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Isotactic Aldehyde Polymers

Kurzmitteilung

by

GIULIO NATTA, GIORGIO MAZZANTI, PAOLO CORRADINI, and IVANO W. BASSI

DR. ALFRED HÜTHIG VERLAG GMBH · HEIDELBERG

From the Istituto Chimica Industriale, Politecnico of Milano, Italy

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Linear polymers having a polyacetalic structure were prepared for the first time by H. STAUDINGER¹), by polymerizing formaldehyde.

Acetaldehyde has been polymerized to linear, amorphous polymers, soluble in acetone, by polymerizing the monomer either in the solid state²), or in the liquid state³).

CONANT and co-workers⁴) described the polymerization of some aliphatic aldehydes to amorphous polymers under very high pressure (12,000 atm.).

Very recently NOVAK and WHALLEY have confirmed that the polymers of acetaldehyde, propionaldehyde, n-butyraldehyde and n-valeraldehyde obtained by polymerization under very high pressure are amorphous, but the polymers of isobutyraldehyde and of n-heptaldehyde proved to be crystalline⁵). However the crystalline structure of these two polymers has not been described.

In the course of our studies on stereospecific polymerizations, we were able to prepare, independently, crystalline polymers of several aldehydes and to prove their isotactic structure. In this preliminary communication we wish to summarize briefly some results of our work.

We have found that at low temperature ($-78^{\circ}\text{C}.$) and atmospheric pressure, in the presence of a small quantity of some organometallic compounds, such as $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Zn}(\text{C}_4\text{H}_9)_2$, and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, acetaldehyde, propionaldehyde, iso and n-butyraldehyde and a great number of other similar aldehydes can be readily polymerized, yielding crystalline, high molecular weight products.

¹) H. STAUDINGER, Die hochmolekularen organischen Verbindungen, J. Springer-Verlag, Berlin 1932, S. 280-287.

²) M. LETORT and A. J. RICHARD, C. R. hebdomadaire Séances Acad. Sci. **240** (1955) 86.

³) M. LETORT and P. MATHIS, C. R. hebdomadaire Séances Acad. Sci. **249** (1959) 274; J. FURUKAWA, T. SAEGUSA, T. TSURUTA, H. FUJII, A. KAWASAKI, and T. TATANO, Makromolekulare Chem. **33** (1959) 32.

⁴) J. B. CONANT and C. O. TONGBERG, J. Amer. chem. Soc. **52** (1930) 1668; J. B. CONANT and W. R. PETERSON, J. Amer. chem. Soc. **54** (1932) 628.

⁵) A. NOVAK and E. WHALLEY, Can. J. Chem. **37** (1959) 1710, 1718.

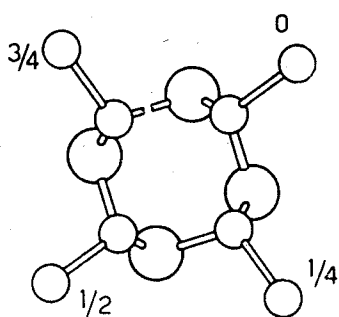
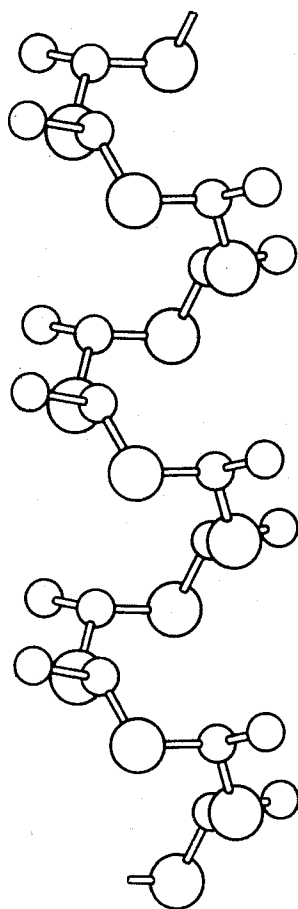
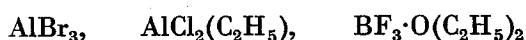


