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Collective Interactions in Polymerization Processes at Low Temperatures and in Polymers with Conjugated Bonds*

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POLYMERIZATION KINETICS AND THE REACTIONS OF FREE RADICALS AT RELATIVELY LOW TEMPERATURES

There are as yet not many experimental studies in this field, but the interest of scientists in this field has grown rapidly in the last few years.

The phenomenon of the violent, almost explosive, polymerization of a solid monomer at the instant of melting seems most striking. This was observed even in the forties by Letort,[1] Hinshelwood,[2] Norrish,[3] and later by Enikolopyan (of the Institute of Chemical Physics) for the case of acetaldehyde. The reaction proceeds as fast as melting can occur without the use of catalysts, whereas slightly above or slightly below the melting point the reaction practically does not proceed at all.

As was shown by Enikolopyan, the same phenomenon is observed at the melting point of formaldehyde. There are many statements in the literature of the occurrence of a violent polymerization reaction at the melting point of other monomers at low temperatures (e.g., styrene and methyl methacrylate). When the melting points of the substances are above 0°C., this phenomenon is not observed or may be observed only as a small increase in velocity. For example, Abkin has reported that the latter situation takes place in the melting of maleic anhydride (56°C.)

Kargin, Kabanov, et al.[4] deposited a monomer and a catalyst in the form of two molecular beams *in vacuo* on a glass surface cooled with liquid nitrogen. When the deposit reached a certain temperature, an explosive polymerization reaction took place. The monomers tested were: methyl methacrylate, styrene, acetone, acrylonitrile, methacrylonitrile, acrylamide, isoprene, etc. The substances used as catalysts were magnesium, lithium, mercury, lithium chloride, beryllium chloride, molybdenum trioxide, etc. It was found that styrene, isoprene, and α-methylstyrene reacted violently on melting. Other monomers (in particular, formaldehyde) showed a violent, often explosive, polymerization at considerably lower temperatures, apparently at the transition point of the deposit from the amorphous to the

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crystalline state. Above or below this critical temperature the reaction takes place very slowly. Similar phenomena have been observed by Magat[5] upon illumination of formaldehyde at a temperature of about −196°C.

It is also of interest that the occurrence of a rapid reaction on melting of a mixture of components is observed not only in polymerization but also in other simpler reactions. In the Department of Chemical Kinetics of the Moscow State University, Chaĭkin,[6] and Lishnevskiĭ and Sergeev[7] several years ago observed violent chlorination and hydrochlorination reactions when mixtures of chlorine or, respectively, hydrogen chloride, were melted in the presence of ethylene or isobutylene.

As early as the twenties, Semenov and Shal'nikov[8] directed molecular beams of sulfur and cadmium onto a surface cooled with liquid air. Under the same experimental conditions as were used by Kargin and Kabanov, they observed an explosive reaction when a certain critical temperature below −100°C. was reached.

In the Department of Chemical Kinetics of the Moscow State University, Gurman and his associates[9] have observed a violent reaction of recombination of free radicals at −115°C. in a frozen 25% solution of H_2O_2 in H_2O. The radicals were generated at −196°C. by ultraviolet irradiation, and were detected by the electron paramagnetic resonance (EPR) method. At temperatures above or below −115°C., the radicals are stable for long periods of time. Without the irradiation, the system 25% H_2O_2 + 75% H_2O shows a phase transition just at −115°C. on the heating curve. Thus, the rearrangement of the crystal structure or the transition from the amorphous to the crystalline state causes a sufficiently rapid motion of the radicals to bring about a rapid rate of recombination.

We also recall that mixtures of finely divided alkali or alkaline-earth oxides with the oxides and chlorides of Group IV elements react to form complex compounds far below the melting point, at the polymorphous transition point of one of the components. This phenomenon has been studied in an especially detailed fashion by Urazov and his students. As Evdokimov[10] of the Institute of General and Inorganic Chemistry showed, this process takes place even when the chloride is in the vapor state. He studied a system consisting of any of the alkaline-earth oxides and germanium chloride vapor. For the various oxides, the temperature of polymorphous transition (with concomitant reaction) occurs between 200 and 640°C., while the melting points of the oxides are of the order of 2000°C. This observation shows that the oxides become penetrable by the molecules of the vapor during the phase transition.

Peculiarities of Polymerization at Low Temperatures in a Liquid Phase with Initiation by Penetrating Radiation, Light, or Catalysts

It has been known for a long time, especially from industrial experience, that the polymerization rate of liquid isobutylene under the action of acid catalysts increases with decreasing temperature.

Under the action of gamma-rays, isobutylene also polymerizes at low temperatures (e.g., at −80°C.) with a considerably higher rate than at 0°C. Here a high molecular weight polymer is formed at low temperatures while at ordinary temperatures (e.g., at 0°C.), products of low molecular weight are formed. The rate of radiation-induced polymerization of liquid isobutylene and its solutions in electron-acceptor solvents is strictly proportional to the intensity of the gamma-rays; this indicates an ionic mechanism of the process.

Abkin[11] has shown that the polymerization rate of acrylonitrile in solution increases (by about seventeen times) as the temperature is lowered from −50 to −112°C., with a sharp concomitant increase in the molecular weight of the polymer obtained. As is known, at temperatures above 0°C., the rate of this reaction decreases with decreasing temperature. Thus, the rate of the polymerization reaction occurring in solution has a minimum and increases either at higher or lower temperatures. Abkin ascribes this phenomenon to the transition from a radical mechanism characteristic of elevated temperatures to an ionic mechanism characteristic of low temperatures.

Enikolopyan in the Institute of Chemical Physics has studied the polymerization of isobutylene in the liquid state under the influence of penetrating radiation over the temperature range from −20 to −120°C. The rate of reaction increases with decreasing temperature (by a factor of about 16 in the stated range), obeying the Arrhenius equation, but with an apparent negative activation energy $E = -2.47$ kcal./mole. The rate of the radiation-induced polymerization turned out to be strictly proportional to the intensity of the radiation. The rate of polymerization is equal to $I\bar{P}$, where $\bar{P}$ is the average degree of polymerization and I is the rate of generation of active centers. I is proportional to the radiation intensity, which is, of course, independent of the temperature. Unfortunately, $\bar{P}$ has not been measured as a function of the temperature, but there is every ground for believing that $\bar{P}$ increases with decreasing temperature.

Polymerization of Methyl Methacrylate

As is known, Goode, Fox, et al.[12] showed in 1958 that a syndiotactic polymer is formed from liquid methyl methacrylate at low temperature under the influence of light in the presence of a peroxide. However, at ordinary temperatures under the same conditions, an atactic polymer is obtained. Obviously, the reaction takes place by a radical mechanism. Thus, a stereospecific polymer was obtained for the first time in a homogeneous medium. Enikolopyan has studied the kinetics of the low-temperature polymerization of methyl methacrylate in the temperature range from 25 to −48°C. under the same conditions as in the study of Goode et al., i.e., with free-radical initiation. In particular, it was shown that the light absorption by the peroxide was constant over the studied tem-

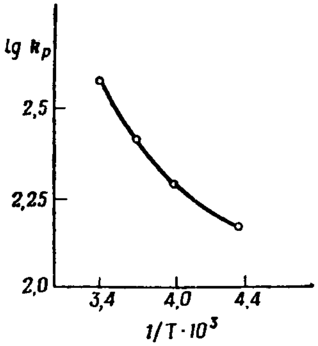

Fig. 1. The dependence of k_p on $1/T$ for methyl methacrylate.

perature range. The same experiment was carried out also for vinyl acetate. The rate of polymerization was proportional to $I^{1/2}$.

The time for chain growth was determined by the rotating-sector method, the rate of the reaction by dilatometry, and the degree of polymerization by viscometry. The rate constant for chain growth k_p was calculated by the commonly used equations. In polymerizations at temperatures above 0°C., k_p and the activation energy corresponding to it agreed with the data of other authors (Melville et al.) However, at lower temperatures the Arrhenius equation is no longer obeyed (Fig. 1). The effective energy of activation decreases with decreasing temperature. The values of the rate constant observed at low temperatures are considerably greater (approximately three times as great) than the values obtained by extrapolating the data obtained at higher temperatures by the Arrhenius equation to these low temperatures (−48°C.). The experimental curve shown in Figure 1, as it seems, cannot be obtained by assuming a formula for the rate constant for chain growth containing two terms:

$$k_p = k_{\text{syndio}} + k_{\text{isotact}} = A_1e^{-E_1/RT} + A_2e^{-E_2/RT}$$

As Enikolopyan showed, the relation which he obtained cannot, apparently, be explained from the generally accepted point of view that the polymerization process (whether radical or ionic) consists of a series of elementary events in each of which one molecule of the monomer is added.

By the rotating-sector method, Enikolopyan determined the time τ for chain growth in the low-temperature polymerization of illuminated methyl methacrylate to which a peroxide had been added. According to the ordinary theory, the time τ is determined by the rate of initiation and the rate of chain termination. It turned out to be independent of the temperature (or, in other words, the rate constant for recombination of radicals is independent of the temperature). The time τ_u between two successive acts of addition of two monomer molecules to the polymeric radicals must be

$$\tau_u = 1/k_p[M]$$

Hence, the kinetic chain length, i.e., the number of elementary acts in the chain, is

$$\nu = \tau/\tau_u = k_p[\mathrm{M}]\tau$$

In the absence of chain transfer (as was rigorously proved by Melville[13] for the polymerization of methyl methacrylate), the usual theory leads to the equation $\nu = \bar{P}$ (for chain termination by disproportionation) or $\bar{P} = 2\nu$ (for chain termination by recombination). However, Enikolopyan found experimentally that $\bar{P} = \nu$ only at temperatures above 0°C., while as the temperature was lowered, $\bar{P}/\nu$ increased, attaining a value of 6.5 at −48°C.

