Current noise in thin polymer films near an insulator–metal transition

O. A. Skaldin and O. A. Selezneva
Physics Department, Bashkir Science Center, Russian Academy of Sciences, 450025, Ufa, Russia

(Submitted 2 June 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 1, 31–34 (10 July 1992)

Current fluctuations near an insulator–metal transition in thin polymer films have been studied. The measured spectral density of the current noise is described by $S(\omega) \propto A\omega^{-\gamma}$, where $\gamma \leqslant 1$. The critical growth of the mean square fluctuation, $\langle \delta U^2 \rangle \propto \exp(\alpha U)$, is the reason why there are no clearly defined thresholds for the transition process. This process appears to be probabilistic.

A central problem in research on conducting polymers is the mechanism for the conductivity in oriented polymer thin films. Of particular interest are polymer systems in which an insulator–metal transition and the inverse transition are observed.[1–3] Attempts to study such systems run into difficulties because the results are not very reproducible. In particular, after a cycle of transitions the polymer does not return to its original state in terms of the conductivity parameter σ. The reason may be either a long relaxation time t_r or irreversible effects which occur in the polymer during the flow of an electric current. It thus becomes important to study the fluctuations in the electric current up to the point at which the transition begins.

In this letter we are reporting a study of the low-frequency current noise of a conducting polymer, namely polydiphenylenephthalide (PDP), near an insulator–

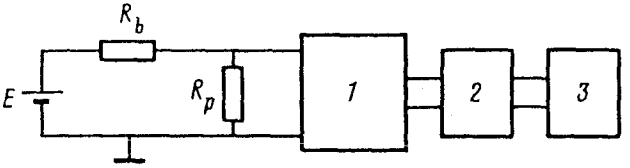

FIG. 1. Block diagram of the experimental apparatus. E—Voltage source (an array of batteries); R_b—ballast limiting resistance; R_p—polymer sample; *1*—Unipan-237 preamplifier; *2*—Kh6-8 correlator; *3*—microcomputer.

metal transition. Figure 1 shows a block diagram of the experimental apparatus for studying the current fluctuations. The voltage from the sample is fed to a preamplifier, then to a Kh6-8 correlator, and then to a microcomputer. The experiments were carried out over the frequency range 0.2–10.0 Hz. In these experiments we used polymer films on glass substrates with a conducting coating of In, Cu, or constantan. The coating was deposited by a centrifuge method. We also used free-standing films. The thickness of the centrifuge films was 200–300 nm, and that of the free-standing films was 1 μm. These film thicknesses were monitored by an interference method.

The current which flows through a polymer sample can be thought of as consisting of a steady-state component and a fluctuating component: $I(t) = I_c + \delta I(t)$. According to the measurement layout, the voltage fluctuation $\delta U(t) = R_p \delta I(t)$ across the polymer film is detected, where R_p is the average resistance of the sample.

A basic characteristic of a fluctuation process is the spectral density[4] $S(\omega)$. Since there is no dispersion in the dielectric constant [$\epsilon(\omega) = \text{const}$] in the frequency range of these experiments, the spectral density of the polymer is given by[4]

$$S(\omega) = U^2(1 + R_p/R_b)^{-2} S_{R_p}/R_p^2, \tag{1}$$

where U is the applied voltage, R_b is the ballast limiting resistance (it limits the current), and S_{R_p} is the spectral density of the fluctuations in the resistance of the sample. The calculations can be simplified by rewriting expression (1) in the form

$$S(\omega) = U^2 \Sigma(\omega) R_b^2 R_p^2/(R_b + R_p)^4, \tag{2}$$

where $\Sigma(\omega) = \langle \delta\sigma^2(\omega) \rangle/\sigma_0^2$ is the spectral density of the relative mean square fluctuation of the conductivity of the polymer sample. On the basis of physical considerations, the latter expression is valid if $\Sigma(\omega) \ll 1$, i.e., if the fluctuation component of the average conductivity of the sample, σ_0, is small. This condition corresponds to a state of the polymer film far from the transition. In our case, the simultaneous correlation function is $\langle \delta\sigma^2(\tau) \rangle/\sigma_0^2|_{\tau=0} \leqslant 10^{-2}$; i.e., the approach outlined above is completely correct.

