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Electronic Structure and Optical and Paramagnetic Properties of Macromolecules with Conjugated Bonds

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ABSTRACT

The electronic structure and optical and paramagnetic properties of macromolecules with conjugated bonds were studied. Their electronic structures were described by use of such modern theoretical techniques as the unrestricted Hartree-Fock method based on the Hubbard Hamiltonian. Paramagnetic and optical properties were explained on the basis of this theory.

INTRODUCTION

At present, ideas about the electronic structure of macromolecules with conjugated bonds and their allied physicochemical aspects are being rapidly developed [1-3]. Considerable progress has also been made in gaining a deeper understanding of the properties of

these compounds, thanks to the development of theoretical and experimental methods of research. Just as in any other field of knowledge, the theoretical apparatus is called upon to explain the already existing hypotheses and to propound fresh ideas in thinking up new experiments, while the experimental techniques, whenever possible, should serve as a tool for testing the validity of the theories and to provide grounds for further theoretical advancement. In any case, this mutual enrichment and complementation of the theory and experiment alone can vouchsafe success. In the area under review, till recently there was a gap between theory and experiment. Theoretical efforts were largely concentrated on solving a model problem (often, rather farfetched), whereas experimental investigations centered around model systems with different electron-interaction potentials, analysis of various approaches, and methods for solving such problems. Particular attention was paid to the nature and method of describing all the possible phase transitions in the system. It cannot be altogether affirmed that these efforts were absolutely fruitless with regard to the theory of electronic structure of macromolecules with conjugated bonds. On the contrary, effective calculation methods have been worked out and a clearer insight has been gained into the essential details of electron interaction in the system.

Experimental investigations, in turn, have suffered as a result of a lack of a sound theoretical basis; nevertheless a vast wealth of experimental information has been accumulated which clearly shows that the electronic structure, and probably the paramagnetic properties, are of paramount importance.

Without concealing the difficulties, we shall attempt to present, in an easily accessible manner, the problems in the field of the electronic structure, paramagnetic and optical properties of macromolecules with conjugated bonds and many other physical and chemical questions.

Polymers with a system of conjugation today find extensive application in engineering and technology as highly thermostable structural materials, binders, and fillers. All these properties owe their origin largely to the system of conjugation along the main chain of the macromolecule. High thermostability results from the substantial binding energy which arises from additional π -bonds. The atomic binding energies in conjugated systems exceed the corresponding energies of saturated systems by about 30-40 kcal/mole.

The rigidity of macromolecules, and consequently, the strength of the product as a whole, depends on the stability of the molecular core relative to the distortions in the valence and torsional angles. One merit of polymers with a system of conjugation in practical

application is their ability to transmit physical and chemical interactions over long distances.

Polymers with a system of conjugation are produced by a multitude of different synthesis methods under various conditions. They can be produced on catalytic systems or by thermal and radiation polymerization in bulk or solution. Despite their various origins, many of the physical and chemical properties of polymers with a system of conjugation do not depend on the conditions and methods of synthesis, but constitute an inherent characteristic feature of the polymers. For instance, such properties are paramagnetism, exhibited as an EPR signal with $g \approx 2$, coloration, longwave optical absorption, semiconductor characteristics, and several others. The polymers with a system of conjugation formed in synthesis are mostly linear in structure. The highly developed conjugation system in these polymers is responsible for their high affinity to form molecular associates. Therefore the solubility of these polymers is determined, in addition to this affinity, by other factors as well, which hinder such association, i.e., coplanarity of molecules and side groups which break up the supermolecular structures. Generally their average molecular weight varies from 500 to 5000. On passing on to a two-dimensional (planar) conjugation, many of the properties (paramagnetism, semiconductor characteristics, longwave absorption intensity) are augmented, and the polymers lose their solubility.

So far only one-dimensional polymers with systems of conjugation have been studied in detail, both experimentally and theoretically, and therefore there is every reason to consider this class of polymers.

Polyphenylacetylene (PPA) was the first such polymer to be synthesized [4], and even today it is the polymer that has been exhaustively studied. Innumerable allied polymers have been synthesized since then. Most of them are either amorphous or weakly crystalline. Those of the polymers with systems of conjugation which are highly crystalline ($\approx 60-80\%$) have been synthesized on stereospecific catalysts. Another class of polymers exists, however, capable of forming single crystals of macroscopic sizes.

Until recently, little was known about paramagnetic properties. At one time it was believed that paramagnetic properties were not to be observed in linear conjugated molecules whose cores lie on one plane, and paramagnetism was attributed to the disruption of the molecular arrangement planarity and conjugation, and the formation of diradical states. Later, it was established theoretically that paramagnetism may be observed even for plane conjugated molecules if all the bonds are formally saturated [5, 6]. While two or three

plausible hypotheses have been propounded to explain the origin of paramagnetism in conjugated polymers, no serious advances have been made in interpreting paramagnetic behavior (exhibited in the form of EPR signals) under the influence of external interactions, such as a change in the aggregate state (liquid or solid), presence or absence of oxygen, the effect of solvent nature etc. All these have to be interpreted in terms of the microscopic theory of paramagnetism in polymers with systems of conjugation. This question, however, needs further clarification. The nature of spatial distribution of paramagnetic centers and the behavior of the relaxation properties of spin systems are still incomprehensible. These problems have just been begun to be studied within the framework of the general physico-chemical theory of the PSC.

Only quite recently have the optical properties been interpreted on the basis of the latest advances in the theory of the electronic structure of macromolecules with conjugated bonds. Previous experimental facts suggest that a limiting wavelength exists for the optical absorption as the conjugated chain length increases ad infinitum. These results were initially reported by Broecker et al. for linear polyenes [7-11]. They have already been established for almost all the one-dimensional systems investigated (except for certain dyes). In addition to the intense optical absorption in the shortwave region (< 560 nm), low intensity optical absorption is observed in the longwave region. This absorption has been found to be of electron transition nature and associated with the properties of individual molecular compounds [12]. Two types of optical absorptions were attributed to electron transitions at two different groups of electronic states: shortwave absorption is associated with one-electron excitation, whereas longwave absorption originates from transitions to collective, excited states. These two groups of electronic states naturally arise as a result of electron correlation effects—a factor certainly to be taken into account in describing the structure and properties of macromolecules with conjugated bonds.

In addition to several interesting properties, polymers with a system of conjugation exhibit many specific chemical and catalytic properties. Of late the catalytic properties have been attributed to two factors—paramagnetism and the system of conjugation.

It is well established that the polymers with a system of conjugation in some cases may act as inhibitors of thermooxidation destruction, polymerization, etc. [13, 14]. In certain other cases the properties of such polymers might be exhibited, on the contrary, in the catalysis of polymerization, in cis-trans isomerization reactions, etc. [15, 16]. Such duality in properties has not as yet been explained reliably from a theoretical point of view, although the factors

mainly responsible for such properties, and the influence of the type and concentration of such polymer additives on their catalytic or inhibiting action are already known. Depending on the concentration, a compound may either catalyze or inhibit different chemical processes. A direct relationship between such properties and the paramagnetic centers in polymers with conjugated systems has been established. A comprehensive investigation has been made into the relationship between paramagnetic centers, their concentration, and the rates of induced or inhibited chemical processes. The properties and the laws which govern the rate of thermal chemical reactions, their direction depending on the content of paramagnetic centers are today collectively known as the effect of the local activation [17, 18]. A surprising yet practically important feature of this effect is that the paramagnetic centers are hardly used up in the polymer-induced catalysis of many chemical conversions. Probably, the reason for this is that in many cases the paramagnetic centers do not act directly by themselves but stimulate a certain substrate which brings out its catalytic reactivities.

Today the relationship between the specific electronic structure of the polymers with systems of conjugation and their physicochemical properties has been thoroughly investigated. This relationship, incidentally, is two-sided: a change in the external conditions leads to a change in the electronic structure, and, conversely, a change in the electronic structure gives rise to a change in many physicochemical properties. Despite the diversity of existing relations and their complexities, nonetheless, the continuous system of conjugated bonds is the decisive factor. Therefore, we shall begin our discussion with a description of the electronic structure of macromolecules with conjugated bonds.

ELECTRON STRUCTURE OF MACROMOLECULES WITH CONJUGATED BONDS

The basic element essential for a clearer understanding of the physical and chemical properties of any chemical compound is a correct idea of its electronic structure. The theory of the electronic structure of compounds and the polymers with a system of conjugation has undergone radical evolution since Hückel put forward his first ideas and methods. Of the several suggestions proposed by Hückel, perhaps, only one has retained its significance till today—the need for only π -electrons, and to a lesser extent σ -electrons in describing the properties of such polymers. This idea has repeatedly been

revived over many years and is still important today. At present, methods are known which "work" only in π -electron approximation without accounting for the groups of σ -electrons (or taking account of them only indirectly, say, by a choice of parameters), that make it possible to give an adequate description of the properties of the PSC.

