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Electronics of thin layers of wide-band polymers

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Contents

Abstract. The history of the creation of conducting polymers is reviewed and their properties are considered. Some special charge-transport features of phthalide-containing polymers — the injection mechanism, high conductivity, and the dependence on boundary conditions — are described. Conditions for a polymer film transition to highly conducting and superconducting states are examined. Prospects for the application of wide-band polymer materials in electronic devices are discussed.

1. Introduction

Studying ordering and various related phenomena in two-dimensional and one-dimensional systems (polymer chains, edges of faces, etc.) attracts great attention from both the general theoretical viewpoint and application to various concrete objects and conditions.

V L Ginzburg [1]

In 2000, the Nobel Prize in chemistry was awarded for work on conductive polymers to a Japanese chemist Hideki Shirakawa and two American scientists, Alan G MacDiarmid and Alan J Heeger. The main scientific results were obtained by these scientists in the late 1970s; Shirakawa developed the technique of a selective synthesis of two modifications of polyacetylene (*trans* and *cis* forms) [2], and MacDiarmid and Heeger suggested and realized a method for achieving a virtually metallic conductivity in this polymer [3]. In fact, they laid the foundation of a new scientific area; at present, many thousands of researchers from various countries are involved in solving related problems [4].

An important role in the establishment of the new area belongs to an appropriate theoretical model suggested as long ago as 1979 [5]. We note that it was based on theoretical results obtained shortly before by the Soviet physicist Brazovskii [6].

The problem of the preparation of conducting polymers can be divided into two global parts. The first is related to the necessity of creating polymer materials whose chemical structure favors the formation of delocalized electron states — bands or levels of charge transfer. This problem was solved by synthesizing polymers with the valence π electron conjugation.

For the molecules of organic materials, the main chemical bonds are those of the σ and π type [7]. They differ in the symmetry and shape of related electron clouds. The 'skeleton' of an organic molecule is formed by σ bonds, which have a rotational symmetry. If the interaction of π electrons is added to a σ bond, a double bond is formed. The clouds of the π electrons have an elongated shape in the form of a dumbbell; therefore, no rotation about a π bond is possible. But these elongated clouds not only can take part in a pairwise overlap to form localized (nonconjugated) bonds but also exhibit itinerant behavior, contributing to delocalized (conjugated) bonds. The variety of types of chemical bonds and the related dynamic activity of electrons in organic materials underlie the possibility of changes in conductivity that are inconceivable for inorganic dielectric materials.

Two typical representatives of such polymers are displayed in Figs 1a and 1b; in Fig. 1c, a new electrically active polymer having no conjugated valence electrons along the polymer chain is shown.

The second problem is related to the absence of free charge carriers in polymers; the lack of such carriers prevents achieving high conductivity, as can be seen from the simple

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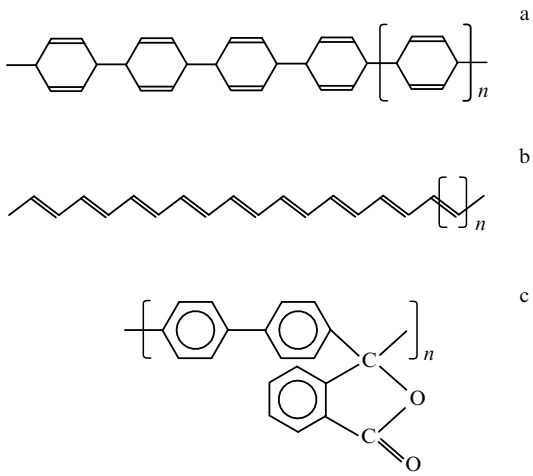

Figure 1. Electroconducting polymers: (a) polyphenylene; (b) polyacetylene; and (c) electroactive polymer polydiphenylenephtalide.

relation between the current J and the voltage U:

$$J \sim en\mu U\,, \tag{1}$$

where e is the electron charge, n is the concentration of charge carriers, and μ is the charge-carrier mobility.

To solve this problem, it has been suggested to introduce special low-molecular additions (dopants) into the polymer material. The dopants play the role analogous to that of doping impurities in inorganic semiconductors such as silicon or germanium. The difference is that a doping impurity in semiconductors leads to the formation of donor or acceptor energy levels in the energy gap of the semiconductor in accordance with the relation between the energy of electron affinity of the impurity and the bottom energy of the conduction band of the semiconductor (the first ionization potential of the impurity and the energy of ionization of the semiconductor [8]). Doping can change the energy spectrum of electrons because of a redistribution of intrinsic (polymer-related) states. Polaron, bipolaron, and even soliton states can thus arise [9].

Recent studies in this area have led to results of colossal importance, which are now widely used in various fields of engineering. The most interesting ones seem to be the suggestions regarding the application of such materials in planar electroluminescent displays [10], thin-film transistors [11], spintronics [12], etc.

However, it was already revealed in the first works [13, 14] devoted to the electric conductivity of polyarylenephthalides that a sharp increase in conductivity can be observed even in nonconjugated polymers (although not to very high values).

2. Conductivity of nonconjugated polymers

Paper [15] published in 1981 for the first time reported the possibility of achieving large values of conductivity in nonconjugated polymers without using the doping procedure.

The authors of [15] described a sharp (jump-like) decrease in the electric resistance R of thin films of polymer insulators and of 'polymer-insulator – metal' composites subjected to uniaxial compression. They used films of lavsan, polyimide, polypropylene, and polytetrafluoroethylene (teflon) with a thickness $d = 2-30$ μm. The pressure was varied using Bridgman anvils from several hundred bars to 30 kbar. At the pressure $P = 10$ kbar and room temperature, the lowest values of R of some of the systems studied did not exceed the resistance characteristic of metal samples, e.g., Ti, of the same size with the conductivity 10^4 $(\Omega\ \mathrm{cm})^{-1}$ under conventional conditions. But the character of the dependence of R on the film thickness d and temperature T indicates that the effect revealed apparently cannot be interpreted as a well-known phase transition of the insulator – metal type. A similar phenomenon was revealed upon compression of systems such as polypropylene – copper or teflon – copper ($d = 70-200$ μm).

The authors of [16] studied the effect of high pressure and the combined effect of high pressure and shear deformation on the conductivity of polymer – metal composites. As a polymer, they selected polyethylene, polypropylene, teflon, polyvinylchloride, and polyacrylamide; and as a metal filler, finely disperse copper, tin, iron, and aluminum or graphite in the form of powders with particle dimensions of $0.01-0.1$ μm and $1-10$ μm, respectively [17]. The following specific features of the transition of polymers into a low-resistance state have been noted in [15 – 17.

(1) An unusual temperature dependence of resistance for deformed samples. As the temperature increased from 77 to 340 K, the resistance measured at a constant pressure $P > P_c$ remained unaltered; in the course of subsequent heating up to 400 K, it decreased in accordance with the law

$$R = R_0 \exp\left(\frac{E}{kT}\right); \tag{2}$$

the activation energy E then decreased with an increase in both P and the angle of rotation of the anvils α during deformation.

(2) A nonlinear character of the resistance dependence on the sample thickness. It was established experimentally that for polymer – metal samples in the form of disks with the area $S = 0.8-7.1$ cm^2 and thickness $d = 70-170$ μm, the dependence of R on the geometrical parameters at constant pressures ($P > P_c$) and temperatures has the same character as that observed in [15]; i.e., it increases nonlinearly with increasing the polymer layer thickness.

(3) Anomalously low resistances of samples (lower than even those of the leads-in).

Based on the experimental results in [15, 16], a conclusion was made that the jump in the resistance caused by the effect of uniaxial pressure and shear deformation on the polymer composites is not related to the formation of conducting channels of contacting particles in the spacer.

Based on a generalization of these unusual results, the authors of [17] developed a model of pressure-stimulated injection of charge carriers from the metal into the conduction band of the insulator. According to this model, the compression of a substance causes the decomposition of surface states that play the role of electron acceptors. It cannot be excluded either that because of an increase in the polarizability, the bottom of the conduction band of the polymer insulator simultaneously decreases (Fig. 2). As a result, at some pressure $P = P_c$, the structure of the energy bands near the metal – insulator interface proves to be favorable for carrier injection, although this process either is not realized at all or has an extremely low efficiency at $P < P_c$.

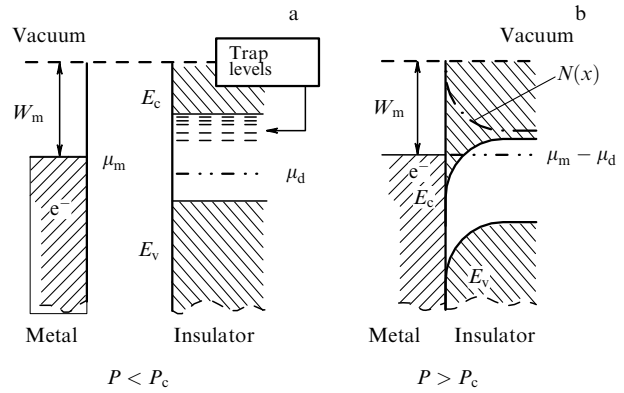

Figure 2. Qualitative picture of energy bands in a metal – insulator system: (a) pressure on the polymer film $P < P_c$ and (b) $P > P_c$. E_c is the energy of the bottom of the conduction band of the insulator; E_v is the energy of the top of the valence band of the insulator; μ_m and μ_d are the Fermi levels of the metal and insulator, respectively; and W_m is the electron work function of the metal. The dashed line in Fig. 2b shows the distribution of injected electrons in the insulating film [17].

An analysis of the results of subsequent investigations allows somewhat expanding the approach to the problem under consideration and formulating it based on a wider and, at first glance, paradoxical aspect, namely, whether an effective charge transfer (comparable to that in metals) is possible in nonconducting materials.