Let us consider the spectral density of the fluctuations in the voltage across a polymer film on a copper substrate (Fig. 2a) with a conductivity $\sigma_0 \simeq 10^{-11}$ S/cm and with an average film resistance $R_p \sim 3 \times 10^5$ Ω. The film thickness is $h \sim 200$ nm. The overall $S(\omega)$ dependence can be approximated by a function $S(\omega) \sim A\omega^{-\gamma}$. Note that

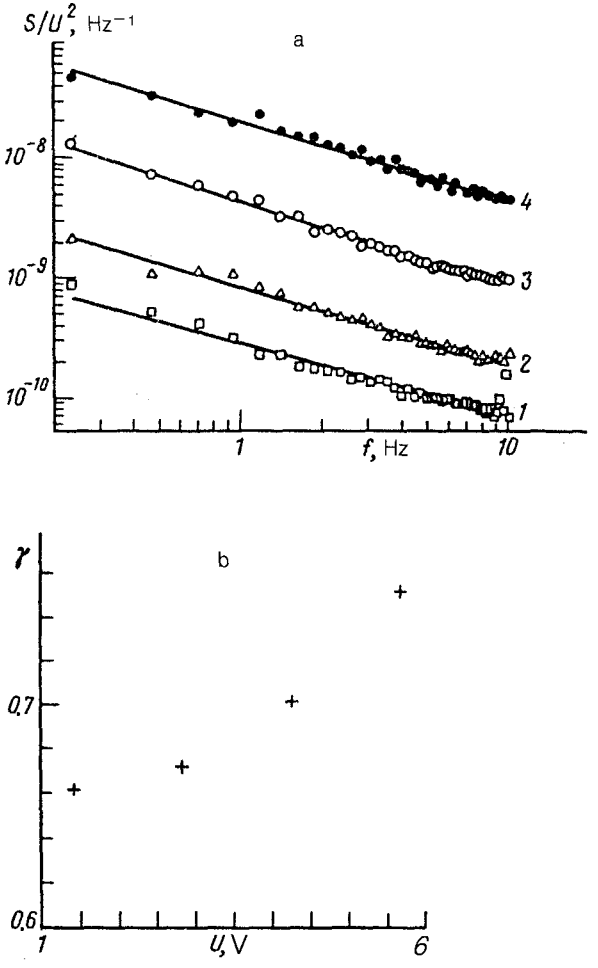

FIG. 2. a: Experimental results on the spectral density of the current noise. *1*—$U_1 = 1.4$ V; *2*—$U_2 = 2.9$ V; *3*—$U_3 = 4.3$ V; *4*—$U_4 = 5.7$ V. b: The coefficient γ versus the applied voltage U for a film deposited by the centrifuge method.

the coefficient γ depends on the applied voltage U (Fig. 2b), and it varies from 0.5 to 0.8 as the transition is approached. At low currents (~ 10 μA) its value is $\gamma \sim 0.5$. This value is apparently typical of the spectral density of the noise due to hydrodynamic fluctuations of a Boltzmann electron gas.[5,6] The measurements on the free-standing film show that the coefficient is $\gamma \sim 1$ near the transition. The presence of a current noise in a conducting system with a spectral density $S(\omega) \sim \omega^{-1}$ corresponds to the model of current noise in thin conducting filaments with $r/h \ll 1$ (Ref. 5; r is the radius of a filament, and h is its length, which is equal to the film thickness in our case). As was shown in Ref. 7, the transition which occurs in polymer systems of this