The author will attempt below to give another type of mechanism for the reaction of chain growth at low temperatures.

Radiation-Induced Polymerization in a Solid Monomer

A series of papers have appeared in the last few years (Mesrobian, Bamford, Magat, Morawetz, Ballantine, et al.[14]) studying polymerization in a solid phase under the influence of illumination at low temperatures. As was shown by Magat, the rate of polymerization under illumination is ordinarily 10–15 times as fast in a solid phase as in a liquid phase, even if the temperature in the solid phase is lower.

In many cases of the radiation-induced polymerization in solid monomers, the so-called post-effect is observed. This is a prolonged continuance of the reaction after cessation of the irradiation. This phenomenon has been studied in especial detail by Morawetz[15] with the polymerization of crystalline acrylamide at 25°C. In this case, the post-effect continues for days. After 100 hr., the extent of conversion amounted to only 20%. Morawetz considers this post-effect to be the result of highly retarded occurrence of the chain-growth reaction, while the considerable rate of reaction found during constant irradiation is the result of an even greater decrease in the rate constant for chain termination. On comparison with the data of Dainton,[16] the former process turns out, according to Morawetz, to be 10^5 times as slow as the reaction in a solution of acrylamide at the same temperature, while the latter process is 10^9 times as slow. The constants k_p and k_g were obtained by Morawetz by comparison of the experimental data on the time dependence of the extent of conversion polymerization with the theoretical curve derived from the usual kinetic equations for polymerization.

However, we must keep in mind the fact that Dainton and Tordoff also observed a strong post-effect in their study of the polymerization of acrylamide in solution. This post-effect continued for many hours with gradually declining rate. However, as they showed, this post-effect does not have a direct relationship to the value of the rate constant for chain growth. The time for chain growth was determined by Dainton by the rotating-sector method in a steady-state reaction (upon irradiation);

the value turned out to be only 30 sec. Hence, Dainton considered that the post-effect is associated with temporary chain scission or with shielding of the free radical, or, as he considered more probable, the process takes place by the transformation of the active polymeric radical into an inactive form with its free valence on the nitrogen atom. In either the former or latter case, the activity of the radical may be restored again by the action of thermal motion (in the latter case, by way of the reverse transformation of the radical into the active form). In these cases, after long quiescence the chain begins again to grow rather rapidly either by prolongation of the same chain or by starting a new one. Since processes of transformation of active forms of the radical into inactive forms take place very slowly in comparison with the rate of chain growth up to the time when the latter is temporarily interrupted, the post-effect will naturally continue for an extended period of time.

The post-effect in the polymerization of solid acrylamide may be of an analogous nature.

Many authors (for example, Morawetz) have associated the existence of appreciable reaction rates in the radiation-induced polymerization in solid monomers with the crystal structures of the monomers. The hypothesis has often been advanced that the relative positions of the monomer molecules turn out to be near to orientations of the reacting molecules most favorable for the chain-growth reaction. Thus, in a paper presented at this Symposium, Bensasson and Marx[17] stated that the decrease in the energy of activation for chain growth is a result of the favorable orientation of the monomer molecules in the crystal. We note that this type of favorable orientation of the radical and the monomer cannot in itself bring about a decrease in the activation energy with respect to its value in the liquid state. In the latter case, as in the gaseous state in which the activation energy is 4–5 kcal./mole, only those particles react which happen to have favorable orientations when they collide. Orientation in the crystal thus may affect only the value of the coefficient of the pre-exponential term. Many authors have overlooked this consideration. The present author advances the hypothesis that such a favorable orientation in the crystal makes it possible for the polymeric ion or radical to attach, not just one neighboring monomer molecule, but an entire chain of molecules within a region in which the crystal is ideal. This question will be discussed in detail below, while the phenomenon of energy transfer at low temperatures will be discussed next.

Let us turn to the experimental facts. For the sake of definiteness and brevity, we may spend time only on the studies conducted along this line in recent years in the Institute of Chemical Physics in the laboratories of Tal'roze, Voevodskiĭ, and Buben, and in the Institute of Petroleum-Chemical Synthesis in the laboratory of Polak. Tal'roze and Frankevich[18] studied the electrical properties which appeared in polyethylene and paraffin on heating samples which had previously been irradiated in the solid state. The irradiation was carried out with fast (1.5×10^6 v.) electrons at liquid-nitrogen temperature, as well as with hard x-rays. At the same time, the electron paramagnetic resonance spectra of the free radicals were determined. The free radicals in these systems are stable at low temperatures and begin to disappear by recombination only upon heating to a certain temperature. In the case of paraffin, these are alkyl radicals, which disappear primarily at temperatures from −33 to −13°C. In the case of polyethylene (as was shown especially clearly by Voevodskiĭ and Buben[19]), they are alkyl and allylic radicals. The former vanish in the range from −3 to +27°C., and the latter from +70 to +90°C. By measuring the electrical conductivity at the same time, Tal'roze and Frankevich found a burst of electrical conductivity at the same or slightly higher temperatures than those at which radical recombination takes place. During this burst, the electrical conductivity of the irradiated material increases by two or three orders of magnitude over that of the unirradiated material. This phenomenon may be due to the fact that the local generation of energy due to recombination of a pair of radicals may be able to eject an electron in the conduction band (forming a "hole").

This hypothesis becomes especially significant in connection with some new experiments of Tal'roze and Frankevich. They have found an analogous burst in the electrical conductivity upon heating a polymer of triethyleneglycol dimethacrylate containing radicals remaining within it after polymerization (at 25°C.). The appearance of an e.m.f. which attained a value of several volts was also observed here. Apparently, this is evidence of the long mean free paths of electrons (or of "holes") in certain collective energy levels in this system.

Certain new data have also been obtained on the migration of excitation energy along a saturated hydrocarbon chain.

Voevodskiĭ, Buben, and their associates[20] have irradiated with fast electrons the following: (*1*) saturated hydrocarbons; (*2*) benzene; (*3*) saturated compounds in the molecules of which one or two of the hydrogen atoms at the end of the chain have been replaced by phenyl groups. The alkyl chain consisted of eleven CH_2 groups. As is known, secondary alkyl radicals are formed in saturated chains on irradiation. In benzene, phenyl radicals are formed with a radiation yield 20–30 times as small as with the saturated hydrocarbon. Thus, in both cases the radicals are formed by the ejection of a hydrogen atom. It turned out that on irradiating the substituted benzenes, radicals of the phenyl type are formed almost exclusively. However, the radiation yield was two or three times larger than in pure benzene, as calculated for the direct effect. These data show the possibility of migration of energy along the saturated hydrocarbon chain to the benzene rings.

Tal'roze and Gusynin[21] have studied the quenching action of carbinols (C_1–C_9) on the luminescence of dioxane solutions activated by terphenyl. It was found that the efficiency of the quenching action of the alcohol molecule increases linearly with the length of the hydrocarbon chain. If the efficiency of quenching is determined by the collision of excited dioxane molecules with the OH group itself, then the efficiency of quenching should be the same for all alcohols (at equal molar concentrations). The discovery of a linear law shows that quenching takes place in the collision of an excited dioxane, molecule with any part of the alcohol molecule. On the other hand, it was found that the corresponding hydrocarbons (in which the OH group is lacking, of course) show practically no quenching action in this medium. These experiments are direct proof of the possibility of long-range migration of energy along the saturated hydrocarbon chain to the OH group of the alcohol.

Another example of very long-range energy transfer is given by the experiments of Kolbanovskiĭ, Polak, and Shcherbakova,[22] conducted in the Institute of Petroleum-Chemical Synthesis of the Academy of Sciences of the Soviet Union. They showed that on irradiation of frozen heptane containing excitation acceptors (e.g., aromatic compounds) in 10^{-2}–$10^{-4}M$ concentration at -196°C., the yield of radiolysis products is decreased. Thus the radius of transfer may be estimated to be approximately 100 A.

These results agree with the data of Porter and his associates,[23] who studied the transfer of energy in a methylcyclohexane–isoheptane medium. During the gamma-irradiation in the presence of approximately 10^{-3} moles of triphenylmethane, these authors found an increased yield of triphenylmethyl radicals due to transfer of energy from the solvent. However, since the products of radiolysis of the medium were not measured in the study of Porter, the study by Polak and his associates seems to be a more direct proof of energy transfer in these systems. From Porter's data, the radius of transfer may be estimated to be about 60 A., a value which is close to that given by Polak's data.

