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Abstract

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ON THE QUESTION OF THE RELATION BETWEEN THE CRYSTALLIZATION OF ALDEHYDES AND THE FORMATION FROM THEM OF POLYMERS OF THE POLYOXYMETHYLENE TYPE

(Presented by Academician B. A. Kazanskii, January 13, 1960)

As is known (1), thermally stable high-molecular-weight polyoxymethylenes possessing valuable practical properties can be obtained from formaldehyde. However, attempts to obtain analogous stable polymers from other aliphatic aldehydes have so far not been successful. Nevertheless, in the course of these investigations very interesting data were obtained, in particular, on the relation between the crystallization of acetaldehyde and its polymerization. Thus, it was shown (2) that polymerization occurs at atmospheric pressure only upon melting of acetaldehyde crystals. However, the crystallization conditions decisively affect the yield and properties of the polymer (3). Acetaldehyde thoroughly purified from oxygen (peroxides) and water does not polymerize; at the same time, when the content of water and alcohols exceeds a certain value, substantial inhibition of the reaction occurs (4). The polymers obtained are unstable even at temperatures close to room temperature and, depending on the nature of the depolymerization initiator, may undergo the latter by both radical and ionic mechanisms (5).

There are several papers on the question of the polymerization of butyraldehyde. This phenomenon was discovered by Bridgman and Conant (6), who obtained an unstable polymer of butyraldehyde at room temperature and a pressure of 12,000 atm. The melting temperature of butyraldehyde at atmospheric pressure is $-99°$; it therefore seemed quite probable that, at a pressure of about 5000 atm, its crystallization would occur at room temperature. Indeed, at a pressure of 4000 atm the melting point of benzene, nitrobenzene, bromoform, and a number of other compounds is 80–90° higher than at atmospheric pressure. The main aim of the present work was to clarify the question of whether preliminary crystallization of butyraldehyde is necessary for its polymerization under high pressure.

Fig. 1

Figure 1: Fig. 1

Experimental Part

Purification of butyraldehyde. To the butyraldehyde were added 1-2 drops of conc. H_2SO_4, several pieces of ignited $CaCl_2$, and the mixture was allowed to stand until it had almost completely been converted into parabutyraldehyde, which was washed with water, dried over $CaCl_2$, and distilled in vacuo (b.p. 126-127°/24 mm, n_D^{20} 1.4261, mol. wt. 207; mol. wt. calculated for $(C_4H_8O)_3$, 216). The parabutyraldehyde was placed in a Favorskii flask, conc. H_2SO_4 was added (1 drop), and it was heated on a water bath in an atmosphere of nitrogen purified from oxygen by passage through pyrophoric copper heated to 200°, deposited on silica gel. The butyraldehyde distilling off under these conditions contained up to 2% water*. To remove the latter, butyr—

butyraldehyde was distilled on a column with glass packing of 15 theoretical plates, in a nitrogen atmosphere. After distillation of the azeotropic mixture with water (b.p. 68.0°; 10.1% water [7]), the butyraldehyde fraction was collected as an oily aldehyde with b.p. 74.7-74.8°/760 mm, n_D^{20} 1.3792-1.3793; according to the literature [7], b.p. 74.78°/760 mm, n_D^{20} 1.37915. In a number of experiments, before fractionation on the column the butyraldehyde was dried with Drierite [8,9].

Experimental procedure. To clarify whether preliminary crystallization of butyraldehyde is necessary for its polymerization under pressure, experiments were carried out in a multiplier equipped with two glass windows. The design of the multiplier (Fig. 1) is analogous to that described in [10]. Butyraldehyde was poured into the channel of the high-pressure block 5, with windows 6 and stopper 7. Then oil was fed by a pump into the low-pressure block 1, the force from piston 2 being transmitted through rod 3 to the "mushroom" 4, which, moving, compressed the butyraldehyde. The apparatus is designed for a pressure of 8000 kg/cm^2 at ordinary temperature. The pressure in the channel of the high-pressure block was determined by calculation from the multiplication coefficient (the correction for friction was taken as equal to 10% of the calculated pressure). During an experiment, an illuminator was attached to one of the windows of the multiplier, and to the other, for measuring the intensity of the transmitted light, a photocell connected to a mirror galvanometer.

