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Abstract

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ON THE ROLE OF PHASE TRANSITIONS IN THE POLYMERIZATION PROCESSES OF MONOMERS IN THE SOLID STATE

From a number of works published in recent years it follows that polymerization reactions of monomers in the solid state can be divided into two groups: fast (in the limiting case, explosive) ($^{1-6}$) and slow ($^{7-9}$). Explosive polymerization reactions are initiated both by chemical methods (with simultaneous condensation of vapors of monomers and various initiators onto a deeply cooled wall ($^{1-4,6}$)) and by the action of high-energy radiation (^{5}). Therefore it may be assumed that the explosive character of the process is connected not so much with the nature of the particles causing polymerization as with the special conditions arising in a system of ordered monomer molecules.

From the data available in the literature it follows that the slow polymerization of crystalline monomers proceeds at considerably lower rates and is characterized by considerably higher activation energies for the chain-growth reaction than the polymerization of these same monomers in the liquid phase (in the case of acrylamide, for example, 25 kcal/mole in the solid phase, instead of 7-10 kcal/mole in the liquid (^{9})). At the same time, the very fact that rapid polymerization occurs at very low temperature compels one to suppose that, under certain conditions, the formation of polymer chains in the solid phase can take place with very small, practically zero, activation works. It has been possible to show that explosive polymerization of a number of monomers (acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methyl methacrylate, etc. (^{3,4,6})) can be induced at temperatures considerably lower than the temperatures at which slow polymerization of their irradiated crystals has repeatedly been observed.

To elucidate the mechanism of rapid polymerization in the solid phase, we studied the conditions for carrying out explosive polymerization in frozen molecular mixtures of monomers and active particles, using as examples the systems acrylonitrile (m.p. −83°)—magnesium and methyl methacrylate (m.p. −50°)—magnesium, applying for this purpose the method of thermal analysis and observation of frozen molecular mixtures in polarized light. To obtain molecular mixtures we used a modified version of an apparatus described earlier (^{1,4}) (Fig.

Fig. 1

Figure 1: Fig. 1

1). The joint vacuum condensation of the vapors of the monomer and the metal was carried out on a glass plate 1, ground to the end of a copper cylinder 2, which was cooled with liquid nitrogen. The temperature change in the condensate layer was recorded with the aid of a thin (0.1 mm) copper-constantan thermocouple 3, one of whose junctions was located directly on the surface of the glass plate, and the other in the body of the cooled cylinder. The readings of the differential thermocouple were recorded with a sensitive electronic potentiometer EPP-09. To carry out measurements, a thin (0.03 mm) layer of the molecular mixture of monomer and initiator, in a ratio of approximately 100 : 1, was slowly deposited on the surface of the glass plate. Condensation was carried out

at such a rate that the temperature in the layer did not rise above −160°. After condensation was complete, the condensate layer was a vitrified homogeneous transparent film containing, according to (2), magnesium-organic radicals "trapped" in the monomeric glass. Next, the liquid nitrogen was removed from the copper cylinder, after which the cylinder was slowly heated (at a rate of 2 deg/min). The temperature of the cylinder was measured with a copper-constantan thermocouple 4, one junction of which was placed in the body of the cylinder and the other in liquid nitrogen. Characteristic thermograms are presented in Fig. 2. It is seen that explosive polymerization, accompanied by considerable heat evolution, occurs either at −160° (curve 1) or at −135° (curve 2). The degree of conversion in this case reaches 100%.

Fig. 1. Schematic of the apparatus (left—general view; right—cooled cylinder with thermocouples)

Thermograms of a condensate containing no active centers, obtained under analogous conditions, show that at these temperatures two exothermic transitions occur in frozen acrylonitrile (curve 3). The first transition can be observed visually by the turbidity of the transparent condensate layer. It is associated with crystallization of the monomeric glass upon reaching the Tammann temperature. The nature of the second transition is less clear. It is probably associated with additional ordering processes in the microcrystalline mass formed as a result of the first transition. Both transitions are irreversible and are not reproduced upon repeated cooling and heating of the condensate *.

Thus, the experiments described show that rapid polymerization of acrylonitrile at temperatures far below the melting point is closely connected with the mobility of molecules that occurs during phase transitions in solids—in the present case, with the glass-crystal transition.

Such a transition is always "held in reserve" if the monomer is in a glassy state. This condition is fulfilled when vapors are condensed on a surface cooled to a

Figure 2

Figure 2: Figure 2

temperature at which the monomer molecules undergo inelastic collisions with the surface.

It should be noted that, for explosive polymerization to occur, it is not necessary for the entire volume of solid monomer to attain the temperature at which molecular mobility arises. It is often sufficient to heat, for example, only the surface layer. In this case the heat released during its polymerization heats the subsequent layers, and the process proceeds like a thermal explosion. Analogous phenomena are observed upon thickening layers (the appearance of a temperature gradient) of molecular mixtures of monomers and initiators during condensation on a surface cooled to the temperature of liquid nitrogen.

