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# Chain Paramagnetic Processes and the Nature of Paramagnetic Centers of Polymers with Conjugated Systems

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## ABSTRACT

This paper is concerned with analysis of the basic regularities of the kinetics of formation of polymers with a conjugated system. The experimentally found regularities are explained in terms of the proposed chain branched polymerization mechanism. The principal role in the chain polymerization mechanism is played by paramagnetic centers which are formed from the diamagnetic macromolecules of the polymer in the process of synthesis. The formation of paramagnetic centers is also due to the chain mechanism. It has been established that the thermal effect of the reaction leads to localized overheating of the emerging heterophase of the polymer, which has important consequences for the kinetics of polymerization and the rate of formation of paramagnetic centers.

As was first shown in 1959, polymer substances with a system of $\pi$-electron conjugation feature, in EPR absorption spectra, narrow single signals ($\Delta H$ = 5 to 15 oersteds) with a g-factor close to that of the free electron, which correspond to a content of $10^{15}$ to $10^{19}$ unpaired electrons per gram of the substance [1]. Such an EPR signal was observed for various classes of polymers with a conjugated system (which will be termed "conjugated polymers" for brevity), differing in chemical nature, structure, and synthesis technique. Therewith, it was established that the intensity of the EPR signal and the associated concentration of paramagnetic centers increase with the conjugation chain and, as one passes from soluble to crosslinked structures, may even be higher. The temperature dependence of the signal in the range of 77-300°K virtually obeys Curie's law. At $T \gtrsim 300°K$, the intensity of the signal usually grows. With further cooling, the EPR signal intensity may not return to its initial value prior to heating [2]. Narrow EPR signals occur in conjugated polymers in a wide temperature range, with the properties exhibited in the condensed phase being retained in the solution.

The processes of hydrogenation, halogenation, and oxidation, which disrupt the continuity of the conjugation chain of macromolecules, are responsible for a lower content of paramagnetic centers, down to concentrations undetectable by the EPR technique ($< 10^{11}$ spin/g) [3].

The waveform and intensity of the EPR signal have nothing to do with the mechanisms of the polyreactions yielding conjugated polymers, but are determined primarily by the degree of conjugation and structure of the resulting macromolecules.

The first publications on the subject were soon followed by a great number of works corroborating the described phenomenon for various types of conjugated polymers synthesized from various monomers or formed as a result of intramolecular transformations of various high molecular weight compounds. All experimental data have allowed consideration of the presence in objects under examination of stable spins detectable by the EPR technique as one of the basic characteristics of polymer conjugation. The high stability of paramagnetic centers of conjugated polymers permits their being distinguished from the "stuck" active radicals formed in the process of synthesis or processing, the latter being characterized by a different structure of the EPR signal and disappearing during dissolution, reprecipitation, and heating. The specific features of paramagnetic centers, however, are not limited by those mentioned above, and there is ample evidence of their influence upon the structure, reactivity, catalytic and electrophysical properties, as well as, probably, the biological activity of polyconjugated systems [4-6].

Therefore, the problem of the nature and mechanism of formation of paramagnetic centers of conjugated polymers is currently topical and demands solution.

## INTERMOLECULAR INTERACTIONS IN CONJUGATED POLYMERS AND THE EFFECT OF LOCAL ACTIVATION

As was already pointed out in the earliest studies into the chemistry of conjugated polymers [7], one of the characteristic properties of these compounds is their ability to form relatively strongly bonded $\pi$-complex associates persisting even in solution. It was assumed that intermolecular $\pi$-electron interaction is responsible for such behavior of conjugated polymer macromolecules [8]. Considering this problem with due account for the presence of stable spins in conjugated polymers, one may assume three types of intermolecular interactions responsible for complexing: (1) $\pi$-electron interaction between two diamagnetic polyconjugated molecules; (2) interaction of a molecule containing free spins with that having valence-saturated bonds; and (3) interaction between two spin-containing ("radical") molecules.

The resulting complexes were previously called, respectively, M-M, M-R, and R-R complexes [9]. Evidently, the bond energy of these complexes increases generally in this series. Of greatest interest for further consideration are complexes formed by two radical molecules, i. e., R-R complexes and, out of all possible types of R-R complexes, only those with $\pi$-radicals. In conjugated molecules, the unpaired electron occupies a 2p-type orbit and may be delocalized in the system. The high strength of associates of conjugated polymer macromolecules is due, firstly, to the presence of a great number of M-M type contacts between their conjugated systems and, secondly, to the presence of unpaired electrons, ensuring additional stability similar to that of M-R and R-R complexes. Both factors may produce an appreciable effect, especially if the macromolecular chains are close to each other.