Fig. 1

A series of experiments on the polymerization of butyraldehyde was carried out in an ordinary multiplier for 7000 kg/cm^2 with a working volume of $\sim$ 70 cm^3; the pressure was measured with a manometer for 10000 kg/cm^2. Butyraldehyde

* Determined approximately by titration in pyridine solution with Fischer reagent.

was loaded by means of a syringe into a lead ampoule with a narrow outlet, which was then squeezed shut and sealed, after which the ampoule was placed in the channel of the high-pressure block. The latter was filled with a mixture of glycerin and water (50%) and the necessary pressure was produced. Before loading, the ampoule and syringe were flushed with purified nitrogen. Up to 5 ampoules could be loaded into the multiplier at once. The solid polymer obtained was usually insoluble in acetone and alcohol; however, it dissolved somewhat in benzene, chloroform, and carbon tetrachloride. The amount of solid polymer formed was determined by weighing after washing with acetone and drying by blowing with air.

Results of the investigation. In [11] it was shown that butyraldehyde does not polymerize at 3000 atm. To determine the minimum pressure necessary for formation of a solid polymer, experiments were carried out in lead ampoules at higher pressures. It was found that polymerization does not proceed at 4200 kg/cm^2. Thus, in one of the experiments, in 19.5 hours and at the indicated pressure no noticeable quantities of polymer were formed. At 5200 kg/cm^2, a solid polymer formed in the same time in an amount of several percent. Raising the initial pressure to 6200-6300 kg/cm^2 usually led to formation of polymer in 40-80% yield in 17-20 hours. Addition of benzoyl peroxide significantly accelerated the process* at 6300 kg/cm^2; however, at a pressure of 4200 kg/cm^2 no solid polymer formed even in the presence of benzoyl peroxide. Thus, at 6300 kg/cm^2 in 2 hours without additives the yield of polymer was zero, whereas in the presence of 1.8% benzoyl peroxide it was 73%; at 4200 kg/cm^2 in the presence of 2 and 3.7% benzoyl peroxide, no appreciable amounts of polymer were obtained even after 67 h.

The data given above show that an increase in pressure by a comparatively small amount (from 4200 to 5200 kg/cm^2) causes the formation of a solid polymer. The question arises whether the polymerization of butyraldehyde is a consequence of crystallization and subsequent melting, analogous to the polymerization of acetaldehyde. However, our attempts to polymerize butyraldehyde by repeated freezing and thawing at atmospheric pressure did not lead to a positive result. A study of the dependence of the polymer yield on time at an initial pressure of 6300 kg/cm^2 also indicated that polymerization is hardly connected with the moment of melting of the crystals. Thus, in one of the experiments the polymer yield at 6300 kg/cm^2 after 2, 4, and 18 h was, respectively, 0, 2.5, and 34.3%.

The most convincing results were obtained in experiments carried out in a multiplier with windows. In the first experiment, pure butyraldehyde was charged into the multiplier and a pressure of about 7000 kg/cm^2 was created. During 17 h the intensity of the light passing through the substance in the apparatus did not change. On unloading it was found that 3.5% polymer had formed in the

* Initiation of the polymerization of butyraldehyde at 12000 atm by small amounts of oxygen and peroxides was first established in works [12,13].