Fig.1. Model of the chain of isotactic polyacetaldehyde in the crystalline state

Crystalline polymers of butyraldehyde and of other aldehydes higher than the acetaldehyde have been prepared by us, also operating in the presence of other catalysts which are known as generally promoting cationic polymerizations, such as



Crystalline acetaldehyde polymers are not extractable by ether or by acetone at their boiling temperature, contrary to the amorphous polymers. By this way the highly crystalline products can be separated from the amorphous ones, which may be present in the crude polymer.

In the case of the polymers of higher aldehydes, such as *n*-butyraldehyde or isobutyraldehyde, low molecular weight oily polymers which are present only to a very limited extent, can be separated by extracting the crude with acetone.

By successive extractions with di-isopropylether or with benzene at their boiling temperature, solid fractions (corresponding to 10 ÷ 20 % of the total polymer), showing a low crystallinity, can be separated. The residues after the above referred to extractions are highly crystalline at X-rays, and are almost insoluble in the usual organic solvents.

The degree of crystallinity of the obtained polymers is very high and comparable to the one of the more crystalline isotactic polymers of α -olefins such as isotactic polypropylene.

Rigorous proof of the polyacetalic structure of our polyaldehydes and of the regularity in the succession of the configuration of tertiary carbon atoms along the chain, has been obtained through the resolution of the X-ray structure of polyacetaldehyde. Fiber spectra of this polymer, in which more than one hundred reflections have been observed, are con-

sistent with a unit cell containing 16 monomeric units corresponding to the following data:

$$a = b = 14.50 \text{ \AA} \quad c = 4.8 \text{ \AA} \quad N = 16 \quad \text{Space group} = I 4_1/a$$

The space group is the same as the one found for polyvinyl cyclohexane⁶). The 16 monomeric units contained within the unit cell must necessarily arrange themselves four by four around the two 4_1 and the two 4_3 screw axes allowed by the space group. The structure of polyacetaldehyde is necessarily isotactic, because the chain has a helicoidal (fourfold) conformation, imposed by the symmetry conditions of the space group. Preliminary calculations lead to a model of the macromolecule (Fig. 1)