The ability of molecules to concentrate the energy of ionizing radiation apparently increases considerably with increasing conjugation. Barkalov, Berlin, Gol'danskiĭ, and Dzantiev in the Institute of Chemical Physics have studied the radiation-induced polymerization of phenylacetylene in ethyl acetate and nonane solutions. As is known, a proportionality between the yield of polymer (for a given total dose) and the concentration of the monomer is obeyed quite precisely in ethyl acetate. However, in the polymerization of phenylacetylene, it was found in both solvents that the yield of polymer (for low degrees of conversion) is practically independent of the monomer concentration in solution if this concentration is greater than 5–10%. The yield of polymer remains the same, even in a system of monomer without solvent. All of this indicates practically complete transfer of the energy absorbed by the solvent to the monomer and the polymer radicals. Apparently, this is associated with the presence of especially strong conjugation in these polymers. The replacement of the aromatic substituents by cyclohexyl rings or aliphatic chains causes a considerable decrease in the effect due to the fact that these polymers are conjugated only in the main polymer chain.

The experimental data on the peculiarities of polymerization reactions occurring at low temperatures can hardly be explained on the basis of the ordinary theory developed for higher temperatures. There are as yet too few new data for the creation of a theory of the phenomenon with which the author is concerned. Without any pretense of constructing such a theory, the author will attempt below to present a working hypothesis, but this only in a purely qualitative form.

Qualitative Hypothesis of the Nature of Low-Temperature Polymerization

It may be that a radical in a crystal of a monomer is able to join itself directly to a group consisting of a considerable number of monomer molecules. Together with other authors, I suggest that the monomer molecules are arranged in a relative orientation favorable for the polymerization reaction. Thus, there is an apparent "preorientation" for the production of macromolecules in the crystal, which does not exist in the homogeneous liquid. This factor brings about the occurrence of a faster polymerization reaction in the solid than in the liquid under the action of irradiation.

The explosive process of transformation from a monomeric to a polymeric state in a solid at a definite temperature (far below the melting point), as observed by Kargin, Kabanov, et al.[4] for a group of monomers, and by Magat[5] for formaldehyde, is highly reminiscent of the rearrangement which takes place just as vigorously in strongly supercooled solid solutions of metals. A classic example of this is the martensitic rearrangement in steel, in which the γ-form is instantaneously (diffusionlessly) transformed into the α-phase.

Since the composition and alternation of carbon atoms is not changed on polymerization, a diffusionless rearrangement is possible in this case as well. However, there is this difference, that in polymerization the process is associated with a change in the valence bonds, i.e., with a major redistribution of the electron density about the carbon atoms. (In addition, as was stated above, the rearrangement in a mixture of metal oxides or of oxides and chlorides of metals leads to a chemical reaction in which complex compounds are formed. This reaction is probably associated with redistribution of the electron density.)

Hence it would seem that in the case of polymerization the process must show an appreciable energy of activation. Each act of union of one molecule of monomer to the radical would have to be associated with the same activation energy ($\sim$5 kcal./mole) as in the liquid state. The existence of a "preorientation" might bring about a large increase in the coefficient of the exponential term in the rate constant of the reaction, but it could not lower the activation energy. Nevertheless, the activation energy of the polymerization reaction in the solid monomer is considerably lower than in the liquid monomer at ordinary temperatures.

However, we must keep in mind the fact that a "preorientation" creates highly favorable conditions for transfer of the energy liberated in the elementary act of addition of one monomer molecule (probably in the form of electronic excitation energy). This energy proceeds to activate a neighboring molecule of monomer, and thus ensures the occurrence of the next elementary act without any thermal activation, etc. Thus, the entire "preorientation" of n molecules of monomer is transformed almost instantaneously, in the period of time necessary for the displacement of the carbon atoms ($\sim 10^{-13}$ sec.), into a polymer chain by means of such an energy chain reaction. The reaction of chain growth is interrupted only when it meets a lattice defect at which the favorable arrangement of the molecules is disturbed. We note that the violent, explosive type of polymerization was observed for a number of solid monomers only at the melting point or at some considerably lower temperature, which may not have been determined precisely. Kargin, Kabanov, et al. associate this temperature with a nonequilibrium transition from the glassy state of the monomer to the crystalline state.

Over the rest of the temperature range, a slow polymerization reaction takes place in the solid crystalline monomer. Nevertheless, this reaction is as a rule 10–15 times as fast as in the liquid monomer at low temperatures.

This slow process of radiation-induced polymerization of the solid monomer at low temperatures may be represented as follows.

The action of the radiation creates in the crystal primary radicals by ejecting hydrogen atoms from the sites in the molecules where they are most weakly bound. Probably, a hydrogen atom may be most easily ejected from molecules situated at lattice defects. These primary radicals R are not very reactive because their free valences are not favorably oriented with respect to the double bond of the monomer molecules in the crystal. This explains the low rate of the process of radiation-induced polymerization. (It is known from quantum-mechanical calculations that in reactions such as $D + H{-}H \rightarrow D{-}H + H$, the process occurs with a low energy of activation only in the favorable case in which the three atoms lie practically on a straight line. With a perpendicular orientation, the activation energy is quite considerable.) Nevertheless a radical occasionally reacts with a monomer molecule at the double bond. Thus a secondary radical R—C—C— is formed, in which the free valence is already oriented favorably for further polymerization. The energy liberated in this reaction proceeds to excite an electron in a neighboring molecule, etc. As a result, a polymer chain with a free valence at the end is formed practically instantaneously.

Thus, the process proceeds as if in jumps with long pauses between them. The author sees herein, in particular, an explanation for the phenomenon of the post-effect, as well as for the frequently observed gradual increase in the rate of polymerization at the beginning of steady irradiation of the solid monomer. The chain of reactions is finally broken as a result of the rare event of recombination of the terminal valences of two chains (bimolecular process).

If the polymerization mechanism is ionic, then ion pairs of opposite signs are ordinarily formed by the action of the radiation at sites of lattice defects. The direct recombination of the ion pair is highly hindered by steric factors. Neutralization by means of capture by this primary ion pair of an electron (by the positive ion) and a hole (by the negative ion) from the collective system of the monomer is also rather rare. The energy liberated in this process, just as in the case of radical polymerization discussed above, makes possible a simultaneous act of immediate polymerization of *n* molecules in the crystal. The number *n* is again determined by the lattice defects. The electron and the hole formed in the last act in the growth of the chain are transferred to the defect. As a result, a new stable ion pair is formed at the end of the chain. Final chain termination takes place as a result of the rare event of direct recombination of a stable ion pair (monomolecular process). There is a post-effect when the reaction of chain generation occurs faster than direct recombination, and no post-effect in the converse situation.

At the melting point or slightly higher or lower, the molecules of the monomer retain their regular arrangement characteristic of the crystal, but the molecules acquire a certain mobility. This mobility is reminiscent of that of the molecules in the liquid, although not completely equivalent. This factor facilitates the reaction of the primary radical (or ion pair) with the nearest molecule of monomer, since it permits the primary radical quickly to acquire an orientation favorable for reaction.

After this act, the practically instantaneous polymerization reaction of the entire "crystallite" follows immediately, since defects can no longer retard the chain growth.

A similar situation occurs at the transition point from the glassy to the crystalline form of the monomer or, in general, at all points of phase transition. In both cases, conditions are thus created for rapid polymerization of an explosive type.

In the development of the energy chain mentioned above, the transfer of the energy liberated in any given act in the reaction to the next monomer molecule may take place in the form of electronic excitation energy.

The presence of the excitation energy leads practically instantaneously to a reaction of addition of monomer molecules to the polymer radical in a fashion similar to photochemical processes. The activation barrier is surmounted by means of this excitation energy, as in the predissociation phenomenon. The energy liberated in the reaction is again transferred so as to excite the next molecule of monomer, and the chain grows. A qualitative estimate made at the request of the author by Adirovich[24] shows that the boundary between the polymeric and monomeric parts of the chain must move with a velocity of the order of 10^4 cm./sec. Thus, a chain of 1000 links will be formed in a time of $\sim 10^{-10}$ sec.

Thus, we may draw the following picture of the energetic state of the electron in the process of rapid chain growth. The electron first occurs in the excited state with an energy E_e (after one reaction), then in the ground state (at the moment of the following reaction) (see Fig. 2).

The hypothesis presented here is one for which there is yet no firm basis. In a perfect region of the crystal, the excited level becomes collective, and

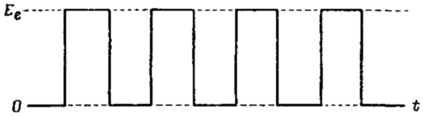

Figure 2

is a level of the excited crystal as a whole. Thus, the electron may move freely throughout the crystal with the velocity of electronwaves.

In addition, we suggest that the ground state of the monomer crystal is also to a considerable extent a collective level, and here we have the basis for the phenomenon.

Undoubtedly, such a collectivization of the ground state of the π-electrons occurs in conjugated systems. However, the regular sequence C=C C=C C=C . . . C=C* found in the crystalline monomer is similar to a conjugated system. It is true that there are no single bonds between the C=C molecules in the monomer crystal. Yet, the possibility of rather frequent tunneling of electrons and holes in monomer crystals is not at all excluded, although the distance between the carbon atoms of two different molecules is greater than that within one molecule. This leads to a certain degree of collectivization of the π-electrons in the ground state of the monomer crystal. However, then the natural question arises whether every elementary reaction in the chain requires the raising of the energy of an electron to the level E_e, then a decay to the ground state, and then a new excitation to the same level, E_e, etc. Is it not sufficient for just one electron simply to remain in this collective level in order to bring about an actually simultaneous process of polymerization of n molecules of the monomer at once? Thus, the energy liberated in the first act of addition of one monomer molecule to the primary radical is used in exciting a monomeric system of n molecules. Thereupon, a simultaneous concerted act of transformation of all n molecules of monomer at once into a polymer chain takes place. This process will take place similarly to the predissociation of complex molecules.

