aldehyde polymerization followed along these lines: most investigations were carried out within the corresponding groups of polyaldehydes, and until very recently little cross-fertilization occurred between the different fields of polyaldehydes.

When one examines the literature of aldehyde polymers, it is clear that the polymers of formaldehyde were the most thoroughly studied. In fact, when Butlerov attempted to make methylene glycol or its dehydro product, formaldehyde, in 1859 (1), he obtained the polymer.

Classic examinations of formaldehyde polymerization followed the initial studies but with limited success (2). The polymerizations were carried out usually in aqueous solutions. At first it was the sometimes annoying instability of formalin solutions that attracted the investigators rather than a genuine interest in the white solid that precipitated from these solutions.

Progress was made when Staudinger embarked on an intensive investigation into formaldehyde polymerization. For more than a decade he worked in this area, and many basic concepts of polymer chemistry, such as polymer homologous series, end groups of polymers, and polymer stability, were derived from the results of his studies of polyformaldehyde (3).

Staudinger found that known polyoxymethylenes differed in molecular weight and end groups. He characterized  $\alpha$ -polyoxymethylene, polyformaldehyde with two hydroxyl end groups,  $\beta$ -polyoxymethylene, polyformaldehyde with a sulfate end group,  $\gamma$ -polyoxymethylene, and  $\delta$ -polyoxymethylene with base-stable methoxyl end groups. All these polymers were of relatively low molecular weight and had a degree of polymerization of up to 100. Eupolyoxymethylene was obtained from the spontaneous polymerization of liquid formaldehyde at low temperatures. It was a high-molecular-weight polymer but, like the low-molecular-weight polyoxymethylene, it was reported to be unstable and to degrade back to monomer at elevated temperatures.

Acylation and alkylation experiments on the polyoxymethylenes were carried out by Staudinger.

As much as the study of formaldehyde polymers had aided in the development of the concept of macromolecules (small molecules linked together by chemical bonds), the instability of polyoxymethylenes actually delayed the full recognition of this idea, because the suggestion that macromolecules were merely "associates" of small molecules could not unhesitatingly be rejected.

By 1932, when work on a number of polymers started to change science and technology, the work on formaldehyde polymers came to a standstill.

Several years later work at the du Pont company was started in an attempt to study the reaction of pure formaldehyde. The preparation of high-molecular-weight polymers was one of the objectives. The earlier samples of polyformaldehyde had been brittle and commercially unattractive. MacDonald (4) was able to establish conditions for making high-molecular-weight formaldehyde polymers that were tough, attractive, and stable. Additional stabilizations of polyformaldehyde were carried out by end-capping of the hemiacetal ends with acyl and alkyl end groups and by the addition of other appropriate stabilizers.

The work on formaldehyde polymerization led ultimately to the commercialization of formaldehyde homopolymer by the du Pont company; this acetal resin was called Delrin.

The publication of the MacDonald patent was the beginning of the modern era of polyaldehyde investigation. A number of laboratories started to work on various aspects of aldehyde polymerization, not only on formaldehyde polymerization. Nearly two thousand papers and patents have appeared on polyformaldehyde alone in the last decade, and the number of papers and patents on higher polyaldehydes has reached about three hundred.

In the course of early formaldehyde work it was found that formaldehyde could be trimerized to a cyclic trimer (5), which was called trioxane. This trimer is easily purified and is a source of pure formaldehyde. It was found that it forms polyoxymethylene, which is the same as the polymer obtained from formaldehyde. The reason for the polymerization of trioxane was initially not known, and the possibility of a radical polymerization was discussed. One of the polymerization techniques for trioxane, the "sublimation polymerization," became the precursor of the now very popular "solid state" polymerizations.

In the early 1950's it was found that trioxane polymerization was a cationic polymerization and that a great number of acids, particularly Lewis acids (6), could be used as initiators.

Subsequently trioxane was copolymerized with many comonomers that were capable of cationic polymerization.

The Celanese Corporation and Farbwerke Hoechst have worked out the trioxane homo- and copolymerization in greater detail, and a random copolymer based on trioxane (7) is now produced under the trade name Celcon and Hostaform.

These copolymers consist of polyoxymethylene chains which contain ethylene oxide linkages as "zipper jammers," beyond which polymer degradation from the chain ends does not occur. Because of these block points the copolymers do not have to be end-capped, but they do have to be stabilized by base or thermal treatment, to remove the unstable polyoxymethylene ends.

Polymers of higher aliphatic aldehydes are relatively new. To accomplish the polymerization, techniques that were rather sophisticated at the time of their discovery thirty of forty years ago, such as very high pressures (8) or low temperatures, had to be employed (9). We know now that many ionic initiators will cause higher aldehydes to polymerize, but low temperatures must still be used. Polymers of higher aldehydes are capable of existing in stereoregular form, and isotactic and atactic polymers have been prepared and characterized.

Several difficulties that were initially recognized in formaldehyde polymerization have turned out to be amplified in higher-aldehyde polymerization. The most important difficulty is low ceiling temperature. The whole problem of polymer stability, however, which includes end-capping and autooxidation, is also more severe in the case of higher polyaldehydes.

Progress has been made in the understanding of the stereoselectivity of the higher-aldehyde polymerizations, cyclopolymerization of appropriate dialdehydes, polymerization of optically active aldehydes, and the polymerization of aldehydes with functionality that does not interfere with polymerization. The whole field of copolymers has barely been touched. Copolymers of higher aldehydes with formaldehyde and copolymers of higher aldehydes with each other and with other comonomers have recently been reported.

Whereas aliphatic aldehyde polymers were not studied until rather recently, polymers of the corresponding haloaliphatic aldehydes, particularly polychloral, are very old (10). It appears that polychloral is probably the oldest known synthetic polymer; it was described by Liebig as early as 1832. Recent work on polychloral and other haloaldehyde polymers will be discussed in a subsequent paper by Dr. I. Rosen.

## REFERENCES

1. A. M. Butlerov, *Ann.*, **111**, 242 (1859).
2. F. Auerbach and H. Barschall, *Studien über Formaldehyd—Die festen Polymeren des Formaldehydes*, Julius Springer, Berlin, 1907.
3. H. Staudinger, *Die Hochmolekularen organische Verbindungen, Kautschuk und Cellulose*, Springer, Berlin, 1932.
4. R. N. MacDonald (to E. I. du Pont de Nemours Co.), U.S. Pat. 2,768,994 (1956).
5. L. Pratesi, *Gazz. Chim. Ital.*, **14**, 139 (1884).
6. A. K. Schneider (to E. I. du Pont de Nemours Co.), U.S. Pat. 2,795,571 (1957).
7. C. T. Walling, F. Brown, and K. W. Barte, (to Celanese Corporation of America), U.S. Pat. 3,027,352 (1962).
8. P. W. Bridgeman and J. B. Conant, *Proc. Natl. Acad. Sci., U.S.*, **15**, 680 (1929).
9. M. Letort, *Compt. Rend.*, **202**, 767 (1936); M. W. Travers, *Trans. Faraday Soc.*, **32**, 246 (1936).
10. J. Liebig, *Ann.*, **1**, 194, 209 (1832).

Received by editor September 9, 1966

Submitted for publication September 9, 1966