A fundamental criterion in testing the validity of the electronic structure theory is that the calculated and experimental characteristics of electron optical transitions should be in agreement, and several of the properties observed may be predicted and interpreted. One important characteristic of long conjugated molecules is the behavior of the longwave part of the optical absorption spectrum, depending on the length of the continuous conjugation chain. This property is associated with the gap in the electron excitation spectrum. It is known that as the length of conjugation in linear conjugated molecules increases, the position of the longwave part in the optical absorption spectrum tends to its limiting value of ~ 560 nm (~ 2.2 eV). One possible way to explain this phenomenon within the framework of the Hückel model is to introduce two values for the resonance integrals of "single" and "double" bonds [19, 20]. The experimentally measured values of bond lengths, however, are in many cases inconsistent with the predictions of the theory. Thus, for cyclic polyenes, for example, in the 18-annulene, not two but three bonds were found to alternate [21, 22], and consequently, there should not be any gap in the excitation spectrum calculated by the Hückel or the PPP method because three bands exist in the spectrum: filled, empty, and one half-filled bands with a zero gap. As the conjugation length in linear polyenes increases, the bond lengths at the middle of chain tend to be the same and the difference between "single" and "double" bonds vanishes [23, 24]. It is not justified to extrapolate the bond alternation observed in the lower members of the homological polyene series to great lengths. The alternation in butadiene, hexatriene, etc. is exclusively associated with the molecular end effects. For a linear polyene with seven double bonds there is hardly any difference in the bond lengths in the middle of the chain [25-27]. The lengths calculated for linear polyenes, taking into account all the valence electrons [28] also suggest that the molecular configuration with equal bond lengths is preferable from the viewpoint of energy aspects. In a general form the bond length alternation is associated with the Peierls theorem [29]. This theorem asserts that in homoatomic one-dimensional systems the configuration with a finite alternation of bond lengths is the most stable. Such a coupled distortion in bond lengths gives rise to a gap in the excitation spectrum and causes a decrease in the total energy of the system. The physical meaning of the Peierls theorem lies in the following. In an

equibonded homoatomic one-dimensional chain in which each atom contributes one electron to the system, the electron levels of such a system, in the one-electron approximation, form a half-filled band in the ground state. Alternation of bond lengths, i.e., a shift of every second atom in the same direction, can be looked upon as perturbation V of the electron and nuclear system. This perturbation connects the levels from the filled and empty bands symmetric relative to the Fermi surface. The correction to almost degenerated upper levels from the filled band is linear in V and negative, while the correction to deeper levels and to the energy of nucleus-nucleus repulsion is proportional to V^2 . As a result, the total energy of the chain decreases, and the equi-bonded arrangement of the atoms becomes unstable relative to the transitions to an alternatively bonded state. Other mechanisms, however, are also possible for the generation of a gap in the excitation spectrum, which lead to a decrease in the total energy of the system (for instance, conductor-insulator transition due to electron-electron interaction suggested by Mott [30, 31] or the electron-phonon interaction leading to the formation of superconducting gap) without any alternation in bond lengths. Hence, if the energy gain in one of the gap formation mechanisms exceeds the gain in the bond alternation mechanism, then the later is highly suppressed. Such a situation is, probably, realized in one-dimensional conjugation systems.

Today, electron correlation is commonly believed to play a decisive role in the emergence of gaps in the excitation spectrum. Even as early as 1930 Slater [32] suggested that, depending on the internuclear distances and electron interaction intensity, a system (Slater was discussing a chain of hydrogen atoms) might exist in paramagnetic or in antiferromagnetic state. The gap in spectrum is qualitatively explained as follows. Electron-electron repulsion constrains the electrons to remain in their "own" atoms (though, of course, exchange interaction will permit them to "exchange" their sites). Optical excitation of an electron is brought about by its transition to one of the adjacent atoms. Such a transition is hindered, however, by the electrostatic repulsion from that electron which is already on this atom. There is no way in the usual SCF-MO one-determinant methods to account for such Coulomb correlation interactions. It is precisely this difference in the description of such interactions that is responsible for the different values predicted for the gap width in excitation spectra by methods which do or do not account for the electron correlation (in the SCF-MO methods the correlation effects are taken into consideration, say, by a many-determinant technique of configuration interaction).

The simplest and the most effective method at present available

to describe the electronic structure of monomers with conjugated bonds is the unrestricted Hartree-Fock method constructed on the basis of the Hubbard Hamiltonian [33]. The Hubbard Hamiltonian is apparently the simplest model Hamiltonian, which allows the electron correlation to be described most adequately. This Hamiltonian is composed of two terms $H = H_1 + H_2$. The matrix elements of the operator H_1 are the usual Coulomb and resonance integrals occurring in the Hückel method with slightly different renormalized values [34]: for carbon atoms the Coulomb integral is

$$\alpha = \langle \varphi_{\mu} | H_1 | \varphi_{\mu} \rangle$$

$$\beta = \langle \varphi_{\mu} | H_1 | \varphi_{\mu \pm 1} \rangle = -2.4 \text{ eV}$$

$$\langle \varphi_{\mu} | H_1 | \varphi_{\nu} \rangle = 0$$

for $\nu \neq \mu, \mu \pm 1$, while φ_{μ} are the basis functions used in the MO method, and are the usual $2p_z$ functions. If H_1 is a one-electron operator, then, in order to describe the correlation effects, the operator H_2 should be a two-electron operator dependent on the spin functions of the interacting electrons. The matrix elements of the H_2 operator can be represented in a simple way as follows:

$$\gamma = \langle \varphi_{\mu\alpha}^2(1) | H_2 | \varphi_{\mu\beta}^2(2) \rangle = \langle \varphi_{\mu\beta}^2(1) | H_2 | \varphi_{\mu\alpha}^2(2) \rangle$$

where

$$\langle \varphi_{\mu\alpha}^2(1) | H_2 | \varphi_{\mu\beta}^2(2) \rangle = \gamma$$

denotes that, if an electron 1 with a spin function α is at the atom μ , where an electron 2 with a spin function β already exists, then their mutual repulsion will be γ ($\gamma = 5.42 \text{ eV}$). The interaction of electrons with identical spin projections has been accounted for by the antisymmetry of the wave function. Only the Hubbard Hamiltonian by itself is not adequate to describe the electron correlation. Such a method

is needed in constructing the wave function free from any limitations on the interdependence of the steric and spin parts. One successful technique is the unrestricted Hartree-Fock method.

In spite of the considerable progress already made in understanding the electronic structure of monomers with conjugated bonds through the Hubbard Hamiltonian, the shortcomings of such a restricted approach are self-evident. Firstly, the real electron-electron interaction in the system is essentially long-range. Therefore, we are not justified in limiting the electron-electron interaction only at one center. In order consistently to take account of the electron interactions, it is essential to include in the Hamiltonian those terms which account for the interaction of the electrons separated by any distance. Secondly, in the Hubbard method, a value of 5.42 eV is chosen for the parameter of the repulsion between the electrons at an atom for matching the calculation with the experiment, but such a value is too low. According to different estimates, this parameter should be somewhere between 9 and 14 eV. These obvious shortcomings of the Hubbard method have been overcome in a paper [35] where a new technique has been suggested for the calculation in π -electron approximation, a method taking full account of all the non-zero electron interactions in the system. In this new scheme the parameter for the repulsion of electrons at different atoms is determined by the Mataga-Nishimoto formula. The unrestricted Hartree-Fock method is also used in constructing the wave functions and the energy of the system. For the values chosen for the repulsion parameter, the gap in the spectrum was found to be ~ 2 eV.

The unrestricted Hartree-Fock technique based on Löwdin's alternant molecular orbital method [36] was first applied to cyclic polyene systems by Misurkin and Ovchinnikov [34]. They determined the wave functions and the energy spectrum. This method was subsequently used in determining these very parameters in a linear polyene [25], polyacene [37, 38], polycumulene [25], and polyphenylacetylene (PPA) [26, 27]. These calculations showed a gap in the excitation spectrum; thus, for polyenes $\Delta E = 2.2$ eV, $\Delta E_{\text{exp}} = 2.2$ eV; for linear polyacenes $\Delta E = 1-2$ eV; for cumulenes $\Delta E = 1.2$ eV, $\Delta E_{\text{exp}} = 0.8-1.0$ eV, for PPA, $\Delta E = 1.5-2.2$ eV depending on the conformation. Besides, the structure of the wave functions should, of course, be specific in the alternant molecular orbital method: for the electron states there is no spin degeneration for the spatial parts of the wave functions, i.e., each molecular orbital is occupied by only one electron with a definite spin projection. Besides this method, a few more attempts were made to describe the electron structure of conjugated systems to obtain a state with a gap in the excitation spectrum [39-44].