We will attempt here with a single example from ordinary kinetics to create a basis for the assumption of a simultaneous transformation of n molecules in the crystalline monomer into a polymer. In fact, we assume here a simultaneous concerted motion of the nuclei and a redistribution of the electron density throughout the assembly of n molecules. As is well known, the detachment of a hydrogen atom from an allylic radical requires the expenditure of an energy q corresponding to the equation:

$$H_3C—CH{=}CH—CH_2 \rightarrow H + H_2C{=}CH—CH{=}CH_2 - q$$

However, this means that the redistribution of the electron density and the

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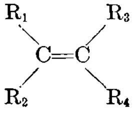
* We write C=C for brevity, instead of


$$R_1R_2C{=}CR_3R_4$$

carbon atoms takes place simultaneously, in one act, upon detachment of the hydrogen atom. If the reaction were to take place in stepwise fashion:

$$H_3C—CH{=}CH—CH_2 \rightarrow H + CH_2—CH{=}CH—CH_2 - Q_1 \qquad (1)$$

$$CH_2—CH{=}CH—CH_2 \rightarrow CH_2{=}CH—CH{=}CH_2 + Q_2 \qquad (2)$$

the energy required to detach a hydrogen atom would be Q_1, i.e., much larger than the actually observed value $Q_1 - Q_2 = q$.

It is considerably more difficult to explain on the basis of this hypothesis the peculiarities in the polymerization of liquid monomers and their solution at low temperatures. These peculiarities consist in the fact that the rate in the liquid state either increases with decreasing temperature, or decreases more slowly than it should from extrapolation to low temperatures of the values of the rate constant for chain growth $k_p = A \exp [-E/RT]$ characteristic of room temperature and above. The apparent activation energy decreases, either because of a real decrease in E or because of an increase in the coefficient A. If regularly oriented (as in the crystal groups or complexes of molecules were formed in the liquid, and the free radical were, upon encountering such a complex, to add at once these n molecules, then the peculiarities of polymerization in the liquid state at low temperatures might be explainable on the basis of the hypothesis given above.

Unfortunately, it is difficult to find a basis for the appearance of such complexes because of the weakness of the van der Waals forces. In addition, even if such complexes were to form, the number of them would change very little with decreasing temperature in a homogeneous liquid or in solution. The question arises whether there may not yet be some special reasons for the appearance of such oriented complexes in the liquid. If the polymerization reaction is due to ions or ion pairs, then the Coulombic forces which give rise to the formation of solvate shells might be the source of the formation of the complexes. In addition, complexes might be formed by means of adsorption on the walls of the vessel or on the polymer formed in the liquid. In the paper of Abkin[25] given at this Symposium, some very interesting data are given on the role of the walls of the vessel in the radiation-induced polymerization of styrene in an ethyl chloride solution at a temperature of −78°C. It was found that the rate of polymerization increases linearly with the ratio s/v, that is, the surface/volume ratio of the vessel. The rate approaches zero as the ratio s/v approaches zero. This seems to show that the reaction takes place in the layer of monomer adsorbed on the wall of the vessel.

Worrall[26] has observed a large increase in the rate of polymerization of isobutylene at low temperatures when additional solid objects were introduced into the vessel. Medvedev and Kristal'nyĭ[27] have also observed this effect in the presence of various powders. The finer the powder was (for the same weight) (i.e., the greater the surface of the solid), the larger the effect. The effect of increase in the rate did not depend much on the chemical nature of the powders.

Adler, Ballantine, and Baysal[28] have indicated in a paper given at this Symposium that the polymerization reaction takes place in a liquid at the surface of the clumps of polymer, causing them to grow into formations easily visible in the microscope.

Thus, there is some reason for supposing that polymerization in a liquid also is associated with the formation of regularly oriented groups of monomer molecules. In the author's opinion, this will permit us in the future to explain the peculiarities of the polymerization in these liquids at low temperatures.

This is the qualitative picture of the simultaneous transformation of an entire crystalline monomer into a polymer chain.

It is hoped that it will be possible in the future to find a basis for this conception, and thus to elucidate the chemical consequences of the conception of collective levels in monomer crystals for the chemistry of polymerization processes. This is similar to the current elucidation of the role of collective levels in the explanation of certain physical properties of conjugated polymers, which will be discussed in the following part of this paper.

Physical Properties of Conjugated Polymers

Before proceeding to the results of ESR studies of the new classes of polymers, we will review the fundamental types of ESR signals in the systems which have thus far been studied extensively.

Basic Types of ESR Signals

1. Free Radicals with an Unpaired Electron Localized on a Definite Atom

In most cases of interest to organic chemists (radicals containing atoms having nuclear magnetic moments), characteristic ESR spectra appear, with a hyperfine structure due to the interaction of the unpaired electron with the magnetic moments of the surrounding nuclei. Several examples are given below.

Figure 3 shows the ESR spectra of hydrogen and deuterium atoms. These spectra were obtained from a frozen solution of ferrous ions in acidified water enriched in deuterium (Bubnov and Shelimov). The solution was irradiated with light from a mercury lamp at −196°C. As may be seen from the figure, the hydrogen atoms, having a spin of $^1/_2$, give two lines in the hyperfine structure, with a spacing of 500 oersteds. The deuterium atom, with a spin of unity, gives three lines, corresponding to the three possible projections of the nuclear spin (-1, 0, $+1$), with a spacing of 78 oersteds. The given spacings between lines in both cases are in very close agreement with the values of the splitting obtained by Rabi in atomic beams. This indicates the absence of any interactions occurring in the solid between the H and D atoms and the surrounding medium.

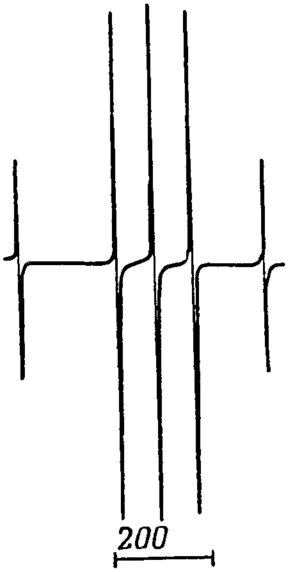


Fig. 3. ESR spectra of hydrogen and deuterium atoms. Scale: 200 oersteds.

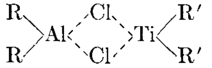
Fig. 4. ESR spectrum of the methyl radical. Scale: 25 oersteds.

In Figure 4 is shown the spectrum of the methyl radical, as obtained by the photolysis of polydimethylsiloxane (Bubnov). The spectrum consists of four lines with uniform spacing between them (25 oersteds), and with an intensity ratio of 1:3:3:1 This spectrum is the result of the interaction of the unpaired electron on the carbon atom with the three equivalent protons of the methyl group. Four states are possible, corresponding to the various orientations of the spins of the three protons:

$\uparrow\uparrow\uparrow$ a priori probability = 1
$\uparrow\uparrow\downarrow$ a priori probability = 3
$\uparrow\downarrow\downarrow$ a priori probability = 3
$\downarrow\downarrow\downarrow$ a priori probability = 1

Carbon (C^{12}) has no nuclear spin.

In the reaction of aluminum alkyls with titanium halides, complexes are formed, which are polymerization catalysts. If we select the compound $(C_5H_5)_2TiCl_2$, then both components and the reaction product are found to be soluble in toluene and benzene. Here, as has been shown by a structural analysis carried out by Natta,[29] the structure of the product may be represented by the formula



$$R_2Al\langle Cl_2 \rangle TiR'_2$$

There must be one unpaired electron in this compound. Correspondingly, Shilov et al.[30,31] in the Institute of Chemical Physics have found an ESR signal which has a poorly resolved hyperfine structure when the bridge atoms are Cl.

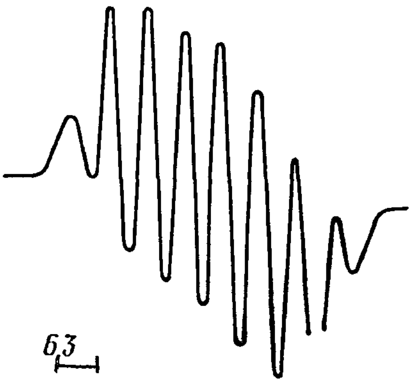
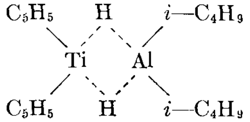


Fig. 5. The ESR spectrum of the complex



$(C_5H_5)_2Ti(H)_2Al(i\text{—}C_4H_9)_2$

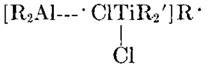
Scale: 6.3 oersteds.

The replacement of one or both chlorine atoms by hydrogen leads to the formation of new complexes whose ESR spectra show well-resolved hyperfine structures (Fig. 5). A calculation of this structure showed that the spin electron density is distributed among the aluminum, the titanium, and the two hydrogen atoms.

Digressing from the question under discussion, the author will consider the question of the role of complexes of the Ziegler type which are polymerization catalysts.

Natta has already found that the light-blue complex whose structure was just discussed shows a weak catalytic activity.