At present, no direct data are available in polymer chemistry on the strength of R-R complexes. Nevertheless, whatever data are available on the strength of bonds in individual compounds that may serve as models of interactions in polymers, for example, hexaphenylethane [10, 11] or a biradical dimer similar to the Chichibabin hydrocarbon [12], indicate that the lower limit of the strength of R-R complexes is 10 to 20 kcal/mole. In what follows, we shall consider the possible mechanism of formation and the significance of R-R complexes for a better understanding of paramagnetism and the specific physicochemical properties of conjugated polymers. The processes of complexing involving conjugated polymers containing paramagnetic centers with diamagnetic molecules are of particular interest for they promise unusual relationships between the physicochemical properties of a complex and concentration as well as type of paramagnetic centers. In fact, as far back as 1962, paramagnetic centers were found to produce an activating effect on the reactivity of the diamagnetic molecules forming complexes with them [13] and to affect the physicochemical and electrophysical properties of conjugated polymers [14, 15]. By now, the effect of local activation has been demonstrated by numerous instances of accelerated accumulation of paramagnetic centers in the case of thermal and other actions on monomer and polymer substances, inhibition or catalysis of thermal or thermooxidative destruction, initiation or inhibition of polymerization processes, catalysis, with the aid of conjugated polymers, of various reactions and enhancing their own reactivity [16, 17].

The effect of paramagnetic centers on the physical properties of conjugated polymers manifests itself in lower fluorescence yield, shorter lifetime of photocarriers, and lower electric conduction activation energy.

Thus, the effect of local activation encompasses a broad range of phenomena of scientific and practical interest. At present, whatever is known about the mechanism of the effect of local activation boils down to the following. In a reaction complex, "paramagnetic center-diamagnetic molecule," spin quantum numbers $S^2$ ($S = 1/2$) and $S_z$ ($S_z = 1/2$) must be maintained. None of these quantum numbers will change if the diamagnetic molecule enters a triplet state with simultaneous reorientation of the spin of the paramagnetic center:

$$R\uparrow \ldots M\downarrow \rightleftharpoons R\downarrow \ldots \uparrow M\uparrow$$

This means that we are dealing with a new adiabatic reaction pathway of the diamagnetic molecule for which transition between states with different multiplicity are no longer forbidden. When this new pathway is energetically preferable, it will lead to a higher reaction rate. Such a situation occurs in the case of an uncatalyzed reaction of cis-trans isomerization of substituted ethylene [18]. Here, two reaction pathways are possible [19] (Fig. 1): (1) a pathway with a low activation energy and a low pre-exponential factor (transmission coefficient) whose value is lower than usual by 5 to 7 orders of magnitude because of the forbidden transitions from a singlet (S) to a triplet (T) surface; and (2) a pathway with a "normal" pre-exponential factor, but a higher activation energy than (1). In the case of an uncatalyzed reaction, the rate of reaction (1) turns out to be greater than that of reaction (2). In principle, this reaction rate may be further increased by raising the pre-exponential factor, i. e., through a higher probability of S-T transitions due to the fact that transitions between states with different multiplicity are not forbidden any more. When cis-trans isomerization of substituted ethylene, in particular, dimethyl maleinate, was catalyzed with stable radicals, it was established [20] that, with the

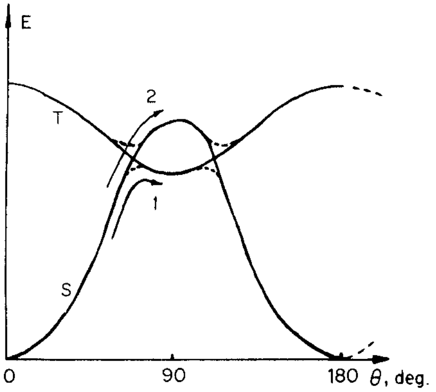

FIG. 1. Possible pathways of isomerization of substituted ethylene: (1) pathway with changing multiplicity; (2) pathway without changes in the reagent's multiplicity. $\theta$ -angle of rotation around the double bond.

activation energy being invariable, the rate of the catalyzed reaction is higher by 5 orders of magnitude than that of an uncatalyzed reaction, and the increase was accounted for by similar effects.

## NATURE OF PARAMAGNETIC CENTERS OF CONJUGATED POLYMERS

The mechanism of formation and the nature of paramagnetic centers of conjugated polymers were discussed in many works. However, they have not yet been completely understood because of their complexity. Of all the advanced hypotheses, three have been accepted: the double radical hypothesis [21], the hypothesis of states with charge transfer (ion-radical hypothesis) [22, 23], and the hypothesis of thermal population of lower triplet levels [24].