In all these approaches a gap is obtained in the excitation spectrum because the electron correlation effects have been given due consideration. Nonetheless, the energy gap is not attributed to the paramagnetic-antiferromagnetic transition mechanism in all these methods. In some papers the same result is believed to arise due to the transition to a state with alternating charges on the atoms, and such an alternation is believed to be preferable from the viewpoint of energy aspects. In the paper by Popov [45], convincing arguments have been put forward to demonstrate that for those values of the parameters which are most consistent with the description of all the physical properties, the antiferromagnetic state is the lowest (with regard to energy) ground state. In the antiferromagnetic state, however, there is no true alternation of spin densities on the atoms; moreover, the spin densities are zero. But it can be seen that the system is nevertheless antiferromagnetic from the long-range character of the spin correlation function [46]. This somewhat unexpected result is a sequel of the well-known fact that the wave function of the ground singlet state derived in a one-determinant method (UHF being precisely such a method) is the eigenfunction of the operator S_z with the eigenvalue $S_z = 0$ rather than being the eigenfunction of the operator S^2 .

Therefore, there is an urgent need for methods of constructing wave functions with the eigenvalue $S^2 = 0$. An effective method is the Van Leuven projection method [47]. The results reported by Misurkin and Ovchinnikov [46] were obtained exactly by this method. Figure 1 shows the qualitative pre- and post-projection behavior of spin functions.

In those situations where the antiferromagnetic state is the ground state, it is possible that elementary excitations, magnons, may exist in the system. This phenomenon is based on the fact that, in any sufficiently long, ordered (in any manner), system there exist corresponding -ons, i.e., the elementary longwave excitations of the whole system which violate the order. Phonons, for instance, are collective excited states of small-order displacement of the nucleus from its equilibrium. Precise theorems exist to explain the collective excitation spectrum and its relation with the properties that disturb the system symmetry. Lange [48] proved a theorem showing that a system with disturbed symmetry has an excitation branch without an energy gap, if the interaction in the system has a finite or even exponentially decreasing range. Anderson [49] demonstrated an inverse theorem, namely, that, if a branch exists in the collective excitation spectrum beginning from zero, then there is a corresponding operation which interrelates the states of the set of all degenerated states. Stern [50] investigated the relationship between these direct and

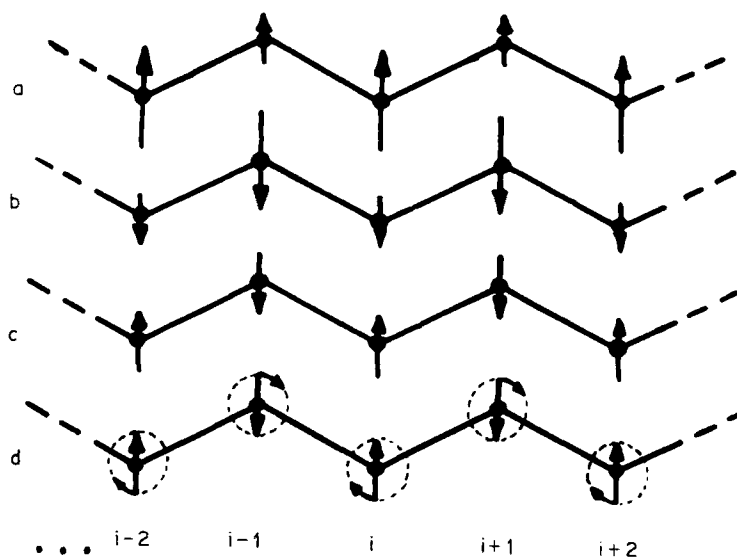


FIG. 1. Distribution of spin densities in the absence of projection for electrons with (a) α spin and (b) β spin; (c) the resultant spin density; (d) qualitative representation of the vanishing spin densities on atoms after the spin projection. The long-range nature of the spin correlation function takes the form of synchronized "rotation" of electron spins. A fragment of the antiferromagnetic chain is shown on all figures.

inverse theorems, and found that a branch of the collective excitation beginning from zero appears for any lowering of the system's symmetry. All these arguments are also fully applicable to long conjugated systems for which the ground state is the antiferromagnetic state, and perturbation in the ground state (creation of triplet excitation) gives rise to low-frequency excitations (spin waves or magnons).

One of the possibilities of phenomenological description of magnons is that these collective excitations can be looked upon as a small-order shift between the phases of adjacent precessing electron spins. The case in which the phase difference between the first and last positions of the electron spins is π in the whole length of the system, corresponds to the state of the least energy level. It is clear, that the longer the system ($\sim N$), the less is the change in the energy of interaction between the two adjacent interacting electrons as compared with the nonexcited states. Consequently, the energy of magnons

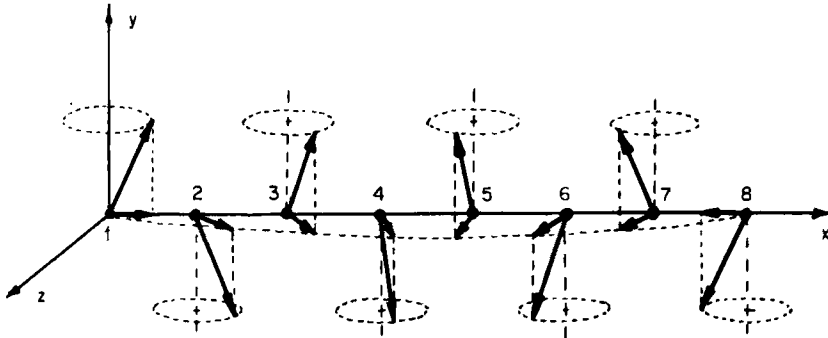


FIG. 2. Graphic representation of the lower triplet collective excitation. There is a nonzero projection of spin state only on the z -axis. These states are the eigenvalues of the operator S_z with $S_z = 1$.

is inversely proportional to the chain length $1/N$ (see Fig. 2 and ref. [51]).

Another possibility of phenomenological description of collective spin excitation lies in the following. Alternating spin directions of electrons on adjacent atoms* correspond to the ground state. If the direction of one spin is reversed by expending energy $Q (= I - A$, where I is the ionization potential and A is the electron affinity), this energy is compensated by the gain in the exchange energy if account is taken of the delocalization of the excitation over the whole system. Such an excited state, which is paired triplet states of a "particle" and a "hole", lies near the ground state (see Fig. 3). Similar methods of describing collective excited states have been sufficiently simplified but still form the subject matter for thorough theoretical attempts to describe weakly-excited spin states of the system. For the one-dimensional systems the dependence of the collective excitation energy on the level number (excitation "momentum") takes the form

$$E_n = (U/N) n \quad (1)$$

*The alternating directions of spins have to be understood in the dynamical sense. The stationary spin density at each atom is zero, see Fig. 1.

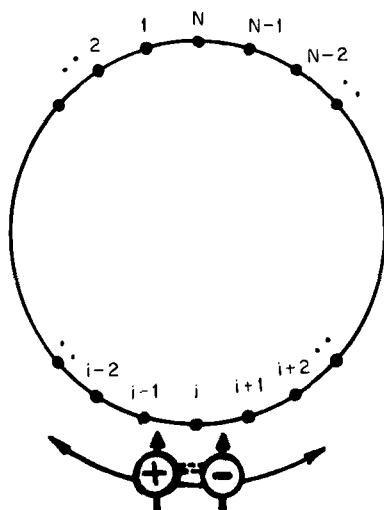


FIG. 3. Collective triplet excitation in the form of a delocalized bonded triplet state of an electron (minus sign) and a hole (plus sign). The arrows show the electron spin projection direction. Only one of the possible localized states is shown. After an account of delocalization, (1) excitation energy decreases, and (2) electron densities on all atoms vanish, but the spin (triplet) state of excitation is preserved.

where N is the number of conjugated π -electrons in the system, n is the number of the level (momentum), and U is a parameter equal to 15-20 eV, depending on the system under consideration. Strictly speaking, a number of these states exist, differing in excitation momentum. The exact expression for the spectrum of triplet excitations of cyclic polyene, obtained by Ovchinnikov [52] is

$$E_n = \frac{4\pi\beta}{N} \left[\frac{I_1(2\pi|\beta|/\gamma)}{I_0(2\pi|\beta|/\gamma)} \right] n \quad (2)$$

where β and γ are the resonance and Coulomb integrals of repulsion of two electrons in the same atom in the case where their spins have opposite projections; I_0 and I_1 are the Bessel functions of imaginary

argument of zero and first order, respectively. This is, incidentally, one of the few exact results known in the many-electron theory.