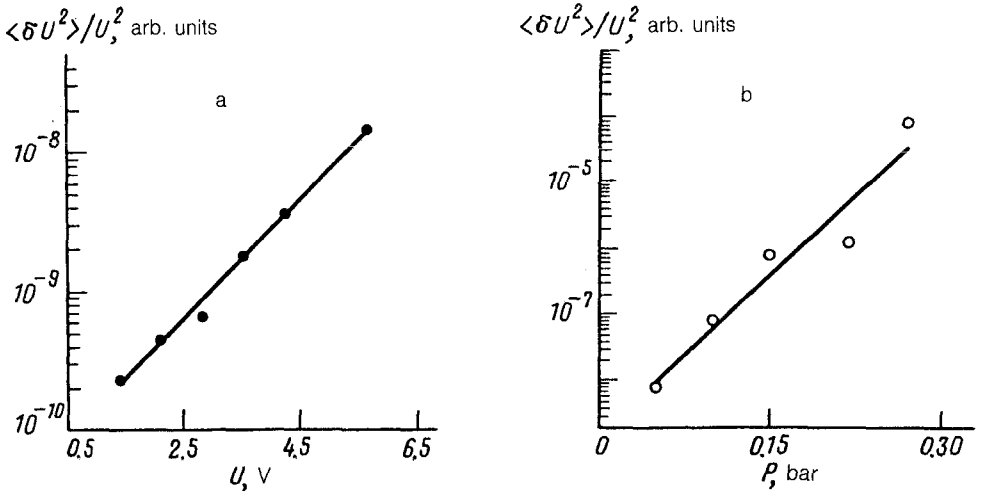

FIG. 3. Relative mean square fluctuation $\langle \delta U^2 \rangle / U^2$. a—As a function of the voltage U at $P = 0.16$; b—as a function of the pressure P at $U = 1.4$ V.

sort causes the entire surface of the film to divide into conducting channels with dimensions $20 \leqslant r \leqslant 300$ nm. The entire polymer film is thus an insulating matrix in which conducting filaments are embedded. The surface number density of these filaments is $\rho \sim 10^4$–10^5 cm^{-2}. In this case the condition for the appearance of an ω^{-1} noise holds well, since the condition $r/h < 1$ holds.

Lachinov *et al.*[3] have reported an anomalous electron instability of polymers subjected to uniaxial pressure. The change in conductivity, by a factor of 10^{11}, was interpreted as reflecting a phase transition similar to a Mott transition in the system.[8] It is accordingly interesting to examine the behavior of the mean square current fluctuation in the polymer film as a function of the applied voltage U and the uniaxial pressure P. As was shown above, the voltage fluctuations $\delta U(t)$ were measured in our case. Let us examine the mean square voltage fluctuation $\langle \delta U^2(\tau) \rangle|_{\tau=0}$ as a function of U and P, i.e., $\langle \delta U^2 \rangle = F(U,P)$. We fix the pressure at some constant value $P = P_0$, and we vary the potential difference applied to the polymer film. In this case the quantity $F(U,P_0)$ is approximated by an exponential function of U (Fig. 3a). If we fix the voltage, $U = U_0$, and vary the pressure P (Fig. 3b), we obtain the behavior of the quantity $\ln F(P)$, which also increases linearly with increasing pressure. On the whole, the quantity F is a function of two arguments: $F \simeq A \exp(\alpha U + \beta P)$. In other words, $F(U,P)$ has an inversion symmetry with respect to U and P. This result leads to the conclusion that there is a common mechanism for the increase in the current fluctuations and that the insulator-metal transitions initiated by different factors are of the same nature. In the case at hand, these factors are the constant voltage U and the uniaxial pressure P.

It can be concluded from the results presented above that the insulator–metal transition in polymers is not a structural phase transition in the standard sense of the

term. Evidence for this conclusion comes from the absence of clearly defined thresholds in the voltage and the pressure and also from the exponential growth of the relative conductivity fluctuation [see (2)]: $\langle \delta\sigma^2 \rangle / \sigma_0^2 \sim \langle \delta U^2 \rangle \sim \exp(\alpha U)$. Apparently all we can say is that there is a probabilistic transition at given values of U and P. In other words, as U or P is raised, the probability for the formation of a system of conducting channels increases. This circumstance makes it doubtful that Mott transitions occur in systems of this sort.[3]

[1]N. S. Enikolopyan, L. N. Grigorov, and S. G. Smirnov, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 326 (1989) [JETP Lett. **49**, 371 (1989)].
[2]V. M. Arkhangorodskiĭ, E. G. Guk, A. M. El'yashevich *et al.*, Dokl. Akad. Nauk SSSR **309**, 603 (1989) [Sov. Phys. Dokl. **34**, 1016 (1989)].
[3]A. N. Lachinov, Yu. A. Zherebov, and V. M. Kornilov, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 742 (1990) [JETP Lett. **52**, 103 (1990)].
[4]Sh. M. Kogan, Usp. Fiz. Nauk **145**, 285 (1985) [Sov. Phys. Usp. **28**, 170 (1985)].
[5]Yu. A. Klimontovich, *Statistical Physics*, Nauka, Moscow, 1982, 608.
[6]Yu. A. Berlin, S. N. Beshenko, V. A. Zhorin *et al.*, Dokl. Akad. Nauk SSSR **260**, 1386 (1981).
[7]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)].
[8]B. Lundberg, B. Sundgvist, O. Inganas *et al.*, Mol. Cryst. Liq. Cryst. **118**, 155 (1985).

Translated by D. Parsons