According to the first hypothesis, paramagnetic centers are formed through local uncoupling of $\pi$ -bonds of the polyconjugated macromolecular fragment. Then, the unpaired electrons occurring in each of the two conjugation regions are stabilized, and their recombinations are impeded, primarily, by steric hindrances. In the case of an infinite polyene chain, whose atoms lie in the same plane, transition to a triplet state corresponds to 20 to 30 kcal/mole, which renders such dark processes highly improbable. There are two factors facilitating the formation of biradicals in the course of synthesis and subsequent transformations of real conjugated polymers. Firstly, it is the fact that these systems are usually noncoplanar because of the side functional groups preventing planar arrangement of the polyconjugated skeleton of the molecule. In this case, the bonds are under tension, and the energy of transition to a triplet state may be substantially reduced. Secondly, in the course of synthesis of conjugated polymers, temperature may rise considerably because of the thermal effect, thereby making transition to a triplet state more probable. The biradical theory of formation of paramagnetic centers, put forward by one of the authors, has been quantitatively advanced by Pople [25, 26] who has termed the occurrences of disturbed conjugation, leading to formation of paramagnetic centers, as "structural defects".

The second hypothesis concerning the paramagnetism of conjugated polymers is based on the assumption that these systems have closely spaced polar states between which an electron is transferred along with formation of ion-radical centers [22, 23].

And, finally, according to the most recent hypothesis, conjugated polymers feature lower triplet levels whose energy decreases with increasing conjugation length N as U/N, where U $\sim$ 15 to 20 eV. With respective lengths of the uninterrupted conjugation chain, the energy of the lower triplet states may be commensurate with thermal energy kT, and these states may be populated thermally.

Among the above-mentioned possible causes of occurrence of paramagnetic centers, the least probable is the ion-radical hypothesis. Such a conclusion is prompted by the theoretical data on the positions of triplet levels in conjugated carbon-chain polymers, which are about 1.5 eV away from the ground state, as well as by experimental data. In particular, as there is no relationship between the dielectric characteristics of monomers or the medium in which the polyreaction takes place and the kinetics of accumulation or the content of paramagnetic centers, the absence of maxima corresponding to the frequency dependence of the tangent of the dielectric loss angle in the case of paramagnetic fractions of certain polyarylenes, and a number of other regularities are indicative of a total absence or an insignificant quantity of polar states in conjugated polymers. However, in the case of conjugated systems containing heteroatoms, ion radicals may exist. Thus, the hypotheses as to the origin of paramagnetic properties of conjugated carbon-chain polymers that will be discussed and studied further include the biradical hypothesis and the hypothesis of thermal population of lower triplet levels. As far as the biradical hypothesis is concerned, since unpaired electrons practically do not interact, their behavior in experiments must be the same as with normal stable radicals. In particular, the EPR absorption line must more often be observed as a narrow irregularly broadened line as a result of a hyperfine interaction with the protons of the chain and side groups, while the hyperfine structure of the signal is frequently not observed because of the extended region of delocalization of the electron and wide distribution of polymers by the lengths, structures, and conformations of the conjugation chain. As to the possibility of observing the lower triplet levels with the aid of an EPR signal, the signal should evidently be rather narrow because of the extended region of delocalization of the triplet excitation, and this signal must be highly saturated because of the weak relation between the triplet excitation and acoustic vibrations of the molecule.

It was recently found that the signal which was previously considered to be a singlet is, in fact, a superposition of at least two signals of different widths and relaxation properties. The degree of saturation of the narrow signal is greater, and the broad signal seems to exhibit a hyperfine structure [27]. These new experimental data suggest that the two types of signals are due to two different causes: the broad signal whose saturation is relatively low and which features a hyperfine structure is due to stable radicals whose delocalization region is estimated to involve 5 to 7 links of the macromolecule; the narrow signal is due to the populated lower triplet levels [28].

## MECHANISM OF ACCUMULATION OF FREE SPINS IN CONJUGATED POLYMERS: "PARAMAGNETIC AVALANCHE"

It would be impossible to lay down the fundamentals of the chemistry and physics of conjugated polymers without understanding the mechanism and kinetics of accumulation and disappearance of paramagnetic centers in the process of formation and subsequent transformations of conjugated macromolecular structures. Indeed, the structure and properties of conjugated polymers can be controlled only if there is adequate information on the mechanism and kinetics of accumulation of paramagnetic centers. There can be no doubt that to solve this problem is of great scientific and practical importance, for the effect of paramagnetic centers on the structure, strength, thermal stability, and electrophysical and physicochemical properties of conjugated polymers and materials on their basis is well known. This problem may also be of a fundamental importance in studies of the biological activity of natural conjugated macromolecules and their role in biological processes in nature.

The obvious urgency of this problem notwithstanding, the attention it has so far received is far from sufficient. At present, we know very little about the kinetics of accumulation of paramagnetic centers during synthesis of conjugated polymers and heat treatment of the so-called individual and polymer substances with a developed polyconjugated system. Nevertheless, we can already distinguish the following general regularities.

