The Crystallinity of Polyaldehydes

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Recently a few reports[1-3] on the stereospecific polymerization of aliphatic aldehydes were published, but the properties of these polymers remain hardly known[3]. As the crystalline property of the polymer is very interesting from practical point of view, we have examined the crystalline properties of some aldehyde polymers, i. e. the polymers of propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, *n*-caproaldehyde, *n*-enauthaldehyde. The polymerization was carried out in hydrocarbon solvent such as heptane or toluene, with triethylaluminum as catalyst, at the temperature −80 or −40°C. In usual procedure we used 20 ml. of solvent, 0.0014 mol. of catalyst and 10 ml. of monomer.

All of the polymers obtained are crystalline. The X-ray diffraction patterns of powders of these polymers treated under various conditions are shown in Figs. 1—5. When treated with boiling chloroform or benzene for several hours, all of these polymers give sharper X-ray diagram than the untreated. As shown in Figs. 1, 3, 4 and 5, the samples swelled in some

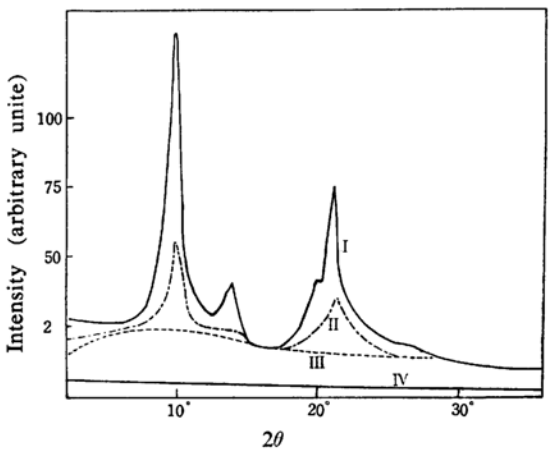

Fig. 1. The X-ray diffraction patterns of poly-propionaldehydes.
- I Sample treated with boiling chloroform for 8 hr. (polymerization at −78°C).
- II Sample swelled in chloroform. Amorphous part assumed.
- III Amorphous parts assumed.
- IV Pattern by air.

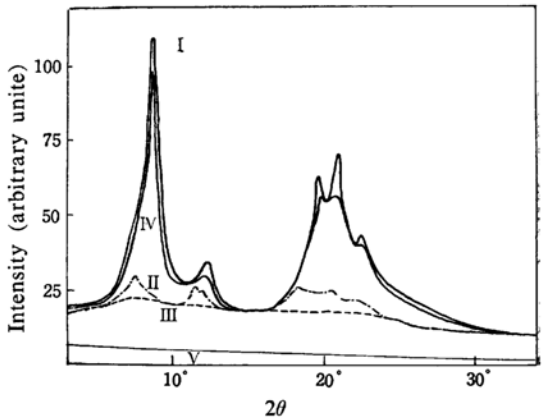

Fig. 2. The X-ray diffraction patterns of poly-*n*-butyraldehydes.
- I Sample treated with boiling chloroform for 6 hr. (polymerization at −80°C).
- II Sample partially depolymerized (gel-form).
- III Amorphous parts assumed.
- IV Untreated sample (polymerization at −40°C).
- V Pattern by air.

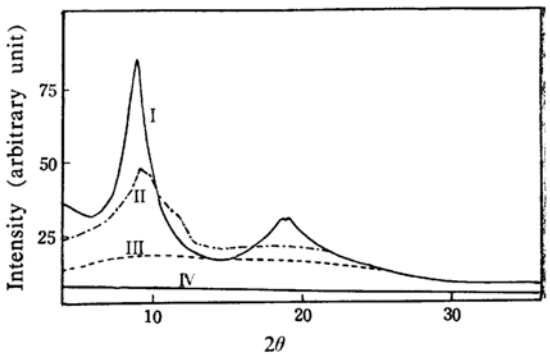

Fig. 3. The X-ray diffraction patterns of poly-isobutyraldehydes.
- I Sample treated with boiling chloroform for 6 hr. (polymerization at −78°C).
- II Sample swelled in chloroform.
- III Amorphous parts assumed.
- IV Pattern by air.

organic solvents were also examined by X-ray diffractometer. The untreated polymers of *n*-butyraldehyde depolymerize in certain condition to give gel-substances, whose patterns are shown in Fig. 2. Generally, the polymer which was kept at higher temperature than 170°C, partially depolymerized to give more diffused patterns.

Assuming the amorphous parts are given by dotted lines in each diagram, (the pattern of amorphous parts will be discussed in detail later,) we calculated the crystallinity of the polymers by integral intensity; as following

1) G. Natta et al., *Makromol. Chem.*, **37**, 156 (1960).
2) J. Furukawa et al., ibid., **37**, 149 (1960).
3) O. Vogl, *J. polymer Sci.* **46**, 261 (1960).

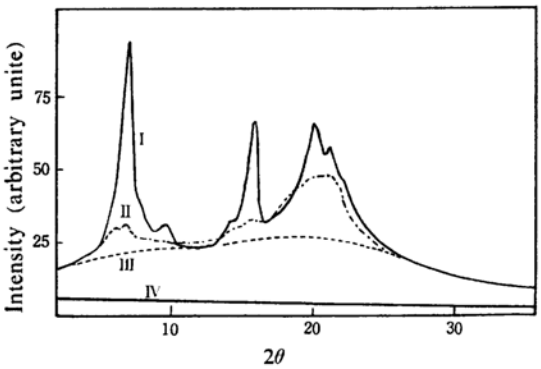

Fig. 4. The X-ray diffraction patterns of poly-*n*-caproaldehyde.
I Sample treated with boiling benzene for 6 hr. (polymerization at −78°C).
II Sample swelled in benzene.
III Amorphous parts assumed.
IV Pattern by air.

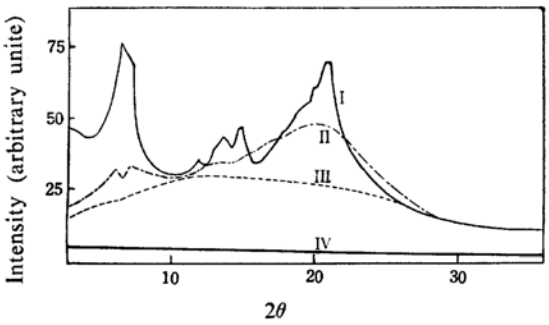

Fig. 5. The X-ray diffraction patterns of poly-*n*-enauthaldehydes.
I Sample treated with benzene.
II Sample swelled in benzene-chloroform.
III Amorphous parts assumed.
IV Pattern by air.

about 40% for poly-propion-, 45% for poly-butyr-, 49% for poly-isobutyr-, 37% for poly-*n*-capro-, 32% for poly-*n*-enauth-aldehyde. These polymers are crystalline even in untreated state and can not be dissolved in usual organic solvents, but are capable to be made a film by calendering at higher temperature than 100°C. The essential difference between the polymers obtained at −80 and −40°C, and the difference between the polymers prepared in heptane and toluene could not be found in the case of poly-*n*-butyraldehyde. At higher temperature than −35°C, the polymers could not be obtained. The kinetics of the polymerization will be reported later.

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