Already in the first works devoted to the investigation of the electrical strength of film coatings, published in the late 1920s and early 1930s, certain deviations from the expected behavior of electrophysical parameters of the materials with decreasing film thickness were noted [18, 19]. It was also found that films of some native oxides sometimes do not prevent the passage of large (even superconducting) currents [20]. In the same oxides, an effect of electrical forming was actually discovered, which in the 1950s became more widely known as the effect of electron switching in connection with the discovery of the effect of electrical memory in films of inorganic semiconductors [21] and then in polymers [22].

Concerning these unusual electronic properties of organic materials, the authors of [23] wrote that the experimental discovery of a number of 'strange metals' has reopened the problem of the low-temperature behavior of interacting Fermi systems. The current understanding of the physics of metals is based on Landau's guess that the electron – electron interaction is insignificant at low energies. "The last two decades have seen the experimental discovery of a number of 'strange metals' whose behavior is apparently not well described by the Fermi-liquid theory. Examples include quasi-one-dimensional organic conductors [24], a two-dimensional electron gas in the presence of disorder [25] or magnetic fields [26], some 'heavy-fermion' compounds [27], and high-temperature superconductors. These experimental discoveries have prompted theorists to reconsider the circumstances under which the Fermi-liquid theory breaks down and what 'non-Fermi-liquid' metals can exist" [23].

The data on the experimental and theoretical results accumulated to date allow supposing that the fundamental features of the behavior of organic polymeric and inorganic insulating films have a common origin; therefore, the study of polymers can also be useful from the general scientific standpoint.

We note that thin (compared with bulk samples) micron-thickness layers of normal metals under certain conditions can also have enhanced conductivity and even superconductivity. In thin solid films, phenomena such as the effects of proximity and anomalous proximity, electroforming effects, soft and recoverable breakdown, A- and B-fritting, and the effect of single-electron switching can occur.

The proximity effect is the appearance of superconducting properties in a nonsuperconducting material near its boundary with a superconductor at distances that are smaller than the coherence length of a Cooper pair. At slightly greater distances, we speak of the anomalous proximity effect.

Electroforming is the phenomenon of a significant and, in essence, irreversible change in conductivity caused by a strong electric field. This phenomenon can be due to Joule heating, redistribution of a space charge, or phase transformation of the insulator. Electroforming is not identical to electrical breakdown, which occurs at much greater voltages.

Fritting is the phenomenon of the appearance of conducting bridges. A-fritting is the process of a breakdown of chemical bonds in the insulator under the effect of an electric field [20], which is accompanied by the fusion of the metal of the contacts. The liquid metal forms a conducting bridge between the contacts. Upon B-fritting, the voltage at the contacts is too small to cause melting. But because the film thickness is also small (about 5 nm), the conducting bridges consisting of the material of the contacts can be formed even without their melting.

Many of these phenomena have several relatively formal parameters in common. In particular, in the experimental sandwich-type structures, e.g., metal – insulator – metal (MIM), such phenomena are also observed at thicknesses d of insulating films that are smaller than a certain critical value. For example, the effects of anomalous proximity manifest themselves at film thicknesses $d \sim 10-50$ nm; effects of electroforming, at $d \sim 100-500$ nm; 'soft breakdown' like switching and fritting effects, at $d \lesssim 1-2$ μm. For films of normal metals located between superconducting 'banks,' the critical thickness can reach 50 μm.

Such a restriction on the critical thickness for the appearance of conduction in a polymer film is sometimes ascribed to the parameters of charge carriers such as the depth of penetration of the surface charge or the coherence length of Cooper pairs, and the high conductivity to a resonance tunneling through the relatively wide potential barrier of a specific structure. In recent years, this list of 'thickness-related' phenomena has been extended by the effects of spintronics; correspondingly, a new parameter has been introduced for their description, the coherence length of electron spin. In paper [12] devoted to studying spin valves, the coherence length of electron spin for an organic superconducting material was determined experimentally; its value was about 140 nm. The metallic 'banks,' i.e., the electrodes between which the film is placed in virtually all these experiments, appear to be necessary as a reservoir of free charge carriers that are lacking in the polymer interlayer.

The most complex component of the problem of charge transfer in metal – polymer samples is that of the transformation of the electronic structure of the polymer insulator whereby it becomes a good conductor of electric current. No common concept of the role of a polymer in the process of charge transfer exists to date. The spectrum of possible suppositions is rather wide; as an explanation of conductivity in the polymer, a number of mechanisms have been suggested,

from the simplest ones, related to the short-circuiting of electrodes because of the existence of holes in the polymer film or dendrite formation [28], to the generation of soliton-like excitations in the polymer chain [29], high-temperature superconductivity [30], or electron 'levitation' [31].

At present, however, the problem of the main features of electron switching and the mechanisms of high conductivity of polymer thin-film systems remains open.

The theoretical description of the phenomenon of coherent charge transfer in thin films of wide-band polymers (with the conduction band width 4.2 eV), just like the construction of empirical models, has encountered serious difficulties. It has been necessary to explain the existence of a relatively high concentration of free charge carriers in an insulating material, the absence of evident prerequisites of an efficient charge transfer, i.e., a proper energy band structure (a partly filled band) and the low (from the energy standpoint) level of action leading to significant transformations of the electronic properties of the material, etc.

In addition, there is a geometrical aspect of the problem that must be taken into account. The highly conductive state of the polymer film is inhomogeneous over its volume. In this state, the film is divided into conducting channels (domains) surrounded by an insulating polymeric matrix. Several experimental works have been devoted to estimating the density and dimensions of such domains. In particular, in [32], these estimations were performed based on the results of measurements of leakage currents; in [33], an original technique was suggested for the visualization of conducting domains using a layer of a nematic liquid crystal; and in [34], the domains were observed using transmission electron microscopy. Good agreement was established between the estimates obtained by these different methods. In particular, the channel diameter varied from 10 to 50 nm. In [34], a fine structure of channels was revealed; isolated 'filaments' of this structure have the diameter about 1 nm.

In a theoretical model, it is therefore expedient to account for the fact that the electrically conducting region is, in essence, a cylinder whose diameter is much smaller than its height. The electron free path can then be greater than, comparable to, or smaller than the diameter of the conducting domain.

In addition, there exists a problem of the 'transition' resistance, which arises at the boundary between the polymer and the metallic electrode. This resistance can be due to the 'leakage' resistance or some potential barrier that inevitably arises at the contact between a polymer and a metal.

Added to these problems is the necessity of accounting for the specific chemical nature of polymer materials and the strong tendency of nonconjugated polymers to charge localization effects.

Unfortunately, many of the models that have been suggested to date have a limited application because they were developed with the purpose of explaining a single experimental fact. Most frequently, the efforts have been directed at explaining the extremely high conductivity of an organic material.

Indeed, the experimental data show that the conductivity of an organic medium is limited by the conductivity of metals used as the material for the electrodes. If a metal in the superconducting state is chosen as the material for the electrodes, then a transition into the superconducting state is observed in the superconductor – polymer – superconductor system [35]. It is apparently for this reason that Little's idea [37] of the possibility of high-temperature superconductivity (~ 800 K) in polymer materials was reanimated and developed on a new level in [30, 36]. However, Keldysh's critical remarks [38] concerning Little's model, which were made as long ago as 1965, are fully applicable to these theoretical constructions as well.

In [31], one additional experimental circumstance was used for the construction of a model of high conductivity in polymers. We speak of the so-called effect of pinching of a current passing through the polymer film and the appearance of conductivity channels whose diameter is much smaller than their length, i.e., $d/l \ll 1$, where d is the channel diameter and l is its length. The authors of [31] investigated the possibility of the occurrence of waveguide energy levels that permit electrons from metallic electrodes to penetrate into the channels and move in them with a negligibly small energy dissipation. A simple, in the opinion of the authors of [31], model of such a channel was suggested, and estimates elucidating the essence of the waveguide levels were made. However, it is difficult to analyze the applicability of this model for the explanation of the available results of measurements because of the lack of concrete parameters; this hinders the use of this model in experimental investigations.

A mechanism of a soliton-like propagation of a specific excited state along a polymer molecule was suggested in [29]. In fact, the model of soliton-like transport in polyacetylene (Fig. 1b) was extended to the phenomena of charge transfer in a more complex molecule of polydiphenylenephthalide (Fig. 1c). The authors of [29] were forced to use very serious restrictions and assumptions. They supposed that the polymer has a structure with a doubly degenerate ground state, as in the case of polyacetylene. The transition between these states is provided by the propagation, along the polymer chain, of a soliton excitation caused by successive breaks in bonds between the side group of the macromolecule and the skeleton part. According to the authors of [29], the breakage of these bonds results in a change in the type of hybridization (the hybridization of the sp^3 type is replaced by the sp^2 hybridization) and a rotation of the side group through $\pi/2$. Hybridization is the interaction of close-in-energy electrons of one atom with those of another atom. Upon the formation of a chemical bond, new (hybrid) electron clouds appear in this case. In the process of sp^3 hybridization, the 2s and 2p electrons of a carbon atom interact with electrons of other atoms to form four totally identical sp^3 hybrid orbitals directed to the vertices of a tetrahedron whose center is occupied by the carbon atom under consideration. Before the hybridization, one of the s electrons of the carbon atom passes onto a free 2p level. In the case of sp^2 hybridization, one s electron and two p electrons of the carbon atom form three identical sp^2 hybrid clouds directed at 120° to one another. It is obvious that the transition from one type of hybridization to another cannot occur without a change in the total energy of the molecule, but this contradicts the principal postulate of the model regarding the degeneracy of the ground state.

In this connection, we consider a series of works devoted to the experimental investigation of electron switching in metal – polymer – metal (MPM) systems under the effect of pressure, electric field, temperature, boundary conditions, etc.

In the last several decades, a large body of experimental data have been accumulated in this field. The table displays some data on nonconjugated polymers exhibiting high conductivity induced by various methods, but always in the

Table. Polymers in which the effects of electron switching (ES) or a high-conductivity state (HCS) were observed.