(1) The concentration of paramagnetic centers increases, during

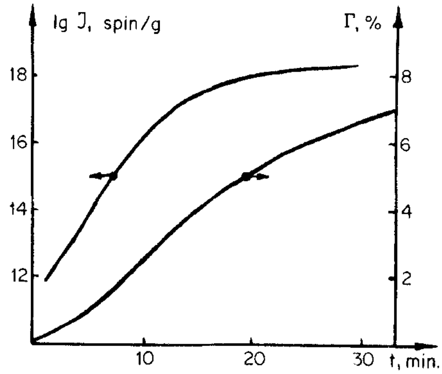

FIG. 2. Time dependence of the paramagnetic center concentration (J), in spin/(gram of formed polymer) and polymer conversion (Γ, %) during synthesis of polyphenylacetylene at 150°C.

synthesis of conjugated polymers, with autoacceleration at the early stages of the polyreaction, when the viscosity of the system is still low and rapidly reaches the maximum for given conditions (Fig. 2) [3].

(2) Addition to individual low molecular conjugated compounds (such as anthracene, naphthacene, pyrene) of their polymer analogs containing paramagnetic centers drastically speeds up the process of dehydropolycondensation of monomer compounds at 300-450°C, with formation of colored paramagnetic polymers. At the same time, not only the rate of accumulation of paramagnetic centers increases, but also the induction period is fully eliminated (Fig. 3) [29, 30]. A similar effect of local activation is observed in some other cases of thermolysis of aromatic and heterocyclic monomers, as well as in the polyreactions employed for synthesis of conjugated polymers at lower temperatures ($\lesssim$ 70-80°C).

(3) As was revealed while measuring the EPR signal intensity in the course of thermal polymerization at the reaction temperature and at a lower temperature at early stages, the drop in the reaction mass temperature leads to a lower EPR signal intensity. If the temperature is raised again to the initial level, the EPR signal intensity reassumes the value it had prior to cooling (Fig. 4).

(4) Interaction between conjugated polymers and active radicals results in a lower concentration of paramagnetic centers. The same effect is attained when polyconjugated polymers are partially hydrogenated or halogenated, whereby the continuity of the conjugation chain is broken [31].

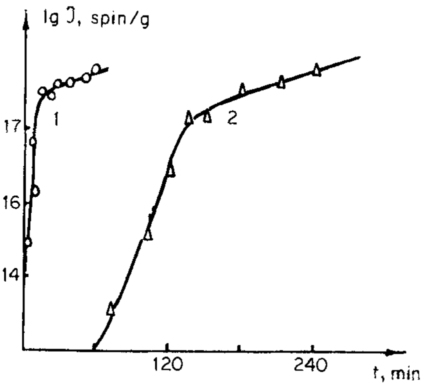

FIG. 3. Time dependence of the paramagnetic center concentration during dehydropolycondensation of anthracene (1) in the presence and (2) in the absence of polyanthracene additives at 450°C, with addition of 1% by weight of polyanthracene containing $5 \times 10^{18}$ spin/g.

The foregoing suggests that the process of accumulation of paramagnetic centers has much in common with the branched chain reactions studied by Semenov and his followers [32]. However, the formation of paramagnetic centers in conjugated polymers is in many respects so peculiar as to warrant considering it as a new type of branched chain processes. Since, as has been mentioned above, paramagnetic centers may be accumulated both in the course of synthesis of conjugated polymers and in the case of, for example, thermal action upon the already synthesized polymer under external isothermal conditions, consider both cases separately.

## ACCUMULATION OF PARAMAGNETIC CENTERS

### Accumulation in a Synthesized Polymer Under Isothermal Conditions

In this case, the primary act of the process of accumulation of paramagnetic centers is triplet excitation causing formation of stable double radicals or ion-radicals (if the polarity of the medium is high). The resulting paramagnetic centers are relatively stable macromolecular compounds with free spins delocalized over extended conjugation regions. In real systems, the macromolecules of conjugated polymers form $\pi$-complexes, therefore, the resulting free spin interacts, with a

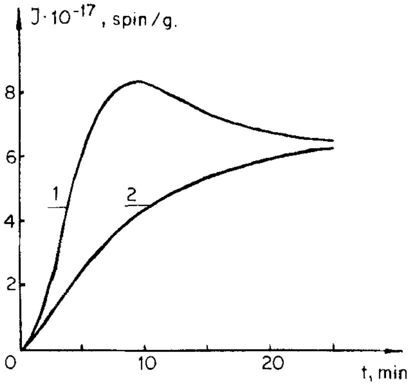

FIG. 4. Time dependence of the paramagnetic center concentration during bulk polymerization of phenylacetylene: (1) measured in the cavity of an EPR spectrometer, thermostat temperature -150°C; (2) measured after cooling, at 20°C.