The exactly solvable Hubbard model makes it possible to classify the electron states of long conjugated molecules. Firstly, there is a group of ion states—the bonded localized states of electrons and holes generated when an electron passes to one of the neighboring atoms. The number of these states is $N2^N$, where N is the number of identical centers (atoms) of a molecule. Intensive optical transitions to these states are possible. The group of these levels is separated from the ground state by an energy gap. The optical transitions to these states correspond to the shortwave region in the optical absorption spectrum.

The second group of levels is composed on $N(N - 1)2^{N-1}$ double-ion states. Higher excited states also exist. Another group of levels is formed of homeopolar states. The very name of these excited states suggests that the electron density is not subject to redistribution in the transition from the ground state to the excited one. These levels are, by their very nature, collective excited states of the whole electron system. The homeopolar states can be classified by the eigenvalues of the operator S_z . Thus, we have the singlet ($S_z = 0$), the triplet ($S_z = 1$), and other groups of levels of any integral multiplicities. Among them the singlet and triplet levels are of great practical interest. In particular, the longwave optical absorption is attributed to the transitions to homeopolar singlet levels. The energy gap of homeopolar states asymptotically tends to zero as $N \rightarrow \infty$. A schematic representation and a classification of these levels are shown in Fig. 4.

For molecular systems more complicated than the regular cyclic polyenes it is not possible to obtain exact results to determine the spectrum of low homeopolar states. An approximate method has been suggested [26] for solving this problem. As the electron correlation effects ultimately determine the spectrum of lower levels, special methods have to be introduced in describing the electron properties that may account for the electron interactions in the system. The two-particle Green function method is a convenient technique. In this case, the equation for the two-particle Green function contains three-particle and higher order Green functions in succession. The chain of sequentially coupled equations should break up somewhere. The main impediment is that it is difficult to say which of the physical approximations causes the rupture in the chain at one stage or another and what assumptions are made there upon. Fortunately, Martin and Schwinger [53] succeeded in demonstrating that the equation for the two-particle Green function is sufficient to express it as a combination

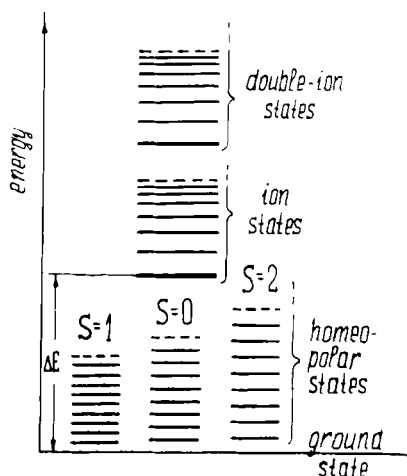


FIG. 4. Classification of the electron levels of a molecule with a system of conjugation. The group of homeopolar levels has been divided into singlet, triplet, ... , levels, of which the triplet states are the lowest energy levels. Ion, double-ion, etc. states have lower fringes for the level positions (energy gaps). For ion levels this gap is equal to the least energy of intensive optical absorption ΔE .

of one-particle Green functions and that this representation may correspond to the random phase approximation. On one hand, this technique considerably simplifies the mathematical formulation of the problem and provides an easy method of solving it; on the other hand, it gives a definite physical meaning to such an approximation. In the language of the configuration interaction method, the random phase approximation accounts for all the single-excited and a part of the double-excited configurations.

Equations so derived for the Green function are nonlinear, and consequently, assumed to describe not only the stationary states, but also certain excited states near the ground state. The spectrum of low-lying collective levels is determined by adding an additional small term to the Green function of the ground state, then linearizing the equation with respect to the small parameter. From a physical point of view, the criterion of the smallness of the term added to the Green function of the ground state implies that the change in the spin densities on the atoms during the transition from the ground state to excited states should be small. A comparison of the excitation spectra obtained by exact and approximate methods for cyclic polyene

containing N atoms revealed satisfactory agreement: $E_{\text{exact}} = 23.9/N$ eV, and $E_{\text{approx}} = 23.2/N$ eV. Therefore, there is every reason to believe that the approximate method will give similar satisfactory results for the systems to which exact methods cannot be applied as well. A method has been proposed [26] for calculating the collective excitation spectra of almost any conjugated carbochain system. Here, as in the unrestricted Hartree-Fock method, there are only two parameters, β and γ , determined previously.

Since, as will soon be clear from the subsequent pages, the low-lying triplet and singlet levels are of no less importance for the physicochemical properties of polymers with a system of conjugation, it is interesting to determine the parameter U for systems that are more important, from a practical viewpoint, than cyclic polyenes, and its variation induced by conformational violations in the macromolecule structure. Figure 5 shows the dependence of the parameter U , given by the relation (1), on the conformation disturbances for cyclic polyenes: (1) the resonance integrals of bonds between the i -th and $(i + 1)$ -th atoms were chosen from the relation

$$\beta_{i,i+1} = \beta_0(1 - 0.1 \cdot x_i q)$$

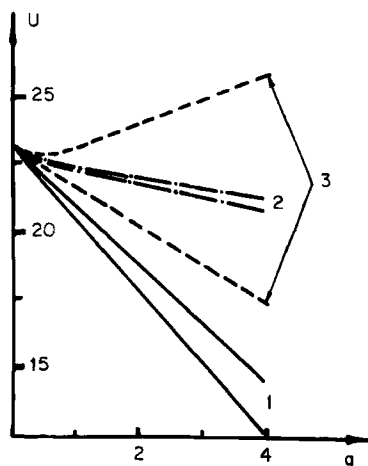


FIG. 5. Dependence of the parameter U on the magnitude of conformation violations in the cyclic polyene chain. See text for an explanation of the symbols.

where $q = 0, 1, 2, \dots$ is the parameter of disorderedness, and x_i are random numbers uniformly distributed in the interval $(0, 1)$; (2) for cyclic polyenes composed of 34 atoms, the resonance integrals of bonds between the 2-3 and 18-19 atoms changed $\beta_{2,3} = \beta_{18,19} = \beta_0(1 - 0.1q)$; (3) the same as in case (2), but the bonds between 2-3 and 19-20 atoms were ruptured. Methods (2) and (3) correspond to partitioning a cyclic polyene into even-even and odd-odd parts as regards the number of atoms contained. Violation of conformation in the macromolecule structure results in that elimination of degeneration corresponding to excitation momentum energy in both directions of the ring in a perfect system. The changes in the spectral pattern and the gap caused by such conformation violations are negligible.

It is surprising that the energy of the low-lying triplet excitation and the energy gap of one-electron excitation in the Hückel method have the same asymptote $\sim 1/N$. We found that in the systems investigated (polyenes and PPA) and for sufficiently long conjugated chains, the coefficient of proportionality between these parameters is about 0.7-1.0. It is not very clear, however, whether this coincidence is purely accidental or whether there is any other physical meaning behind it. In the latter case it would be possible to eliminate cumbersome computations in determining low-lying excitation spectra; nevertheless, further detailed investigation is needed to discover the possible relationship between the energy gap determined by the Hückel method and the collective excitation energy.

In addition to the low-lying triplet states, branches of collective excitation of any integral multiplicities exist, beginning from the zero level (having the asymptote $\sim 1/N$). Among these states, the singlet states succeed one another as regards the energy level. Their energy coincides with the energy of the low-lying triplet levels to an accuracy of $\sim 1/N^2$. Probably, Fukutome was the first to point out the importance of low-lying triplet levels in explaining the paramagnetic properties of conjugated polymers [41]. The importance of low-lying singlet levels in understanding longwave optical absorption and its relation to the paramagnetic properties of conjugated polymers has been discussed elsewhere [54, 55]. In a general case the role of singlet and triplet low-lying levels may be reduced to the following. If the triplet levels lie close to the ground state and their energies are comparable with the thermal energy kT , then these levels could be populated, and make a thermal contribution to the paramagnetism observed in the polymers with systems of conjugation. Optical transitions to singlet collective levels are possible. Despite the delocalization nature of excitation, the probability of optical transition

is, nevertheless, different from zero [56, 57]. Such transitions are said to be responsible for the longwave optical absorption of MCB. As the singlet levels are isoenergetic with the triplet levels to an accuracy of $\sim 1/N^2$, the same order of correlation should be observed in the relationship between the optical and paramagnetic properties of the PSC. Such a dependence was, indeed, observed for the molecular-mass fractions of some members of the PSC series [54, 55].

