

Metal-like state induced in a polymer film by a change in the boundary conditions at the film surface

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An insulator–metal phase transition has been induced experimentally in a metal–polymer–metal sandwich by changing the boundary conditions at a metal–polymer interface. The boundary conditions were changed by virtue of a change in the work function of the electrode metal at the melting point of the latter. © 1995 American Institute of Physics.

Since the late 1980s various investigators have reported observing an anomalously high conductivity in certain electrically active polymers.^{1–5} Various physical methods have been used to produce this high-conductivity state.^{6–8} The nature of these methods suggests that this phenomenon depends on the concentration of nonequilibrium space charge in the polymer. In the present letter we demonstrate that it is possible to produce a highly conducting state in undoped polymers by changing the boundary conditions at a polymer–metal interface.

Here is the idea underlying the experiments. We know that band curvature occurs at a metal–polymer interface as the result of an equalization of the Fermi levels. The potential energy of the carriers, $V_b(z_0)$, at a distance z from the interface determines the magnitude of the curvature:⁹

$$V_b(z) = \begin{cases} V_0 - 2\pi e^2 N(z - z_0)^2 / \epsilon, & 0 < z < z_0, \\ V_0, & z > z_0, \end{cases}$$

where z_0 is the depth to which the surface charge N propagates into the interior of the polymer. According to various estimates, z_0 varies over an order of magnitude, depending on the nature of the polymer and the method used to estimate it.^{10,11} We will work with the average value¹¹ $z_0 \sim 3 \mu\text{m}$. Note that this value is comparable to the thicknesses of the films on which a switching to a highly conducting state has been observed.^{3–8} Working from the expression for $V_b(z_0)$, we can estimate the surface charge density $N = \epsilon W_0 / 2\pi(ez_0)^2$, where $W_0 = \varphi_p - \varphi_m$, and φ_p and φ_m are the work functions of the polymer and the metal, respectively. By varying N we can thus change the relation between the work functions of the polymer and the metal. We know¹² that certain metals, e.g., indium, undergo particularly sharp changes in φ_m when they melt. If this metal is used as one of the electrodes, the surface charge at the polymer–metal interface may change sharply at the melting point. By analogy with thermally stimulated switching,¹³ we would expect this change to give rise to a highly conducting state in the polymer sample.

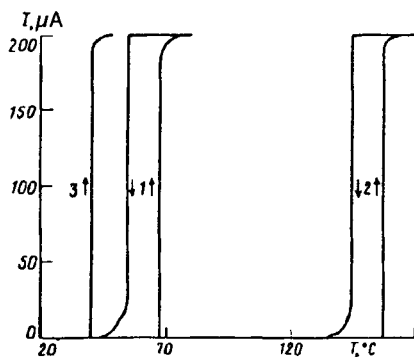


FIG. 1. Temperature dependence of the current through a metal-polymer-metal system in which the following metals are used as the upper electrode: 1—Wood's alloy; 2—indium; 3—gallium. The arrows show the directions in which the current changes during heating and cooling of the sample.

As the polymer in the experiments we used films of polyphthalidilenebiphenylilene¹⁴ (PPB) ranging in thickness from 1 to 10 μm . The test sample was a metal-polymer-metal sandwich in which one of the metal electrodes was a low-melting metal or alloy, e.g., indium, gallium, or Wood's alloy.

Figure 1 shows the temperature dependence of the current flowing through the polymer film. At the melting points of these metals, each of the test samples undergoes a transition from an insulating state with a conductivity $\sim 10^{-14}$ S/cm to a highly conducting state with $\sim 10^{-1}$ – 10^{-3} S/cm. More than 10^3 cycles of this temperature-induced switching were recorded.

Let us look at the changes in the conductivity of the polymer film as the temperature is raised in the case of Wood's alloy. At room temperature the polymer sample has a conductivity $\sim 10^{-14}$ S/cm. As the temperature of the measurement cell is raised to 40–45°C, fluctuations of the current arise in the measurement circuit (Fig. 2). The resistance of the sample decreases to 1–10 M Ω . This region of current fluctuations exists as the temperature of the measurement cell is raised all the way to the melting point of the upper electrode. The current-voltage characteristic is nonlinear in this case; its shape is characteristic of space-charge-limited charge transport.