lower exchange energy, with the $\pi$-electrons of the complex-forming chains as well. In such complexes with spin "transfer," the probability of an S-T transition becomes greater, and the energy gap may become somewhat narrower. Hence, with respective energy expenditures, the probability of the $\pi$-bond in these complexes being uncoupled, when activated by the electron exchange interaction with a free spin, becomes higher. The resulting biradical becomes a stable double radical. In other words, a single spin initiates, with a certain probability, two new ones, which gives rise to a branched chain process that we have termed "branched paramagnetic chain" or "paramagnetic avalanche."

With due consideration for the branched chain pattern of the reaction and the high value of the pre-exponential factor ($10^{13}$ to $10^{15}$ sec$^{-1}$), the rate of the process is high and steadily increasing, which brings about accumulation of stable paramagnetic centers detectable by the EPR technique at early stages of the polyreaction, even at relatively low temperatures. Therewith, there is a certain relationship between the rate of formation and nature of the polymer, on the one hand, and the kinetics of development of paramagnetic chains, on the other. The accumulation of paramagnetic centers is accompanied by inhibition of the chain growth, caused by their recombination with formation of the above-considered spin-spin complexes (R-R complexes) or by their irreversible destruction as a result of the broken continuity of the polyconjugation chain or spin inactivation in a reaction with impurities.

If the kinetics of formation of conjugated polymers proper is put aside, branched paramagnetic chain processes in general can be represented in the following simplified way.

Formation of primary paramagnetic centers:

$$\downarrow P_i \uparrow \xrightarrow{K_i} \uparrow P_i \uparrow \qquad (1)$$

Formation of complexes with spin transfer, branching, and chain propagation:

$$P\uparrow + \uparrow P_1 \downarrow \underset{K_{-ST}}{\overset{K_{ST}}{\rightleftarrows}} [P\uparrow \circlearrowright \downarrow P_1 \uparrow] \xrightarrow{P_p} P\uparrow + \uparrow P_1 \uparrow \qquad (2)$$

$$P_1\uparrow + \uparrow P_2 \downarrow \underset{K_{-ST}'}{\overset{K_{ST}'}{\rightleftarrows}} [P_1\uparrow \circlearrowright \downarrow P_2 \uparrow] \xrightarrow{K_p'} P_1\uparrow + \uparrow P_2 \uparrow, \text{ etc.} \qquad (3)$$

Inhibition of the chain growth as a result of formation of spin-spin complexes:

$$\uparrow P_i \uparrow + \uparrow P_K \uparrow \underset{K_{-d}}{\overset{K_d}{\rightleftarrows}} [\uparrow P_i \uparrow \circlearrowright \downarrow P_K \downarrow] \qquad (4)$$

Disappearance of the paramagnetic chain as a result of disturbed conjugation or spin inactivation:

$$P_i\uparrow + X \xrightarrow{K_t} XP_1, \qquad (5)$$

Here $P_i$ is a conjugated polymer molecule with i conjugation links; arrows stand for the ground state ($\downarrow\uparrow$) and a triplet state or a stable double radical ($\uparrow\uparrow$), X are impurity molecules capable of reacting with the spins of a stable radical, $K_i$, $K_{ST}$, $K_d$, and $K_t$, are the rate constants of, respectively, formation of excited primary biradicals and stable double radicals; formation of a double radical in the case of local activation [reaction (2)]; slowing down [reaction (4)], and disappearance [reaction (5)] of paramagnetic centers.

Assuming that, in a first approximation, the rate constants of the above elementary processes are independent of the conjugation system size, we obtain the following system of equations for defining the kinetic law of accumulation of paramagnetic centers:

$$d[\mathrm{PMC}]/dt = K_i P + K_p[\mathrm{CST}] - K_d[\mathrm{PMC}]^2 + \kappa[\mathrm{PMC}]^2 - K_t[\mathrm{PMC}]\ X$$

$$d[\mathrm{CST}]/dt = K_{ST}[\mathrm{PMC}]\cdot P - K_{-ST}[\mathrm{CST}] - K_p[\mathrm{PMC}] \qquad (6)$$

Here [PMC] and [CST] are the concentrations of paramagnetic centers and complexes with spin transfer, respectively, and K is the equilibrium constant of reaction (4). If the quasistationarity condition is satisfied ($d[\mathrm{CST}]/dt = 0$), system (1) takes the form of an equation similar to that proposed by Semenov [32] in his theory of branched chain processes for the case of the so-called negative interaction of chains:

$$d[\mathrm{PMC}]/dt = K_i P + K_r[\mathrm{PMC}] - K_t[\mathrm{PMC}]\cdot X - K_h[\mathrm{PMC}] \qquad (7)$$