Polymer	Effect	References
Polyethylene	HCS	[16, 22, 39, 40]
Polyferrocene	ES	[55]
Polypropylene	HCS	[15, 16, 32, 35, 40–49]
Polytetrafluoroethylene	HCS	[16, 35, 40, 50]
Polyvinylchloride	HCS	[16, 50]
Polyacrylamide	HCS	[16, 50]
Poly-N-vinylcarbazole	ES	[51]
Polycrystalline terphenyl	ES	[50]
Polyimide	HCS	[15, 35, 40]
Polystyrene	ES	[53]
Polymethylmethacrylate	ES	[53]
Langmuir–Blodgett films	ES	[54]
Polydivinylbenzene	ES	[55]
Polysiloxane	ES	[55]
Polyurethane	HCS	[55]
Silicone rubber	HCS	[16]
Polydimethylsiloxane	HCS	[46]

absence of doping. In spite of the data given in the table, there is no definite answer to the question of whether high conductivity is possible in thin polymer films, what the conditions for its appearance are, and what the mechanism of charge transfer in this case is. This is apparently caused by the existence of frequently controversial information, in particulars, concerning various theoretical constructions.

3. Diphenylphthalide-based polymers

Over the last decades, a new scientific area has been developed, the electronics of thin films of electrically active polymers. But why does this concern precisely thin films and to what extent are these films thin?

With decreasing the material thickness below a certain value, various factors, previously insignificant, start affecting the appearance of new properties (including electronic ones), which are frequently quite interesting from the standpoint of practical application.

The possibility of creating organic films, including polymeric ones, with fantastic physical properties exists. With decreasing the film thickness, the surface effect increases significantly. This manifests itself especially strongly in the case of metal–insulator contacts.

In what follows, we do not distinguish the concepts of an insulator and a polymer, unless specially stipulated, because we consider polymers having a wide energy gap E_g and, therefore, satisfying the criterion that is frequently used to distinguish between semiconductors and insulators: for an insulator, the inequality

$$E_g > 2 \text{ eV}, \tag{3}$$

is satisfied, whereas the reverse inequality relates to a semiconducting material.

We note that the main paradoxicality of the phenomena described in this review consists in the fact that the efficient charge transfer (electric conductivity) occurs in materials all of whose properties indicate that they are insulators.

Figure 3 displays a simplified energy-band structure of a three-layer MPM structure in the version where both metals are the same and the electron work functions for the metal and the polymer are also the same. This is the so-called case of

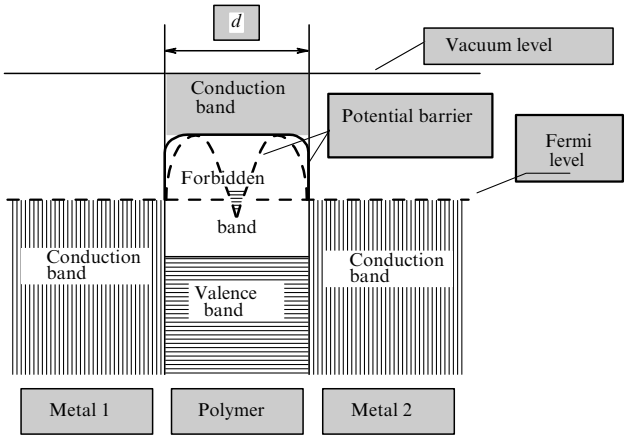

Figure 3. Energy-band diagram of a three-layer metal–insulator–metal structure: d is the thickness of the insulator; the continuous solid line in the insulating layer shows the shape of the potential barrier in the case where d is greater than the depth of penetration of the surface charge; the dashed line corresponds to the case where d is less than the depth of penetration of the surface charge; and the short horizontal lines in the middle part of the potential barrier correspond to electron states.

direct bands; using a polymer in such a structure, an ohmic contact can be obtained most frequently. We do not consider the details of the mechanism of electric contact establishment. We only state that the existence of an insulator (with a large energy gap) between two metallic electrodes can prevent the passage of a charge current between the electrodes when the thickness of the insulating interlayer is sufficiently large. In this case, the insulating layer plays the role of a potential barrier of a rectangular shape whose height is determined by the difference between the work function of the metal and the energy of electron affinity of the insulator.

With decreasing the thickness of the insulating film, the charges concentrated near the opposite boundaries of the contact under consideration may begin to interact with one another, leading to a distortion of the potential barrier shape. The largest thickness of the film at which the interaction between the boundary charges occurs can be assumed to be twice the penetration depth of the surface charge (which is a parameter of the contact). The interaction of near-surface charges can lead to the formation of a local energy minimum in the middle of the barrier; this minimum can in turn lead to the intersection of the Fermi level with the curve describing the potential barrier envelope.

In this hypothetical version, new electron states can arise in the middle of the barrier at the Fermi level, significantly increasing the barrier permeability to electrons. Gaining a control over such states would mean creating a fundamentally new electron hybrid nanostructured metalorganic material.

In the early 1980s, a new polymer — polydiphenylenephthalide [56] — was synthesized at the Institute of Organic Chemistry (Ufa Research Center, Russian Academy of Sciences), which opened the way to synthesizing a number of new compounds. Its optimized three-dimensional geometry is shown in Fig. 4.

As was established later using the method of quantum-chemical calculations [57], a remarkable feature of these polymers is that with a change in the length of one of the bonds in such a molecule to a certain magnitude, a second energetically stable state can arise that is characterized by the

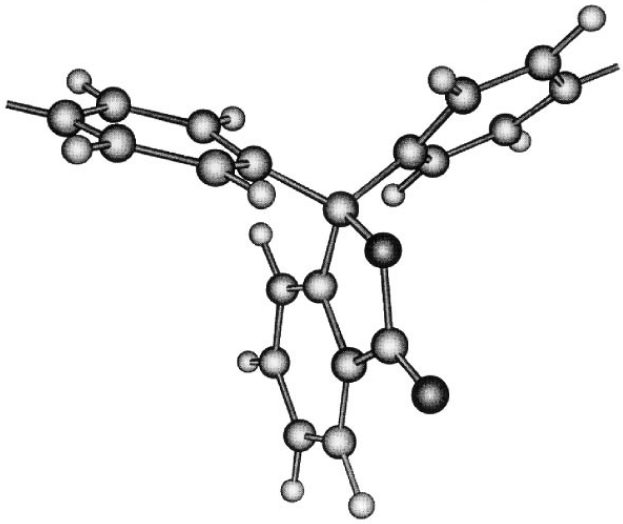

Figure 4. Optimized spatial structure of a monomer unit of polydiphenylenephthalide molecules: small spheres denote hydrogen atoms; large spheres, carbon atoms; and large dark spheres, oxygen atoms.

existence of electron levels in the region of previously forbidden energies.

To perform quantum-chemical calculations of the polymer structure (Fig. 1c), the semiempirical Austin Model 1 (AM1) method [58] was used to optimize the chemical structure of organic molecules and the pseudopotential method of the valence effective Hamiltonian (VEH) [59] was used with the data obtained in terms of the AM1 method as the initial parameters. We note that the authors of [57] studied properties of an isolated chain, although it is obvious that taking the intermolecular interactions into account may be important for the understanding of the relevant phenomena. In all cases, the geometry was optimized using monomeric and/or dimeric units, whereas the electron structure was determined for periodic boundary conditions with a monomeric unit. Calculations in terms of the VEH method yield the electron energy band structure. Figure 5 shows the optimized geometry for three different cases.

In a neutral system (Fig. 5a), the central carbon atom in the backbone chain is quaternary (sp^3 hybridization), and the C_6H_4 group (which must enter the main chain of the polymer) is in the benzoid state. Benzoids are monocyclic aromatic compounds with delocalized π electrons, because π bonds in the cyclic group are conjugated. Moreover, the distance from both phenyl groups (in the main chain) to the central quaternary carbon atom turned out to be 1.50 Å. The distance between the central atom and the nearest oxygen atom in the side group (C – O spacing) is equal to 1.47 Å. The torsion angle between the planes of phenyl groups inside the monomer is about 65°, which indicates a weak conjugation degree along the polymer chain.

The calculation started from the initial geometry in which the central carbon atom was in the sp^2 hybrid state, the bonds surrounding the carbon atom lay in the same plane, and the oxygen atom was not bound to the central carbon atom. The procedure of optimizing the molecule geometry was stopped at a local minimum with a slightly increased formation heat compared with that of the neutral ground state. The phenyl groups retained the benzoid type. The structure around the central carbon atom was contracted, which led to a decrease in

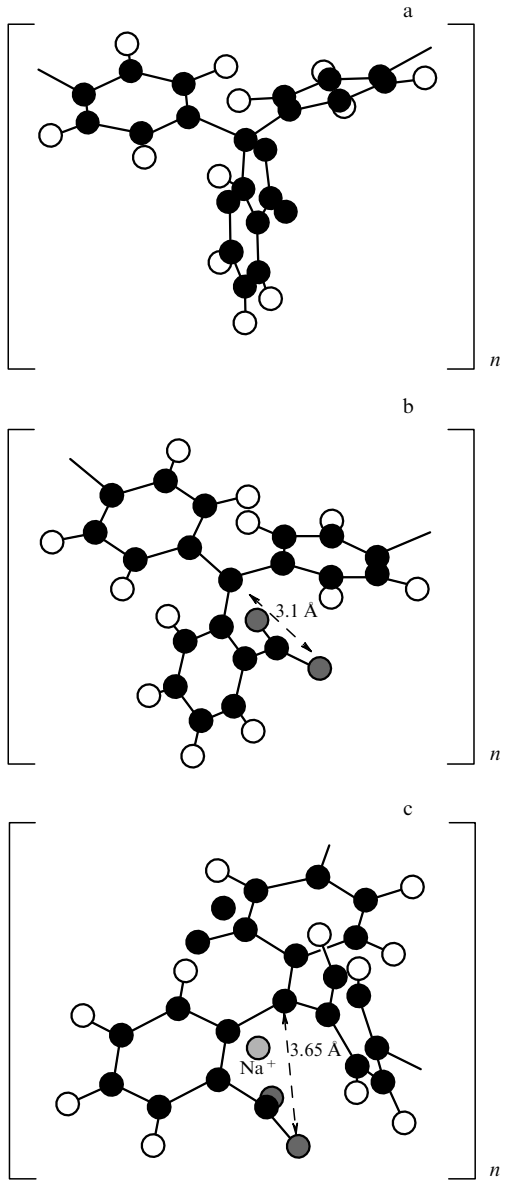

Figure 5. Optimized geometry for three different cases: (a) a neutral molecule in the ground state; (b) the molecule in the state with a greater total energy, which corresponds to an open lacton (containing a –C(O)–O– group) cycle at the place of the –(CO_2)– group in the lateral benzene ring; and (c) alloying by adding one electron and a counter-ion Na^+ to the molecule.

the length of the bonds. The distance from the carbon atoms of the phenyl groups to the central carbon atom was now about 1.44 Å, whereas in the geometry of the neutral ground state, it was equal to 1.50 Å. The C – O spacing in this case was 3.10 Å. A separate preliminary calculation of the reaction coordinates for isolated polymer chains showed that the magnitude of the activation barrier is not more than the actual difference in the heats of formation of these two optimum configurations. The local energy minimum is very shallow; therefore, the shape with an open cycle in the neutral molecule is very unstable. However, intermolecular interactions, including those caused by the dipole moment, reduce the attraction between the positive carbon atom and negative carboxyl group and lead to a stabilization of the chemical structure. This apparently indicates that the shape with an open bond can be formed as a

result of the action of external forces in the solid state, when the surroundings of the polymer chains are capable of stabilizing the higher energy state.