On the basis of his experiments, Shilov arrived at the conclusion that the catalytically active form is the intermediate complex, which may be represented in a general form by



$$[R_2Al\text{---}\cdot Cl\underset{\overset{|}{Cl}}{Ti}R_2']R\cdot$$

(biradical type)

or

$$[R_2Al\text{---}Cl\underset{\overset{|}{Cl}}{Ti}R_2']^+R^-$$

(ion pair)

Most probably, the true structure is intermediate between these two. One of the alkyl groups, weakly bound to the rest of the complex, shows certain properties of free radicals (e.g., it may disproportionate with another suitable particle), but it is almost incapable of recombination. Hence, the reaction of titanium halides with triethylaluminum takes place almost instantaneously, with the liberation of ethane and ethylene, while trimethylaluminum forms the stable complex mentioned above. In reactions with olefins, the $\cdot CH_3$ (or CH_3^-) in this complex is replaced by a longer radical capable of disproportionation with other CH_3 groups. Hence, as Shilov showed, together with the consumption of the olefin, the liberation of methane and the formation of a light-blue inactive complex take place.

Of course, the general question arises whether the so-called ion pairs in certain cases are not intermediate entities between ionic and biradical structures.

2. Free Radicals with Delocalized Unpaired Electrons (Electrons Not Fixed on Any Particular Atoms in the Molecule)

If the frequency of exchange is sufficient, each unpaired electron is situated in the same average field of the nuclear spins. As Anderson has shown, we observe here a narrow single paramagnetic resonance line corresponding to the average (zero) value of the magnetic field of the nuclear spins.

Figure 6*b* shows the ESR spectrum of the free radical diphenylpicrylhydrazyl (DPPH) in benzene solution. The spectrum shows a typical hyperfine structure (due to interaction with the nitrogen nuclei). The total width of the spectrum is ~50 oersteds. In the solid state, in which the molecules exchange their unpaired electrons with a sufficient frequency (collective level), the spectrum is a single narrow line (Fig. 6*a*).

Figure 7 shows the ESR spectrum of guanylic acid which had been irradiated with gamma-rays. This monomer is one of the components of the complex biological polymers, the nucleic acids. As we may see, the spectrum consists of a series of hyperfine-structure lines with a total width of about 100 oersteds. In the polymer ribonucleic acid, in which the unpaired electrons appearing upon gamma-irradiation are delocalized, a narrow (8–9 oersted) ESR line without hyperfine structure is observed (Fig. 8) (data of Blyumenfel'd).

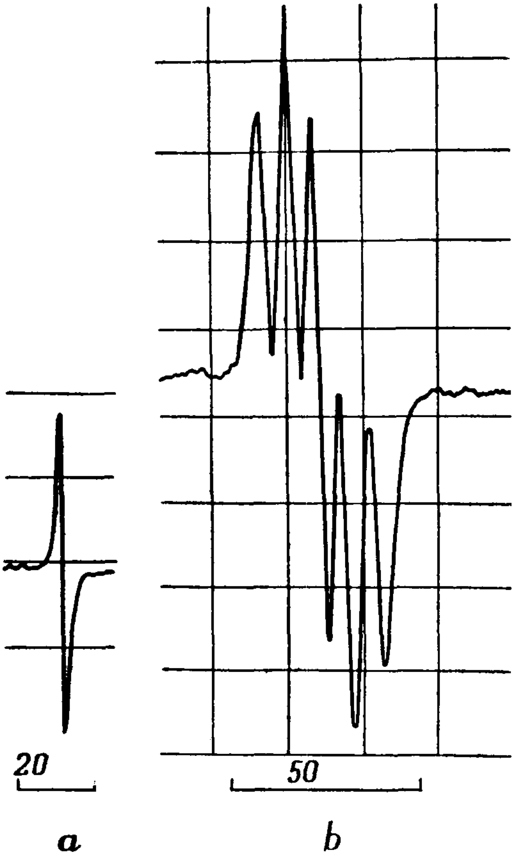


Fig. 6. ESR spectra of diphenylpicrylhydrazine: (*a*) in the solid state; (*b*) in benzene solution. Scale: (*a*) 20 oersteds; (*b*) 50 oersteds.

3. Unpaired Electrons with a Strong Collective Interaction

In this case, an exceedingly great broadening of the ESR signal (hundreds or thousands of oersteds) and an asymmetry of these broad lines are observed. Two types are widely known: (*a*) metals of high electrical conductivity, in which the intensity of the signal is small; (*b*) ferromagnetic

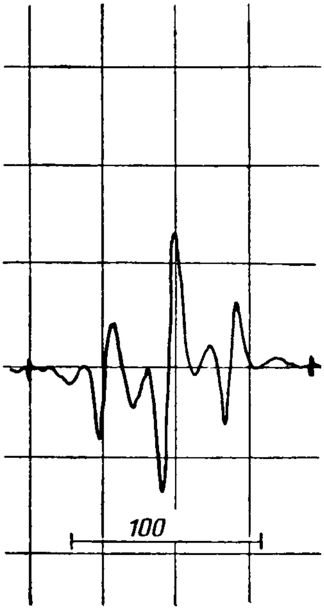


Fig. 7. ESR spectrum of gamma-irradiated guanylic acid. Scale: 100 oersteds.

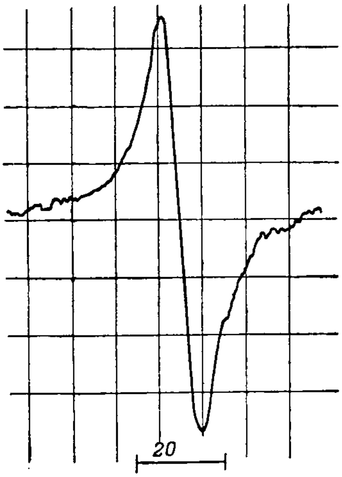


Fig. 8. ESR spectrum of ribonucleic acid. Scale: 20 oersteds.

and antiferromagnetic materials, in which powerful internal magnetic fields occur, leading to a very high intensity of signal. In Figure 9 is shown the ESR signal of the typical antiferromagnetic material Cr_2O_3.

Thus completing the brief description of the classification of ESR signals, we will now proceed directly to the theme of the second part of this paper.

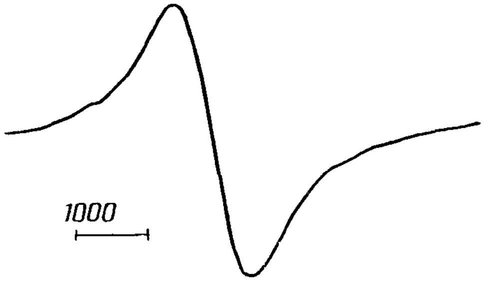


Fig. 9. ESR spectrum of Cr_2O_3. Scale: 1000 oersteds.

ESR Spectra of Conjugated Polymeric Systems

During 1959, new magnetic effects in organic structures were discovered by the ESR method which were associated with the appearance of narrow, and broad ESR lines. We shall begin with the problem of the narrow lines. As early as 1948, Kozyrev[32] in Kazan found a narrow ESR signal in hydrocarbons with conjugated double bonds in the solid state. Here the intensity of the signal increased with the length of the conjugated chain. The experiments were carried out at a single temperature (room temperature). Apparently Kozyrev interpreted this phenomenon incorrectly as the result of excitation into the triplet (biradical) state, which approaches so closely to the ground state as the conjugation increases that it becomes appreciably occupied even at room temperature. Analogous results were later obtained from various conjugated systems by various foreign and Soviet authors. In the middle of 1959, a paper by Matsunaga[33] appeared which showed that in the case of the conjugated hydrocarbon, dinaphthoquinone, the narrow ESR signal observable in the crystalline state increases in intensity upon a decrease in the temperature according to the Curie law. Apparently, this excludes the interpretation of the effect as being due to excitation to the triplet state. However, Matsunaga assumes that in solution a very small fraction of the molecules forms bimolecular complexes with greatly lowered (to considerably less than kT) energies of excitation to the triplet state. These complexes are frozen in the solid state, and give the observed signals. We should note that the signal disappears in solution.

At the Mendeleev Congress in March, 1959, the author reported very briefly in a review paper[34] that, according to the experiments of Blyumenfel'd and Berlin,[35,36] narrow ESR signals appear in conjugated polymeric systems. The detailed articles of these authors appeared in the latter part of 1959. Above all, the presence of narrow signals was shown in polyphenylacetylene, and then in other conjugated polymeric systems (polyphenylene, the polymer of tetracyanoethylene, polyphthalocyanine, polyaminoquinones). The signals persist when the polymer molecules are dissolved.

In the paper of Topchiev, Kargin, Krentsel', Polak, Davydov, et al.[37]

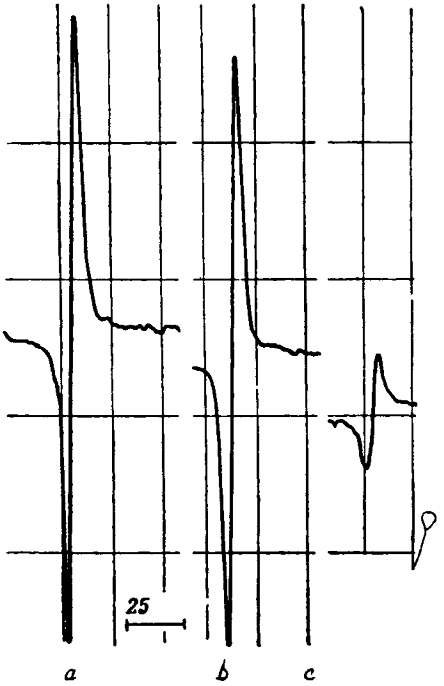


Fig. 10. ESR spectrum of polyphenylacetylene: (*a*) in the solid state; (*b*) the same amount in benzene solution; (*c*) the same as (*b*), but diluted fivefold. Scale: 25 oersteds.

published in September, 1959, it was reported that narrow ESR signals occur in heat-treated polyacrylonitrile samples.

