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1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

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The Influence of the Nature of the Initiator and the Phase State of Acetaldehyde on the Chemical Structure of Macromolecules Formed during Its Polymerization

Polymerization of monomers in the solid state is characterized by a number of kinetic features associated with the specificity of initiation and chain propagation in a solid body ([1,2]). Of no less interest is the clarification of the question of the influence of the nature of the initiator and the phase state of the monomer on the polymerization mechanism and on the structure of the products formed.

For this purpose, the most suitable objects of investigation may be monomers capable, in principle, of forming polymer chains of different chemical structure. One such monomer is acetaldehyde; as is known, in the liquid phase acetaldehyde can yield, depending on the catalyst chosen and the polymerization conditions, either polyacetaldehyde (both atactic and stereoregular) ([3,4,5]), or polyvinyl alcohol ([6]).

We investigated the polymerization of acetaldehyde initiated by metallic sodium and magnesium, in the crystalline and glassy states and during melting. Sodium and magnesium were chosen as initiators because, as had been established earlier, certain carbonyl-containing compounds in the solid state polymerize in the presence of these metals with cleavage of the C–O bond ([7,8]). At the same time, liquid acetaldehyde in the presence of sodium amalgam at low temperatures polymerizes with the formation of polyvinyl alcohol ([6]).

The starting substances were subjected to additional purification. Acetaldehyde of "pure" grade was dried for 24 hours over ignited magnesium sulfate; dissolved air was removed from it by repeated freezing and thawing in vacuum, and half of the amount taken was distilled into an ampoule with calcium hydride, in which the acetaldehyde was kept for 15 min. Then half of the amount of acetaldehyde contained in this ampoule was distilled into a clean ampoule, from which, after repeated freezing and thawing in vacuum, the acetaldehyde was distilled into ampoule 1 (Fig. 1). Acetaldehyde purified in this way did not polymerize spontaneously upon melting, which indicates its high degree of purity.

Metallic sodium was purified by repeated distillation in vacuum. Magnesium (in powder form) was not subjected to special purification. The frozen mixture

Fig. 1. Apparatus diagram

Figure 1: Fig. 1. Apparatus diagram

of acetaldehyde and initiator (Na or Mg) was obtained by joint condensation of the components in vacuum onto a cooled surface. In doing so, an improved procedure was used, described earlier in a number of papers ([2,8,9]).

The apparatus used for this purpose is shown in Fig. 1. The system was evacuated to a vacuum of 10^{-5} mm Hg, and, with stopcock 2 closed, gaseous acetaldehyde was fed by means of stopcock 3 from ampoule 1 into flask 4 up to the required pressure; the pressure was monitored with manometer 5. Then the surface of sphere 6 was cooled to the required temperature by means of liquid nitrogen or a cryostat, and, heating furnace 7 (into which the initiator was placed ···

Na or Mg) and, by opening stopcock 2, the initiator and acetaldehyde were simultaneously condensed onto the surface of bulb 6 for a specified time. The rate of acetaldehyde feed was regulated by the pressure in flask 4 and the diameter of capillary tube 8, and the rate of evaporation of the initiator by the voltage on the winding of furnace 7. The temperature of the condensate layer was recorded with a thin ribbon thermocouple (9) (15 μ thick) and recorded by means of a high-sensitivity EPP-09 electronic potentiometer.

Fig. 1. Apparatus diagram

It had been established beforehand that, when acetaldehyde is condensed in the absence of an initiator onto a surface cooled to −196°, a transparent vitrified layer of acetaldehyde is formed. As is seen from Fig. 2, which shows the thermogram for heating this layer (curve 1), on heating the acetaldehyde begins to crystallize at a temperature of about −160°, and crystallization continues up to the melting point of acetaldehyde. When acetaldehyde is condensed onto a surface cooled to −150°, a layer of crystalline acetaldehyde is formed. In the thermogram of the condensate layer obtained under these conditions (Fig. 2, curve 2), there is no rise associated with the release of heat of crystallization.