The addition of an electron and of a compensating ion to any of the three geometric configurations under consideration shows that the structure with an open cycle becomes stable. The energy of stabilization of the monomer is about 113 kcal mol^{-1}. The bond lengths indicate that the phenyl group continues to be of the benzoid type as before. The largest change is observed in the distances from the phenyl groups to the central carbon atom, which decrease from 1.50 to 1.43 Å. The bond lengths along the polymer chain become almost equal to each other. It can be seen from Fig. 5c that the C – O bond is broken (the C – O spacing is equal to $\sim$ 3.65 Å). This suggests that the central carbon atom has the sp^2 rather than sp^3 hybridization, as in the neutral state. We note for comparison that the opening of the C – O bond is a well-known phenomenon in the case of phenolphthalein, which has a chemical structure resembling the structure of the monomer of the polymer under consideration.

In Fig. 6, we compare the densities of valence states corresponding to the three geometric configurations of the molecular structure considered above. It is obvious that the differences in the predicted structures should easily be detected by photoelectron spectroscopy. The magnitudes of the gap in the energy band calculated via the VEH method are as follows: 4.0 eV for the initial neutral polymer, 1.6 eV for the form with an open bond, and 1.1 eV for the doped polymer. The optical absorption edge in the initial polymer is 4.2 eV, which agrees well with the results of calculations of E_g by the VEH method.

The investigation of geometric optimization with a monomer used as the unit cell shows that two different geometric structures with a relatively small difference in the total energy of the ground states can be realized in polyarylenephthalides.

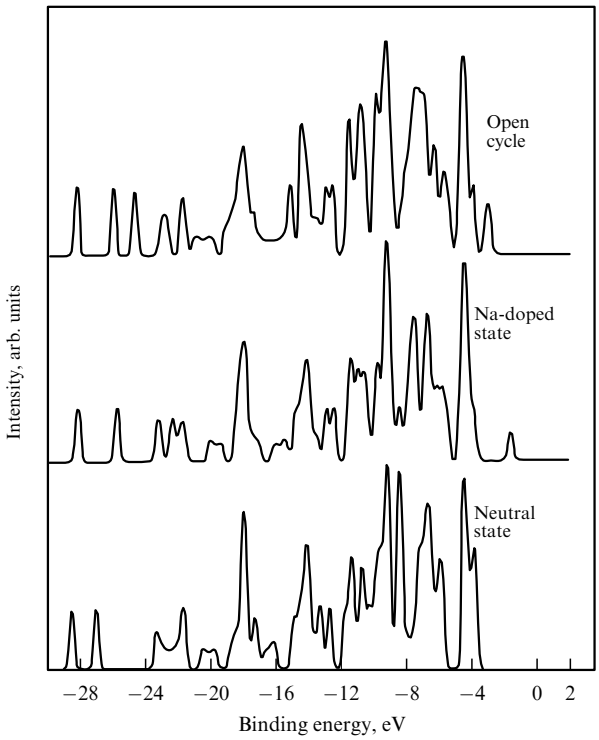

Figure 6. Comparison of the densities of valence states corresponding to the three states shown in Fig. 5.

Thus, numerical investigations have shown that the individual molecules of polydiphenylenephthalide have two energetically stable geometric configurations. The first corresponds to the neutral ground state, which is characterized by the widths of the energy gap between the top occupied and bottom vacant orbitals equal to 4.2 eV. The second configuration is determined by a modified set of lengths of intramolecular bonds and a nonzero spectrum of electron states in the region of forbidden energies. However, the stability of this state is insufficient to ensure its actual existence. But its stability increases (the local minimum becomes relatively deep) if the molecule captures an electron and becomes a negative-charge ion. In this case, the calculations predict the appearance of a new deep electron level in the energy gap.

From the standpoint of the model shown in Fig. 3, this result means the hypothetical possibility to control the shape of the potential barrier and its permeability to charge carriers by the generation of electron states inside the energy gap.

However, the results of calculations based on the experimental data on measurements of the energy characteristics of the polymer by X-ray photoelectron spectroscopy (XPS) [60] were insufficient to correctly understand the properties of this material.

Direct experiments that would allow observing the transition of the molecule from one neutral state into another state with a modified distribution of electrons and bond lengths were required. The main problem was in the correct choice of the means of acting on the molecule and of the method of recording the results of such an action. Therefore, a direct experiment was carried out in which the transition under consideration had to occur as a result of the interaction of electrons having small thermal energy with organic molecules. Molecules whose chemical structure was close to that of the monomeric unit of the polymer were selected. The smallness of the electron energy in this case is a very important factor, because experimental conditions should be created that would be maximally close to the conditions under which the processes occur in real polymer samples through which electric current passes. The scheme of such an experiment is shown in Fig. 7.

The collision of an electron with the molecule occurs under conditions of a deep vacuum. The result of the subsequent interaction can be restored by studying the products of this interaction depending on the energy of impinging electrons.

It was established in [61] that there exists a stable configuration of negative molecular ions with a broken C – O bond. This means that the result of the interaction of the

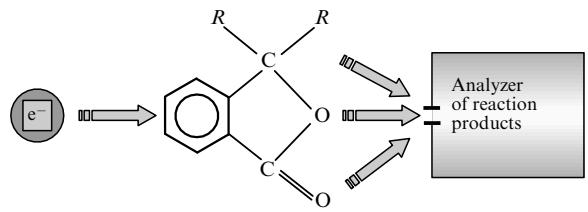

Figure 7. Scheme of the experiment on investigating the mechanism of interaction of model molecules with low-energy electrons. The reaction products were analyzed using a mass spectrometer of negative ions.

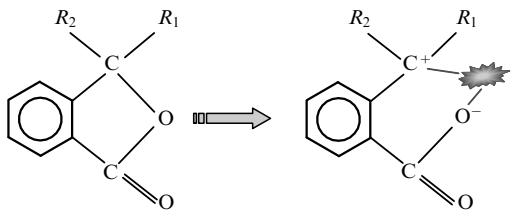

Figure 8. Scheme of the model concept of the process of breaking C – O bonds in molecules modeling a monomeric polymer unit.

electron and the model molecule can be represented as in Fig. 8; this mechanism does not exclude the possibility of the processes of interaction of the polymer molecule with an excess charge to develop in accordance with this scenario.

Such a change in the internal structure of the molecule must lead to changes in the charged state of some atoms; in particular, the carbon atom in the backbone chain of the polymer molecule should acquire a positive charge, while the oxygen atom in the side chain should become negative. This should reduce the potential barrier separating neighboring π-conjugated parts of the skeleton part of the molecule and thereby increase the probability of charge transfer along the chain. In the language of the energy band model (see Fig. 3), this process must lead to the appearance of deep electron levels located, according to the calculations in [57], almost at the Fermi level. It follows from these calculations and experiments that by changing the rate of injection of charge carriers into the polymer film, one can substantially control the electric conductivity of wide-band nonconjugated polymers. The available experimental work [62 – 69] generally confirmed this conclusion. Complex investigations permitted revealing many new physical phenomena in organic polymeric objects with a nontraditional conductivity.

To emphasize the nontraditional character of such materials, it is convenient to call them electroactive, in contrast to well-known electroconducting materials, which are mainly conjugated polymers. This means that most electroconducting polymers have double bonds in the molecule structure, whose reactivity (and, consequently, energy) depends on the number of such bonds (i.e., these bonds affect one another), whereas in polymers based on diphenylphthalide, the active double bonds of the different parts of the molecule are independent of each other.

To demonstrate the uniqueness (from the standpoint of physics) of electroactive polymers, the diagram shown in Fig. 9 schematically displays the main effects that are mostly new not solely for polymer materials.

Somewhat arbitrarily, all the effects can be divided into three large groups. The first group includes electrooptical phenomena; the most interesting of these is the effect of electroluminescence revealed in polymers [63]. The second group comprises unique phenomena of which only one was known previously — the effect of electron switching in a field. This effect was considered in sufficient detail in [73].

The third group includes quantum phenomena, such as the induced superconductivity [67]; some phenomena characteristic of metals, e.g., field-induced or cold electron emission from a polymer film [71]; phenomena occurring at the atomic level, which can certainly be ascribed to nanoelectronics, e.g., the effect of electron memory, which allows using the probe of a scanning electron microscope to repeatedly produce the total cycle of recording – erasing – recording information in film regions with an area of a few dozen square nanometers; or the closely related (in its physical essence) phenomenon of dimensional quantization in a polymer film, which manifests itself in that zero-dimensional objects — so-called quantum dots — can be created in the polymer under certain conditions.

4. Effect of pressure on the conductivity of thin films of electroactive polymers

The uniqueness of the electronic properties of polymeric materials is well exemplified by the effect of pressure on the conductivity of relatively thin polymer films.