Blyumenfel'd and Berlin showed that: (*1*) the intensity of the signal does not depend on the method of preparing the polymer, but is determined by the length of the conjugated chain, and is retained upon solution, even at the highest dilutions (Fig. 10). That is, it is a property of the polymer molecule, rather than of the solid polymer as a whole. These data exclude the hypothesis of Matsunaga at least, as applied to these polymeric compounds.

It was also found that (*2*) the temperature dependence strictly obeys the Curie law over the temperature range from +150 to −196°C. That is, the paramagnetic signals are not due to thermal excitation to the triplet state.

Voevodskiĭ and Tikhomirova[38] showed that the narrow signals in amorphous carbons are also due to the system of conjugated bonds of the condensed aromatic rings of the carbon, rather than indicating the presence of true free radicals, as was thought previously. Thus, a new effect was in fact found in 1959, characteristic of conjugated systems, and especially strongly manifested in conjugated chains in macromolecules.

The appearance of a narrow signal may be considered to be an indication of the extent to which the electrons are unpaired in conjugated systems.

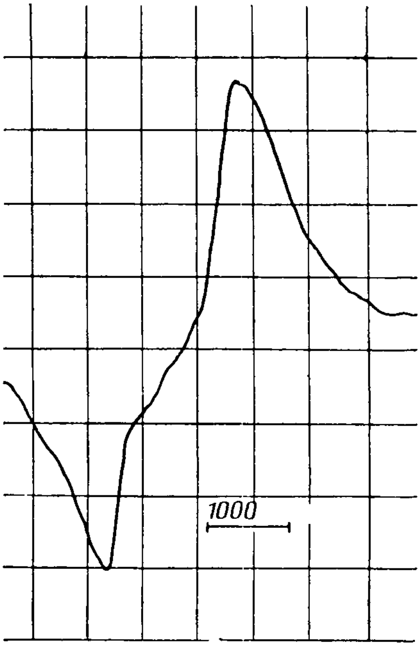


Fig. 11. ESR spectrum of deoxyribonucleic acid (DNA). Scale: 1000 oersteds.

If we know the intensity of the signal and the absorption caused by one unpaired electron (under given conditions of measurement), we may determine the extent of unpairing, i.e., the number of unpaired electrons per gram and, hence, per molecule. In monomeric conjugated systems, the number of unpaired electrons per molecule is found to be a small fraction (10^{-4}–2.5×10^{-3}), and for soluble conjugated polymers it is not larger than $^1/_5$. Since the extent of unpairing is a fractional number, we apparently may not speak of any individual unpaired electron, but only of the extent of unpairing of the electron cloud as a whole. The fractional value of the extent of unpairing in the molecule obviously cannot be explained by assuming that one of the molecules contains an unpaired electron while the others do not, since all of the molecules in the solution are, of course, identical.

It follows from all that has been said above, apparently, that the unpairing is associated not with the excited, but with the ground, state of the molecule. There is as yet no theoretical explanation for this effect.

We shall proceed to the study of magnetic effects associated with the appearance of broad ESR lines.

An article was published in early 1959 by Blyumenfel'd, Kalmanson, and the Chinese graduate student Shen Peĭ-Gen',[39] who discovered new magnetic properties of nucleic acids and their complexes with proteins. They found exceedingly broad (700–1000 oersteds) asymmetric ESR lines of high integrated intensity in native nucleic acids and nucleoproteins. A typical ESR spectrum of native deoxyribonucleic acid is given in Figure 11.

If we estimate the concentration of unpaired electrons on the assumption that these compounds are ordinary paramagnetic materials, we obtain tremendous values (10^{21}–10^{22} unpaired electrons per gram). However, the width, form, and temperature dependence of these lines are different from the corresponding characteristics of paramagnetic materials. These completely unexpected magnetic properties of biopolymers which according to previous conceptions should be diamagnetic have been studied in detail in the laboratory of Blyumenfel'd.[40] It was found that these compounds are characterized by a positive static magnetic susceptibility, which decreases upon increase of the magnetic field according to a hyperbolic law. Thus, a distinct saturation effect is observed, as is characteristic of ferromagnetic materials. However, in distinction from all known ferromagnetic materials, there is no residual magnetic moment when the external magnetic field is removed. For a number of substances the behavior of these signals upon lowering of the temperature is reminiscent of the change in the ESR spectra of compounds of the type of Cr_2O_3, MnO, and other typical antiferromagnetic materials. On the other hand, the saturation at relatively low fields is reminiscent of ferromagnetic materials. We note that Bothner-By, Balazs, and Gergely[41] reported at the 4th International Congress of Biochemistry in late 1958 that their data give evidence of the presence of strong internal magnetic fields in DNA.

It is clear from all of the existing experimental material that this is a collective phenomenon due to the existence of separate regions (individual domains) within which unpaired electrons interact strongly. The manifestation of the effects found by Blyumenfel'd is closely associated with the maintenance of the ordered structure of the biopolymer. When the structure is destroyed (as by heat denaturation), the effects vanish, while with additional formation of structure (as in the formation of complexes with proteins), the effects are intensified. Analogous specific magnetic properties have been discovered in this laboratory in native tissues containing nucleic acids (Kalmanson), in natural nucleoproteins (Kulibakin), and in growing bacterial cultures (Samoĭlova).

An analogous peculiar "pseudoferromagnetism" has also been observed in many polymers with conjugated double bonds; these polymers, as a rule, contain heteroatoms or metal atoms in the conjugated chain, as well as electron-donor or electron-acceptor groups.[36,42] These new polymers have been synthesized in the laboratory of Berlin. As in all polymers with conjugated double bonds, these polymers give narrow ESR lines of the type described above. However, in this case, in the solid state this narrow signal is superimposed on a broad line of great integrated intensity. As in the case of the nucleic acids, the manifestation of the broad signal is accompanied by a positive static magnetic susceptibility exhibiting a distinct saturation effect. Upon solution of the polymer, the broad line and the positive magnetic susceptibility disappear, while the narrow signal remains. Thus, the broad line is characteristic of the structure of the solid polymer as a whole, although its appearance also depends on the properties of the individual polymer molecules. Analogous magnetic properties (broad ESR lines) have been found in Blyumenfel'd's laboratory in certain crystalline monomers having a rather branched system of conjugated bonds (certain dyes, hydroxy derivatives of organic condensed hydrocarbons). As in the case of the polymers, these effects vanish upon solution.

All of the new magnetic properties of the polymeric systems described above give evidence of the existence either of collective levels in which the electrons occur in a delocalized form throughout the system (the narrow ESR lines) or of regions having strongly interacting clouds of collectivized electrons (the broad ESR lines).

Thus, in the light of the new data, individual macromolecules, and sometimes also the ordered aggregates of macromolecules, must be considered from the standpoint of their electronic structure to be single, integral systems. Undoubtedly, these peculiarities of electronic structure must have a strong effect on the physical and chemical properties of such substances.*

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* Anomalous magnetic properties of nucleic acids have attracted the attention of many scientists during the last years. A confirmation of effects discovered in Blyumenfel'd's laboratory was obtained with natural nucleoproteins and phages by Zimmer et al.,[59] with DNA, RNA, and purine and pyrimidine bases compressed under 15,000 atm. by Blois and Maling,[60] and with DNA by Redhardt.[61] At the same time it was clearly understood that the magnetic effects observed were of a collective nature and resembled those of ferromagnetism, and this compelled all scientists to especially elaborate treatment of the question whether the effect observed could be due to minor ferromagnetic inclusions of iron or its oxides. Ferromagnetic admixtures, even as traces, may cause signals of the intensity observed. It will be noted that nucleic acids always contain small amounts of paramagnetic metal ions, in particular of iron, inherent in their structure in a concentration of approximately one ion for 150–200 nucleotides.[62] These ions proper cannot exhibit the above-mentioned effects, but their amount is comparable to that of iron, for instance, if all the amount of the latter were present in a ferromagnetic state sufficient to cause a resonance signal. Thus chemical techniques that are incapable of distinguishing between ferromagnetic iron and paramagnetic ions appears inadequate for analysis of these admixtures. Since the effect is not specific, minor ferromagnetic particles that could have been occluded in the process of preparation may imitate the phenomena observed.

Indeed, A. A. Alexandrov, V. Yu. Gavrilov et al[63] found that in certain cases the effect may be accounted for by such admixtures. On the other hand a number of experiments shows that the abovementioned properties are inherent in the biological material and exist irrespectively of admixtures incorporated from outside.[64]

Taking into consideration the collective ferromagnetic nature of the effect, it will be noted that minor ferromagnetic inclusions into the organic structure, stabilized or even created by the polymer itself out of paramagnetic ions, might provide an explanation for many facts observed. The physical nature of these anomalous magnetic properties is not yet established. Ferromagnetic inclusions inherent in biopolymers or formed in the course of synthesis of polymers with conjugated bonds, and a strictly defined spatial configuration may appear to be responsible for the effect. However, there is a fair amount of information in favour of the suggestion that unpaired electrons are inherent in the organic structure, the latter ensuring their collective interaction. Further extensive investigations are necessary for the elucidation of this problem.

