CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, K. S. MINSKER,

1962

SovietRxiv

Abstract

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CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, K. S. MINSKER,
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ON THE MECHANISM OF HOMOGENEOUS RADICAL STEREOSPECIFIC POLYMERIZATION OF VINYL CHLORIDE IN ALDEHYDES

Along with heterogeneous stereospecific polymerization on catalytic systems of the Ziegler–Natta type, works have recently appeared in the literature devoted to the synthesis of stereoregular polymers of a high degree of crystallinity by the method of homogeneous free-radical polymerization. One of the most interesting cases of this type of process is the polymerization of vinyl chloride in the presence of aldehydes ($^{1-6}$). As was shown in these works, the reaction was induced by initiators of free-radical polymerization (azobisisobutyronitrile, benzoyl peroxide, aldehyde peroxides, etc.).

The introduction into the polymerization system of typical inhibitors of radical processes confirmed the free-radical mechanism. Such inhibitors as powdered rhombic sulfur, iodine, hydroquinone, and quinhydrone, taken in an amount of 1% of the weight of the monomer, completely suppressed the reaction of free-radical polymerization of vinyl chloride in an aldehyde medium. Without inhibitors, polymerization in the dark proceeded with normal yields. Let us note that in the absence of inhibitor and initiator, polymerization of vinyl chloride in aldehydes (in particular aliphatic ones) did not take place. Only under ultraviolet irradiation with a PRK-2 lamp for 1.5 hr was the formation of a stereoregular polymer with a yield of up to 10% observed. Judging from the literature data, stereoregular polyvinyl chloride obtained by homogeneous stereospecific polymerization in aliphatic aldehydes is characterized by a syndiotactic sequence in the arrangement of monomer units in the macromolecule (^{1,6}). The 20 experimentally found sharp reflections with interplanar spacings in the range 5.26 Å ÷ 1.14 Å (^{1,5}) are characteristic of a stereoregular polymer and are fairly well indexed on the lattice of a syndiotactic structure (^{7}).

The value of the ratio D_{635}/D_{692}, which, as is known, is a measure of the crystallinity of syndiotactic polyvinyl chloride (^{1,6}), determined from IR spectra of films not subjected to additional crystallization, proved to be 4.7. This is greater than the analogous value reported in works (^{1,6}), where its maximum value is 4.3 (^{1}), while the usual values are 2–2.7 (^{1,6}).

However, up to the present time the mechanism of homogeneous stereospecific free-radical polymerization of vinyl chloride in aldehydes has remained unclear. The available material made it possible only to focus attention on the following experimental facts:

1. The reaction medium (1,3,4) is responsible for the stereospecific free-radical polymerization of vinyl chloride at ordinary temperatures ($-20 \div +60^\circ$).
2. The solvents that make it possible to obtain syndiotactic polyvinyl chloride of a very high degree of ordering are aldehydes and, first of all, aliphatic aldehydes (1,6).
3. The carbonyl group is not responsible for the formation of stereoregular-

of polyvinyl chloride (4). Thus, in aliphatic aldehydes a highly crystalline polymer is obtained, whereas in esters, amides, ketones, etc., an amorphous one is obtained.

4. The nature of the substituent in aldehydes has a substantial effect on the stereospecificity of the polyvinyl chloride formed (2,4).

In this connection it has been pointed out that the cause of the formation of crystalline polyvinyl chloride should be sought in the structure of complexes consisting only of aldehyde and vinyl chloride (4,5). The latter has also been confirmed by specially designed experiments on polymerization of the monomer in acetic (or butyric) aldehyde, carefully purified from peroxide compounds, under the action of γ-radiation without introducing foreign initiators. The electron diffraction pattern of the polymer obtained contained 19 reflections and was analogous to the electron diffraction pattern of sample 2 presented in (5). In the general case, the stereospecificity of the process of homogeneous free-radical polymerization, which ensures orientation of the adding monomer units to the growing macromolecule with formation of alternating *d*- and *l*-stereoconfigurations, is due to the presence of a sufficiently large and polar substituent at the double bond (8). Owing to this, the rate of orientation of the adding monomer units increases. In this sense, the production of a stereoregular syndiotactic polymer must be due to the formation of associates that increase the polar substituent in the monomer.

It appears to us that the schematic structure of the associates may be described as a six-membered ring:

[[schematic six-membered associate: C=C, Cl, O, C, H, R, $\oplus, \ominus$ charges and arrows]]

Then the monomer may be regarded as a vinyl compound containing a sufficiently large polar substituent at the double bond, which leads to the creation of the necessary conditions for obtaining syndiotactic polymers (8–10). The proposed ideas explain all the earlier and newly obtained experimental data. Thus, in studying the effect of the monomer:aldehyde ratio, within the range from $1:0.1$ to $1:10$, on the degree of crystallinity, it was found that at a component ratio of 1 : 1, or with an excess of aldehyde, the maximum stereoregularity of the polyvinyl chloride achieved (19 reflections in the electron diffraction pattern) practically did not change (Fig. 1, *a*, see insert p. 1091), whereas even a certain excess of monomer already led to partial amorphization of the polymer (Fig. 1, *b*). At a monomer:aldehyde ratio of 1 : 0.7, and with further increase in the vinyl chloride content in the reaction mixture, complete amorphization of the polymer took place (Fig. 1, *c*). Similar amorphization was also observed upon introducing into the reaction mixture small additions of substances capable of competing in the formation of the corresponding associates (for example, water*). It is interesting that additions of ethyl chloride** (hydrogenated monomer) within the range from 0.01 to 1.5 mol had practically no effect on the stereoregularity of the polymer. The proposed structure of the associates is in agreement with the results of experiments on the polymerization of vinyl chloride in various classes of organic compounds containing a carbonyl group: amides, esters, ketones, acids and their anhydrides (4), as well as in additionally examined acid halides.

When the characteristic functional groups of these classes of organic compounds are compared with the aldehyde group, it is evident that the most stable six-membered associates with vinyl chloride can be expected only in the case of aldehydes. Ketones, acid anhydrides, and acid halides are not capable of forming stable cyclic associates with vinyl chloride, while in the case, for example, of acids, only energetically less favorable seven-membered associates are possible.

It could have been assumed that the formation of associates is connected with the α-hydrogen atoms in the aldehyde, which possess sufficiently high mobility. However, comparison of the electronograms of polymers obtained in an acetaldehyde medium (Fig. 1, *a*), chloral (Fig. 2, see insert, p. 1091), and acetyl chloride (the type of electronogram is similar to Fig. 1, *b*) leads to the conclusion that cyclic associates are responsible for the formation of the crystalline polymer, and that their presence is due to interaction of the aldehyde group of the solvent with the

$$> C^{H}_{Cl}$$

group of the monomer.

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Received
11 XII 1961

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* Acetic or butyric aldehyde saturated with water in the presence of vinyl chloride.
** Aldehyde:monomer ratio 1 : 1 (mol:mol).

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Note: Figure translations are in progress. See original paper for figures.