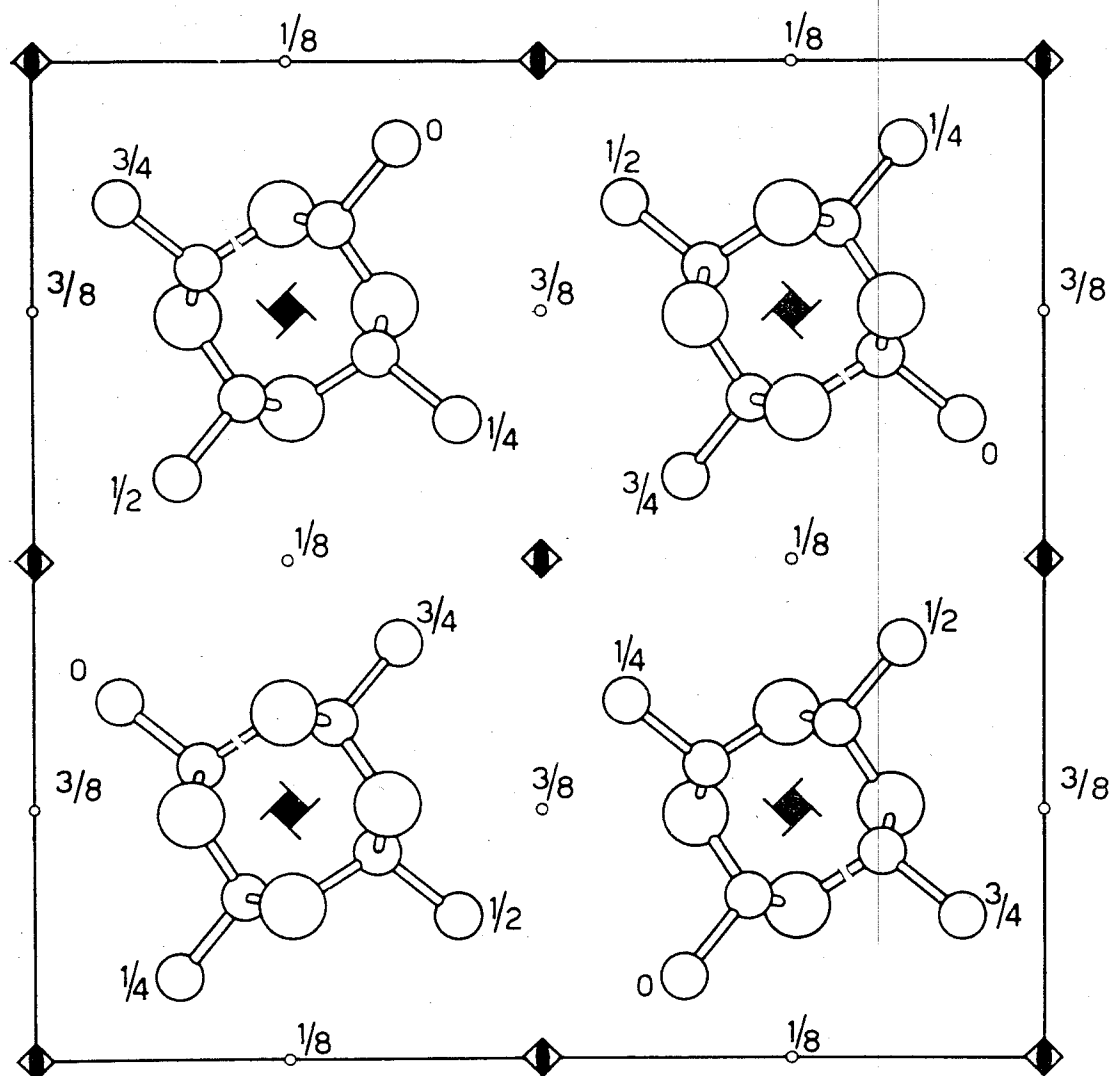


Fig. 2. Model of chain packing of isotactic polyacetaldehyde in the crystalline state

⁶) G. NATTA, P. CORRADINI, and I. W. BASSI, *Makromolekulare Chem.* **33** (1959) 247.

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defined by internal rotation angles $A = -135^\circ$, $B = 85^\circ$ (for comparison, polyvinyl cyclohexane $A = -151^\circ$, $B = 83^\circ$) and to the model of chain packing shown in Fig. 2. In this model, VAN DER WAALS interchain contacts are realized only between hydrogen atoms, the lowest carbon-carbon distances being all higher than 4.1 Å. The inner position of oxygen atoms imbedded in the crystals in a very compact chain, and screened by the methyl groups, may justify the very low solubility of acetaldehyde polymers, even in polar solvents.

The X-ray structure of other polyaldehydes is very similar to the one given for polyacetaldehydes. Also in this case, space group considerations are sufficient to establish the isotactic structure of the chain.

The most relevant unit cell data for some polyaldehydes are compared in Table I.

Table I. X-Ray data of some crystalline isotactic polyaldehydes

Polyaldehyde	Unit cell constants		N	d	Space group
	a (Å)	c (Å)			
Acetic	14.60	4.79	16	1.14	$I 4_1/a$
Propionic	17.52	4.78	16	1.05	$I 4_1/a$
n-Butyrric	20.01	4.78	16	1.00	$I 4_1/a$

N = number of monomeric units per unit cell d = X-ray density