In the subsequent pages we shall consider in detail the relationship between the electronic structure of MCB and their optical and paramagnetic properties. But it is already clear that in this class of molecules, all the physical and chemical properties are so closely intermingled and each property exerts such a strong influence on the other, that there is urgent need for an overall and comprehensive investigation into all these interrelations, by use of the latest experiment techniques and theoretical methods.

PARAMAGNETIC PROPERTIES OF CONJUGATED MACROMOLECULES

Paramagnetism is an inherent property of macromolecules with conjugated bonds. At present, it can be asserted that almost all the members of the series of polymers with systems of conjugation exhibit paramagnetism. What is paradoxical here is that it is far easier to explain why one rare system or another does not possess paramagnetism, than to explain the reasons for its occurrence in most macromolecules with conjugated bonds. Another interesting aspect is that, at first sight, it seems that paramagnetism shows a weak dependence on the method of synthesis of polymers with systems of conjugation. The polymerization method (radical, ion, polycondensation), the temperature regime, and other factors have hardly any influence on external characteristics, except for the intensity of EPR signal which is a direct experimental image of the paramagnetic properties. In almost all cases a single inhomogeneously broadened line with a g -factor close to that of the free electron, with a half-width of 3-15 gauss was observed. The EPR signal intensity usually varies from 10^{15} to 10^{19} paramagnetic centers (PMC) per gram. With increasing degree of conjugation, especially in passing over to a two-dimensional conjugation, the EPR signal intensity increases. The PMC are highly sensitive to external interactions like dissolution, and temperature variations.

In this paper we shall not deal with the origin of paramagnetism

in graphite and in products obtained by high-temperature treatment of carbon-containing substances, (this question is, incidentally, very interesting in itself) but we shall examine the paramagnetism which is developed during polymerization at moderate temperatures ($t \leq 200^\circ \text{C}$).

In principle, there may be a multitude of reasons for paramagnetism. If the paramagnetic state is classified against the causes responsible for it, then we can tentatively distinguish a few types of paramagnetic states:

(1) The σ radicals formed during the rupture of σ -bonds, as a rule, exist at an atom (C, N, and others) in sp^3 hybridization. Examples are the radicals formed during hydrogen abstraction, mechanical destruction of saturated compounds and many others. The radical CH_3 may serve as a model. Such radicals are extremely active, their lifetime being very short (except for special cases). Probably, the σ radicals do not have any significance in relation to the paramagnetism of the polymers with systems of conjugation as they can readily isomerize to π radicals.

(2) The π -radicals in which an unpaired electron exists in a p-type orbit may be delocalized over the conjugation system. Examples of such radicals are most of the stable radicals (DPPH, nitroxyl, trimethylaryl, and other radicals), radicals formed as a result of rupture of π -system in macromolecules with conjugated bonds, and terminal radicals formed in radical polymerization of acetylene monomers, etc. Allyl or any polyenyl radical may serve as an excellent model for investigation into the paramagnetism in polymers with systems of conjugation. The π -radicals are essential for the description of paramagnetism in the PSC. Here we have to take account of the factors (steric and energetical) which stabilize the π -radicals or hinder their recombination.

(3) Diradicals are of the same nature as the π -radical, but differ in that both the unpaired electrons exist on the same molecule. The reason why the diradicals should be distinguished as a separate class is that both the radicals are spatially inseparable, and the external conditions (in particular, the temperature) may determine the molecular multiplicity. All the known diradicals are formed either from conjugated systems of high steric hindrance, or from systems having low S-T transition energy. The Chichibabin diradical is an excellent example of a diradical model. Diradicals also make their contribution to the paramagnetism observed in the polymers with systems of conjugation. Berlin [58] was the first to point out the importance of diradicals in understanding the paramagnetic properties of the polymers with systems of conjugation. The diradical theory of paramagnetism proposed by Berlin was further developed by Pople

[59]. Pople calculated the cyclic polyene in Hückel and PPP approximations in the alternating bond-length model. He also determined the energy needed for the transition into a state with two regions of ruptured conjugation. He called such ruptures in the conjugation "defects." In essence, however, such states are no less than diradical states. An interesting fact that follows from the work of Pople is that energy as low as 0.5-1.0 eV is sufficient for the transition of a cyclic polyene to a two-defect state. Today, by the "defect theory of paramagnetism" we mean the origin of radical states due to any rupture in the continuous conjugation chain of the PSC. This hypothesis is believed to be well established, as there is a direct relationship between the x-ray diffraction analysis data on crystallinity and the EPR signal intensity [60, 61]. Although the calculation methods for the electron structure which do not take into account the electron correlation effects, in particular, the Hückel method or the PPP method, are unsatisfactory for describing the properties of polymers with systems of conjugation, the ideas suggested by Berlin and Pople have still proved fruitful. In fact, a perfect conjugation system should not give rise to paramagnetic states, which are the ground states. It is evident that only a disruption in the conjugation system, "defects" in the structure, ought to cause the appearance of such states. From this viewpoint, the structural defects could be π -radicals, charge-transfer states, especially, diradicals.

(4) Ion-radicals are formed in heteroatomic systems. Ion-radicals or charge-transfer complexes can hardly be formed in systems composed of carbon and hydrogen atoms alone, as the formation of diradicals in these systems is more advantageous from the point of view of energy. Ion-radicals may be essential in describing the paramagnetic properties of heteroatomic conjugated systems, particularly, in polar solvents where the solvation energy renders such formations stable.

(5) Paramagnetism is induced as a result of thermal population of low-lying triplet levels [62]. This theory explains the existence of paramagnetic states at higher temperatures, the growth in the EPR signal intensity with increasing temperature, and the deviations from the Curie law observed. The existence of low-lying triplet levels, and the consequent paramagnetism may be taken as theoretically established facts. Many experimental results have confirmed this theory.

The classification given above is purely conditional. It is, nonetheless, the generally accepted classification. Several facts (in particular, the independence of EPR signal parameters in relation to the polymerization method and aggregate state) clearly suggest that the origin of EPR signals in all the PSC is, in all probability, the same. The narrowness of the EPR signal, in the generally accepted

interpretation [63], demonstrates that the spin state in the system is subjected to considerable delocalization, and the nonuniform broadening is determined by the superfine interaction with a large number of protons.

Of the current theories, special mention should be made of the theory of generation of diradicals and the theory of thermal population of lower levels during polymerization or subsequent transformations of the MCB. Both these theories are based on the experimental fact that the EPR signal intensity of polymers with systems of conjugation increases on heating above room temperature, and that structural order is somewhat disrupted during x-ray or electron microscopic examination.

As already mentioned, it is essential to discover the most important and decisive characteristics of macromolecules with conjugated bonds in order to gain a fuller understanding of their physical properties and their interdependences. Such characteristics are, apparently, the electronic structure and the conformation of macromolecules. For those whose main conjugation chain is of the polyene type, the most advantageous conformation is the arrangement of atoms in one plane. Depending on the nature of the system in hand, various factors do, to a certain extent, hinder this arrangement: for instance, the functional side groups or substituents, violation in the addition of monomers to the polymer chain during polymerization, intermolecular interactions which distort the core, etc. In all these cases the electronic structure and conformation of the macromolecules with conjugated bonds undergo significant changes. Herein lies one distinction of such systems from saturated molecules, which yield fairly easily to the external action without any significant changes in their electronic structure or energy.

The formation of diradicals (defects in the structure of macromolecules) during synthesis of polymers with systems of conjugation is not surprising. It should be borne in mind that the polymerization which leads to the formation of macromolecules with conjugated bonds is in fact an essentially rapid exothermic process and the heat of polymerization of substituted acetylene monomers, for instance, is ≥ 15 kcal/mole. (If no precautions are taken, even a thermal explosion may take place during polymerization in bulk.) As already mentioned, the macromolecules with conjugated bonds exhibit high affinity for formation of intermolecular associates mainly by overlapping the π -electrons of the systems of conjugation. Probably, the macromolecules thus synthesized immediately form associates that can be regarded as a polymer heterophase. The heterophase surface is very active to monomer addition reactions; apparently, the rate of heat transfer from such polymer formations is inadequate to maintain thermal

equilibrium with the outer medium, and the polymer heterophase thus seems to be overheated locally. The fact that the temperature of the polymer formations could be far higher than might be expected from the mean temperatures of the reaction mass, throws some light on the reasons for the generation of paramagnetism during PSC synthesis. Indeed, there is no plausible theory that could have predicted a rapid increase in paramagnetism at moderate temperatures ($\sim 150^\circ\text{C}$). If we assume, however, that the polymer formation temperature is, say, 100°C higher, then many of the forbidden energy processes may take place at noticeable rates. The fact that locally overheated regions do exist in the PSC formation has been indirectly supported experimentally. An additional and highly significant factor that aids the formation of paramagnetic centers when the conjugation system breaks up is that the polymer systems, as already mentioned, are formed in a stressed state. The energy needed to rupture the conjugation in such systems is less than what can be expected for a plane-ordered molecule. It is difficult to assess the contribution of entropy factors when the degree of freedom of the molecule with a ruptured conjugation is increased, but it is obvious that this effect certainly promotes the formation of paramagnetic centers.

