Electroluminescence in thin polymer films with a nondegenerate ground state

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The results of investigations of electroluminescence in thin films of an electroactive polymer of the polyphtalidylidenearylene class are presented. The investigations were carried out on an experimental structure of the three-layer "sandwich" type: InO_2–polymer–metallic electrode (Cu,Cr). It is established that the changes in the electroluminescence induced by electric field correlate with the dynamics of high-conductivity channel formation in the polymer film. The analysis of the spectral composition of radiation showed that polaron states participate in the recombination.

1. INTRODUCTION

Electroluminescence recently discovered in a new class of polymers, polyphtalidylidenearylenes (PPA),[1] can be used to provide information on the dynamics of electronic states in electric fields in polymers with a nondegenerate ground state. A high sensitivity of the new method is particularly important, when we are dealing with a small amount of the substance studied or with samples with multiphase structure and with a large difference in the concentration of different phases. In particular, the latter is realized in thin PPA films, when a new phase with anomalously large conductivity arises in the polymer sample.[2] According to the results reported in Ref. 3, the new conducting phase accounts for 10^{-5}–10^{-6} of the dielectric phase. Therefore traditional electric methods provide only integrated characteristics. The resonance methods have not yet yielded satisfactory results either. Yet, the problem of the high-conductivity state (HCS) in unconjugated polymers of the PPA class is extremely important.

Recently, high conductivity of several polymers has been reported. In particular, apart from the PPA, the HCS was observed in isotactic and atactic polypropylene.[4,5] As a rule, this state arose when the polymer film was subjected to electric field. However, it was shown later that a similar state could be created by uniaxial pressure[6] or by nonstationary heating.[7] In each case the low values of external factors attract attention. Thus the relevant value of the electric field is $\sim 10^2$–10^3 V/cm, of pressure $\sim 10^5$ Pa, and of temperature 240 K or even 160 K. The corresponding changes in conductivity amount to 10^{14}. These changes occur in some parts of the sample rather than in its whole volume. These regions, by analogy with the ones arising in the "switching" effect in amorphous semiconductors and glasses,[8] were called longitudinal domains.[3] According to various estimates,[3,9] the width of these domains ranges from 10 to 500 nm, while their length is equal to the sample width. According to Ref. 10, the conductivity of these domains exhibits metallic character down to helium temperatures. Evidently, the experiments allowing to investigate the creation of conducting domains could give a clue to the understanding of the origin of anomalously high conductivity in thin polymer films. In this connection, the electroluminescence is the method which makes it possible to combine the integral process of charge transfer through the polymer film and the individual processes of pair recombination of charges having opposite signs. To realize the electroluminescence in thin PPA films, there are necessary prerequisites, such as the injection mechanism of charge generation from electrodes into the polymer, and strong enough photoluminescence, which occurs via polaron states.[11]

In this connection, the aim of the present study is the investigation of electroluminescence generation conditions and the relation of this phenomenon to the dynamics of the high-conductivity state in polymers with a nondegenerate ground state.

2. TEST SAMPLES AND EXPERIMENTAL PROCEDURE

Polyphtalidylidenearylenes are a new class of aromatic, high-molecular, heat-resistant, and film-forming polymers synthesized recently.[12–14]

In the present study of the PPA electroluminescent properties we used poly(3,3'-phtalidylidene-4, 4'-biphenylylene) (PPB). PPB had the molecular weight $(50–80) \cdot 10^3$ depending on the synthesis conditions. The softening point was 440 °C. The polymer is soluble in common organic solvents such as chloroform, dichloromethane, and 1,1,2,2-tetrachloroethane. A good PPB solubility makes it possible to remove impurities and fabricate polymer films to study their various properties.

