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Fig. 1

Figure 1: Fig. 1

Abstract

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RADICAL POLYMERIZATION AS AN ENERGETIC CHAIN PROCESS CARRIED OUT WITH THE AID OF AN EXCITON

(Presented by Academician N. N. Semenov, 15 VII 1960)

1. On the basis of an analysis of experimental data on polymerization at low temperatures, N. N. Semenov (1) put forward the idea that, under geometrically favorable conditions, the addition of monomer molecules to a growing polymer chain is accomplished not in a series of successive acts of overcoming activation barriers, but as a result of a collective electronic interaction which, upon excitation, leads to a redistribution of valence bonds in the system. The present article is an attempt at a quantum-mechanical concretization and development of these ideas.

2. Let us consider a polymer radical $\dot{R}_\nu$ and a monomer molecule $A = A$ in a configuration favorable to the addition reaction (ν is the number of molecules in the polymer). If interaction with the σ-bonds and the side bonds in the molecule and in the polymer is neglected, then the reaction

$$\dot{R}_\nu + A = A \rightarrow \dot{R}_{\nu+1}$$

reduces to a three-electron interaction, analogous to the reaction

$$K + LM \rightarrow KL + M$$

(K, L, and M are monovalent atoms). The curves in Fig. 1 show the change in the electronic energy ε of the system polymer radical + monomer along the reaction path. As the independent degree of freedom x we choose the distance between the terminal atom C in the polymer and the nearest atom C, participating in the double bond, in the monomer molecule. As is known, the electronic energy of the system, calculated in the adiabatic approximation, plays the role of the potential energy of nuclear motion (2, 3).

Fig. 1

In the state of separated components (the right-hand edge of the diagram), terms 1, 2, 3, and 4 refer to the ground and three lowest excited states of the system. The difference $\varepsilon_2 - \varepsilon_1$ is equal to the excitation energy of the unpaired electron in the terminal atom C of the radical $\dot{R}_\nu$; $\varepsilon_3 - \varepsilon_1$ is equal to the excitation energy of the molecule $A = A$; $\varepsilon_4 - \varepsilon_1$ is equal to the energy of adiabatic rupture of the π-bond. In specifying the relative positions of terms 2 and 3 for the separated components of the system we were guided by data on the potential curves of diatomic molecules, according to which the excitation energy of a molecule is, as a rule, greater than the difference of the atomic levels from which the ground and excited molecular states under consideration arise (4, 5). The position of term 4 relative to terms 2 and 3 is immaterial, since the corresponding potential curves do not perturb one another upon crossing.

The theoretical determination of the height of the activation barrier ε_{act} of the reaction $\dot{R}_\nu + A = A \rightarrow R_{\nu+1}$ (curve 1) requires knowledge of the form of the potential-energy surface ([6]). Application of Polanyi' s rule ([7]): $\varepsilon_{\text{act}} = 11.5 - 0.25q$ leads to the value $\varepsilon_{\text{act}} \approx 5 \div 6$ kcal/mole. Approximate quantum-mechanical calculations, as well as experimental data, give results close to this ([8]). According to ([3,9]), $\varepsilon_{\text{act}} \approx 1 \div 3$ kcal/mole.

Let us take the mean value $\varepsilon_{\text{act}} = 3$ kcal/mole $= 0.13$ eV/molecule. At 20°C, $\varepsilon_{\text{act}} = 5\,kT$, while at −196°C, $\varepsilon_{\text{act}} = 19\,kT$. If each act of monomer addition required thermal activation, the rate of polymerization would be small, especially at low temperatures.

The polymerization process could develop without receiving energy from the thermostat (surrounding medium) if a sufficient part of the heat of reaction went directly to activation of the next act of monomer addition (energy chain ([10])). Let λ denote the probability of concentration, on the reaction degree of freedom, of all the energy released in the reaction. Let ε_0 and ε_N be the energy localized on the reaction coordinate at a polymer length equal, respectively, to ν and $\nu + N$ molecules. Calculation shows that

$$\varepsilon_N = \frac{\lambda}{1-\lambda} q + \lambda^N \left(\varepsilon_0 - \frac{\lambda}{1-\lambda} q \right). \tag{1}$$

From the condition $\varepsilon_{N|N\to\infty} \geqslant \varepsilon_{\text{act}}$ it follows that, for favorable arrangement and orientation of the monomer molecules, the polymerization process will be nondecaying if

$$\lambda \geqslant \lambda_0 = \frac{\varepsilon_{\text{act}}}{\varepsilon_{\text{act}} + q} \approx 0.13. \tag{2}$$