In Eq. (7),

$$K_r = \frac{K_{ST}K_{p'}P}{K_{-ST} + K_p}$$

and

$$K_h = (2K_d - \kappa)$$

It should be emphasized, however, that although Eq. (7) is, from the standpoint of formal kinetics, identical with the above-mentioned equation of Semenov, it describes, in fact, a fundamentally new mechanism of a branched chain reaction that we have termed "paramagnetic avalanche." Integration of Eq. (7) gives the expression (8) for the time dependence of the paramagnetic center concentration:

$$[\mathrm{PMC}] = \frac{[\mathrm{PMC}]_0\{b + \sqrt{q} + (2C/[\mathrm{PMC}]_0)[\exp(\sqrt{q}\cdot t] - b + \sqrt{q} + (2C/[\mathrm{PMC}]_0)\}}{b - 2[\mathrm{PMC}]_0 K_h + \sqrt{q} + (\sqrt{q} + 2[\mathrm{PMC}]_0 K_h - b)\exp(\sqrt{q}\cdot t)} \qquad (8)$$

where

$$q = (K_r P - K_t X)^2 + 4K_h K_i P$$

$$b = K_r P - K_t X$$

$$c = K_i P$$

and $[\mathrm{PMC}]_0$ is the initial paramagnetic center concentration. Analysis of Eq. (8) suggests that: (1) the paramagnetic center accumulation curve has the S-shape typical of autocatalytic processes; (2) at infinite time, the paramagnetic center concentration reaches a limiting value:

$$[\mathrm{PMC}]_\infty = [\mathrm{PMC}]_0 \frac{b + \sqrt{q} + (2C/[\mathrm{PMC}]_0)}{\sqrt{q} - B + 2[\mathrm{PMC}]_0 \cdot K_h}$$

(3) as the $[\mathrm{PMC}]_0$ increases, the rate of accumulation of spins in the autoacceleration region increases, too, i. e., the effect of local activation is manifest in the process; (4) as the first-order [or second-order, reaction (5)] termination rate increases, the induction period of the process is extended, while the limiting paramagnetic center concentration decreases at $t \to \infty$; (5) the reversible nature of slowing down of the chain growth [reaction (4)] must be responsible for an increase in the paramagnetic center concentration and a decrease in the number average molecular weight, with increasing temperature. Indeed, under these conditions, the complex equilibrium constant decreases hence, dissociation of R-R complex associates ("quasi-molecules") takes place with formation of stable radicals; (6) in the case of a major contribution of the reaction in which the chain disappears [reaction (5)], the rate of accumulation of paramagnetic centers and its temperature dependence are, all other things being equal, determined by the inhibition constant ratio and the disappearance of the paramagnetic chain. Note also that, in the case where $[\mathrm{PMC}]_0 = 0$, Eq. (8) transforms to a kinetic law characterizing a branched chain process with negative chain interaction, derived by Semenov [32].

Let us now turn to the second case, where paramagnetic centers are accumulated in the course of polymerization.

### Accumulation in the Course of Synthesis of Conjugated Polymers

In this case, the formation of paramagnetic centers should be considered together with that of polymer macromolecules. In accordance with three portions of the S shaped curve of paramagnetic center accumulation, namely, the induction period, autoacceleration portion and saturation portion, one may assume that they determine the following basic processes. During the induction period, a small number of diamagnetic high-molecular polymer fractions are formed (low initiation constant, high propagation constant), which, for the above discussed reasons, either pass into a biradical state or their length becomes sufficient for such a value of the energy of the lower triplet levels, so that the latter are populated with high efficiency. At any rate, for subsequent processes to occur, it is important that a stable free spin of any nature should be present.

Then, according to the mechanism of the effect of local activation under the effect of paramagnetic centers of conjugated polymers, the rate of formation of macromolecules and their passing into a paramagnetic state drastically increases. The greater the number of paramagnetic centers, the higher the rate. An additional stimulus for accelerating the polymerization and increasing the number of paramagnetic centers is the rise in the reaction mass temperature due to the exothermal effect of the reaction. These processes correspond to the second portion of the paramagnetic center accumulation curve. The third portion of the curve corresponds to establishment of thermal and kinetic equilibrium in the system.