In principle, although it has not been strictly established, another explanation showing paramagnetism to be a common property of polymers with systems of conjugation is that, despite the apparent differences in the polymerization methods, a chain-radical polymerization process sets in at later stages of polymerization after the formation of a certain amount of fairly long molecules. It has already been proved that the paramagnetic centers in a system activate several chemical processes, especially radical reactivity, which is a manifestation of the effect of local activation. For almost all the polymerization methods leading to the formation of polymers with systems of conjugation, the time dependence curves of polymer yield and variation of concentration of paramagnetic centers have a distinct S-shape; this is a clear indication of the autocatalytic or chain mechanism of polymerization. Perhaps, the induction period corresponds to the accumulation of a certain minimum amount of paramagnetic centers, which, in due course, through the local activation mechanism, either activate the radical polymerization process or act as initiators of "paramagnetic chains." If the radical polymerization were a common process, then, of course, trapped radicals, incapable of recombination might exist, especially in conditions where the mobility of macromolecules is hindered by their rigidity or higher capacity to form π -complex associates. While such a mechanism could be used to explain the generation and existence of permanent paramagnetism, with a

temperature dependence obeying the Curie law, then thermally stimulated paramagnetism calls for new ideas to be developed to explain its existence.

If the temperature dependence of the EPR signals of polymers with systems of conjugation are investigated after a considerable lapse of time after their production, especially in solution, i.e., when the system exists in thermodynamic equilibrium with the surrounding medium, then it could hardly be expected that a moderate variation in the temperature would lead to such a sharp change in the EPR signal intensity. Here, there is obviously insufficient energy to induce action of this type.

The increasing EPR signal intensity with increasing temperature probably results from the thermal population of low-lying triplet levels. An adequate theory has been developed [62] to explain the thermally stimulated paramagnetism. Without going into the finer details of the theory and computations, it may be mentioned that the low-lying triplet levels lie close to the ground state, and as the conjugation length increases, the energy of the first triplet level tends asymptotically with $\sim 1/N$, where N is the number of conjugated π -electrons. It is obvious that the probability of population of these levels increases with the increasing conjugation length. For real polymers with systems of conjugation the molecular weight distribution (MWD) has to be averaged out in order to determine the EPR signal intensity and its temperature dependence. Averaging was carried out over the "tail" of the MWD and, as expected, took the form $\rho(N) = 1/N \exp \{-N/\bar{N}\}$. An expression has been derived [54, 55] for static magnetic susceptibility and its temperature dependence for a system of populated low-lying triplet levels (the static magnetic susceptibility being linearly related to the number of paramagnetic centers and therefore, to the EPR signal intensity):

$$\chi = (2 \mu^2 g^2 / kT) (\pi^2 u / \bar{N} kT)^{1/4} \exp \{-2\sqrt{u/\bar{N}kT}\} n_{\pi} \quad (3)$$

Here u/\bar{N} is a parameter equal to ~ 1 eV, μ is the Bohr magneton, g is the g -factor, k is the Boltzmann constant, and n_{π} is the number of π electrons per gram of the specimen. In this paper the EPR signal observed is expressed as the sum of two terms: one term depends on permanent paramagnetism the temperature dependence of which obey the Curie law, $\sim 1/T$; and the second term depends on thermal-excited paramagnetism. The thermal-excited contribution predominates at higher temperatures, i.e.,

$$\chi(T) = a/T + bT^{-5/4} \exp \{-cT^{-1/2}\}$$

where a , b , and c are certain constant parameters specific to a given system; they are determined by the least square method from a comparison with the experimental curve. For example, for one of the PPA specimens, it was found that $a = 4.5 \text{ cm}^3\text{-deg/g}$, and it corresponds to the number n of paramagnetic centers, $n = 6.1 \times 10^{18} \text{ g}^{-1}$; in other words, one ruptured conjugation bond per 1000 $-\text{CH}=\text{C}_6\text{H}_5-$ units; $b = 1.03 \text{ cm}^3\text{-deg}^{5/4}$; $c = 187 \text{ deg}^{1/2}$. Figure 6 shows the experimental points plotted for the PPA specimen; curve (1) gives to the contribution from permanent paramagnetism while curve (2) relates to thermally excited paramagnetism. The same diagram also shows the temperature dependence of static magnetic susceptibility calculated by Eq. (3). In the calculation, the ratio u/\bar{N} was taken to be 0.76 eV. It is obvious that the experimental and theoretical curves are in satisfactory agreement. In our opinion, the critical standpoint maintained by Bloor et al. [60] is unfounded. This paper reports the results obtained in an investigation into the absorption and reflection electron spectra, and the EPR spectra of polymers formed during the polymerization of diacetylenes of the general

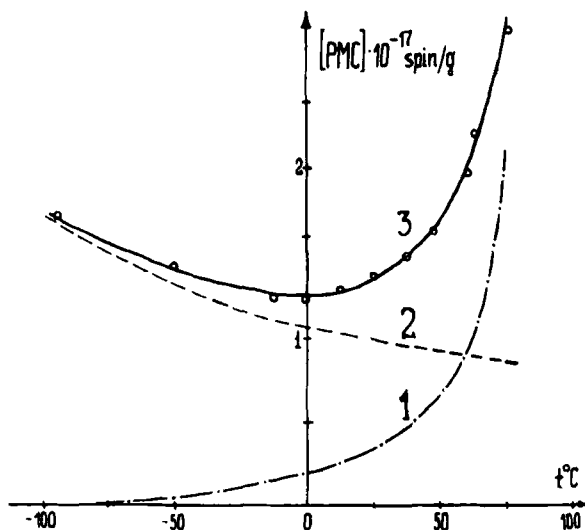
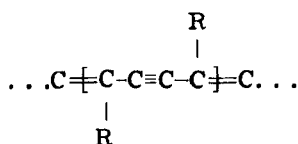


FIG. 6. Theoretical dependence and decomposition of EPR signal intensity in relation to temperature variations for the PPA specimen. See text for an explanation of the symbols.

structure $R-C\equiv C-C\equiv C-R$, where R is $-\text{CH}_2-\text{O}-\text{SO}_2-\text{C}_6\text{H}_4-\text{CH}_3$. Polymer single crystals of macroscopic sizes were found to be formed under specific polymerization conditions, and the longwave optical absorption and the typical EPR absorption line with $g \approx 2$ were not detected for these single crystals. Both the properties reappear on passing over to polycrystals. On the basis of these results the authors attributed the phenomena of paramagnetism and longwave optical absorption to defects in the molecular structure polymer and extended these ideas to all the other polymers investigated. Earlier [64] it was found that the polymer formed had the following structure:



The bond energy in this case is quite different: single, double, and triple bonds are distinctly visible on the Raman spectra. Calculations by the Hückel method for such polymer molecules with alternating bond lengths give a finite value to the energy gap in the excitation spectrum: $\Delta = |\delta| \sqrt{7}$, where the meaning of δ is obvious from the notation:

$$\beta_{\text{C}\equiv\text{C}} = \beta_{\text{C}=\text{C}} + \delta,$$

where we define

$$\beta_{\text{C}-\text{C}} = \beta_{\text{C}=\text{C}} - \delta$$

and β is the resonance integral of the Hückel method. We found earlier that the energy gap in the collective excitation spectrum is proportional to the gap derived in the Hückel approximation. For the polymers investigated we could not, therefore, observe either the longwave optical absorption or EPR absorption owing to the large gap in the collective excitation spectrum. These properties quite probably arise as a result of the "defects", as the authors presumed; alternatively, they may be due to the thermal population of low-lying triplet levels and optical transitions to homeopolar singlet levels

during possible equalization of the bond lengths in passing on to a polycrystal specimen. Perhaps both mechanisms are realized simultaneously. In a recent paper [65], one of a series of investigations into the physicochemical properties of these polymers, the existence of two types of paramagnetic centers was reported: their existence depends on the degree of polymerization. A specimen which had not undergone complete polymerization exhibited EPR signals with an anisotropic g factor specific to the stable triple radicals existing at the terminal atoms of the growing polymer molecule; a completely polymerized specimen gave the usual EPR signal, characteristic of conjugated polymers, with an isotropic g factor and paramagnetic centers concentration of about $3 \times 10^{15} \text{ cm}^{-3}$. The authors attributed this signal to the thermal-activated mobile defects. In addition to giving this as the cause of the single EPR signal with an isotropic g factor, however, the authors put forward another possible explanation in interpreting such signals in many other systems. If diradicals or π -radicals are present in a system, in other words, if defects exist in the structure of macromolecules, under conditions suitable for sufficient mobility, they may partially recombine to give rise to an equilibrium between associated diamagnetic and dissociated paramagnetic molecules. An excellent model of such transformations is the behavior of the Chichibabin diradicals in solution [66], where the steady concentration of paramagnetism at 25°C is supposed to correspond to 4% of the dissociated molecules, and the increase in the paramagnetic properties with increasing temperature is attributed to further dissociation. Figure 7 shows a qualitative picture of such conversions. The stable triplet radicals present in incompletely polymerized specimens might be exactly those radicals, or more probably, the products of isomerization of triplet radicals, whose dissociation and association govern the EPR signal, depending on the temperature. The symbatic decrease in the molecular mass of PPA with increasing EPR signal intensity on heating may be said to support this viewpoint. The phenomenon of paramagnetism has been explained by Stevens and Bloor [67] in a similar way. Other interesting observations are associated with the time dependence of the variations in the EPR signal intensity with varying temperature.