Using the experience of Ref. 15, we chose the following experimental procedure. As a hole injecting electrode, we used indium oxide, and as an electrode injecting electrons, copper or chromium. An indium oxide layer was deposited on the surface of polished glass by indium oxidation in the oxygen atmosphere. Thus, we obtained a semitransparent
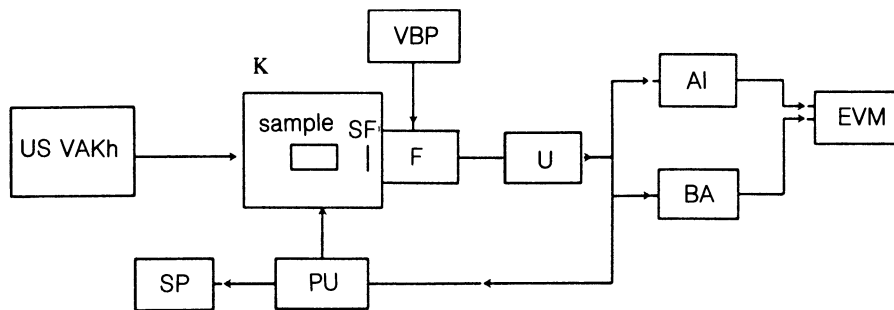
FIG. 1. Diagram of the experimental setup: US VAKh—registration device for CVC, K—light-tight chamber, O—sample, SF—a set of light filters, F—PM, VBP—high-voltage block, U—signal amplifier, AI—pulse analyzer, BA—time analyzer, EVM—computer, PU—preamplifier, SP—X-t recorder. AI and VA form a part of a universal storage UNO-1024.

electrode. The film was grown on the surface of this electrode by centrifuging from a $CHCl_3$ solution. The polymer thickness was 0.8–1 μm. The second electrode was deposited by vacuum thermodiffusion. Before that the polymer film was heated at about 100 °C in a vacuum for one hour to get rid of the remaining solvent and other impurities.

The electroluminescence was detected with the help of a setup shown in the diagram (Fig. 1). The setup made it possible to study independently and simultaneously the kinetic dependence of the electroluminescence intensity with a time constant 1 s, the time structure of the light flux with a high resolution, the density of pulse amplitude distribution for the electroluminescence, and to estimate the spectral composition of the electroluminescence by light filters.

The test sample was placed into a light-tight chamber. The photocathode of the photomultiplier (PM) was on the side of the semitransparent electrode. The electroluminescence detection was carried out by counting photons in the one-electron regime. The PM signal was amplified and then processed independently and simultaneously in three channels. In the first channel the PM pulses were integrated. The result, in the form of a kinetic curve $I_{el} \propto t$ was recorded on tape. The second channel enabled us to estimate the density of EL pulse amplitude distribution by an amplitude analyzer. The third channel made it possible, with the help of a time analyzer, to estimate with a good resolution (the smallest channel width ~10 μs) the time structure of the light flux from the sample by counting

pulses at successive time intervals. The equipment was calibrated by a brightness standard comprising a scintillation solution of diphenyloxazole labeled by ^{14}C atoms. The information obtained with the help of the analyzers was stored in a computer and then processed, as necessary, according to the experimental requirements.

3. EXPERIMENTAL RESULTS

The experimental structure InO_2–polymer film–Cr possessed diode properties. Its typical current–voltage characteristic (CVC) is shown in Fig. 2. The asymmetry of the curves for different polarity of the voltage across the film is quite apparent.

The electroluminescence intensity versus the current flowing through the sample is shown in Fig. 3. The electroluminescence of both polymer samples has a voltage threshold, U_{th}, above which it arises. The magnitude of this threshold is different for different polarity. The functional dependence of the radiation intensity on the current is close to $I_{el} \sim I_{cur}^{1.8}$, where I_{el} is the electroluminescence intensity, and I_{cur} is the current through the sample.

Figure 4 shows the electroluminescence spectrum of the polymers studied. The radiation maximum is in the region of 500 nm and coincides with the long wavelength band of the PPB photoluminescence. As the applied voltage is varied, the maximum is not shifted, only its intensity is changed. Often, near the maximum, extra radiation
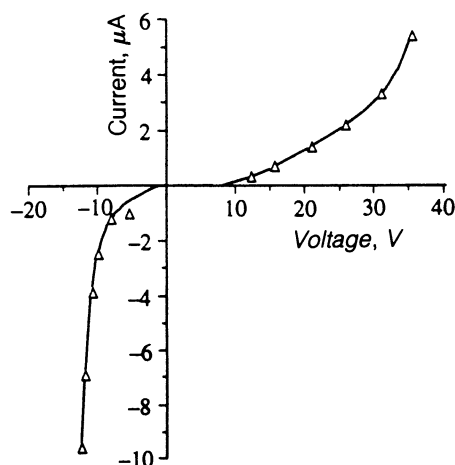

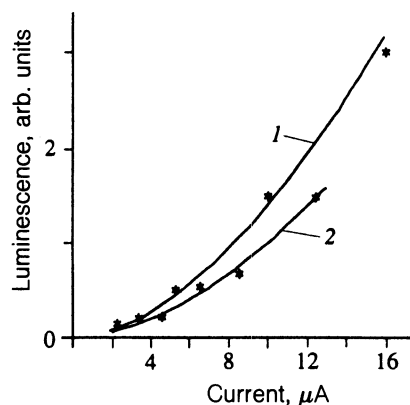FIG. 2. CVC of the polymer film in the InO_2-PPB film–Cr structure.

