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POLYCONDENSATION OF ACETALDEHYDE ON DEHYDRATING SILICIC ACID GEL

(Presented by Academician V. A. Kargin, May 5, 1962)

In the works of V. A. Kargin and co-workers ([1,2]) it was shown that ordering of monomer molecules as a result of complex formation or by some other means makes it possible to carry out the polymerization (polycondensation) of a number of monomers, whereas at the same temperatures and pressures under ordinary conditions polymerization proves impossible for thermodynamic reasons ([3–5]). Ordering of monomer molecules apparently should also occur upon their adsorption on various surfaces. If the adsorbent is at the same time a dehydration catalyst, then on such a surface one may expect polycondensation reactions to proceed with the liberation of water.

In studying the dehydration of silicic acid gels in an atmosphere of acetaldehyde vapors, we found that, under conditions of continuous removal of water vapor from silica gel on its surface, even at room temperature, a polycondensation reaction of acetaldehyde takes place. Polycondensation was carried out by drying silicic acid hydrogels, washed free of salts with distilled or acidified (pH 4) water, in acetaldehyde vapors, in a desiccator over calcined $CaCl_2$. The initially colorless hydrogels acquired toward the end of drying a coloration that gradually changed from yellow through brown to black. Control gels, which were dehydrated under the same conditions and in the absence of aldehyde vapors, remained colorless.

Apparently, under conditions of continuous removal of water vapor on the surface of silica gel, the reaction proceeds

$$(n+1)\left[CH_3-C\begin{matrix}=O\\ \backslash H\end{matrix}\right] \xrightarrow{-n\,H_2O} CH_3-[-CH=CH-]_n-C\begin{matrix}=O\\ \backslash H\end{matrix}$$

Attempts to remove the reaction product from the pores of silica gel with ordinary organic solvents proved unsuccessful. Therefore, in order to extract the polycondensation product, we had to dissolve the silica gel in a 1 N NaOH solution, which, after dissolution of the silica, acquired a reddish-brown color corresponding to the coloration of the organic polymer that had passed into solution. This polymer was readily extracted from the resulting alkaline solution

Fig. 1. IR spectra of the products of acetaldehyde polycondensation: a – before heating the silica gel with polymer; b –after heating the silica gel in air; c –after heating in air the polymer isolated from the pores of silica gel

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with benzene and, after evaporation of the latter, was a viscous reddish-brown substance soluble in ordinary organic solvents.

We believe that in this case acetaldehyde is converted into partially oxidized polyene aldehydes with similar molecular weights. To test the proposed structure of the polycondensation products, we recorded the infrared absorption spectra of polymer films deposited on a NaCl plate (Fig. 1a)*. The band in the region 1600-1630 cm^{-1} is assigned to the absorption of conjugated C=C bonds, and the band at 1680-1720 cm^{-1} is due to absorption by C=O groups conjugated with double bonds. In addition

* The infrared spectra were recorded on a UR-10 spectrometer.

as in work ([6]), in the region 1000-1300 cm^{-1} an increase in the general background is observed.

Heating silica gel with polymer in the pores for 2 h at 120° and for a further 1 h at 150° in air leads to the result that the transformation product of acetaldehyde (after dissolving the silica gel in alkali) acquires a dark-brown color, is insoluble in benzene and CCl_4, and dissolves only partially in acetone. This can be explained by further polycondensation during heating, leading to cross-linking of polymer molecules. In the IR spectrum of this polymer (Fig. 1b) there is a shift toward lower frequencies and an increase in the absorption intensity of the band belonging to conjugated C=C bonds, which indicates an increase in the conjugation chain ([7]). Similar treatment of the polymer extracted from the gel without preliminary heating of the latter leads to disappearance of the band corresponding to conjugated C=C bonds (Fig. 1c), which may be caused by oxidation and reactions of the diene-synthesis type.

Fig. 1. IR spectra of the products of acetaldehyde polycondensation:
a –before heating the silica gel with polymer;
b –after heating the silica gel in air;
c –after heating in air the polymer isolated from the pores of silica gel.

Independent confirmation of the proposed scheme is provided by the results of investigating this system by the EPR method.* Immediately after carrying out polycondensation at room temperature, the samples do not give an EPR signal, but heating them for several minutes in air at 100-150° causes the appearance of an EPR spectrum characteristic of polyconjugated systems, in the form of a symmetric singlet with a line width of 10 Oe. Upon further heating of the

Fig. 2 and Fig. 3: graphs

Figure 2: Fig. 2 and Fig. 3: graphs

sample, a decrease in signal intensity is observed up to 200°, at which the signal is practically not observed (Fig. 2, 1). The change in signal intensity upon cooling and in subsequent heating-cooling cycles is represented by curves 2 and 3 in Fig. 2.**

At the same time, the temperature dependence of the signal intensity for the polymer isolated from the preliminarily heated gel has a different form (Fig. 2, 4, 5). The polymer extracted from unheated gel gives a very weak signal (at the noise level of the instrument), which agrees with the low intensity in the IR spectrum of the band of conjugated C=C bonds (Fig. 1a).