By analyzing such dependences, one can single out some common features of changes in the conductivity of films of nonconjugated polymers inherent in different methods of its initiation, which are listed below.

(1) Anomalously low values of external actions that induce transition into the high-conductivity state (HCS) in the polymer. For example, when using pressure as an external factor, these values are lower by six orders of magnitude than those predicted by the theory; in the case of an electric field, by three orders of magnitude. No data on other external factors have been revealed in the literature.

(2) The threshold character of the phenomenon. The transition into the HCS occurs after the external field reaches a certain critical value.

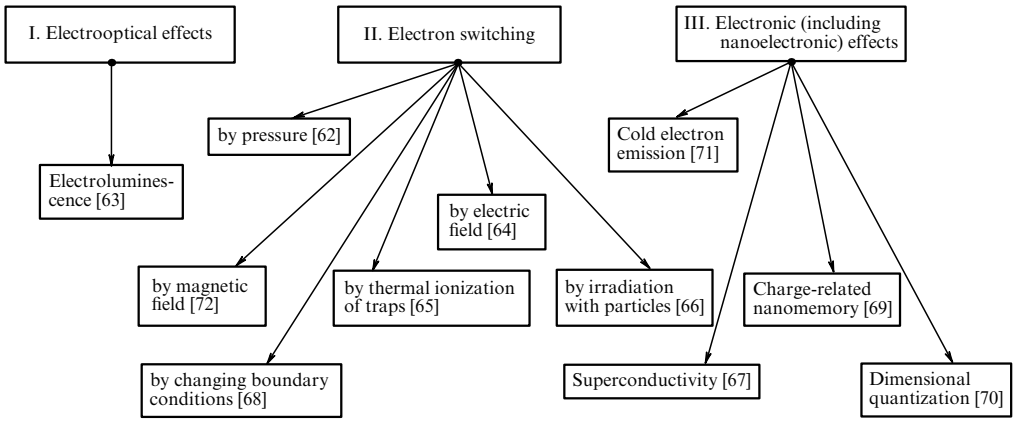

Figure 9. Systematization of electron effects observed in polymers with a nonconjugated system of valence π electrons, in particular, in polyarylenephthalides.

(3) The change in the conductivity of a polymer film frequently occurs jump-like from the insulating into a metal-like state with an increase in the conductivity by 12 – 16 orders of magnitude.

(4) In the HCS, the conductivity of the polymer exhibits a truly metallic temperature dependence down to ultralow (liquid-helium) temperatures.

(5) In a polymer sample that is in the HCS, charge instability can be realized, which leads to the reverse transition into the insulating state.

(6) As a result of the phase transition into a metal-like state, the polymer sample is divided into highly conducting domains separated by an insulating matrix. The conductivity within one domain reaches extremely high (for organic systems) values, e.g., $\sim 10^{12}$ $(\Omega\ \mathrm{cm})^{-1}$ according to some estimates [65], which exceeds the conductivity of copper by seven orders of magnitude.

We consider the main features of the phenomenon in the example of the effect of uniaxial pressure on the conductivity of polymers.

Figure 10 displays the dependences of the electric current passing through a polymer film 0.3 μm thick on the magnitude of the uniaxial pressure applied to the film at various fixed voltages. The conductivity of the polymer in the initial state is $\sim 10^{-12}$ $(\Omega\ \mathrm{cm})^{-1}$ and is independent of the pressure up to certain values. In a narrow range of pressures near the critical value P_c (in this case, $P_c = 0.4$ MPa), the conductivity of the sample begins increasing with increasing the pressure. After the value P_c is reached, the conductivity sharply (in Fig. 10, almost vertically) increases by several orders of magnitude. As the pressure increases further, the conductivity saturates at the level $\sim 10^{-3}$ $(\Omega\ \mathrm{cm})^{-1}$. Measurements of the temperature dependence (in the range 1 – 350 K) of thin polymer films at pressures $P > P_c$ showed that this dependence had a metal-like character: the resistance of the sample decreased with decreasing the temperature.

It was established in [74] that an increase in pressure in the near-threshold region at a fixed bias across the polymer sample changes the character of charge-carrier injection into the film. It was also revealed that the concentration of electrons and their mobility are significantly enhanced in the polymer compared with the same parameters for holes, which changes the type of the majority charge carriers after the transition into the HCS.

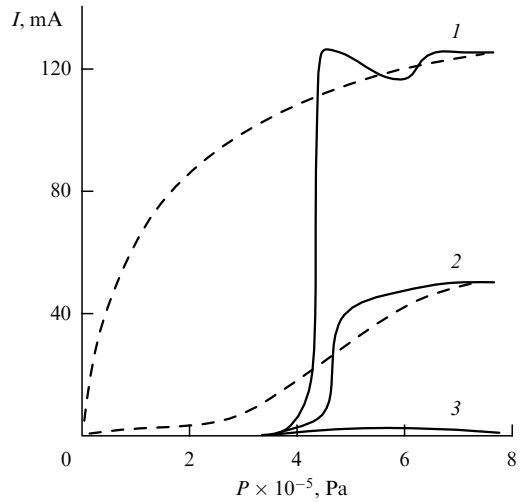

Figure 10. Variation of the current passing through a sample as a function of the uniaxial pressure acting on a film.

5. Electron switching induced by changes in boundary conditions

In this section, we consider details of a unique (in its importance for both the fundamental science and the applied field) phenomenon: the electron switching induced by changes in boundary conditions at the metal – polymer interface.

The essence of the phenomenon is rather simple. If in a steady-state contact, e.g., such as shown in Fig. 3, we begin somehow to change the position of the Fermi level of the metal, then the properties of such a contact also change. The origin of this effect is in the well-known effect of charge transfer from one contacting material to the other until their Fermi levels become equal. This process occurs sufficiently rapidly and, as a rule, is ignored in discussing the stationary properties of contacts. But this in not the case when we consider the contact of a metal with a polymer film whose thickness is comparable to the penetration depth for the charge transferred into the polymer. Because of the anomalously strong interaction of the nonequilibrium charge with the organic surroundings compared with the interaction of such a charge with classical inorganic semiconducting materials, e.g., silicon or germanium, we can expect significant changes in the electronic properties of polymers in this case.

In principle, there have been some previous attempts to predict such effects theoretically and reveal them experimentally, but these attempts were unsuccessful for various reasons. First of all, a polymer with a large energy gap width was required to produce a large density of stable electron states in the middle of the gap. Most researchers tried to reveal this effect in narrow-gap conjugated polymer materials such as polyacetylene, in which strong exchange effects exist, leading to a smearing of the conducting levels, or, as they are usually carefully called, percolation levels, over a certain energy range. Correspondingly, the depth of charge penetration into the polymer was a few nanometers in such materials, and hence such a surface layer could not exert a significant effect on the conductivity of the entire material. On the contrary, in polyarylenephthalides (in which the first ionization potential is about 6 eV, the energy gap width is about 4.2 eV, and the electron affinity energy is about 2 eV), the depth of penetration of the surface charge is ~ 1 μm [75]. This explains why changes in the conductivity of an MPM system caused by changes in the position of the Fermi level of one of the metals in the system could be revealed when the thickness of the polymer film was less than 1 μm. However, a rather nontrivial question that remains open here is how can we change the Fermi-level position in such cases. The simplest way is to effect a phase or structural transition in the metal. The authors of [76] obtained an analytic expression describing the Fermi level behavior near the critical temperature T_c of a phase transition.

Figure 11 illustrates how a phase transition in a metal can be detected from measurements of the electric current passing through an experimental multilayer MPM structure. The vertical segments of the experimental curves precisely correspond to the melting temperatures of the metals and alloys chosen. We see how large the changes are in the parameter to be measured (here, the current passing through

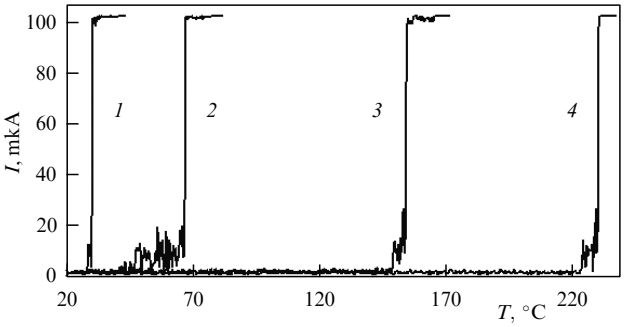

Figure 11. Temperature dependence of the current passing through a sample with different metals used as the M_2: (*1*) gallium; (*2*) Wood's alloy; (*3*) indium; and (*4*) tin. Film thickness, 1 μm; source voltage, 5 V; heating rate, 5 K min^{-1}.

the multilayer). Precise measurements show that the relative variation of the current can reach $10^8 - 10^{12}$. At temperatures below the phase transition, current fluctuations are seen, which increase with increasing the temperature; these are the so-called pretransition fluctuations, which are explained in some works by the gradual layer-by-layer melting (of monatomic surface layers) preceding the phase transition. These are delicate phenomena that can be studied only using complex and expensive methods.

Based on this phenomenon, a new method of nondestructive control of the state of metallic structures is under development at the Institute of Physics of Molecules and Crystals, Ufa Research Center, Russian Academy of Sciences. This method is based on an anomalously high sensitivity of the conductivity of thin polymer films to the energy state of the metal with which the film is in contact. This method allows detecting both a relatively 'simple' melting – solidification phase transition and more complex transformations, e.g., the restoration of a coarse-grain structure occurring at temperatures of the 'structure recovery' [77] in nanostructured metallic samples obtained by severe plastic deformation. A high sensitivity of the method to metallic samples subjected to a relatively small pressure [78] and a sensitivity to stresses accumulated in metallic samples were revealed; with respect to the control parameter, the method proved to be more sensitive than the well-known X-ray diffraction method by almost an order of magnitude. The applicability of the method to studying electronic phase transition was tested on the example of magnetic transitions in metals and one more striking fact was established: this method was sensitive not only to phase transitions but even to simple changes in the orientation of the magnetic moment in magnetic materials.