Earlier it was reported that hysteresis is observed for the temperature dependence of the EPR signal intensity in PPA: after heating and subsequent cooling to the initial temperature, the EPR signal intensity gradually returns to its initial value [68]. The time required for it to regain its initial value increases as the temperature at which the reversal takes place falls [69]. For this phenomenon to be reversible, it is essential that the specimen should not undergo any irreversible changes during heating, i.e., the heating temperature

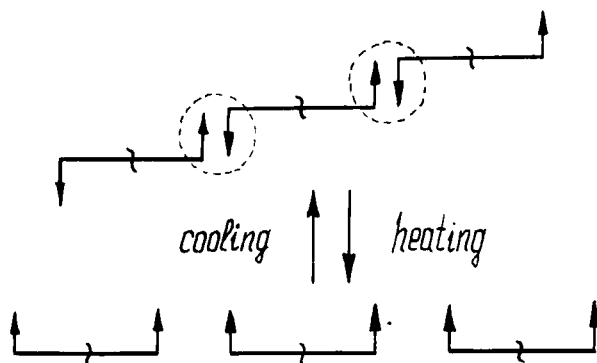


FIG. 7. Possible mechanism for the increase in the paramagnetic properties with temperature increase. At low temperatures paramagnetism is determined by the two terminal radicals of the associated diradical molecules. With an increase in temperature, the equilibrium shifts towards dissociation products with an increase in the paramagnetism observed.

should not, as experience shows, be more than 100°C . It may be assumed that such relaxation phenomena for the EPR signal intensity are related to the conformational transitions in the macromolecule structure (see Fig. 8).

Any conformational disturbance in the structure of macromolecules with conjugated bonds leads to a change in the resonance integrals in the Hubbard model. According to Fig. 5, this, in turn, leads to a change in the parameter U of the model. It is the change in U that determines the change in the contribution of a signal attributed to thermal excitation to the EPR signal observed. As U is contained in the largest factor (in absolute value) of the power exponent of Eq. (3), a small change ($\lesssim 4\%$) in this parameter entails a noticeable change ($\gtrsim 20\%$) in the static magnetic susceptibility. The energy needed to bring about such a change in U , indeed, does not seem to be very great: for cyclic polyenes with $N = 34$, depending on the nature of conformational violations, energy from 0.15 to 1.5 eV is sufficient, and this corresponds to a change of about 2 and 20 cal in the internal energy per gram of the specimen. As the conformation changes affect the molecule as a whole, which furthermore exists in a solid matrix, the characteristic times of the molecular rearrangement should be considerable and depend on the temperature. In our opinion, the merit of this explanation for thermally excited paramagnetism, is,

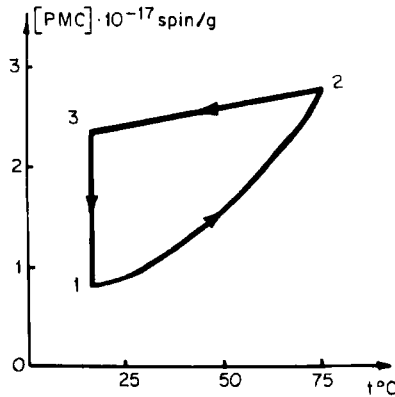


FIG. 8. Temperature and time dependence of the EPR signal intensity for PPA: (1-2) heating at a rate of about 10 C/min; (2-3) cooling at the same rate; (3-1) slow restoration (30-40 hr) of the EPR signal intensity to the initial level.

firstly, that it is the first quantitative explanation of the increase observed in paramagnetism with temperature, in agreement with the experimental results, and secondly, only a small amount of energy is needed to realize this mechanism.

Some new experimental results were recently obtained, which reveal further details of the EPR signals from PSC polymers with conjugated systems. The signal observed, which was previously regarded as a single signal, is, in fact, a superposition of two signals of different widths [64]. The narrow signal ($\Delta H = 2-3$ gauss) is strongly saturated even at low microwave power. The broad signal ($\Delta H = 8-15$ gauss) is not easily saturated. Most probably, the two types of signal correspond to two different types of paramagnetic centers: the narrower EPR signal is characteristic of the thermally excited paramagnetism due to strongly delocalized triplet excitations, while the broader signal results from the permanent paramagnetic states, the structural defects. The EPR signal, was likewise found to have a superfine structure [71, 72] which is probably related to the broad signal. No reliable explanation of these signals has as yet been found. Probably, the question can be cleared up by investigating the relationship between the intensities of these two signals with temperature.

ELECTRON ABSORPTION SPECTRA
AND COLORATION OF MACROMOLECULES
WITH CONJUGATED BONDS

The electron absorption spectra of polymers with systems of conjugation most often take the form of a wide maximum in the range 260-400 nm with an absorption extinction coefficient at $\sim 10^4$ and longwave decay stretching continuously right up to or even beyond the valence vibration region. Figure 9 shows the dependence of the absorption extinction coefficient on the wavelength for the PPA specimen. Other linear representatives of PPA also give rise to similar absorption spectra. The background absorption in the IR region has been found to depend on electron transitions, but is not dependent on either the synthesis or the recording method [12]. The absorption electron spectra of PPA do not in many cases exhibit a fine structure and typical absorption bands. In those cases in which the spectra have a fine structure, no explanation of these bands has as yet been found; at any rate, such an explanation, if any, seems highly doubtful. Since the electron absorption spectra were considered to be unimportant, naturally, they were not investigated in detail.

The following results are nevertheless worthy of mention. For the PPA fractions, higher intensities of the background absorption in the

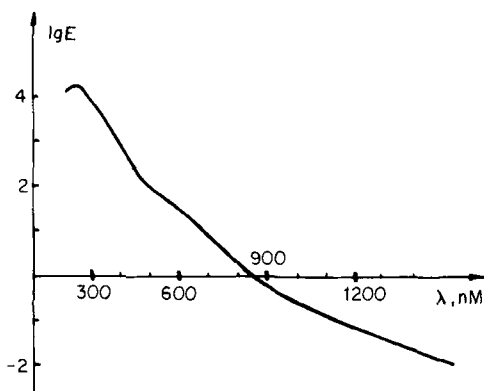


FIG. 9. Absorption extinction coefficient vs. wavelength for the PPA specimen. Analogous, but in most cases, structureless absorption spectra are given also by other linear members of the PSC series.

IR region correspond to fractions of higher molecular mass, and in most cases the absorption maximum does not change its position, i.e., the absorption intensity increases in the longwave region; the EPR signal intensity shows a proportional increase, accordingly.

Thus, the whole range of PPA optical absorption can be tentatively divided into two regions: a region with a wavelength greater than ~ 560 nm, and a region with wavelengths less than ~ 560 nm. The nature of the optical transitions responsible for the shorter wavelength region may vary. Nonetheless, we can distinguish the absorption of the main chain of the conjugation of the molecule, and if there are substituents in the chain, for the absorption of which the dipole moment of the transition is localized at these substituents. PPA, for instance, has a broad absorption peak with a maximum at about 270 nm, and the absorption extinction coefficient in the maximum is $\sim 10^4$. This peak has a slowly falling longwave arm which eventually passes into the longwave region of the absorption. Probably, the absorption maximum is related to the optical absorption of side phenyl substituents partially conjugated with the polyene chain. This absorption (270 nm) shows a small bathochromic shift (~ 5 nm) for the benzene absorption line intensity ($\lambda_{\max} = 265$ nm, $\epsilon = 10^4$). The polyene chain absorption is less intense and is located on the arc of intense absorption of the phenyl ring.