Let us write the basic processes determining the accumulation of a polymer and variations in the content of paramagnetic centers:

$$X + P \longrightarrow XP \tag{9}$$

$$XP + P \longrightarrow XP_2 \tag{10}$$

$$\dots$$

$$P_i \longrightarrow {\uparrow}P_i{\uparrow} \tag{11}$$

$$P_i + P + {\uparrow}P_K{\uparrow} \longrightarrow [{\uparrow}P_I \dots P \dots P_K{\uparrow}] \longrightarrow P_{i+1} + {\uparrow}P_K{\uparrow} \tag{12}$$

$$P_i + {\uparrow}P_K{\uparrow} \longrightarrow {\uparrow}P_i{\uparrow} + {\uparrow}P_K{\uparrow} \tag{13}$$

$$\uparrow P_i \uparrow + P_K \longrightarrow \uparrow P_{i+K} \uparrow \tag{14}$$

$$\uparrow P_i \uparrow \longrightarrow \uparrow P_K \uparrow \longrightarrow \uparrow P_{i+K} \uparrow \tag{15}$$

$$\uparrow P_i \uparrow \longrightarrow \uparrow P_K \uparrow + P_{i-K} \uparrow \tag{16}$$

$$\uparrow P_i \uparrow + X \longrightarrow XP_i \uparrow \tag{17}$$

In this sequence, Eqs. (9)-(11) correspond to the growth of the diamagnetic molecule and its transition to a paramagnetic state. The respective constants determine the duration of the induction period. Then, autoacceleration of the reaction begins. It is caused not only by the higher rate under the effect of paramagnetic centers, but also by the greater number of paramagnetic centers proper. Eqs. (12)-(14) describe these processes, Eq. (12) corresponding to addition reactions promoted by paramagnetic centers (local activation effect) with an effective constant higher than in Eqs. (9)-(11) reaction (13) corresponding to branching of the paramagnetic chain, and (14) corresponding to additional growth of the molecular mass of the polymer. This is followed by an equilibrium being established in the system, which is expressed, mainly, by Eqs. (15-17), where Eq. (15) corresponds to association of two biradicals with disappearance of two paramagnetic centers, Eq. (16) corresponds to a reverse process, and Eq. (17) corresponds to a decrease in the concentration of paramagnetic centers of biradicals on impurities and due to other causes.

In all of the above equations, $P_i$ stands for a diamagnetic polymer molecule comprising i links, $\uparrow P_i \uparrow$ and $P_i \uparrow$ stand for the same molecule in a biradical or a radical state, respectively, X stands for an initiator, an impurity, etc. The equations are written for conditions of varying temperatures, concentrations, etc. It is therefore impossible to solve them in a closed form. Bearing in mind that the processes of polymer formation involve heat release in the course of polymerization and, therefore, cannot be regarded as isothermal, applying formal kinetics to describe the accumulation of paramagnetic centers does not seem to be justified in this case. This is why we shall analyze this case using the following model. Let, at an initial moment $t = 0$, a spherical polymer seed with radius $R_0$ be present in the system. We shall assume that its radius may increase only up to $R'$, which value corresponds to the polymer having been depleted or to appreciable diffusion difficulties arising when the viscosity of the reaction mass grows.

In our assumptions, the volume of the growing sphere corresponds to the degree of transformation of the polymer.

The monomer temperature is assumed constant and equal to $T_0$, whereas the temperature of the growing sphere is assumed constant but different from $T_0$ and determined by the thermal effect of the reaction and abstraction of heat through its surface. The distribution of paramagnetic centers inside the sphere is assumed to be uniform and determined by the acts of their appearance and disappearance. Simplified phenomenological equations for such parameters as concentration J of paramagnetic centers, temperature T, and degree $R^3$ of transformation of the polymer, in such a model, take the following forms:

$$dJ/dt = K_1R^3 \exp\{-\Delta E_1/kT\} - K_2J^2(1/R^3) + K_3J \exp\{-\Delta E_2/kT\} - K_4J \tag{18}$$

$$dT/dt = -K_5R^2(T - T_0) + K_6\,(dR/dt)\,R^2 + K_7A \tag{19}$$

$$dR/dt = K_8 \exp(-\Delta E_3/kT) + K_9\,(J/R) \exp\{-\Delta E_4/KT\} \tag{20}$$

The augend in Eq. (18) for the number of paramagnetic centers represents transition of the diamagnetic macromolecule to a biradical state with activation energy $\Delta E_1$; the first addend stands for recombination of biradicals; the second addend represents new paramagnetic states appearing, under the influence of the existing paramagnetic centers, at a rate higher than that of the process represented by the augend, and corresponds to branching of the paramagnetic chain; and the third addend stands for "linear" disappearance of paramagnetic centers, for example, on impurities or walls. The augend in Eq. (19) for temperature represents the heat abstraction proportional to the surface of the growing polymer sphere, as well as to the difference of the polymer temperature (T) and that of the monomer ($T_0$); the first addend stands for the thermal effect of the reaction; and the second addend stands for the thermal effect of the biradical recombination. The augend of Eq. (20) for the sphere volume represents its increase caused by the acts of monomer addition, while the addend also stands for an increase in volume except that it is due to the paramagnetic centers on the surface. This expression describes a manifestation of the local activation effect, i. e., an additional increase in the