Because of the large number of degrees of freedom and the strong bond between atoms and atomic groups in the polymer chain, and also because of the dissipation of the heat of reaction in the wave, the real values of λ are apparently

smaller than the critical value λ_0. At $\lambda < \lambda_0$ the growth of the polymer will cease very rapidly. According to (1), the chain length is

$$N = \frac{\lg \dfrac{\lambda(\lambda_0 - \lambda)}{\dfrac{\varepsilon_0}{\varepsilon_{\text{act}}}\lambda_0(1-\lambda) - \lambda(1-\lambda_0)}}{\lg \lambda}. \tag{3}$$

If $\lambda_0 = 0.13$, $\lambda = 0.12$, and $\varepsilon_0 = 10\,\varepsilon_{\text{act}}$, then the increase of the polymer chain amounts to only 3 molecules.

3. Repulsion and the associated need for activation energy on the path from the state of separated components to the transition state are due to the exchange interaction, expressed by the integrals α in London' s formula ([6,8])

$$E = E_0 + Q_{12} + Q_{23} + Q_{31} - \sqrt{(\alpha_{12} - \alpha_{23})^2 + (\alpha_{23} - \alpha_{31})^2 + (\alpha_{31} - \alpha_{12})^2}. \tag{4}$$

By contrast, the Coulomb integrals Q decrease monotonically as the components of the system approach one another and contribute to activationless mutual attraction. In works ([11–14]) it has been shown that, in reactions of excited atoms, the specific weight of the Coulomb integrals in the total interaction energy is much greater than in reactions of unexcited atoms. This should lead to an enhancement of attraction in the initial stage of approach of the reacting particles, i.e., to a substantial decrease, and possibly to a reduction to zero, of the activation energy of the reaction of monomer $A = A$ addition to the excited polymer radical $\dot{R}^*_\nu$ (curve 2; $\dot{R}^*_\nu$ is a radical with an excited unpaired electron on the terminal C atom).

In the process $\dot{R}^*_\nu + A = A \to \dot{R}^*_{\nu+1}$, simultaneously with the transfer of the free valence, there must also occur a transfer of excitation energy to

the new terminal C atom in the attached unit of the polymer. The state $\dot{R}^{**}_{\nu+1}$, corresponding to excitation of σ-bonds in the polymer chain, is unstable with respect to a nonadiabatic transition to configuration x_{II}. Thus, in the radical $\dot{R}^*_{\nu+1}$ that has attached a monomer molecule, the unpaired electron proves to be excited, which makes possible the activationless addition of a second, third, etc., molecule, provided that the conditions of favorable position and orientation in the monomer are realized. Transfer of the excitation energy to the $(\nu+2)$-th molecule stabilizes the $(\nu+1)$-th σ-bond, etc. The arrow in Fig. 1 shows how the stabilization process of the $(\nu+1)$-th σ-bond in the polymer would proceed in the idealized case if the condition

$$J_{\nu+1,\nu+2} \equiv \text{Re} \int \Psi^+_{\nu+2} V_{\nu+1,\nu+2} \Psi_{\nu+1}\, d\Omega = \begin{cases} 0, & \text{for } x > x_{\text{III}}, \\ \infty, & \text{for } x = x_{\text{III}}, \end{cases} \tag{5}$$

were satisfied. Here $\Psi_{\nu+1}$ and $\Psi_{\nu+2}$ are the electronic wave functions of the system with the $(\nu+1)$-th and $(\nu+2)$-th molecules excited, and $V_{\nu+1,\nu+2}$ is the interaction operator. From the formula for the transition time of the excitation energy[15]

$$\tau \sim \frac{t}{J_{\nu+1,\nu+2}} \tag{6}$$

it follows that, under condition (5), transfer of excitation from the $(\nu+1)$-th to the $(\nu+2)$-th molecule in the polymer would occur instantaneously in configuration x_{III}, corresponding to the instantaneous "switching on" of the exchange interaction between the states $\dot{R}^*_{\nu+1}$ and $\dot{R}^*_{\nu+2}$.

In reality, transfer of the excitation energy to the $(\nu+2)$-th molecule in the polymer occurs not at a fixed configuration of the atoms, but in the process of formation of the $(\nu+2)$-th σ-bond, analogous to the process of formation of the $(\nu+1)$-th σ-bond shown in Fig. 1. Therefore the stabilization of the $(\nu+1)$-st unit of the polymer chain proceeds not as a transition according to the Franck–Condon principle, but by gradual deformation of curve 2 into curve 1 over the time of one or several vibrations of the atoms. Since the excitation energy of the unpaired electron in the polymer radical $\dot{R}_\nu$ does not depend on the chain length ν, the transfer of excitation energy from molecule to molecule during the growth of the polymer chain will be accompanied by the transition of the stabilized units into a state of vibrational excitation, the released energy being equal to the difference between the energies of the σ-bond in the polymer and the π-bond in the monomer (see Fig. 1).