The appearance of an EPR signal upon the initial heating of the sample and the increase in its maximum intensity in each subsequent cycle may be connected with more deeply proceeding polycondensation processes, leading to the formation of a longer system of conjugated C=C bonds. The sharp change in intensity in the interval 75-150° can be explained if it is assumed that the polyenes obtained form with the surface of the silica gel a donor-acceptor complex, which is destroyed upon heating and restored upon cooling. The formation of such a complex in the present case is apparently connected with the acceptor properties of the silicon atom, determined by its vacant $3d$ orbitals. Such a reversible surface complex is probably analogous to the known molecular complexes of polynuclear aromatic hydrocarbons with such acceptors as I_2, Br_2, chloranil, etc. ([8–10]); these complexes also

* The spectra were recorded on an RE-1301 instrument.
** When the sample was heated, the width of the absorption line did not change.

give EPR spectra in the form of narrow singlets and are reversibly destroyed upon heating (8).

Thus, under conditions of constant removal of water vapor, silica gel is a powerful dehydration catalyst, on whose surface, even at room temperature, a polycondensation reaction of acetaldehyde takes place, leading to the formation of a polymer with a chain of conjugated C=C bonds. The fact that polycondensation evidently proceeds in the adsorption

Fig. 2. Change in the intensity of the EPR signal as a function of temperature: *a*—for the isolated polymer, *b*—for the polymer in the pores of silica gel.

Fig. 3. Sorption isotherms of methanol vapor (1) and water vapor (2) on silica gel containing polymer; methanol vapor (3) on a control sample (black points—desorption).

layer in the pores of the gel is also confirmed by methanol and water vapor adsorption isotherms, recorded by us on a McBain balance at 20° for silica gels

with polymer present in their pores. From Fig. 3 it is seen that the total porosity of such a sample, in comparison with the porosity of the control gel, decreases only by approximately a factor of 2, i.e., complete overgrowth of the pores by the organic polymer does not occur. It should be noted that during adsorption of water vapor, significant chemisorption of water is observed (Fig. 3).

It may also be assumed that, along with adsorption, some polymer molecules become grafted to the surface of the silica gel, since in the course of drying and substantial shrinkage of the gel, rupture of intermicellar siloxane bonds in it is inevitable by a radical mechanism, with formation of macroradicals $\equiv Si{-}O\cdot$ and $\equiv Si\cdot$; in this case, some of the polymer molecules may become grafted to such macroradicals of the gel surface.

Silica gels with analogous properties are also formed in the case of hydrogels washed with acidified (pH 4) water and dried over calcined $CaCl_2$ in vinyl acetate vapors. It follows from this that in the initial stage vinyl acetate undergoes hydrolysis with formation of acetic acid and acetaldehyde, while the latter under these conditions is converted into polyene aldehydes by the mechanism described above.

It seems probable that silica gels containing in their pores polymers with a chain of conjugated bonds may be used as active fillers, at the same time possessing the properties of acceptors of free radicals, since it is known that polymers with a chain of conjugated bonds are inhibitors of radical reactions (11).

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REFERENCES

1. V. A. Kargin, V. A. Kabanov, International Symposium on Macromolecular Chemistry, Section 2, Moscow, 1960, p. 453.

2. V. A. Kargin, V. A. Kabanov et al., *Vysokomolek. soed.*, 3, 426 (1961).

3. V. A. Kargin, V. A. Kabanov et al., *DAN*, 134, 1098 (1960).

4. V. A. Kargin, V. A. Kabanov et al., *DAN*, 139, No. 3 (1961).

5. V. A. Kargin, V. A. Kabanov et al., *DAN*, 140, No. 1 (1961).

6. N. A. Slovokhotova, I. V. Astaf' ev, *Vysokomolek. soed.*, 3, 1607 (1961).

7. E. R. Blout, M. Fields, R. Karplus, *J. Am. Chem. Soc.*, 70, 194 (1948).

8. A. Szent-Gyorgyi, J. Isenberg, S. L. Baird, Jr., *Proc. Natl. Acad. Sci.*, 144 (1960).

9. David R. Kearus, M. Calvin, *J. Am. Chem. Soc.*, 83, 2110 (1961).

10. B. Smallier, *Nature*, 191, No. 4784, 168 (1961).

11. A. A. Berlin, *Chemistry and Technology of Polymers*, No. 7–8, 139 (1960).

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