Electrical Properties of the Polymers

Besides the magnetic properties, another important set of physical properties is the electrical properties. Naturally, the electrical conductivity is determined here by the state of the sample as a whole, rather than simply by the structure of the individual molecules. As has been shown, in conjugated systems of both types (showing narrow or broad signals), generalized levels exist, and apparently there is practically no resistance to the motion of electrons or holes under the influence of an external magnetic field in the conjugated molecule itself, or in the domains as well. Resistance appears only when the electron passes from one polymer molecule to another or from one domain to another. Since a domain is considerably larger in volume than a polymer molecule, we might expect these systems to show considerably larger values of the electrical conductivity. In fact, it has been known for a long time that the polynuclear aromatic hydrocarbons, which form good molecular crystals, exhibit an enhanced electrical conductivity at room temperature as compared with other organic compounds. As Blyumenfel'd has stated, a broad signal has been found for certain compounds of this type.

Tal'roze, Frankevich, and Balabanov[43] of the Institute of Chemical Physics of the Academy of Sciences of the Soviet Union have measured the electrical conductivity of a large number of the new polymers listed above. The polymers were synthesized in the laboratory of Berlin (by Parini, Cherkashin, etc.). It was found here that an enhanced conductivity at room temperature is observed, as a rule, in the same samples that give broad ESR signals. On the other hand, the authors considered the fact that those polymer samples with continuous conjugated chains which give narrow ESR lines without exhibiting enhanced electrical conductivity at room temperature, in many instances, show a very high energy of activation (as much as 50 kcal./mole) of the electrical conductivity. In these cases, the Arrhenius equation ($\sigma = \sigma_0 \exp \{-E/RT\}$) is obeyed very precisely. Tal'roze studied the relation between the activation energy and the coefficient σ_0 for the polymers with narrow and broad ESR signals which they had studied, as well as for various previously known organic compounds, including the polynuclear aromatic compounds. The results of this study are given in Table I and Figure 12, in which the logarithm of the coefficient $\log \sigma_0$ is plotted as the abscissa, and the energy of activation E is plotted as the ordinate. At the same time, for a large number of the samples studied by the ESR method by Blyumenfel'd, the presence of a narrow signal is indicated by the square points (□), a broad signal by the circles (○) and no signal at all by the triangles (△). The inverted triangle (▽) refers to samples for which there are no data on ESR signals as yet. It was found that there is a very distinct relation between the change in the activation energy and in the coefficient σ_0 on going from one sample to another. It is of especial interest that there is a rather good linear relation between $\log n_0$ and E for practically all the samples for which broad ESR lines are

TABLE I
Materials Listed in Figure 12

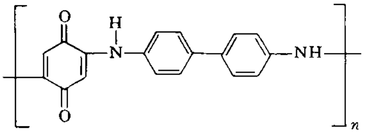
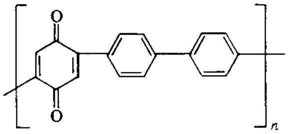
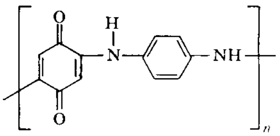
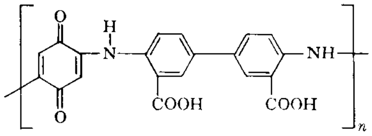
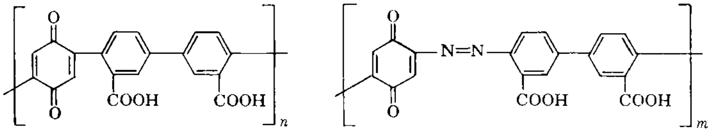
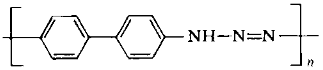
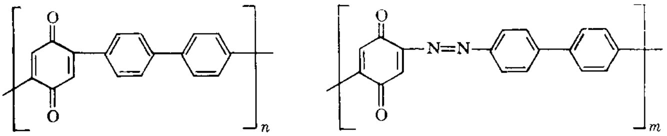
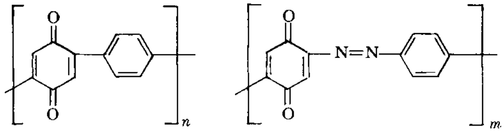
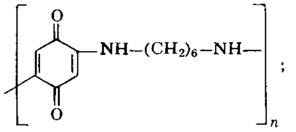
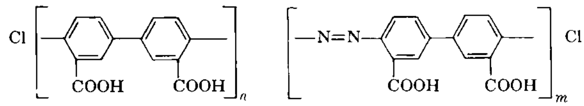
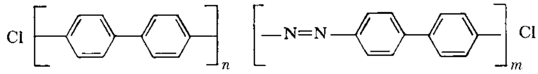
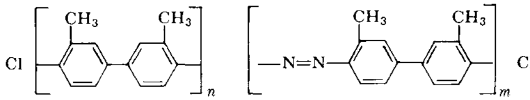
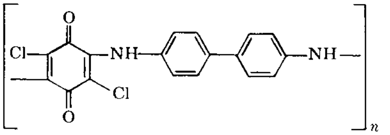
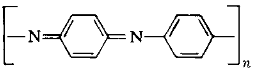
No.	Material and treatment	Reference
1	Polyphenylacetylene (mixture of yellow polymer obtained by polymerization of phenylacetylene at the boiling point and the black polymer obtained on heating the yellow polymer to 400°C.)	
2	Polyphenylacetylene (mixture of black and yellow forms)	
3	Polyphenylacetylene (yellow)	
4		
5		
6		
7		
8	Paraffin	51
9	Same as No. 7, but a different sample	
10		
11		
12	Same as No. 11, but unfractionated, lower molecular weight	
13		
14		

TABLE I (*Continued*)

No.	Material and treatment	Reference
15		
16		Unfractionated, low molecular weight
17	Insoluble fraction of No. 16	
18	 (Heated to 200°C.)	
19	Same as No. 18, not heated	
20	 (Heated)	
21		
22	Complex of No. 21 with copper acetate	
23	Salt of No. 21 with pyridine	
24	Tetrasalicylferrocene	
25	Tetrasalicylferrocene	
26	Complex of tetrasalicylferrocene with Fe^{2+}	
27	Complex of tetrasalicylferrocene with Be^{2+}	
28	Polyphenylacetylene (black)	
29	Copolymer of polyphenylacetylene with hexyne	
30	Same as No. 29, but at different temperature	
31	Polytetracyanoethylene	
32	Polytetracyanoethylene + tetracyanoethylene	
33	Polyphenylacetylene (black), pressed at 260°C., 5000 $kg./cm.^2$	
34	Polyphenylacetylene (yellow), pressed at 200°C., 2000 $kg./cm.^2$	
35	Polyphenylacetylene (black), pressed at 200°C., 2000 $kg./cm.^2$	
36	Copolymer of polyphenylacetylene (yellow) with *p*-diethynylbenzene	
37	Complex of acenaphthene with chloroanyl (1:1)	
38	Same as No. 37, at higher temperatures	
39	Complex of acenaphthene with chloroanyl (1:2)	
40	 (40-75°C.)	

(*continued*)

TABLE I (*continued*)

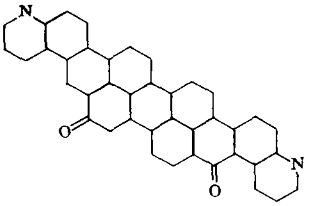
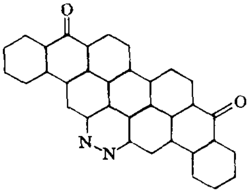
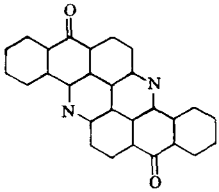
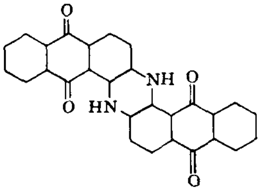
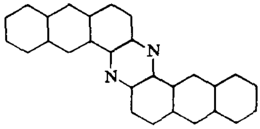
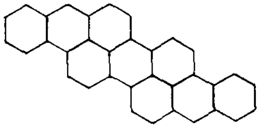
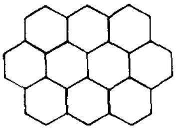
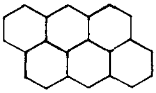
No.	Material and treatment	Reference
41		52
42		52
43		52
44		52
45		52
46		52
47		52
48		52

TABLE I (*continued*)