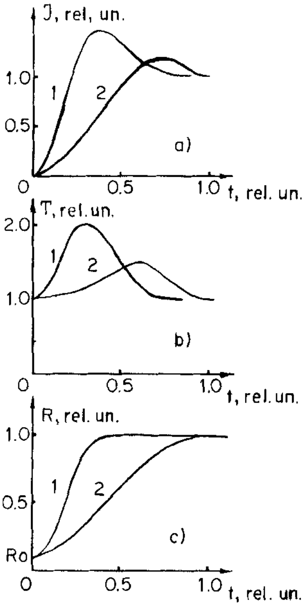

FIG. 5. Qualitative solution of Eqs. (18)-(20) versus time: (a) time dependence of the paramagnetic center concentration; (b) time dependence of local temperature; (c) time dependence of the spherical polymer formation volume. All values, including time, are given in relative units. All curves 1 correspond to a higher local temperature.

polymerization rate under the effect of the paramagnetic centers near the sphere surface.

A qualitative solution of Eqs. (18)-(20) is represented in Fig. 5, where all curves 1 correspond to a higher, as compared to curve 2, local temperature of the growing spherical polymer formations.* The above-mentioned phenomenological approach to describing polymerization processes with due account for temperature variations has, for the first time, made it possible to appreciate the importance of this factor on the kinetics of accumulation of paramagnetic centers and of the polymer. The most essential thing is that the presence of overheated polymer formations "enables" many processed which

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*The system of Eqs. (18)-(20) was solved on an MN-18 analog computer and a BESM-6 computer with partial optimization of the reaction constants and activation energies.

would have otherwise been energetically forbidden. We believe that a substantial distinction of polymerization processes yielding conjugated polymers from similar processes in which saturated polymers are formed is that, in the case where conjugated polymers are formed as a result of intermolecular interactions as early as the initial stages of the reaction, there emerges a polymer heterophase whose mass rapidly increases by virtue of a chain mechanism and which is locally overheated due to the thermal effect of the reactions. (If the rate of heat exchange with the environment is low, the local overheating may cause that of the entire reaction mass and, ultimately, a thermal explosion, which does happen in certain cases when mass polymerization is conducted in large volumes). In many cases, overheating of the reaction mass can be observed experimentally. This accounts for the experimental data indicative of an extreme time dependence of the EPR signal intensity in conjugated polymerization. Besides, the kinetic paramagnetic center and polymer accumulation curves are S-shaped, which is typical of chain processes. Therewith, the rates of the processes corresponding to the autoacceleration portion are also determined by temperature.

## CONCLUSION

We have examined some basic regularities of processes of paramagnetic center accumulation and the kinetics of polymerization. New mechanisms have been assumed to be responsible for these regularities.

The essence of the proposed concepts resides in the following. A polymerization process (irrespective of whether its mechanism is radical, ionic, polycondensation, etc.) is of an autocatalytic nature with saturation normally taking place at the early stages of the reaction. The autocatalytic nature of polymerization is determined, primarily, by the following two factors: (1) the local activation effect, i. e., an increase in the polymerization rate under the effect of paramagnetic centers, both already existing or newly forming, in conjugated polymers, and (2) an increase in the number of paramagnetic centers, due both to the greater number of polymer molecules with subsequent transition of the latter to a radical and/or biradical state and to new branched chain processes that we have termed "paramagnetic avalanche."

The kinetics of polymer and paramagnetic center accumulation is tangibly influenced by inhomogeneity of distribution of the reaction mass temperature which may be much higher at polymer nucleation and formation sites as a result of the thermal effect of the reaction. One of the most pronounced effects is local overheating of the emerging polymer formations at the stage corresponding to autoacceleration of the reaction.

The kinetics of accumulation of paramagnetic centers in the proposed model is also explained. The kinetic regularities of formation of paramagnetic centers have two characteristic features. First of all, the relationship between the content of paramagnetic centers and the polymerization time is represented by an S-shaped curve and, secondly, this curve exhibits an extremum. Both features can be explained in terms of the proposed mechanisms. The former is due to the local activation effect and branched chain paramagnetic processes, while the latter is accounted for by the locally overheated polymer formations. Both processes–polymerization and accumulation of paramagnetic centers–are interrelated and mutually dependent; therefore, they are equally important and cannot be considered singly.

We hope that the proposed concepts and mechanisms hold for all processes yielding conjugated polymers and will help elaborate a unified physicochemical theory of directed formation of conjugated polymers with predetermined properties.

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