The absence of a vibrational structure in the absorption spectra and the absence of even isolated absorption peaks is primarily associated with the averaging out of the optical characteristics, not only over the molecules differing in molecular weight distribution, but also over the isomers and conformer of the same molecular weight. While permanent paramagnetism is an experimental manifestation of structural imperfections of the molecule (i.e., disrupted molecular conjugation), all the molecules are active in optical absorption, and it is impossible to carry out averaging over all the possible wavelengths, orientations, and conformations. Only the general tendencies will show up, and the problem is, therefore, to investigate these tendencies and to explain them.

We shall now take up the longwave region in the absorption spectra of polymers with systems of conjugation. For these compounds we shall consider only the position of the longest wavelength region in the absorption spectrum, the energy of which is equal to the gap in the one-particle excitation spectrum. This energy, as already mentioned, depends on the molecular conformation. For a planar arrangement of the carbon molecules in the polyene chain, the limiting width of the gap in the spectrum is about 2.2 eV; i.e., absorption should not be observed beyond ~ 560 nm. If radical states exist in the system, then the energy of the one-particle molecular orbital

exists at the middle of the forbidden band. Transitions (if they are not forbidden) from the higher occupied molecular orbital to an orbital corresponding to the radical state and from this orbital to lower vacant orbital are possible. The energy of such transitions should at least be less than half the energy of the corresponding gap in the excitation spectrum of diamagnetic molecules, and the optical absorption may stretch to wavelengths of ca. 1200 nm. The chemical compounds absorbed in this spectral range are black in color. In general, there should be continuous distribution of the molecules absorbed between the fringes indicated above, and this distribution should steadily decrease as the wavelength increases. It is, in fact, almost impossible to determine the distribution density of molecules with different widths for the gap in the excitation spectrum. An experimentally determined characteristic is the dependence of the optical absorption extinction coefficient on the wavelength, $\epsilon = f(\lambda)$. In the wavelength range from 500 to 1,200 nm this curve was found [73, 74] to take the form:

$$\epsilon(\lambda) = A\lambda^n \exp\{-\lambda/\lambda_0\}$$

where A and λ_0 are certain parameters characterizing the system under investigation, λ is the wavelength, and n is a constant equal to two or three. Earlier the anomalous longwave absorption observed for shorter polyenes was explained on the basis of the deviation from the equilibrium conformation [73, 74]. Even in such a simple interpretation, it was found that the variations in the conformation of macromolecules, their structural imperfections, might have considerable influence on the physical properties of polymers with systems of conjugation, and in the case under consideration, on the energy of the optical transitions, i.e., on the coloration of chemical compounds. Such explanations, though plausible for a wavelength of 500-1200 nm, cannot, however, reveal the causes of light absorption beyond the second fringe, ~ 1200 nm. Electron absorption proceeds right up to the range > 3000 nm, and in many cases it prevents and sometimes even completely screens out recording of the IR spectra of the polymers.

To explain such observations and the behavior of the longwave region in the absorption spectra, recourse has to be taken to recent ideas about the electron structure of MCB. In a previous section we have already mentioned that the low-lying homeopolar collective levels of integral multiplicities are characteristic of polymers with systems of conjugation. The lowest triplet levels ($S = 1$) were found to be useful in explaining paramagnetic properties. The succeeding

levels, i.e., the singlets ($S = 0$) should be of value in interpreting the causes of longwave optical absorption. Indeed, the spectrum of these levels for a given wavelength N is expressed as:

$$\epsilon_s = (U_s/N)n$$

where n is the number of the level, and U_s is a parameter dependent on the structure of an elementary link in the macromolecule and on its configuration. The optical transitions to collective singlet levels are, in principle, not forbidden [56, 57], and consequently, they should be observed as a rule. In order to describe the longwave optical absorption and its dependence on the wavelength, use was made of the common technique of averaging over the "tail" of molecular weight distribution [54]. The absorption intensity versus the wavelength curve takes the form,

$$\epsilon(\lambda) = A\lambda^2 \exp\{-\lambda/\lambda_0\}$$

where A and λ_0 are certain calculation constants.* This curve is in agreement with the experimental data. In the same paper the relationship between the paramagnetic properties and the intensity of the longwave optical absorption of the polymers with systems of conjugation has been theoretically interpreted and verified experimentally.

The interpretation of longwave optical absorption in terms of the transitions to homeopolar singlet levels likewise leads to a strong dependence of the transition intensity and energy on the molecular conformation. Figure 5 shows the variations in the parameter U (it coincides with U_s to an accuracy of $\sim 1/N^2$) as a function of the model conformational violations in the macromolecule structure. It is obvious that quite diverse possibilities may be realized, but, undoubtedly, what is most important is that when the planar arrangement of the molecular core is disrupted, the probability of optical transitions to the singlet collective levels should increase as a result of the increased linkage of these states with the molecular vibrations. Here too, the conformation affects the physical properties of the polymers and, in the case in hand, it influences the optical properties.

*The authors acknowledge their gratitude to I. A. Misurkin for pointing out the inaccuracy in the formula reported by Berlin [54].

CONCLUSIONS

In the previous sections we examined a number of properties and the behavior characteristic of polymers with systems of conjugation. To a certain extent, of course, these ideas need to be further refined. Nevertheless, if we attempt to draw final conclusions, we may formulate them along the following lines. A system of conjugation is quite essential in explaining the whole set of physicochemical properties, but the presence of this system of conjugation in real molecules with steric functional side groups, especially in intermolecular interactions when heat liberation is intense and the excess heat cannot be quickly dissipated, predetermines the generation of structural defects in the form of disruption in the conjugation chain and generation of radical states. But even in the absence of structural violations in the molecular structure, paramagnetic states might be generated via the thermal population of low-lying triplet levels. Paramagnetism thus induced adds new features to the general picture of the physicochemical properties of such conjugated systems. For instance, they may exhibit catalytic and inhibiting properties as a result of the effect of local activation or the free-radical states inside the forbidden band may undergo splitting, thereby leading to inevitable electro-physical and optical effects.

Therefore, without any fear of being misled, it may be asserted that we see polymers with a system of conjugation as resulting from the presence of a ruptured conjugation.

As we restricted ourselves to the topic under review, we were compelled, against our will, to leave out some of the most interesting experimental and theoretical material. In the first instance, there is the problem of high-temperature superconductivity. Unfortunately, at present it can be said, with almost absolute certainty, that the elegant hypothesis propounded by Little [76] to explain the superconductivity on a system of the type like the polyene core with side polymerizing substituents is not justified for two reasons. Firstly, energy approximately equal to the gap in the one-particle ion excitation spectrum is needed to transfer the charge carrier (electron) into the conductance band. Secondly, in order to realize the Little superconductivity mechanism by electron-electron interactions, we need easily polarizable side substituents which should, on one hand, readily interact with the polyene core and should not, on the other hand, disrupt the conjugation chain of this core. When there is bonding between the polyene core and the polarizing side substituents, the latter will, in all probability, form their own band in the electron level spectrum, and thus, the whole pattern of superconductivity is

disturbed. More convincing theoretical arguments, however, are available to demonstrate that there cannot be any superconductivity in the compounds listed by Little for this purpose. These remarks, however, do not apply to other types of organic compounds which are possible substances exhibiting high-temperature conductivity, such as sandwich-type compounds, organic salts, compounds based on the rare earths, and many others. Successful experimental and theoretical efforts are still being made along these lines.

The electrophysical properties have not as yet been dealt with. They include such interesting problems as semiconductor properties and photoconductivity. These properties, besides being of considerable theoretical interest, are of paramount practical importance.

Several other types of behavior exhibited by the physical properties and chemical interactions may be mentioned. Among them, worthy of mention is only the high affinity of polymers with systems of conjugation for the formation of intermolecular π -complexes with a well developed system of conjugation. There is no doubt that all these specific features might be understood and explained only in terms of a sound theoretical foundation based on concepts of the electron structure of macromolecules with conjugated bonds. Experimental investigations into polymers with systems of conjugation pose questions and problems which cannot be solved without a profound knowledge of the finer details of electron interactions and without a correct description of these interactions.

This review, in all probability, carries more questions and unsolved problems than the ready solutions and answers it gives. Moreover, not all readers will agree with the basic standpoints expressed. However, we firmly believe, that the time is ripe to unite the efforts of theoreticians and experimenters to conduct an all-round study of the problem, and this was, in fact, the stimulus behind the publication of this review. The list of references was, incidentally, compiled at random. Therefore, we apologize to the authors of numerous interesting publications whose works are well known to us, for failing to refer to their works, a situation dictated by considerations of the size of the review.

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