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Abstract

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POLYMERIZATION OF ACETONE

It is known that the transition liquid monomer—polymer is accompanied by a decrease in the entropy of the system. Therefore, from the most general thermodynamic considerations it follows that, in a homogeneous liquid phase, polymerization can occur only with a positive thermal effect (Q). Indeed,

$$\Delta Z = \Delta H - T \Delta S,$$

where ΔZ is the change in the isobaric isothermal potential in the transition monomer—polymer, $\Delta H = -Q$ is the change in heat content, ΔS is the change in entropy of the system, and T is the absolute temperature. For the process to proceed spontaneously it is necessary that the inequality $\Delta Z < 0$ be satisfied, which, when $\Delta S < 0$, is possible only if $\Delta H < 0$ and $|\Delta H| > |T\Delta S|$, i.e., $Q > 0$. The thermal effect of the reaction may be determined as the algebraic sum of the energies of the bonds broken as a result of the reaction and of the bonds newly formed, the values of the former being taken with a minus sign and of the latter with a plus sign.

If the thermal effect of polymerization of carbonyl compounds—for example, acetaldehyde or acetone—is estimated by taking as the energy of the C—O bond in the polymer the average energy of the C—O bond in simple ethers, we find that the thermal effect of polymerization of acetone is −6 kcal/mol, and that of acetaldehyde is zero (the energy of the C=O bond in acetone is 156 kcal/mol, in acetaldehyde 150 kcal/mol, and the average energy of the C—O bond in simple ethers is 75 kcal/mol). Thus, on the basis of this approximate estimate, one may conclude that polymerization of acetaldehyde and acetone in a homogeneous liquid phase is impossible. However, if in the initial state the transition from the monomeric liquid to a system of ordered monomer molecules is effected, i.e., if the entropy of the initial system is decreased, the picture may change substantially. One of the ways of mutually ordering monomer molecules is to freeze it. The transition from a liquid monomer to a crystalline one is accompanied by a decrease in the entropy of the system by the amount of the entropy of fusion. For organic liquids the entropy of fusion usually lies in the range 13 ± 3 cal/deg · mol (^{1}), which apparently is comparable with the change in entropy in the transition liquid monomer—amorphous polymer. A decrease in the entropy of the initial system leads to a decrease in the negative value of the entropy of polymerization. At sufficiently low temperatures the latter may even change sign. In this case polymerization accompanied by a negative thermal effect will become possible. Thus, in some cases the phase state of the monomer in the system should exert a decisive influence on the ability of this monomer to polymerize, as determined by the thermodynamic parameters of the initial and final systems. For example, it is well known that acetaldehyde, which at ordinary pressures is incapable of polymerizing in the liquid phase, readily polymerizes in the solid state near the melting temperature ([2–4]).

Guided by these considerations, we attempted to carry out the polymerization of acetone at the C=O double bond, using the method we developed for low-temperature polymerization in systems obtained by the simultaneous condensation of molecular beams of monomer and initiator onto a strongly cooled wall ([5–7]).

The experiments were carried out in an apparatus and by a procedure analogous to those described in works [5,6]. Metallic magnesium was used as the initiator; its vapors were slowly condensed in vacuum together with vapors of thoroughly dried acetone onto a surface cooled with liquid nitrogen. The acetone:magnesium ratio during condensation was approximately $200:1$. Under these conditions, a layer of condensate was deposited on the cooled wall in the form of a vitrified molecular mixture of acetone and magnesium. As the layer thickens, the distance between its outer, continuously renewed surface and the cooled wall increases. Because of this, the temperature of the outer surface of the vitrified condensate rises continuously and, finally, reaches a value at which a spontaneous process of concerted rearrangements of the monomer molecules begins in the surface layer. In the absence of initiation centers in the system, this process should have led to crystallization of the monomeric glass. In the present case, however, the mobility of the particles arising during the disorder-order phase transition is realized in their instantaneous polymerization. The same phenomenon can be observed when the temperature of the wall on which condensation is carried out is gradually raised. In other words, at the moment when the phase transition in the solid phase takes place, conditions are created that kinetically favor the joining of ordering monomer molecules into polymer chains*. As a result, a polymer of acetone is formed, representing an elastic white mass. The polymer is soluble in its own monomer. At room temperature, polyacetone is very unstable and decomposes with formation of acetone. A sample of polyacetone, when rubbed in the hands, rapidly turns into a drop of monomer. The most stable polymer samples in the absence of oxygen and moisture "live" no more than 10-12 hours. Somewhat more stable was the polymer obtained by condensation of acetone together with traces of vinyl acetate. The ways of stabilizing polyacetone apparently should be sought in blocking the active ends of the polymer chains.

The apparatus for condensation of molecular beams was connected to a viscometer. The design of the apparatus made it possible to prepare solutions of the polymer obtained and to measure the viscosity of these solutions directly in vacuum, without access of moisture and oxygen from the air. The specific viscosity of a solution of polyacetone in acetone, measured in this way in one of the experiments, proved to be 0.6 (at a solution concentration of 0.5 g/100 ml).

Using acetone as an example, this work has shown that, by employing the principle of preliminary ordering of monomer molecules in the reaction system, it is possible to carry out the polymerization of substances that are incapable of polymerizing under ordinary conditions. In the present case, such ordering was achieved through crystallization of the monomer. Conditions kinetically favorable for the formation of polymer chains from ordered monomer molecules arise at the moment when a disorder–order type phase transition takes place in the vitrified monomer.

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* Qualitative considerations concerning the mechanism of formation of a polymer chain in an ordered system of monomer molecules were recently expressed by Semenov [8].

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

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