If the surface on which condensation is carried out is at a higher temperature, then the condensing molecules and radicals have— can migrate over the surface, accommodating themselves to the crystallization nuclei that arise. In this case, instead of a homogeneous amorphous layer, in individual areas of the surface there form intergrowths of well-formed crystals possessing characteristic birefringence. We observed this phenomenon during the vacuum condensation of methyl methacrylate and magnesium vapors onto a glass sphere cooled to −75°, in the apparatus described earlier ([1], [4]). Fig. 3a (p. 346) presents a typical photograph of a radial intergrowth of methyl methacrylate crystals (a spherulite) on the surface of the sphere, taken in polarized light. The characteristic Maltese cross is clearly visible. Polymerization in such a system at −75° proceeds very slowly and is accelerated upon gradual raising of the temperature. The polymerization process can be observed in polarized light by the disappearance of birefringence.

Fig. 2. Thermograms of molecular mixtures of acrylonitrile—magnesium (1, 2) and of pure acrylonitrile (3). T is the temperature of the copper cylinder; ΔT is the temperature difference between the copper cylinder and the condensate.

Examining the surface of the sphere in crossed polarizers with the aid of a long-focus microscope, we convinced ourselves that polymer formation begins at the edges of the spherulites, at the boundaries between individual crystallites and at the sites of cracks. Subsequently the reaction proceeds all the time under heterogeneous conditions at the crystal—polymer boundary. The displacement of this boundary up to the completion of polymerization is clearly observed in polarized light. In Fig. 3b a portion of a spherulite is seen in which polymerization has already taken place (the birefringence has disappeared), and the

* The question of why, in some experiments, polymerization occurs at the first transition and, in others, at the second transition requires additional investigation.

boundary separating this portion from the still unpolymerized one (which possesses birefringence). When the temperature of the sphere surface is raised at a rate of 0.3 deg/min, polymerization is fully completed 3-4° below the melting temperature of methyl methacrylate. The birefringence then completely disappears. Fig. 3c presents a photograph of the very same spherulite as in Fig. 3a, after polymerization in it has completely taken place. The photograph was taken with the polarizers removed. The intergrowth of monomer crystals has turned into an isotropic piece of polymethyl methacrylate that has retained its initial shape with a considerably increased number of cracks.

Thus, using the optical method, we were able to observe a typical picture of "slow" polymerization in the crystalline state, entirely analogous to that observed by Adler et al. ([10]) upon irradiation of acrylamide crystals. It should be emphasized that the joint condensation of methyl methacrylate and magnesium vapors onto a surface cooled with liquid nitrogen, accompanied by the formation of an amorphous layer, leads to explosive polymerization at considerably lower temperatures. In discussing the question of polymerization in the solid phase, N. N. Semenov ([11]) proposed that, owing to the collectivization of electronic levels in a region where the crystal is ideal, the formation of a polymer chain from an ordered molecular template occurs in a single reaction act and does not require activation energy. A concrete scheme for the formation of a polymer chain in an ideal monomer crystal with participation of an exciton has recently been dis-

considered by E. I. Adirovich ([12]). N. N. Semenov' s hypothesis appears very attractive, since it makes it possible to explain the rapid low-temperature polymerization of solid monomers. However, consideration of the experimental data on the polymerization of crystalline monomers shows that in equilibrium ("ideal") crystals of monomers, far from the melting temperature, high conversion rates are usually not observed. They are characterized by "slow" polymerization. Moreover, the polymerization process is accelerated precisely under conditions in which the crystals become defective (for example, upon quenching of melts ([9]) or near the melting temperature).

In all probability, rapid low-temperature polymerization reactions in the solid phase can occur only when the ordering of the reacting molecules is combined with their sufficient mobility. The point is that the formation of a polymer chain in an ideal crystal must immediately lead to the appearance of a defect owing to a change in interatomic distances. As the chain lengthens, the defect will increase, which will inevitably lead to cessation of chain growth and to "freezing" of the active center. For this active center to be reintroduced into the reaction and for the given chain to continue, a local thermal rearrangement of the crystal ("healing of the defect") is necessary, i.e., relaxation of the stress caused by irreversible displacement of the molecules that have entered into the reaction. The observed high activation energies of the chain-growth reaction (especially in post-polymerization) are probably associated precisely with these rearrangements, which limit the rate of polymerization. Such rearrangements take place most readily on the surfaces of crystals or at the sites of cracks and dislocations. Therefore the polymerization of crystalline monomers begins precisely at these sites and proceeds mainly at the crystal-polymer interface ([10]). Factors that facilitate regrouping of monomer molecules at the interface, for example adsorption layers of solvents ([9],[13],[14]), lead to a noticeable acceleration of polymerization.

The situation is different if conditions are created in the solid monomer that ensure rapid migration of defects (their formation and "healing"). In this case the principal limitation on the instantaneous, activationless (according to Semenov) sprouting of chains in an ordered solid phase is removed. Such conditions may arise in a solid, for example, during phase transitions or near the melting point. If the concentration of active centers in the frozen monomer is sufficiently high, then the sudden appearance of molecular mobility, in combination with the ordering that is still preserved, leads to practically instantaneous polymerization.

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