FIG. 3. Electroluminescence intensity versus current. 1—Electroluminescence measurements before the switching into the HCS; 2—measurements after the cycle of direct and reverse switching of the film conductivity.
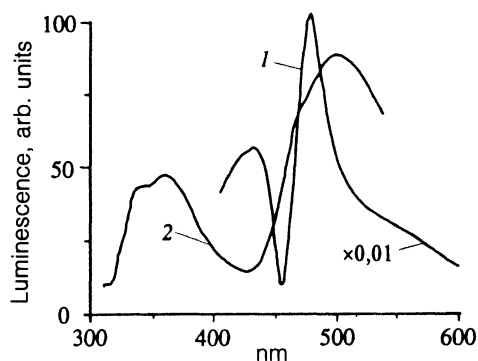
FIG. 4. Electroluminescence spectrum of the polymer film in the InO_2-a PPB film-Cr(1). 2—PPB photoluminescence spectrum.

FIG. 6. Fluorescence and fluorescence excitation spectra of polydiphenylenephtalide. ___—Absorption spectrum, Δ—fluorescence spectrum excited at 280 nm, □—excitation spectrum for the short-wave fluorescence band; *—excitation spectrum for the long-wave fluorescence band.

bands are observed which, as some authors suggest,[15] are the consequence of electron–photon interaction and manifest themselves as a fine structure to the left and right of the main maximum. The same spectral position of the photo- and electroluminescence bands probably implies the same recombination mechanism for the excited states in both cases. From the point of view of possible applications, the quantum efficiency of the electroluminescence is important. In our experiment it is $\sim 10^{-2}\%$.

The radiation has a fluctuating character. A typical time dependence of photon counting ($N \propto t$) is shown in Fig. 5a. Correspondingly, the electroluminescence intensity also has a fluctuating character, which is observed both on the kinetic curve I_{el} registered by a recording potentiometer and on the time analyzer display (Fig. 5a). The mean value of the intensity I_{el} is proportional to the voltage across the electrodes.

The results of the amplitude analysis of the PM output pulses are shown in Fig. 5b. The curve displayed in this figure corresponds to a one-electron peak. For comparison, the amplitude distribution of PM noises is also shown in Fig. 5b (the lower curve). This means that separate photons uncorrelated in time arrive at the PM photocathode, and that the electroluminescence is a random process.

It is worth noting that low-frequency components of period ranging from 0.5 to 5.0 s dominate the kinetic de-
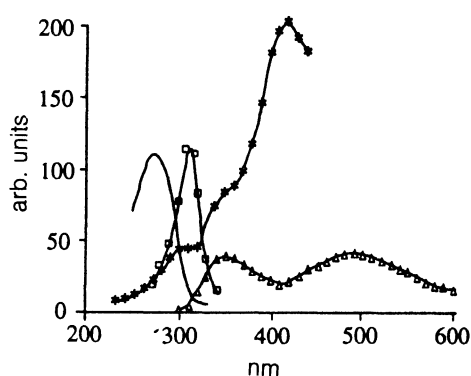
pendence fluctuations. The electroluminescence intensity, in our case, does not exceed $5 \cdot 10^7$ photons/s for $U_{sample} \sim 100$ V.

4. DISCUSSION

The electroluminescence in thin films of poly(3,3'-phtalidylidene-4,4'-biphenylylene) has much in common with the electroluminescence observed earlier in other polymer films. Above all, this includes the threshold dependence of the electroluminescence intensity on the applied field, nonlinear dependence on the current flowing through the sample, radiation in the visible spectral region coinciding with the position of the long-wavelength photoluminescence, and the small value of quantum efficiency ($10^{-(1-2)}\%$).