When the melting point of the upper electrode (68°C for Wood's alloy) is reached, the current in the measurement circuit rises sharply. The resistance of the test cell is 0.1–5 Ω under these conditions. The current-voltage characteristic is linear in this case. As the temperature of the measurement cell is raised further, we see a slight rise in the resistance of the sample. A similar picture is observed when the upper electrode is made of indium or gallium (curves 2 and 3, respectively, in Fig. 1).

As the temperature of the measurement cell is lowered, the changes in the conductivity of the polymer occur in the opposite order. When the crystallization temperature of the upper electrode is reached, there is an abrupt decrease in the current in the measurement circuit, as shown by the arrows in Fig. 1. The apparent reason for the hysteresis here is the nonzero response time of the measurement cell. As the temperature is lowered

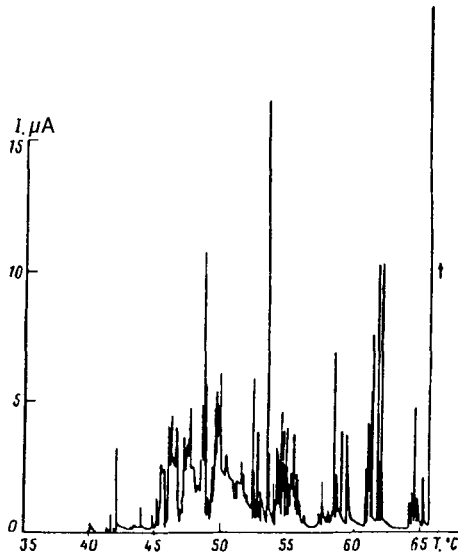


FIG. 2. Fluctuations in the current when the sample temperature is below the melting point of the upper electrode. The arrows show the transition of the sample to the highly conducting state. The upper electrode was made of Wood's alloy.

further, we again see the region of current fluctuations with a sample resistance of 1–10 M Ω . At room temperature the samples goes back into its original insulating state.

One might propose several trivial explanations of these observations. Examples are 1) direct contact between the electrodes due to holes running all the way through the film or other irregularities, 2) dielectric breakdown in regions in which the electric field is locally nonuniform, and 3) a diffusion of the liquid metal through the polymer film. To test these possibilities, we carried out the following experiments.

1. We studied the effect of the thickness of the polymer film on the characteristics of this phenomenon. We used film samples, consisting of one or more layers, prepared by repeatedly building up the thickness of the film in a polymer solution. The effect was observed up to a film thickness of 10 μm , which is an order of magnitude greater than the critical film thickness in the induction of the highly conducting state by such agents as uniaxial pressure and an electric field.⁸

The use of a material which is a liquid at room temperature (mercury) at the upper electrode showed that the switching of the sample to the conducting state does not occur. We should also point out that the metals used in these experiments (Wood's alloys, indium, and mercury) do not wet the polymer film.

2. In a study of the effect of an electric field, we found that the switching effect is observed, regardless of the electrode material and regardless of the polarity of the applied voltage—at fields $\sim 10^2$ V/cm and at potential differences below 10 mV. Even in the field of the contact potential difference, with the external voltage source disconnected, we observe current fluctuations like those in Fig. 2.

3. In analyzing the possibility of metal bridges in the polymer matrix, we observed a dependence of the switching effect on the magnitude of the current. Since the experimental conditions favored diffusion, an increase in the current should have promoted the formation of metal bridges. In our case we observed the opposite effect: As the current was raised by changing the parameters of the measurement circuit, the switching effect became unstable. In the absence of a ballast resistance, the effect was not seen at all.

The possibilities of defects, breakdown, and metal bridges were checked by direct observation of the polymer films in a transmission electron microscope. This study showed that the polymer film is strong and uniform. After repeated switching of the film to the conducting state and back, we observed no holes running completely through the film or any traces of breakdown.

In summary, it has been shown that the generation of surface charge due to a change in the boundary conditions at a polymer–metal interface can lead to an insulator–metal phase transition in a polymer sample. The reason for the transition may be an energy instability of the electron subsystem of the polymer. It was observed in Ref. 15 that the molecular organization of the PPB polymer macromolecule is such that two stable energy states can be realized: a neutral state and a charged state, separated by a relatively low potential barrier. In particular, a transition to the charged state can be facilitated by an interaction of the molecule with a net space charge. An effect of space charge on electron phase transitions in electrically active polymers has been observed previously in experiments on thermally stimulated switching in thin films.⁷ It is apparently important that the concentration of the interacting centers be sufficient to lead to overlap of the corresponding wave functions and to the formation of a metal-like subband, which implements a coherent charge transport.

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