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Abstract

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ON THE QUANTUM THEORY OF RAPID LOW-TEMPERATURE POLYMERIZATION

(Presented by Academician V. A. Kargin on 8 IV 1963)

Polymerization of solid monomers at temperatures of 100°K, proceeding rapidly near phase transitions, is one of the very interesting phenomena in polymer chemistry, the intensive study of which began in recent years ($^{1-3}$). Low-temperature polymerization in the solid phase has the following features: 1) the rate of polymerization in the solid phase is often considerably higher than in the liquid phase* (the rate constant does not obey the Arrhenius law); 2) the experimentally observed activation energy in a number of cases is very small or even negative (^{3,4}); 3) at the temperatures of phase transitions a jump-like increase in the rate of polymerization is observed, and polymerization proceeds at the rate of the phase transition (rapid low-temperature polymerization (R.L.P.) (^{1})); 4) under some conditions, for example under radiation** and mechanical (^{4}) destruction, spontaneous depolymerization is possible. These features led N. N. Semenov (^{2}) to the conclusion that R.L.P. does not fit within the framework of generally accepted ideas about radical, stepwise, and other types of polymerization. For a qualitative explanation of R.L.P., N. N. Semenov proposed a hypothesis according to which R.L.P. is due to the collective interaction of the particles responsible for polymerization (^{2}). In the works of V. A. Kargin and co-workers (^{1}), along with collective interaction, the necessity of phase transitions for the occurrence of the R.L.P. process was emphasized—that is, increased mobility of monomer molecules (realized, for example, near or at the points of phase transitions). In the present note we give the formulation of the problem and the principal conclusions of the quantum theory of R.L.P. due to collective interaction***.

1. Let us consider the process of R.L.P. in a monomeric "preform" (according to N. N. Semenov), located in a monomer crystal consisting of N^1 such preforms, and containing a number of monomers sufficiently large for the legitimate application of quantum statistics. Let the polymerization process be carried out by certain quasiparticles**** (with $\alpha \lesseqgtr 1$ quasiparticles per monomer), interacting with one another. Since the "preform" can be in two states—monomeric and polymeric—each of the quasiparticles responsible for polymerization can likewise be in two states, characterized by different values of the physical parameters (for example, energy, etc.) that

determine these states. We shall call these states "promoting polymerization" and "promoting depolymerization" (or polymerization and depolymer –

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* Although other cases are also known.
** Private communication of N. S. Enikolopyan.
*** A work (^{5}) is devoted to questions of the quantum theory of R.L.P.; the collective character of biopolymer polymerization was indicated in (^{6}).
**** By quasiparticles in what follows we shall understand radical (or conjugated-bond, etc.) electrons, ions, etc.; in other words, any particles responsible for the R.L.P. process, since for the qualitative conclusions of the theory the specific nature of the quasiparticles (different, perhaps, for chemically different monomers) is not essential.

···rization states). Both the polymerization and the depolymerization states of quasiparticles are a consequence of the collective interaction of the electrons and ions of the sample and are determined by a set of quantum parameters that we are not yet able to determine. The task of the theory is to determine the relative number of quasiparticles that are in the polymerization and depolymerization states (N_1 and N_2, respectively) as functions of the physical parameters of the sample; and this problem can be solved without an extensive detailing of the nature of the polymerization and depolymerization states of the quasiparticles. If $N_1 > N_2$, then the sample polymerizes; if $N_1 \ll N_2$, then the sample will be in the monomeric state.

Between quasiparticles that are in the polymerization and depolymerization states, owing to the presence of interaction, there will exist exchange "polymerization" forces due to the overlap of the wave functions of the quasiparticles (an analogue of a homeopolar bond)*. Apparently, these exchange forces are due to both the direct and indirect interaction of the quasiparticles (through quasiparticles belonging to the conduction band of the sample, intermediate atoms, etc.). Such exchange forces will decrease with distance according to a power law and may lead to the formation of "resonance structures" for quasiparticles (according to Pauling (^{7})) between monomers. It is convenient, from the formal point of view, to introduce for the description of the establishment of these structures, or for the description of the two states of quasiparticles, the concept of a "polymerization spin," which in an external force field takes two values—polymerization and depolymerization**. Then a quasiparticle that is in the polymerization state will have the "polymerization" value of this spin, while a quasiparticle that is in the depolymerization state will have the "depolymerization" value. The energy of a quasiparticle will depend on the state of the polymerization spin, and the process of fast low-temperature polymerization may be regarded as a process of ordering of the polymerization spin.

On the basis of what has been said, the physical model of fast low-temperature polymerization consists in the following: exchange interaction (direct and indirect) between quasiparticles responsible for polymerization, each of which may be in two states (polymerization and depolymerization), leads to an ordering of the quasiparticles according to these states, dependent on temperature and on other physical parameters of the sample. This ordering may be described either in terms of Pauling resonance or in terms of polymerization spin.