It was pointed out in Ref. 11 that polaron states are responsible for the generation of the long-wavelength fluorescence band in PPB films. This conclusion was drawn on the basis of the experimental data analysis. Shown in Fig. 6 are the absorption spectra of the polymer film, fluorescence spectrum and fluorescence excitation spectra. The short-wavelength fluorescence (3.65 eV) is due to the recombination of the excited states related to the light absorption in the $\pi - \pi^*$ band of the aromatic part of the

FIG. 5. The results of the time-amplitude analysis of the electroluminescence. a) The photon counting rate versus time. Photons were registered by a time analyzer (UNO-1024) with 1024 channels in the regime of pulse counting at successive time intervals. The channel width was 50 ms and the scale factor along the y axis was $\Delta N = 10^6$ photons s^{-1}/cm. This result was obtained for a constant voltage at the sample electrodes ~ 90 V. b) The density of the electroluminescence pulse amplitude distribution (upper curve). The lower curve represents the amplitude distribution of PM noises.
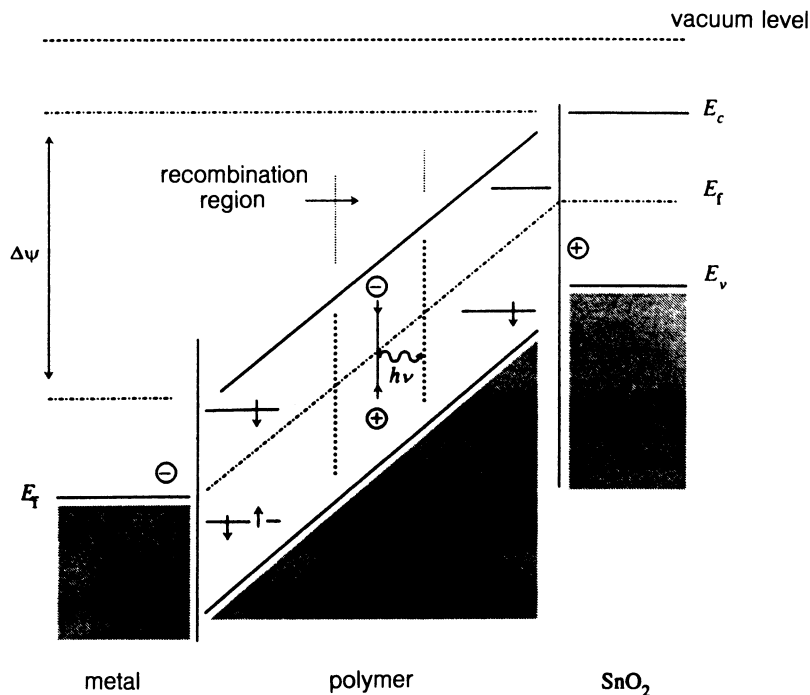
FIG. 7. Energy bands of the metal–polymer–semiconductor (p-type) junction. A voltage $\Delta\psi$ is applied between the metal and semiconductor. Band deformations at the boundaries are not shown for simplicity. E_c, E_v, and E_f are the bottom of the valence band, the top of the conduction band, and the Fermi level respectively. Energy levels are polaron states. On the left, near the metal–polymer junction, electron polaron states are formed (the lower level is completely filled, while the upper one is half filled). The injection of electrons from the metal and of holes from the semiconductor is denoted by ⊖ and ⊕ respectively. The recombination region is shown in the center by dashed vertical lines.

molecule (4.5 eV). The position of the long-wavelength fluorescence band (2.6 eV) and the Stokes shift (0.85 eV) coincide satisfactorily with the estimate on the basis of relations connected with the gap width (E_g) in the electron spectrum and found, using the polaron model of an excited state in a polymer.[16] In this connection, the Stokes shift ΔE_s and radiation energy $\hbar\omega_L$ can be found from the following relations

$$\Delta E_s \sim 0.6\Delta, \tag{1}$$

$$\hbar\omega_L \sim \sqrt{2}\Delta, \tag{2}$$

where $\Delta \sim 0.5E_g$. The following values have been found: $\Delta E_s \sim 1.04$ eV and $\hbar\omega_L \sim 2.42$ eV.