It seems that the effect of electron switching, selected from the large spectrum of new electronic phenomena in nonconjugated polymers, is quite promising from the standpoint of practical application. In the nearest future, the rapid development of nanotechnologies of thin-polymeric-film ultrasensitive sensors capable of obtaining information from any regions of structures that are difficult to access and which are used under complex and hazardous conditions (pipelines, buildings and various other structures, bridges and crossings, aircraft, etc.) is foreseen. Such sensors can function without additional sources of electrical energy in the regime of both continuous investigation and in a stand-by mode, when the actuation occurs after a certain level of hazard is reached. The possible variants of applications of electroactive polymers with a nonconjugated π-electron structure are by no means exhausted, since only the first results of investigations of their nature have been obtained so far.

6. Electron switching with a magnetic field

One of the manifestations of electron switching induced by changes in the boundary conditions at the metal – polymer interface is the reaction of a system to a change in the magnetic state of the substrate.

A magnetic phase transition in the substrate was fixed in the ferromagnet – polymer – nonmagnetic-metal system in [79], where metallic chromium served as the substrate. A sharp change in the conductivity of the working cell at the Curie temperature T_C was also noted for the $CdCo_2$ substrate [80].

In the temperature dependences of the current passing through the experimental cell, the antiferromagnet – paramagnet transition manifests itself in the appearance of regions of anomalous variations of the current. Typical dependences of the current upon heating are shown in Fig. 12 (curves *1* and *2*). In these experiments, two types of chromium samples were used: a high-purity polycrystal (Cr^1) and a single crystal (Cr^2).

At the temperature 280 K, the current passing through the cell is taken as the device zero. The cell is in a low-conducting state. Its current – voltage characteristic, which has an exponential form, can be explained in terms of the model of the Poole – Frenkel effect typical of transfer in insulators.

In the temperature range 310 – 315 K, current fluctuations arise. A further increase in temperature is accompanied by an increasing amplitude of fluctuations. After the temperature reaches 320 K, a sharp increase in the current occurs; the cell passes into a HCS. Analogous results were obtained in [80].

Because the system considered is a sensitive indicator of the magnetic state of the substrate, a natural question arises: what is its reaction to a partial spin ordering of conduction electrons that penetrate into the polymer from the ferromagnet? The point is that the Fermi levels for the conduction electrons in opposite spin states are somewhat different.

The most noticeable manifestation of spin-dependent properties of a material is its magnetoresistance.

Investigations of ferromagnetic-metal – semiconductor – ferromagnetic-metal systems [81, 82] show that changes in magnetoresistance depending on the mutual orientation of

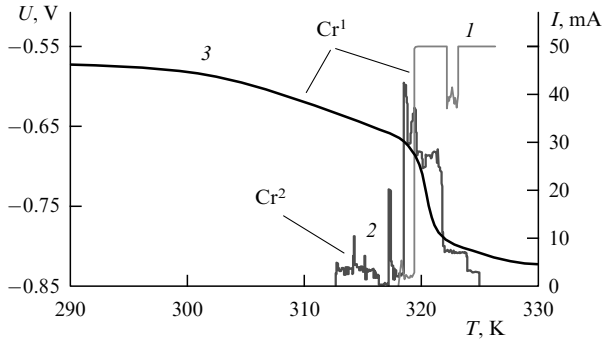

Figure 12. (*1*, *2*) Characteristic temperature dependences of the current passing through a sample upon heating for Cr^1 and Cr^2 samples, respectively; and (*3*) temperature dependence of the electrochemical potential $U(T)$ for the Cr^1 sample.

spins in the ferromagnetic electrodes are possible in these media. A change in the spin orientation in one of the electrodes (with a smaller coercive force) can be achieved by applying an external magnetic field. The degree of spin polarization of the current in [81] was estimated to be less than 0.1%.

Spin injection at the interface between ferromagnetic and nonferromagnetic materials implies the existence of a tunneling barrier at the surface of the contact, i.e., of a surface resistance [83, 84]. If the surface resistance is absent, the spin injection is small. Therefore, of special interest are systems that have a thin tunneling interlayer between two ferromagnetic conductors, which have been called spin valves. The resistance of such a system is minimum at the parallel orientation and maximum at the antiparallel orientation of spins of the ferromagnetic electrodes.

In 2000, P Le Clair et al. [85] revealed that the tunneling magnetoresistance in an Al_2O_3 film placed between two ferromagnets is proportional to the product of the densities of spin-polarized states of the ferromagnetic electrodes. They also noted that the change in the chemical potential in a magnetic field can serve as an indicator of the magnetic state of substances [86, 87].

The ferromagnet – semiconductor – ferromagnet system was suggested for producing spin-polarized transistors [88, 89].

However, in all the systems that have been investigated until recently, the spin-dependent magnetoresistance either was revealed at too low temperatures [12, 90, 91] or was insufficiently large [92, 93].

The authors of theoretical work [94] concerning spin – charge manipulation suggest the use of a rather complex experimental facility, which is difficult for practical realization.

The calculated, sufficiently interesting (from the physical standpoint) cases of magnetoresistance for a system of ferromagnetic heterocontacts [95] could not be checked immediately at the place where the calculations were performed because of technological difficulties. This is especially true for Russia, but even some foreign authors (see [96]) cannot claim the immediate experimental verification of their suggestions.

To construct a device based on the phenomenon of spin polarization, simple structures should be prepared that simultaneously have large magnetoresistance, ferromagnetism, and high conductivity at room temperature, and which allow directionally changing these properties.

The main material used for solving these problems is a tunneling interlayer between ferromagnetic contacts.

In 2002, the authors of [82] showed for the first time that the spin orientation of electrons injected into the organic semiconductor sexithienyl (T_6) can be retained at room temperature at least in the case where the thickness of the separating interlayer between the ferromagnetic electrodes does not exceed 200 nm. This is much greater than the thickness characteristic of the tunneling penetration of electrons equal to 1 – 2 nm. Such an increase in the electron free path related to spin orientation in an organic material is assumed to be caused, at least partly, by the suppression of hyperfine interaction by delocalized π orbitals of sexithienyl.

Thus, the use of an organic transport layer as a separating interlayer instead of a usual insulator is very promising. Of great interest are polymer materials. The possibility of trapping electron states in a polymer layer was suggested for use in current enhancement [96] and creating memory elements [97].

The problem of the existence of high conductivity in low-dimensional systems was also discussed in [98]; the coexistence of high conductivity and ferromagnetism was considered in [99, 100].

In 2004, an experimental work by American researchers Z H Xiong et al. [12] was published in *Nature*, which was devoted to the investigation of a ferromagnet – π-conjugated polymer – ferromagnet system. The authors revealed a difference in the resistance of the working cells with parallel and antiparallel orientations of the magnetizations of the ferromagnetic electrodes and constructed a classical spin valve based on this effect. However, the thickness of the polymeric spacer in such a valve by two orders of magnitude exceeds the thickness of insulating interlayers transparent to tunneling penetration of electrons that are practically applied in spintronics! The measurements were conducted at the temperature 11 K, and the change in the resistance reached 40% at the thickness of the polymer spacer $d = 120$ nm and 10% at $d = 160$ nm.

The ferromagnet – polymer – nonmagnetic-metal system studied in [72] demonstrates a sharp reversible change in the conductivity, but this change occurs not because of a phase transition in the substrate but because of a change in the magnitude of the magnetic field. This effect can be related to a change in the energy level of electron states in a ferromagnet placed in an external magnetic field relative to the position of the Fermi level in the nonmagnetic polymer (Fig. 13).

In the low-conductivity state, any polymer is an insulator involving a completely filled valence band, a wide forbidden band, and an empty conduction band. Under the effect of a small external pressure, a narrow conduction band (of about 0.02 eV, see Fig. 10) appears in the middle of the forbidden band of the polymer [101].

As the external magnetic field varies, the position of the Fermi level of the ferromagnetic substrate is shifted relative to

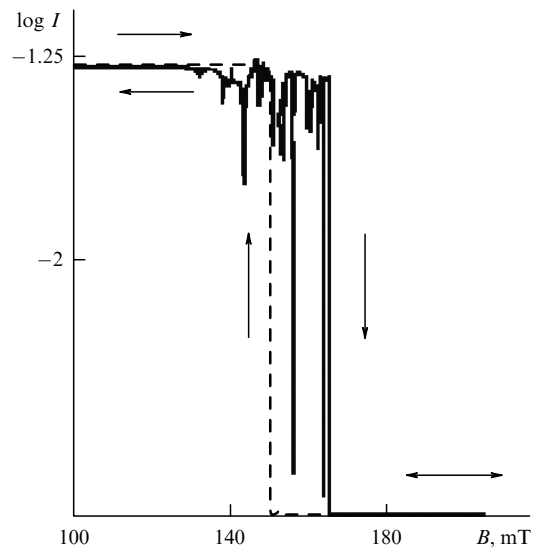

Figure 13. Variation in the current (measured in mA) passing through an Ni – polymer – Cu structure as a function of the magnitude of the magnetic field. Arrows indicate the directions of changes in the magnetic field. The solid line corresponds to an increase in the magnetic field; the dashed line, to its decrease. A voltage of 1 V is applied across the structure. A change in the conductivity by a factor of 10^4 occurs jump-like.

the gap in the allowed states and a sharp transition into a highly conducting state occurs. In fact, we are dealing here with a magnetic-field-controlled charge injection into the polymer transport layer, and the role of spin-dependent phenomena in this case is not yet clear.

7. Charge transfer in films of wide-band polymers at ultralow temperatures

Extremely important information on the mechanism of charge transfer in thin films of nonconjugated polymers has been obtained by studying charge transport at ultralow temperatures using superconducting metals as the electrodes. The possibility of a superconducting current flowing through a nonconjugated-polymer film was clearly demonstrated in [67].