2. The mathematical description of the above model of fast low-temperature polymerization can without difficulty be carried out within the framework of the known methods of quantum field theory (^{8}). For this purpose, let us introduce operator two-component wave functions

$$\psi = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \quad \text{and} \quad \psi^+ = (\psi_1\psi_2),$$

describing the absorption and creation of quasiparticles in the polymerization ψ_1, ψ_1^+ and depolymerization ψ_2, ψ_2^+ states, and write for them equations of motion, choosing one or another model Hamiltonian to describe the behavior of the quasiparticles. It is then not difficult, following (^{9}), to find equations for the mean values $\langle\psi_\alpha^+\psi_\alpha\rangle(\alpha = 1, 2)$ (the averaging is performed both over the quantum-mechanical and over the statistical ensemble), and, both for the stationary and for the nonstationary case, to find, for the cases of two "limiting" models of quasiparticle behavior (the model of delocalized quasiparticles belonging at once to the whole sample, and the model of quasiparticles localized on monomers and forming a monomer lattice), the dependence of the degree of conversion

$$\frac{N_1 - N_2}{N} \quad (N = N_1 + N_2)$$

on the tem-

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* These exchange forces have nothing in common with magnetic exchange forces: the nature of the two states (polymerization and depolymerization) is not connected with ordinary spin, but is determined by a set of quantum parameters.

** For a three-level model the polymerization spin must be "integer."

temperature, the exchange energy of the quasiparticles, and other parameters of the specimen. The qualitative conclusions of these models coincide; however, for lack of space we do not give here the mathematical side of the description of these models.*

We present the principal results of the calculations (using Fermi statistics for the nonlocalized model, and Bose statistics for the localized model):

1. Along with the known types of polymerization (chain, stepwise, etc.), at temperatures below the "critical" temperature θ, which is a function of

the exchange polymerization energy, l.t.p. may occur, caused by collective interaction. L.t.p. is possible (for $T < \theta$) only under the condition that a sufficiently large number of quasiparticles responsible for polymerization exist in the specimen, $N > N_{\min}$ ($N_{\min}$ depends on the parameters of the specimen), and has a "nonactivation" character (negative activation energy). The rate of l.t.p. is determined by the rate of transition of the collective "cloud" of quasiparticles from the monomeric state to the polymeric one, i.e., it is limited only by the rate of rearrangement of the intermonomer distances accompanying the change in the state of the quasiparticles, which makes it possible to explain the connection of l.t.p. with phase transitions.

2. The condition for the possibility of l.t.p. depends strongly on the interaction of the quasiparticles located in a given specimen with neighboring specimens (through the dependence of the indirect-exchange integral on the number of intermediate particles through which the indirect interaction is effected) and with monomeric particles.
3. In a polymerized specimen there exist "polymerization waves," which reduce the degree of conversion; their number depends on the temperature. Polymerization waves are collective oscillations of the density of the polymerization spin and can be detected experimentally (inelastic neutron scattering, Mössbauer effect). From the physical point of view, polymerization waves correspond to elementary excitations freely propagating along the polymerized chain and transferring individual monomers from the polymerization state to the depolymerization state and back.

The existence of quanta of polymerization waves (polymerizons) leads to a number of anomalies in optical phenomena, transport phenomena, and other kinetic processes in polymers with l.t.p., as well as to the existence of resonance phenomena on polymerization waves. In particular, if the polymerization and depolymerization states possess different values of magnetic moment, then paramagnetic resonance on polymerization waves is possible.

Radiation and mechanical destruction of polymers with l.t.p. at doses greater than a certain value leads to the formation of an anomalously large number of monomers.

Radiation and vibrational polymerization of monomers with l.t.p. at doses greater than a certain value leads to a sharp increase in the yield of polymers.

Under certain conditions, "reversible" l.t.p. is possible even far from phase transitions.

The conclusions of the quantum theory of l.t.p. presented by us (naturally, they can also be formulated in a phenomenological language, for example, in terms of an internal polymerization field) make it possible to explain the known experiments on l.t.p. (1–4) and predict a number of effects accessible to experimental verification. For further experimental study of l.t.p. processes, it is of great interest to investigate the influence on l.t.p. of electric and magnetic fields (both constant and alternating), pressure, and ultrasound. It is desirable to carry out the l.t.p. process in the pres—

* A detailed exposition of the mathematical side of the theory will be published elsewhere.

of the indicated physical actions, also taking into account their combination with one another and with radiation and electromagnetic emission.

Thus, one variant of the quantum theory of fast low-temperature polymerization has been considered, conditioned by the collective interaction of quasiparticles (electrons, protons, excitons, etc.) responsible for polymerization.

An essential feature of the theory is the explanation of the activationless character of the process and the possibility, along with explaining the known experiments on fast low-temperature polymerization, of predicting a number of physical phenomena (polymerization waves, resonance phenomena, anomalies in kinetic phenomena, etc.) that allow the theory to be tested.

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