lower part of the apparatus (near tube 7). The latter did not cover the windows of the apparatus; for this reason, and also because there was no crystallization of the aldehyde, the intensity of the transmitted light did not change during the experiment. In the second experiment, butyraldehyde containing 2.8% benzoyl peroxide was charged into the multiplier. During 2.5 h after the pressure was created (7000 kg/cm^2), no substantial change in the intensity of the light was observed. The next reading was taken after 17 h; in this case a sharp decrease in intensity was found; after the pressure had been lowered to the minimum (about 100 kg/cm^2), the intensity of the transmitted light remained just as low. A product containing 10 wt.% polymer (based on the charged butyraldehyde) was discharged from the apparatus. If crystallization of the aldehyde had occurred in this experiment, lowering the pressure would have led to its melting and, consequently, to an increase in the intensity of the transmitted light. Thus, when benzene was compressed in the multiplier, a strong decrease in the light intensity was observed at the moment of benzene crystallization under pressure. After the pressure was lowered, the intensity again increased to its original value. The experiments described above indicate that butyraldehyde is capable of polymerizing under pressure without preliminary crystallization.

In the course of our study, the influence of a number of additives on the polymerization of butyraldehyde, as well as on the depolymerization of its solid polymers, was investigated. The corresponding experimental data will be published separately. Here we shall note only the principal results obtained in this study. The addition to butyraldehyde of water in an amount of ~1.3%, and also of *n*-propyl alcohol (5%), leads to a sharp decrease in the yield of solid polymers.* Hydroquinone (1.5-3%) is an inhibitor of the reaction. Azoisobutyric acid dinitrile, in contrast to benzoyl peroxide, has no noticeable effect on the rate of polymerization under the conditions studied. The polymers obtained at a pressure of 6300 kg/cm^2 were solid plastic substances, unstable at atmospheric pressure. After hydroquinone or quinone is added to the polymer (in an amount of several percent by weight), it becomes more stable and can be stored at room temperature in the open air for several months.

Discussion of the results of the study. The data given above on the influence of additions of water and alcohol reveal a certain similarity to the corresponding data obtained in the polymerization of acetaldehyde at atmospheric pressure and low temperature. At the same time, our experiments have shown that, in contrast to acetaldehyde, butyraldehyde is capable of polymerizing with the formation of analogous polymers without preliminary crystallization. In this connection, the report on the possibility of polymerization of acetaldehyde on alumina at a temperature considerably exceeding its crystallization temperature deserves attention (^{14}). Of great inter-

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* The formation of the unstable liquid polymer described in (11) was due to an impurity of water in the monomer.

est is the fact that butyraldehyde does not polymerize at 4200 kg/cm^2, but can form solid polymers already at a pressure of about 5200 kg/cm^2, although under these conditions it does not crystallize. Possible reasons for this phenomenon will be considered below.

One of the most important factors responsible for the formation of solid polymers of butyraldehyde under pressure is the shift of equilibrium under the action of pressure. Indeed, at atmospheric pressure these polymers are unstable, whereas at a pressure of about 5000 kg/cm^2 they are formed in appreciable amounts. If one takes into account that during polymerization the decrease in volume per mole of the polymer formed is very large (because of the high molecular weight of the polymer), then it is easy to conclude that a comparatively small increase in pressure can lead to a very considerable shift in the equilibrium of the polymerization reaction. Thus, for example, at a degree of polymerization equal to 50 and with a decrease in volume at each step of polymerization (for example, in going from monomer to dimer) equal to 10 cm^3/mol, the equilibrium constant K_N, when the pressure is increased by only 1000 kg/cm^2, increases by 10^9 times; such an increase in K_N corresponds to an increase in the equilibrium concentration of polymer from 1 to 94 wt.%.

There arises, however, the question of why polymerization begins to proceed in the pressure region which, apparently, is close to the crystallization conditions of the aldehyde at room temperature. It is possible that the formation of solid polymers of butyraldehyde occurs under conditions where the arrangement of molecules in the liquid is to a considerable extent ordered, i.e., near the crystallization point (see ([15])). In this case one might expect a substantial decrease in the negative value of the entropy of activation, i.e., a significant increase in the reaction rate. Clarification of this question is the subject of our further investigation.

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