Thus, electronic excitation of the polymer radical makes possible activationless chain growth. With favorable positions and orientations of the monomer molecules (for example, in a crystal), such growth of the polymer chain is a single elementary act of propagation of electronic excitation, in which the excitation energy, passing from molecule to molecule, stitches them into a polymer. The duration of growth and the length of the polymer chain are then determined by the lifetime and the propagation rate of the electronic excitation.

4. Such a process of radical polymerization represents a new aspect of the exciton. As is known, a sufficiently long-lived electronic excitation in a periodic structure does not remain localized on a definite atom or molecule, but moves through the structure in the form of an excitation wave—an exciton[16,17]. The velocity of the exciton is $v \sim a/\tau$, where a is the period of the structure, and τ is the residence time of the exciton at a definite lattice site, determined by formula (6). If the excitation-transfer time τ is less than the time of atomic displacement τ_{at}, then the exciton is a wave of electronic excitation only. For $\tau > \tau_{\text{at}}$ the exciton has time to change the equilibrium positions of the atoms and is a joint displacement of electronic excitation and a local elastic

deformation of the structure. The exciton can be localized at disturbances of periodicity.

Let us consider a polymer $\dot{R}_\nu$ in contact with a "blank" in the form of a periodic monomer structure. The electronic excitation of the polymer is localized on the terminal C atom (at the boundary of the polymer structure), which is the carrier of a free valence. Contact with the monomer makes possible the propagation of the exciton in the form of a self-consistent process of chain growth and excitation transfer. The arrival of the exciton at the end of the polymer chain causes the addition of a monomer molecule, while the accompanying rearrangement of atoms provides the conditions for further transfer of the exciton. Thus, in systems with double bonds capable of existing in two ordered modifications—monomeric and polymeric—a new type of exciton is possible: a wave of electronic excitation accompanied by a wave of inelastic (residual) deformation. For $a \sim 10^{-8}$ cm and $\tau \sim 10^{-13}$ sec, the exciton, and hence the polymerization front, moves with a velocity $v \sim 10^5$ cm/sec. During the lifetime of the exciton ($\sim 10^{-8} \div 10^{-9}$ sec), a chain of length $10^4 \div 10^5$ molecules can be formed. At the polymerization front heat is released equal to the difference between the energies of the σ- and π-bonds; however, in the exciton mechanism considered above, chain development is ensured by transfer of the energy of electronic excitation, and not by the release of heat in the course of the reaction.

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CITED LITERATURE

1. N. N. Semenov, *Chemistry and Technology of Polymers*, **4**, No. 7-8, 196 (1960).

2. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, Ch. XI, 1948.

3. V. N. Kondrat' ev, *Kinetics of Chemical Gas Reactions*, Chs. III, IV, §14, Publishing House of the Academy of Sciences of the USSR, 1958.

4. G. Herzberg, *Spectra of Diatomic Molecules*, N. Y., 1950.

5. R. F. Basher, S. Goudsmit, *Atomic Energy States*, N. Y., 1932.

6. C. Gleason, K. Laidler, G. Eyring, *Theory of Absolute Reaction Rates*, IL, 1948.

7. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Ch. I, §§ 4, 8, Publishing House of the Academy of Sciences of the USSR, 1958.

8. Kh. S. Bagdasaryan, *Theory of Radical Polymerization*, Ch. VII, §2; Ch. VIII, §§ 2, 5; Ch. X, §1, Publishing House of the Academy of Sciences of the USSR, 1959.

9. E. W. R. Steacie, *Atomic and Free Radical Reactions*, 2, Ch. VII, N. Y., 1954.

10. N. N. Semenov, *Chain Reactions*, 1934.

11. J. H. Bartlett, *Phys. Rev.*, **37**, 507 (1931).

12. N. Rosen, S. Ikehara, *Phys. Rev.*, **43**, 5 (1933).

13. J. L. Magee, *J. Chem. Phys.*, **8**, 677 (1940).

14. K. J. Laidler, *The Chemical Kinetics of Excited States*, Oxford, 1955.

15. U. Kozman, *Introduction to Quantum Chemistry*, Ch. 13, IL, 1960.

16. J. Frenkel, *Phys. Rev.*, **37**, 17, 1276 (1931); Ya. I. Frenkel, *ZhETF*, **6**, 647 (1936).

17. G. Haken, *Uspekhi Fizicheskikh Nauk*, **68**, 565 (1959).

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