It was established in [101] that a thin film of polyphthalidyliden biphenylene (PDP) of thickness $d \sim 1$ μm becomes switched into a HCS in the electric field of a relatively low strength, $E \sim 10^2$ V cm^{-1} (which is lower than the breakdown voltage by two orders of magnitude) if a moderate pressure ($P < 10^5$ Pa) is applied to the metallic contacts, which is necessary to ensure a reliable mechanical contact between the metal and the polymer. It was also shown that if the metallic electrodes were in a superconducting (S) state, then the resistance of such a sandwich-like structure did not exceed 10^{-3} Ω, which was the resolution limit for the device that was used.

As the polymer sample, PDP films 1 μm thick were employed, which were prepared by three methods:

(i) a PDP film was applied from a 5–7% solution of cyclohexanone directly onto a polished surface of one of the electrodes by the solution-cast method;

(ii) a film was applied using the centrifugation method onto the surface of one of the electrodes; and

(iii) a preliminarily obtained free film of PDP was pressed between two polished surfaces of the electrodes.

In the last case, a method that is traditional for electron microscopy was employed. After centrifugation of the polymer dissolved in cyclohexanone, its transfer onto an object plate, and subsequent short-time drying at room temperature, the object plate with the film was placed in water, where the film was separated from the glass under the effect of capillary forces. The film floating on the surface of the water can then be transferred either onto an object frame or the metallic electrode.

Tin and niobium with a purity not less than 99.99% were used as electrodes. The electrodes of tin and niobium had the shape of disks 2 mm thick with diameters 3.0 and 5.0 mm, respectively. The metallic electrodes were mounted in rings of an insulating material forming a single surface with them. This surface (a metallic electrode in an insulating frame) represented the contact surface. The polymer film was applied onto one of the contacting surfaces. The second electrode, which had no polymer coating, was pressed to a polymer film under a certain force necessary to ensure a reliable electric contact. The state of the electrode surfaces was controlled using an interference microscope and, in some places, using atomic-force microscopy. The roughness of the surface was not more than 0.1 μm.

The conducting state was registered without using an external source, by the emf method described in [102]. In this case, the magnitude of the noise voltage applied to the sandwich structure at which the conducting state was registered did not exceed 0.5 V cm^{-1}, which is by almost seven orders of magnitude lower than the breakdown voltage of insulating films. The low-temperature resistance measurements and the investigation of the effect of a weak magnetic field on the conductivity were performed using a two-probe method in a liquid-helium cryostat without special shielding of the external magnetic field.

The weak magnetic field was created by a superconducting solenoid and controlled using an InSb Hall probe.

Figure 14 shows the temperature dependence [67] of the resistance of an Sn – PDP – Sn sandwich structure. At $T < T_c$, where $T_c = 3.7$ K is the temperature of the superconducting transition of tin, the contact resistance of the PDP – Sn structure vanishes. As can be seen from the figure, the resistance decrease is by no means sharp, which is characteristic of thin conducting channels and point superconducting contacts (such a structure can be represented as S$_\circ$S, where the symbol $_\circ$ stands for the point contact). At $T < 3.6$ K, no resistance is registered, which agrees with the result in [102]. Analogous behavior of the $R(T)$ dependence in structures with superconducting electrodes was revealed for films of polyimide [103] and polymethylsiloxane [104].

We consider the behavior of current – voltage characteristics (CVCs) of such structures. Figure 15 displays a CVC at $T = 3.45$ K. It can be seen that the CVCs of a sandwich structure have a Josephson-like form; no voltage decrease is observed up to a certain critical current $I_c = 1.25$ mA, but then it proceeds jump-like at $U = U_c$. For $U > U_c$, the CVC is still far from being ohmic, which is characteristic of the resistive state, when superconducting electrons are present along with normal ones. The magnitude of the excess superconducting current can be estimated by extrapolating the CVC to $U = 0$ (see Fig. 15). The anhysteretic behavior of the CVC at $T < T_c$ is characteristic of cases where the elements of the weak contacts between the superconductors are either a point contact or a normal metal with induced superconductivity (N_s) caused by the proximity effect [105, 106]. To identify weak coupling, the temperature dependence of the critical current was investigated. It is known that if the experimentally obtained $I_c(T)$ dependence is analyzed using the formula

$$I_c(T) = \text{const}\left(1 - \frac{T}{T_c}\right)^n, \tag{4}$$

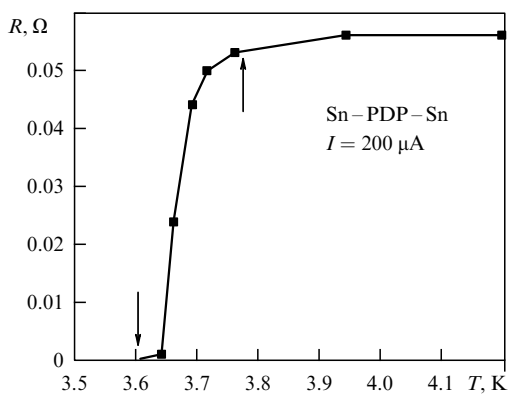

Figure 14. Temperature dependence of the resistance of an Sn – PDP – Sn sandwich structure. Arrows indicate the regions of the superconducting transition.

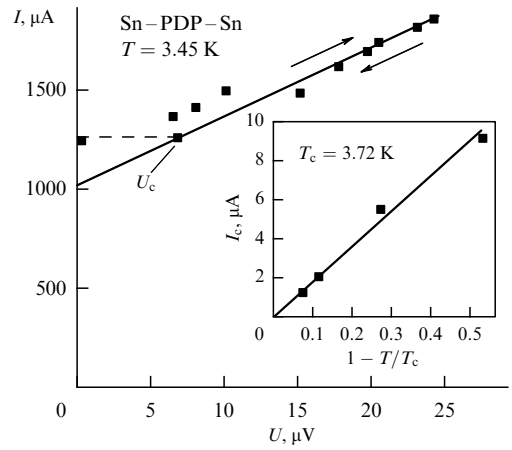

Figure 15. Current – voltage characteristic of an Sn – PDP – Sn structure, which is typical of such structures (its shape is virtually independent of the method of preparation of the PDP film). The dashed line shows the magnitude of the excess superconducting current. The inset displays the experimental dependence of I_c on $(1 - T/T_c)$ for the Sn – PDP – Sn structure.

then the value of the exponent n can indicate the type of weak coupling. Thus, $n = 2$ for the SN_sS junction [107], whereas $n = 1$ in the case of a point contact between two superconductors [106].

The inset in Fig. 15 shows the experimental dependence of $I_c(T)$ on $1 - T/T_c$ for an Sn – PDP – Sn structure. It is seen that in our case, $n = 1$ with a good accuracy for the parameter $T_c = 3.72$ K, which corresponds to the T_c temperature of pure tin. It therefore follows from the analysis of the CVCs of sandwich structures that the weak coupling between the superconductors is realized via a point contact, because the conducting channels in the polymer are very thin and can be represented in the transverse section as points. Precisely the same result was obtained in studying the CVCs of sandwich structures with polydimethylsiloxane [103]. This means that in the superconductor – polymer – superconductor structure, which can be represented as $S_{\circ}P^{S}{}_{\circ}S$, the charge carriers pass through the polymer along thin conducting filaments without energy dissipation. This is possible in two cases:

(a) for ballistic transport, when the free path of a charge carrier between two inelastic collisions in the polymer is $l \gg d$ [67, 102 – 106, 108 – 110]; and

(b) when the channel in the polymer is superconducting, such that $I_c^P > I_c^{Sn_{\circ}P}$ (here, I_c^P is the critical current of the superconducting polymer channel and $I_c^{Sn_{\circ}P}$ is the critical current of a point contact between a massive superconductor and the polymer).

The evidence for the existence of a current of Cooper pairs and of multichannel conductivity in a polymer can be obtained by studying the Josephson effect in Sn – PDP – Sn and Nb – PDP – Nb structures. Figure 16 shows Josephson oscillations of voltage at $I > I_c$ depending on a weak magnetic field ($H \ll H_c$, where H_c is the critical magnetic field for a bulk superconductor) with $H \perp I$. As can be seen from Fig. 16, the Josephson oscillations of voltage caused by the magnetic field have a complex form compared to the Fraunhofer diffraction pattern of an isolated Josephson junction. We note that the resistive state does not destroy the coherence of the wave functions of superconducting electrons at Josephson junctions located on a superconducting circuit; therefore, when the external magnetic field varies, the voltage at the circuit oscillates with the same period but in antiphase with the oscillations of the latter [111].

The observed pattern of oscillations $U(H)$ is characteristic of n parallel Josephson junctions located at a SQUID circuit (superconducting quantum Josephson interferometer), with the essential difference that no definite period of the $U(H)$ dependence exists in our case.

A similar pattern of oscillations is observed at the core boundaries of a high-temperature superconductor, where it is caused by a large number of parallel Josephson junctions [112]. It follows from a comparison of Figs 16a and 16b that an increase in the I/I_c ratio leads to an increase in the amplitude of oscillations $U(H)$. As is known, for two Josephson junctions switched in parallel, the period of oscillations is $\Delta H = \Phi_0/S$, where $\Phi_0 = 2.07 \times 10^{-15}$ T m^2 is the magnetic-flux quantum and S is the area of the region between the two Josephson junctions penetrated by the magnetic flux. With the polymer film thickness about 1 μm, we can estimate the distance L between the junctions. Thus, for the Sn – PDP – Sn structure in the case shown in Fig. 16b, with the ratio $I/I_c = 1.3$, we have $L \sim 5$ μm. In addition, the amplitude of oscillations depends on the type of superconductor that contacts the PDP. For example, the scale of the amplitude of oscillations $U(H)$ for the Nb – PDP – Nb structure is smaller than that for the Sn – PDP – Sn structure.

We also note that when one of the electrodes of a sandwich structure is in the normal state, then no Josephson oscillations $U(H)$ are observed. Such a behavior does not exclude dissipationless transport of charge carriers in the polymer, but seems to exclude the appearance of the superconducting state in the polymer caused by Cooper pairing of electrons in accordance with the classic Bardeen – Cooper – Schrieffer (BCS) theory. This conclusion differs from that obtained when studying organic molecular semiconductors such as pentacene [113], in which the superconducting state appears to be caused by the phonon mechanism of pairing, which is described by the BCS theory.

