

# Electroluminescence in thin polymer films with an anomalously high conductivity

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An electroluminescence has been observed in thin polymer films. It precedes the switching of the film to a highly conducting state.

It has been reported previously that thin films of certain polymers go into a state with an anomalously high conductivity, either spontaneously or upon the application of an electric field.<sup>1</sup> It was later established that such a state can be reached by applying a uniaxial pressure of anomalously low magnitude (about  $10^5$  Pa) to a polymer.<sup>2</sup> A characteristic feature of these effects is the appearance of conducting domains in the films, with a conductivity that reaches<sup>3</sup>  $\sim 10^{14}$  S/cm.

Most of these studies, however, did not take up the question of the electronic properties of the highly conducting state of the polymer or those of the states which preceded it, apparently because of the small size and relatively low density of the domains in the polymer film. The nonlinear current-voltage characteristic which can be detected in the pretransition region in films of these polymers<sup>4</sup> suggested an injec-

tion mechanism, which might be capable of giving rise to an electroluminescence. We accordingly selected the electroluminescence method for this study, since it is one of the most sensitive and informative methods. The test samples were thin films of the polymer polydiphenylenephthalide.<sup>5</sup> The test cell was a multilayer structure in which the polymer film, synthesized by centrifugation on a transparent conducting substrate of  $\text{InO}_2$  on glass, was bracketed by two electrodes. The second electrode, made of Cr, was deposited on the surface of the polymer film by vacuum diffusion deposition. A third, annular electrode was fabricated around the second electrode and grounded, to prevent surface leakage currents. This particular electrode configuration and these particular electrode materials were chosen in an effort to carry out experiments under conditions close to those under which a highly conducting state had been realized previously.<sup>1,2</sup>

A voltage was applied to the sample from an adjustable dc source. A ballast resistance in series with the sample limited the current through the sample in the case in which the sample switched to the highly conducting state, or breakdown occurred. The voltage drop was measured directly at the sample. The electroluminescence was detected in a light-tight chamber with a photomultiplier as detector.<sup>6</sup> The photomultiplier was positioned on the side of the transparent  $\text{InO}_2$  electrode. The intensity of the electroluminescence of a sample reached  $10^7$  photons/s at  $U = 90$  V. The spectrum of the luminescence was determined with the help of cutoff optical filters.<sup>6</sup>

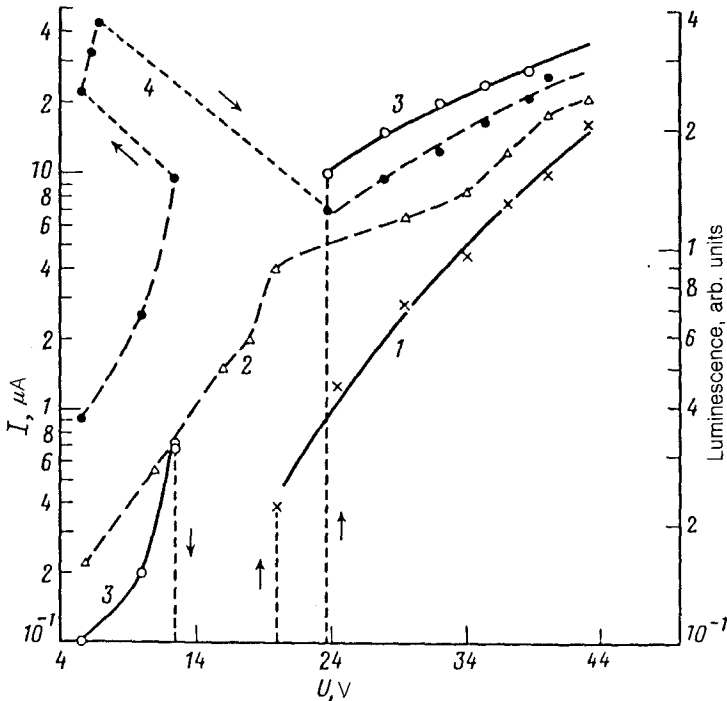


FIG. 1.

Figure 1 shows the intensity of the electroluminescence versus the applied voltage, along with the current-voltage characteristic of the same polydiphenylenephthalide film. The electroluminescence arises when the potential difference across the electrodes reached 6–20 V; the corresponding electric fields are about  $10^5$  V/cm. As the voltage is raised, the electroluminescence intensifies; the dependence is nonlinear and can be approximated by a function  $B_e \propto I^n$ , where  $n \sim 1.5\text{--}4.5$ . The measurement cycle was repeated several times, and the results were found to be satisfactorily reproducible. We should point out that the first appearance of the luminescence requires a potential difference higher than that required for subsequent appearances. It was established in the course of the experiments that reversing the polarity of the voltage applied to the sample has no important effect on the electroluminescence.

How the electroluminescence is related to the electronic switching of the conductivity is important to know. Curves 3 and 4 in Fig. 1 demonstrate this relationship. When a threshold field of 6 V is reached, the electroluminescence arises. Its intensity increases with increasing voltage, as does the current through the sample. When the potential difference across the sample is  $\sim 12.5$  V, however, the polymer film switches to a highly conducting state, as shown by the dashed line in this figure. When this highly conducting state appears, the electroluminescence disappears simultaneously. The current-voltage characteristic is linear, but the electronic instability of this state when the current reaches a critical value  $\sim 44$  mA leads to an inverse switching, to the poorly conducting state. The current decreases abruptly, and the current-voltage characteristic becomes nonlinear again. At the time of this inverse switching of the conductivity, the electroluminescence is “reignited,” and its intensity increases with increasing voltage. There is thus no electroluminescence in the highly conducting state.