The coincidence of the spectral position of the photo- and electroluminescence bands probably implies the presence of polaron states in the latter case as well. Moreover, such a suggestion can mean that on the dielectric branch of the CVC the charge transfer is realized by polarons. A similar picture was observed in the electroluminescence of poly (p-phynylevynilene).[15]

The polaron states form in the polymer band gap two systems of levels: one near the bottom of the conduction band and the other above the top of the valence band. In this case the energy band structure for the metal–polymer–semiconductor sandwich can be represented in the form shown in Fig. 7.[17] In the holes whose injector in our experimental structure is the InO_2–polymer junction. The metal–polymer junction injects electrons, i.e., minority charge carriers. The electroluminescence mechanism can be imagined in the following way (Fig. 7). For a small potential difference $\Delta\psi$ a monopolar hole injection from the semiconducting electrode is realized. A positive charge in the polymer causes deformation of nearby parts of macromolecules, which localizes it, and a polaron state arises. In Fig. 7 it is schematically shown as a hole capture at a

polaron level. The charge transfer in electric field is carried out by a hopping mechanism which manifests itself in a weak activation temperature dependence of the conductivity.[18]

The potential barrier near the opposite electrode interferes with the injection of minor charge carriers, i.e., electrons. As the potential difference $\Delta\psi$ across the electrodes grows, the potential barrier becomes lower and, for a certain value $\Delta\psi_{th}$, electrons are injected into the polymer and get captured at polaron negative levels, as shown in Fig. 7. The recombination of the hole and electron polarons can give rise to the formation of a singlet exciton whose radiative transition provides the electroluminescence.

The nonlinear dependence of the radiation intensity on the current flowing through the polymer film (Fig. 4) can probably be explained through the injection model of this phenomenon.[19] According to this model, the current–radiation relation has the form

$$B_T = b_1 I + b_3 I^2, \tag{3}$$

where B_T is the electroluminescence brightness, I is the current, and b_1 and b_3 are constants. If $b_1 < b_3$, we get $B_T \sim I^2$. The latter means that the recombination process is dominated by the monomolecular decay, and the injection corresponds to the weak current case. For a strong current, instead of (3), we will have a linear dependence. In principle, the transfer of both positive and negative charges in the sample volume leading to recombination radiation can be regarded as intrachannel. The charges move toward each other along the channel and recombine in a certain region of the volume. Such a mechanism is traditionally meant when we are dealing with the electroluminescence in organic materials.[20] It may possibly be the recombination processes that account for the fluctuation character of the electroluminescence shown in Fig. 5(a) and (b), since the
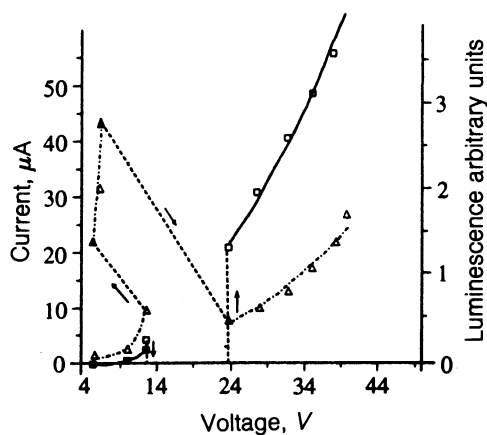
FIG. 8. Electroluminescence intensity versus the voltage across the polymer film and the CVC for the switching in the HCS. The electroluminescence is shown by the solid line and the corresponding CVC by a dashed line. The arrows show the direction in which the electroluminescence intensity and electric current change.

recombination leads to a local deviation from the unperturbed charge distribution in the channel, which is recorded as current fluctuations.[21]

However, the special feature of the polyarylenephtalide thin films is the high-conductivity state induced by various external fields,[2-6] including electric field.

It is believed that the HCS arises in separate parts of the film called conducting domains. It is not clear what the conducting domain is, whether it arises due to the evolution of electronic states of a given local film volume for voltages and currents much lower than critical, or due to thermal processes taking place when the threshold voltage is achieved and exceeded and the sample is "switched." The latter is considered in detail in the literature.[22] There is a lot of evidence that these conducting channels, which result, in one form or another, in carbonization of the organic material or even in electrode melting, have thermal origin.