8. The most promising avenues of further research

(1) One of the main problems that substantially impedes the progress in investigations of polymer conductivity is the lack of a proper physical model. In [101], based on a generalization of experimental results and some estimates, we suggested a working hypothesis concerning the formation of a narrow conduction band in the middle of the forbidden band of a thin polymer film. This idea is by no means new; it was suggested as long ago as 1967 [114] for explaining the effect of electron switching in thin insulating films. Nevertheless, it has not yet received substantial development and confirmation. At the same time, it allows explaining and unifying many experimental facts. In particular, it clarifies why electron switching can be induced not only by an electric field but also by pressure, a magnetic field, changed boundary conditions at the metal – polymer junction, etc. This approach can be formulated as follows: the existence in the polymer of a narrow partly filled band located near the injecting level (the Fermi level of a metal) can affect the charge transfer in the MPM system because of the exponential dependence of the injection current on the difference in the energies of these levels. The relative position of the Fermi level of a metal can be controlled by an external field or some other external

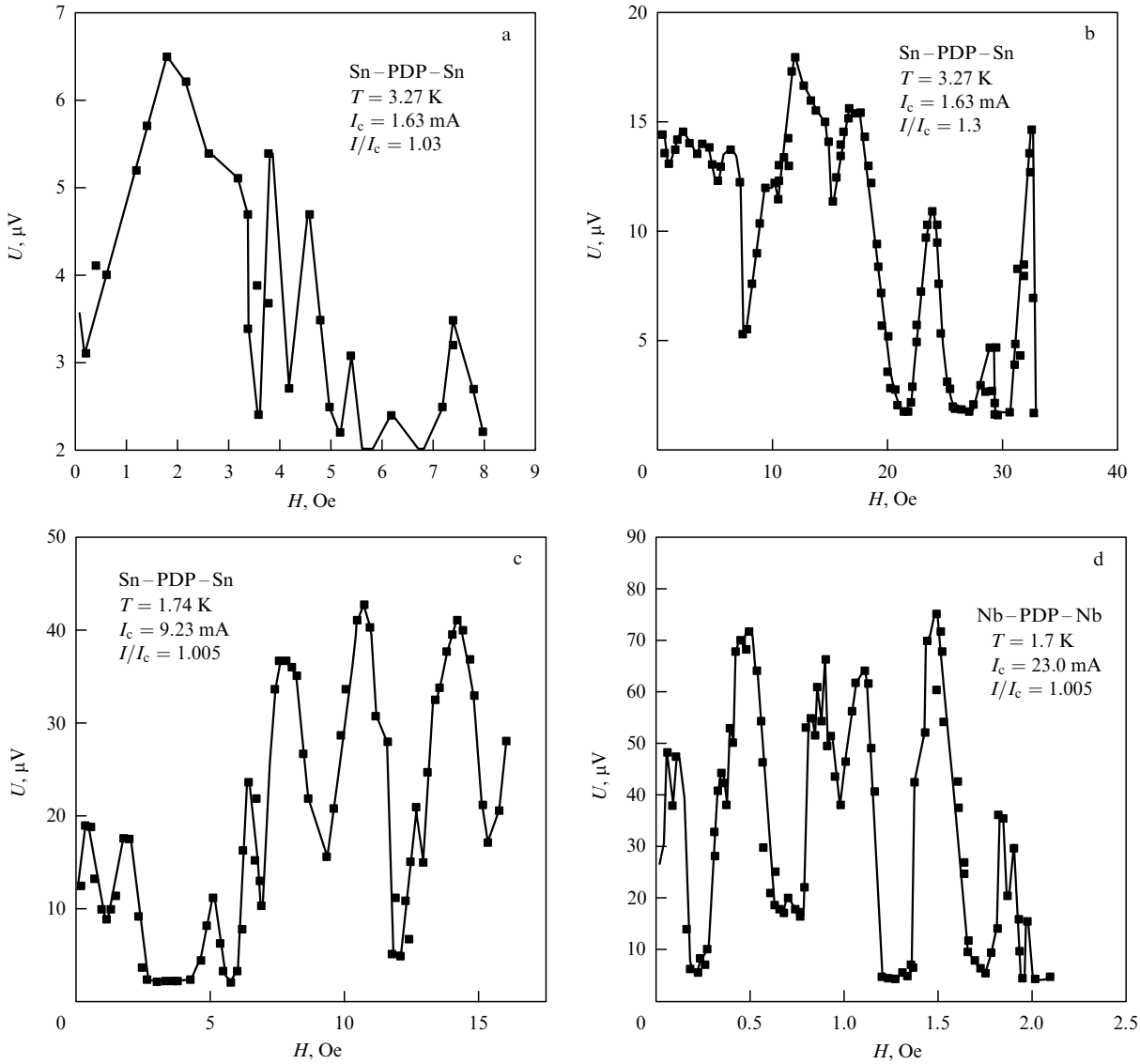

Figure 16. Voltage oscillations in a weak transverse magnetic field in Sn – PDP – Sn structures. The oscillations are due to a network of *n* parallel pairs of Josephson junctions connected in series successively switching-on.

action, thereby permitting the control of charge transfer in this system. Because the external action affects the filling of the narrow band, one more possibility of controlling charge transfer can be used, taking into account that the filling of the band, just like its emptying, leads to the appearance of an insulating state.

(2) Many electronic phenomena considered in this review occur in a limited region of the polymer sample. This, in turn, restricts the region of charge transport to sizes that are comparable to the electron free path in a given material (which is a parameter of charge carriers). Therefore, wave properties of electrons can manifest themselves in the case of such a mechanism of transport.

(3) The small (nanoscopic) size of the charge-transfer regions allows speaking of a certain class of nanoelectronic (in the direct meaning of this word) changes in the electronic properties arising when at least one of the material dimensions decreases to nanoscopic size. It is therefore evident that these phenomena are quite promising for use in nanoelectronics, i.e., for the development of diode and transistor structures based on new principles, which can be controlled using additional actions.

(4) Of great interest is the region of contact of the electroconducting channel with a metallic or semiconducting surface. In the late 1970s, it was suggested to use the properties of contacts of a semiconductor with a metal for the spectroscopy of phonons in the method of microcontact spectroscopy [115]. Recently, in studying the $Si-SiO_2-$ electroactive-polymer junction, dimensional quantization effects were revealed [116], which can be used for the development of hidden information-recording systems, for example. These experiments were performed at room temperature under laboratory conditions. The mechanism underlying this phenomenon has not been completely understood, and the charge localization region in the complex multilayer structure and the laws of transition from the quantum well to a quasi-zero-dimensional structure have not been reliably established. The mechanism of local redistribution of charges leading to the appearance of quantum dots has not been established either. However, the possibility of repeatedly recording, reading, and rerecording information has been convincingly proved using microprobe methods.

(5) There exists the well-known problem of the modification of the electronic properties of metallic or semiconductor

surfaces by applying a thin insulating layer. When using a wide-band polymer material, this manifests itself, e.g., in a significant (dozens of times) decrease in the effective work function of such a system and in the transformation of the spectrum of emitted electrons [117]. This concerns films of by no means tunneling thickness. The thickness of coatings is several dozen or even hundreds of nanometers in this case. The effect by itself can be very useful, e.g., for creating cold field-emission cathodes for flat displays and buffer layers in polymer electroluminescent light sources. However, such a substantial decrease in the effective work function is by no means evident. In particular, the values of the work function of the materials used in [117] were ~ 4.5 eV for tungsten and 4.2 eV for the polymer, whereas the effective work function values were found to be ~ 0.1 eV and smaller. At present, the most common explanation relies on the semiempirical model suggested in [118] based on the very specific structure of the materials and rigid restrictions, which substantially narrows the applicability range of this model.

(6) The average geometric dimension (thickness of the separating interlayer) in a spin valve in [12] is already as large as 140 nm. This indicates that the use of organic materials for creating spin valves is quite promising. Indeed, the main difficulty in the practical preparation of such structures is the application of a film a few nanometers thick to separate two electrodes, which is a very complex process from the technological standpoint. But if such technological difficulties are acceptable and surmountable in the production of known engineering devices, it is hardly expedient to work out special-purpose technology for research purposes, where it is required to repeatedly change the parameters of the system under consideration.

The possibility is being discussed (see, e.g., [119]) of the development of spin filters based on granular structures exhibiting injection magnetoresistance. However, structures of a ferromagnet – granular-film – semiconductor – granular-film – ferromagnet type are much more complex than a ferromagnet – polymer – ferromagnet structure.

It is obvious that we have mentioned only a minor part of the problems that require solution at present. Nevertheless, even what was said is sufficient to see that in the field of organic electronics, in the broad meaning of this term, the number of problems to be solved is now much greater than those that have already been solved. However, in connection with the global expectation of a technological breakthrough in the field of application of organic materials in micro- and nanoelectronics, these problems become extremely topical, and it seems expedient to invest significant effort into their solution.

9. Conclusion

The application of organic materials as elements of electronic devices has long been known; it suffices to recall the early 1950s, when interest arose in searching efficient materials for large-capacity capacitors. The development of copying devices in the 1970s led to the wide use of polymer materials in the key units of these machines. But it is only in recent years that a true scientific and engineering boom has arisen in connection with the possibility of applying organic materials in electronics as a realistic alternative to the application of traditional semiconductors. Polymers are a very good material in this sense, because the electron – phonon interactions in them are very strong and the efficiency of exciton-related processes is very high. In addition, owing to the achievements of chemists dealing with material synthesis, a unique opportunity of obtaining various materials with predicted electronic properties has appeared.

The unusual electrophysical properties of thin polymer films made of materials with a wide band gap are, in our opinion, quite expected from the standpoint of fundamental concepts of charge injection into an organic medium, charge transport, and relaxation. The low thresholds of conductivity switching via various physical fields and the reversibility of these effects open wide prospects for the application of such materials in modern technologies and devices.

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