No.	Material and treatment	Reference
49	Phthalocyanine, 100–500°C.	53
50	Phthalocyanine, 10–100°C.	53
51	Coronene, 220–260°C.	53
52	Anthracene	53
53	Isobenzanthrone	53
54	Anthracene	54
55	Naphthacene	54
56	Pentacene	54
57	Perylene	54
58	Pyrene	54
59	Chrysene	54
60	Anthanthrene	54
61	Isobenzanthrone, 50–250°C.	55
62	Coronene	55
63	Anthracene, 70–204°C.	55
64	Isobenzanthrone	55
65	Fibrinogen	55
66	Phthalocyanine, 130–270°C.	55
67	Phthalocyanine, 270–390°C.	55
68	Phthalocyanine, 60–160°C.	55
69	Copper phthalocyanine	56
70	Zinc phthalocyanine	56
71	Magnesium phthalocyanine	56
72	Pinacyanole	57
73	Orthochrome T	57

not observed. The samples having broad ESR lines are considerably "shifted" away from the straight line in Figure 12 in the direction of larger values of the electrical conductivity at room temperature.[44]

Here the values of the electrical conductivity which scientists in various countries have been able to measure on polymeric materials are highly significant. Thus, Topchiev, Kargin, Krentsel', Polak, and Davydov, and their associates[45,37] in the Soviet Union have been able to prepare by heat treatment of polyacrylonitrile a substance with an electrical conductivity of 10^{-3} ohm^{-1} cm.$^{-1}$ at 20°C. Somewhat later, Pohl[46] (U. S. A.) obtained samples by an analogous method with an electrical conductivity of the same order of magnitude. Epstein and Wild[47] in the United States have prepared samples of copper polyphthalocyanine with $\sigma = 2.5 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ at 25°C. Neill and Weiss[48] in Australia have prepared polyxanthene with $\sigma \cong 10^{-4}$ ohm^{-1} cm.$^{-1}$ at 25°C. The electrical conductivity of the polymeric chelate compound of tetracyanoethylene with copper, which was synthesized in the Institute of Chemical Physics in Berlin's laboratory and studied in the Institute of Electrochemistry of the Academy of Sciences of the Soviet Union by Frumkin, Burshteĭn, and their associates,[49] is 5×10^{-6} ohm^{-1} cm.$^{-1}$ at 20°C. The electrical conductivity of polyphenylamine, which was synthesized in the same laboratory and studied in the Institute of

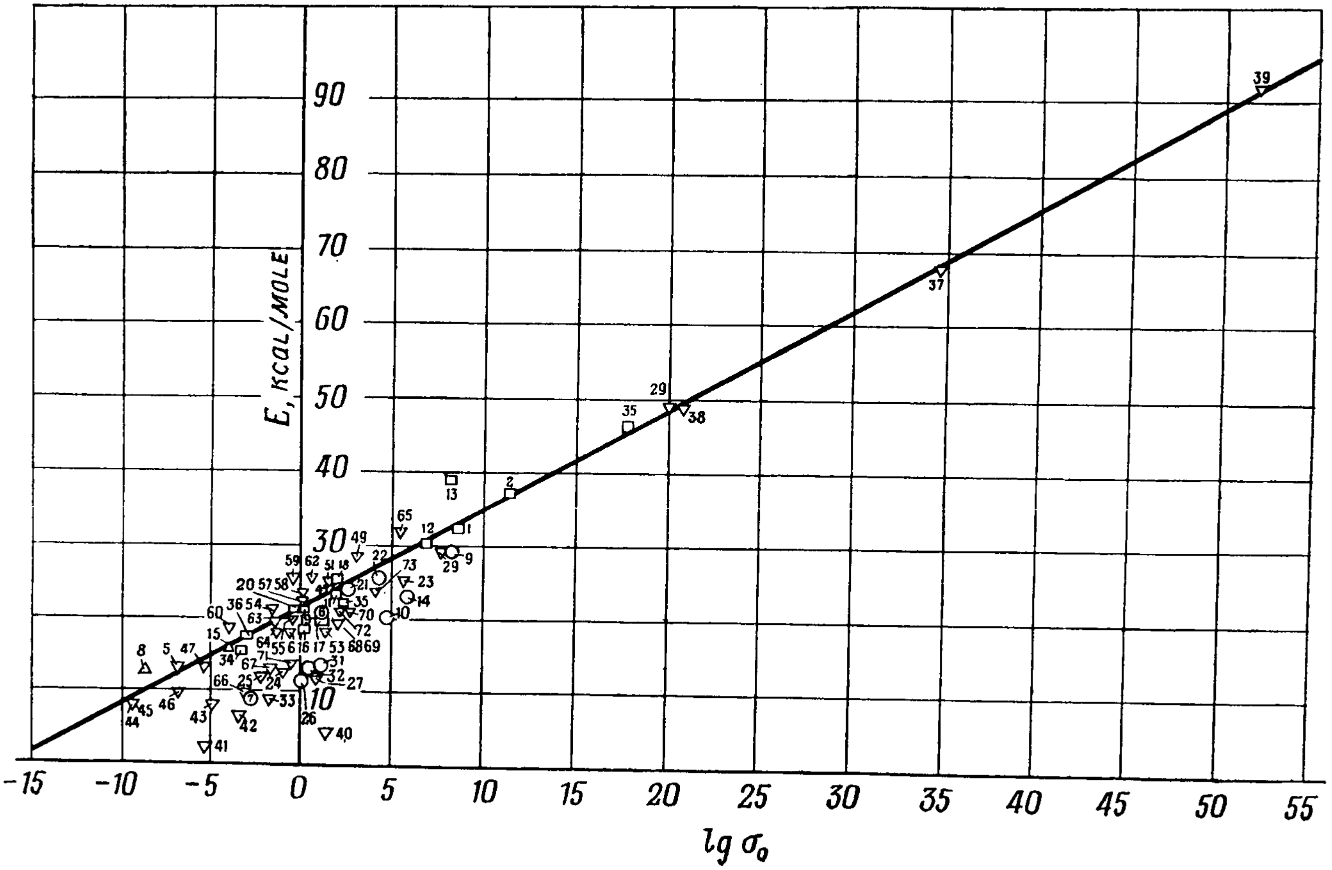


Fig. 12. Relation between the activation energy E and the coefficient σ_0 for the electrical conductivity of organic substances: (○) samples giving broad ESR lines; (□) samples giving only narrow ESR lines; (△) samples not giving ESR signals; (▽) samples whose ESR spectra have not been studied. The structures and treatment of the various couples are listed in Table I.

Chemical Physics, is equal to 10^{-6} ohm^{-1} cm.$^{-1}$ at 25°C. Enhanced values of the dielectric constant are observed in all cases.

It is of interest to note that the samples (corresponding to the points on the upper right-hand part of the line in Figure 12) which show very high values of σ_0 and E, naturally show a very rapid increase in electrical conductivity on heating. Thus, for example, the electrical conductivity of samples of the molecular complexes of acenaphthene and chloranil, prepared by Parini in Berlin's laboratory is 10^{-15} ohm^{-1} cm.$^{-1}$ at 25°C., while at 65°C. this value has risen to 10^{-7} ohm^{-1} cm.$^{-1}$. However, these samples decompose at higher temperatures. The relation derived between σ_0 and E has many kinetic analogs, especially in solid-state processes, in catalysis in particular. There is yet no overall conception of this so-called compensation effect, but recently Roginskiĭ and Khait[50] in the Soviet Union have suggested some theoretical bases for this effect. However, we must emphasize that this effect has never been observed before on a comparable scale, with a change in the coefficient σ_0 by 60 orders of magnitude.

Tal'roze has suggested that the existence of a linear relation encompassing all substances which do not show broad ESR lines and which at the same time have small electrical conductivities at room temperature, together with the sharp deviation from this relation by samples with high electrical conductivities (and with broad ESR lines at the same time) may in the future serve as the basis of a classification distinguishing substances with strong collective interactions and correspondingly high electrical conductivity from those with small collective interactions and correspondingly poor electrical conductivity at ordinary temperatures. In conclusion, I should like to note that the polymeric systems discussed above which give ESR spectra show catalytic properties in certain oxidation–reduction reactions, as preliminary experiments conducted at the Institute of Element-Organic Compounds, the Institute of Petroleum-Chemical Synthesis, and the Institute of Chemical Physics have shown.[58]

This paper has consisted of two parts rather different in character. The first part was devoted to polymerization at low temperatures, while the second part involved the physical properties of new classes of polymers. However, both of these parts were connected to some degree by one general idea consisting in the recognition of the important role of the collectivization of electrons and their energy levels, both in polymerization processes and in physical properties. The role of such conceptions will probably be especially important in the future in the understanding of biochemical processes.

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Synopsis

The first part of the paper is concerned with low-temperature polymerization, and a hypothesis explaining its mechanism is proposed. Physical properties of new classes of polymers are discussed in the second part. The importance of electron collectivization and energy levels both in polymerization processes and in physical properties is emphasized.

Résumé

La première partie de ce travail traite de la polymérisation a basse température et on propose une hypothèse pour en expliquer le mécanisme. Dans la deuxième partie, on discute des propriétés physiques de nouvelles classes de polymeres. On discute de l'importance du rassemblement électronique et des niveaux d'énergie à la fois dans le processus de polymérisation et dans les propriétés physiques.

Zusammenfassung

Der erste Teil der Arbeit befasst sich mit der Tieftemperaturpolymerisation und bringt eine Hypothese zur Erklärung ihres Mechanismus. Im zweiten Teil werden die physikalischen Eigenschaften neuer Klassen von Polymeren diskutiert. Besonderer Nachdruck wird auf die Bedeutung der Elektronenkollektivierung und der Energieniveaus sowohl bei den Polymerisationsvorgängen als auch bei den physikalischen Eigenschaften gelegt.