Polymerization of crystalline acetaldehyde, obtained by joint condensation of acetaldehyde and initiator (Na or Mg) on the surface of bulb 6 cooled to −150°, was carried out in such a way that the acetaldehyde layer was not heated above the melting point. For this purpose the crystalline acetaldehyde containing active centers (which may be formed from acetaldehyde and Na or Mg in the gas [(8)] or solid phases) was heated to −130° and held at this temperature for 10 min. Then liquid nitrogen was poured into bulb 6, the apparatus was opened, and the reaction mixture cooled to −196° was rapidly transferred into warm water. The water-insoluble polymer was washed with water and dried. With this method of carrying out the polymerization and isolating the polymer, the yield was about 30% at a monomer-metal ratio of about 100 : 1 (by weight). The IR spectrum of the polymer is shown in Fig. 3a; as is seen from the figure,

Fig. 2. Thermograms of acetaldehyde: 1 –glassy, 2 –crystalline

Figure 2: Fig. 2. Thermograms of acetaldehyde: 1 –glassy, 2 –crystalline

Fig. 3. Infrared spectra of polymers

Figure 3: Fig. 3. Infrared spectra of polymers

the spectrum exactly coincides with the spectrum of polyacetalde-

Fig. 2. Thermograms of acetaldehyde: 1 –glassy, 2 –crystalline

hydes ([3], [4]). However, in contrast to the polymer obtained in the polymerization of acetaldehyde in the crystalline state under the action of high-energy radiation ([10]), the polyacetaldehyde obtained by us is insoluble in methanol and acetone and gives an X-ray pattern characteristic of stereoregular crystalline polymers (Fig. 4, see insert, p. 672).

Glassy acetaldehyde, obtained by the joint condensation of acetaldehyde and the initiator onto a surface cooled to −196°, and containing 5-10% Na or Mg, does not crystallize up to a temperature of −123.5° (i.e., the melting point of acetaldehyde). Holding such a vitrified layer at −130° for 10 min does not lead to the formation of polymer; upon heating above −123.5°, a polymer is formed, apparently polyvinyl alcohol, which dissolves in water, is precipitated from water by acetone, and rapidly darkens on heating owing to the partial occurrence of a dehydration reaction, which agrees with the data of Japanese investigators ([6]). However, as is evident from Fig. 3b, the IR spectrum of this polymer lacks a number of absorption bands characteristic of the IR spectrum of polyvinyl alcohol obtained by hydrolysis of polyvinyl acetate ([11]). This may be due to the fact that the latter contains a certain amount of unhydrolyzed acetate groups.

If glassy acetaldehyde contains little initiator (from 0.1 to 1%), then at temperatures of −150 to −130° it begins to crystallize; holding such a crystallized layer at −130° for 10 min forms polyacetaldehyde. These data apparently indicate that the crystal lattice of acetaldehyde favors the growth of polymer chains, whereas in the glass their growth is hindered.

Fig. 3. Infrared spectra of polymers. Top: **I**–polyacetaldehyde obtained in the solid state in the presence of magnesium or sodium; **II**, **III**–the same, according to data ([3], [4]); **I**–polyvinyl alcohol obtained upon melting acetaldehyde in the presence of sodium; **II**–polyvinyl alcohol obtained from polyvinyl acetate ([11]).

Thus, we were able to show that the polymerization of acetaldehyde in the liquid and crystalline states in the presence of one and the same

To the article by N. M. Papisov, T. A. Pisarenko, A. A. Panasenko,
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Fig. 4. X-ray diffraction pattern of polyacetaldehyde obtained in the polymerization of acetaldehyde in the solid state in the presence of magnesium

To the article by A. A. Bronstein, p. 715

Fig. 1. Hairs of olfactory cells on the surface of the olfactory lining of a frog. Phase contrast

of the initiator proceeds with the formation of polymers of entirely different structure (a similar result was obtained in the polymerization of diketene ([12])). The data indicating that glassy acetaldehyde does not polymerize at an appreciable rate in the presence of initiators that polymerize this monomer in the crystalline state are consistent with the data on the role of defects in acetaldehyde crystals in its polymerization ([10]).

Another important result, in our view, is the formation of stereoregular crystallizing polyacetaldehyde during the polymerization of crystalline acetaldehyde in the presence of sodium and magnesium. As is known, when ionizing radiation acts on crystalline acetaldehyde, an atactic amorphous polymer is formed ([10]). This difference is unlikely to be due to the amorphizing action of high-energy radiation, since atactic polyacetaldehyde is also formed during post-polymerization. The different structure of the polymer chains formed in crystalline acetaldehyde under different methods of initiation is apparently associated with different mechanisms of polymerization.

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Received
31 I 1964

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