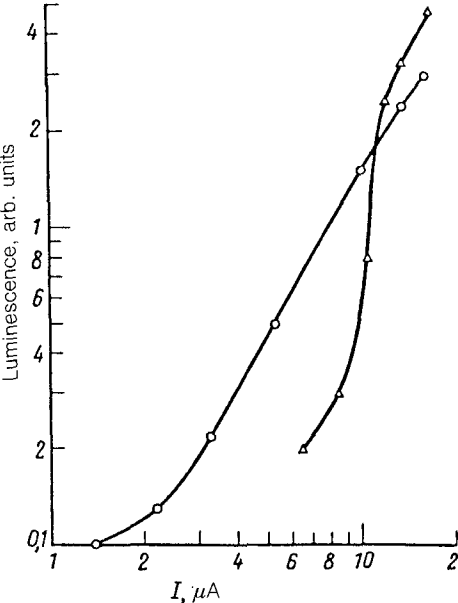


FIG. 2.

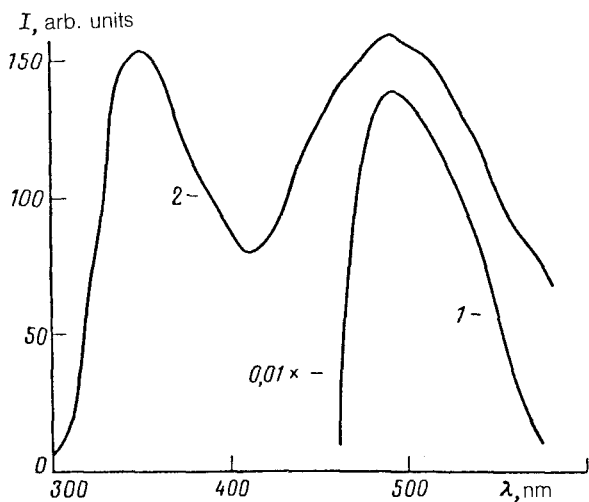


FIG. 3.

On the plot of the luminescence intensity versus the current flowing through the sample in Fig. 2, we see two regimes. At low currents, the plot in Fig. 2 is nonlinear, roughly quadratic. As the current is raised, the plot becomes linear. Analysis of the spectrum of this luminescence revealed a peak at  $\lambda \sim 500$  nm (Fig. 3). The position of this peak does not depend on the magnitude or polarity of the voltage applied to the sample. The electroluminescence peak is close to the photoluminescence peak at  $\lambda \sim 490$  nm. These results may be evidence that the charge transport in thin films of polydiphenylbenzophenone is limited by an injection of charge from the electrodes. In low fields this injection is unipolar. Evidence for this conclusion comes from the presence of a threshold in the electroluminescence, which is usually attributed<sup>7</sup> to the onset of the bipolar injection required for electroluminescence. The conclusion that the injection is unipolar is supported by the circumstance that the electrodes used in these experiments were not ohmic. The fact that there is no electroluminescence in the highly conducting state of the polymer may mean that this luminescence occurs from parts of the film in which metal-like channels arise upon the switching. On the other hand, the absence of an electroluminescence upon the appearance of the highly conducting state can be explained on the basis that the applied electric field is shunted by conducting domains and is not sufficient to excite the electroluminescence. However, we see from Fig. 1 that the field near the threshold for the inverse switching to the poorly conducting state is above the threshold for electroluminescence. Nevertheless, this luminescence arises only after the conductivity is "turned off." This result may mean that the necessary conditions for electron-hole recombination are not satisfied in the highly conducting state. This is apparently what we should expect if the electroluminescence occurs from regions ("conduction domains or channels") which have a metal-like conductivity in the highly conducting state. We can draw the further conclusion that these domains form in the film long before the phase transition to the highly conducting state—not at the time of this transition. For this reason, the trans-

formation of the electronic states in these domains ultimately leads to a transition to a highly conducting state. This conclusion is important, since it is usually assumed that the channels form at the time of the switching.

It would obviously be premature to draw a final conclusion regarding the mechanism for this electroluminescence in thin films of polydiphenylenephthalide. It is clear, on the other hand, that the electroluminescence which we have observed not only will be of assistance in reaching a deeper understanding of the mechanism for this anomalously high conductivity in thin films of certain polymers but will also bring us closer to an understanding of the entire array of charge instabilities in these films.

<sup>1</sup>O. A. Skaldin, A. Yu. Zherebov, A. N. Lachinov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **51**, 141 (1990) [*JETP Lett.* **51**, 159 (1990)].

<sup>2</sup>A. N. Lachinov, A. Yu. Zherebov, and V. M. Kornilov, *Synth. Met.* **44**, 111 (1991).

<sup>3</sup>V. M. Arkhangorodskii, E. G. Guk, A. M. El'yashevich *et al.*, *Dokl. Akad. Nauk SSSR* **309**, 603 (1989) [*Sov. Phys. Dokl.* **34**, 1016 (1989)].

<sup>4</sup>A. Yu. Zherebov and A. N. Lachinov, *Synth. Met.* **44**, 99 (1991).

<sup>5</sup>S. N. Salazkin, S. R. Rafikov, G. A. Tolstikov, and M. G. Zolotukhin, *Dokl. Akad. Nauk SSSR* **262**, 355 (1982).

<sup>6</sup>V. P. Kazakov and V. A. Antipin, *Questions of Physics of the Liquid State*, Ufa, 1986, p. 182.

<sup>7</sup>W. Hwang and K. Kao, *J. Chem. Phys.* **60**, 3845 (1974).

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