Evidently, the electronic formation of the HC domains is of the greatest interest. It was reported[23] that HC domains arise in the process of the film formation from the polymer solution, which means that the channels are the result of structural changes going on in the films, when they are formed from the solution. However, the strong effect of uniaxial pressure on the thin film conductivity discovered later meant that the "spontaneous" conductivity could arise due to a low threshold pressure in such films, since in all the experiments, pressure might have been exerted on the sample surface while the upper electrode was being deposited.

For understanding of the relation between the processes causing the electroluminescence and formation of high-conductivity domains, the result shown in Fig. 8 is of great importance. In this figure the CVC of a PPB film is displayed together with the corresponding voltage dependence of the electroluminescence intensity. The CVC reflects the process of switching into the HCS. The film remains in this state until the current flowing through it

reaches 43 μA. Above this value the HCS is "turned off" due to instability similar to that observed and reported earlier.[11] The CVC sections related to "turning on" and "off" of the HCS are not controlled by the voltage and therefore shown in Fig. 8 by dashed lines. Shown in the same figure is the voltage dependence of the electroluminescence intensity corresponding to the CVC. The electroluminescence is observed only in the low-conductivity state. When the sample is switched to the HCS, the electroluminescence disappears. It appears when the voltage across the sample reaches 5–6 V. The current dependence of the electroluminescence is close to exponential. The electroluminescence arises again, when the samples is "turned off." Then the current dependence of the electroluminescence intensity is governed by a power law.

Experimental results pertaining to the electroluminescence in thin polymer films make it possible to analyze the probability of channel (domain "nuclei") formation on the "dielectric " branch of the CVC.

It is evident that the distribution of such channels on the surface and in the bulk of the film is, most likely, chaotic and due to various inhomogeneities on the electrode surfaces or in the bulk of the polymer film. Is there any relation between the "luminescent" channels and high-conductivity domains? As seen from Fig. 8, the electroluminescence dies out if the sample is switched into the HCS. Hence we conclude that the luminescent channels are shunted by the HCS domains and, therefore, the voltage across the sample electrodes is not sufficient for sustaining the regime of double injection necessary for the electroluminescence.

However, it is worth noting that the voltage across the sample in the HCS varies by up to 8 V, while the electroluminescence threshold is lower. Therefore if there were regions luminescent regardless of conductivity channels, they should manifest themselves at these voltages. Thus, we conclude that the electroluminescence is realized in those parts of the polymer film where high-conductivity domains arise under appropriate conditions.

The absence of the electroluminescence in the HCS could be explained by the metallic character of the conductivity, i.e., the charge transfer is realized in the partially filled conduction band. Under these conditions, the recombination processes characteristic of semiconducting states are greatly inhibited. When the sample is "turned off," conditions for radiative recombination of electrons and holes are created in the channel. This is probably what is observed in Fig. 8: when the current is larger than critical, equal to 43 μA in this case, the low-conductivity state is restored abruptly and the electroluminescence arises.

The electroluminescence observation makes it possible to answer the question, how much the electronic structure of conducting channels is changed, when the polymer is switched into the HCS, and, in particular, to elucidate the electronic character of this switching.

Such processes as polymer carbonization and electrode atom diffusion into the film are likely to lead to significant changes in the electroluminescence parameters measured

before and after the switching. Let us analyze two dependences.

1. The radiation intensity versus the current flowing through the sample (Fig. 3).

2. Spectral characteristics (Fig. 4).

As seen from Fig. 3, before and after the switching the current dependence of the electroluminescence intensity has a power character and the exponents differ by 3%, which is smaller than the experimental error. The corresponding values for the onset of the electroluminescence also differ negligibly and are ~ 20 V in both cases (in Figs. 6 and 3 the voltage has opposite polarities, therefore the values of U_{th} are different).

Spectral characteristics are identical before and after the switching. Hence, two conclusions can be drawn: either the electroluminescence is not sensitive to impurities, such as carbonized molecule parts or metallic atoms diffused into the polymer from the electrodes during switching, or the switching and the related HCS are electronic effects that do not result in irreversible changes in the electronic structure.

As a rule, impurities quench the electroluminescence.[19] Therefore it should be expected that after the switching the impurities in the channels would, on the one hand, decrease the electroluminescence intensity and, on the other hand, lead to the red shift of the electroluminescence maximum. However no effects of this kind have been observed. Furthermore, all characteristics of the electroluminescence are satisfactorily reproduced after the switching.

Thus, we can draw the following conclusions. The electroluminescence in thin PPB films due to radiative recombination of electrons and holes injected from the electrodes occurs below the conductivity switching in those regions of the polymer film where the conducting domains arise. The radiation has a fluctuating character and probably corresponds to current fluctuations that increase near the switching threshold.[23] The stability of electroluminescence characteristics before and after the switching confirms the earlier suggestion that this is an electronic effect. The fact that the positions of the photo- and electroluminescence radiation bands coincide implies that in both cases polaron states are involved in the recombination. Consequently, the electroluminescence in samples of the PPA type can be considered as a result of the exciton–polaron state dynamics used as a technique of the investigation of these states. This is all the more important, since so far, as a rule, experimentalists worked with polaron carriers of one sign, while the phenomenon of electroluminescence in polymer samples testifies that in the process of charge transfer both positive and negative polarons are involved.

[1] V. A. Antipin, I. L. Valeeva, and A. N. Lachinov, JETP Lett. **55**, 545 (1992).
[2] A. N. Lachinov, A. Yu. Zherebov, and V. M. Kornilov, Synth. Metals **44**, 111 (1991).
[3] V. M. Kornilov and A. N. Lachinov, Synth. Metals **53**, 71 (1992).
[4] V. M. Arkhangorodskiĭ, E. G. Guk, A. M. Elyashevich et al. Dok. Akad. Nauk SSSR **309**, 603 (1989) [Sov. Phys. Dokl. **34**, 1016 (1989)].
[5] N. S. Enikopyan, L. N. Grigorov, and S. G. Smirnova, JETP Lett. **49**, 371 (1989).
[6] A. N. Lachinov, A. Yu. Zherebov, and V. M. Kornilov, JETP Lett. **52**, 103 (1990).
[7] A. N. Lachinov, A. Yu. Zherebov, and M. G. Zolotukhin, in *Abstracts of the International Conference on Science and Technology of Synthetic Metals* (Goteborg, Sweden, 1992), p. 324.
[8] S. A. Kostylev and V. A. Shkut, in *Electronic Switching in Amorphous Semiconductors* (in Russian) (Naukova Dumka, Kiev, 1978).
[9] V. M. Arkhangorodskii, A. N. Ionov, V. M. Tushkevich, and I. S. Shlimak, JETP Lett. **51**, 67 (1990).
[10] A. N. Ionov, A. N. Lachinov, M. M. Rivkin, and V. N. Tushkevich, Solid State Commun. **8**, 609 (1992).
[11] I. L. Valeeva and A. N. Lachinov, Khim. Fiz. **4**, 51 (1993).
[12] M. G. Zolotukhin and S. N. Salazkin, in *Abstracts of International Conference on Polycondensation and Related Reactions* (Italy, Gargano, 1990), p. 53.
[13] M. G. Zolotukhin, in *Abstracts of the 2nd European Technical Symposium on Polyimides and High-Temperature Polymers* (Montpellier, France, 1991), p. 14.
[14] M. G. Zolotukhin, A. A. Panasenko, V. S. Sultanova et al. Macromol. Chem. **186**, 1747 (1985).
[15] J. N. Burroughes, D. D. C. Bradley, A. R. Brown et al., Nature **347**, 539 (1990).
[16] S. A. Brazovskii and N. N. Kirova, JETP Lett. **33**, 4 (1981).
[17] A. B. Holmes, D. D. C. Bradley, A. R. Brown et al., Synth. Met. **55**, 1 (1993).
[18] A. N. Lachinov, A. Yu. Zherebov, and M. G. Zolotukhin, Synth. Metals **59**, 377 (1993).
[19] K. C. Kao and W. Hwang, *Electrical Transport in Solids* (Pergamon, 1981).
[20] W. Hwang and K. Kao, J. Chem. Phys. **60**, 3845 (1974).
[21] M. J. Buckingham, *Noise in Electronic Devices and Systems* (Ellis Harwood, 1983).
[22] D. Adler, H. K. Henish, and N. F. Mott, Rev. Mod. Phys. **50**, 209 (1978).
[23] A. N. Lachinov, A. Yu. Zherebov, and V. M. Kornilov, Zh. Eksp. Teor. Fiz. **102**, 187 (1992) [Sov. Phys JETP **75**, 99 (1992)].

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