High-conductivity state of thin polymer films: effects of an electric field and of a uniaxial pressure

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Experimental results on the high-conductivity state of thin films of undoped, unconjugated polymers of the polyarylenephthalide class are reported. The high-conductivity state is reached by applying an electric field or a low uniaxial pressure ~ 0.1–0.4 MPa. The conductivity of this state has a metallic temperature dependence. This state forms by an electronic mechanism.

INTRODUCTION

The high-conductivity state which was recently discovered in undoped, unconjugated polymers such as polypropylene[1] and polydipheylenephthalide[2,3] has attracted much interest. It had previously been assumed that a metallic conductivity was possible only in conjugated organic polymers, whose electronic structure favored the delocalization of π electrons.[4] However, a certain density of these electrons had to be introduced by doping in order to achieve charge transport.[5] Doping generally results in the appearance of polaron-like states (solitons, polarons, bipolarons, etc.), which determine the mechanism for charge transport in such systems.

The results of Refs. 1 and 2, as well as those of Refs. 6 and 7, show that other mechanisms, not involving a doping or conjugation of valence electrons, also operate and can give rise to a much higher conductivity in the organic system. For example, Skaldin *et al.*[6] report a conductivity of at least 10^5 S/cm, and Arkhangorodksiĭ *et al.*[7] report a conductivity of at least 10^{11} S/cm at room temperature and at least 10^{14} S/cm at ~ 3 K. The conductivities reported for doped, conjugated polymers, on the other hand, have so far not exceeded $5\cdot 10^5$ S/cm.

The nature of this anomalously high conductivity has yet to be resolved. It was suggested in Ref. 6 that it is a manifestation of "electronic switching." It was recently reported[8] that a high-conductivity state can arise when an electric field $\sim 5\cdot 10^2$ V/cm and a uniaxial pressure $\sim 10^5$ Pa are applied simultaneously to a polymer film. This effect requires the attainment of a threshold: The transition to the high-conductivity state occurs abruptly once a certain critical pressure P_c is reached. The anomalously low value of P_c has attracted attention; it is much lower than the corresponding value for polyacetylene, which is[9] $\sim 2\cdot 10^{10}$ Pa.

It appears worthwhile to compare the properties of the high-conductivity states reached in various ways in order to add to our understanding of the physical properties of this anomalously high conductivity in thin films of unconjugated polymers. Our purpose in the present study was accordingly to carry out experiments on this anomalously high conductivity induced in thin polymer films, by an electric field and a low uniaxial pressure. We also studied the mutual effects of these agents on the conditions for the formation of the high-conductivity state.

TEST SAMPLES AND EXPERIMENTAL PROCEDURE

As test samples we selected films of polydiphenylenephthalide (PDP): a high-temperature (softening point ~ 600 K), chemically stable, soluble polymer belonging to the class of polyphthalidilidenearylenes.[10] The films were grown by centrifuging from a cyclohexanon solution. The test sample was a three-layer metal-polymer-metal sandwich. The metals used were Cu, Al, Au, Cr, and In. The lower metal layer, up to 1000 Å thick, was deposited by vacuum diffusion on polished glass or silicon plates. The upper layer was either sputtered or, in the case of In, rolled onto the polymer layer. Measurements were taken with electrodes of the same metal and also of different metals. We found no influence of a difference between the metals on the effects in which we were interested.

The pressure dependence of the conductivity was studied by the technique described in Ref. 8. A data acquisition and processing system based on an Élektronika DZ-28 microcomputer was used.

EXPERIMENTAL RESULTS

Figure 1 shows the current through the sample versus the applied pressure at a constant voltage. The conductivity of the polymer film is initially less than 10^{-14} S/cm. When the pressure reaches the critical level, which is 0.4 MPa in this particular case, the conductivity jumps to 10^{-3} S/cm and becomes metallic, with a corresponding temperature dependence. In other words, it begins to increase slowly with decreasing temperature. This trend persists at ultralow, liquid-helium temperatures. Note that the metallic temperature dependence of the conductivity prevails when the conductivity is sufficiently low. In certain cases we detected this behavior at a sample conductivity $\sim 10^{-5}$ S/cm. In its high-conductivity state, the film has a pronounced conductivity anisotropy, described by $\sigma_\perp/\sigma_\parallel \sim 10^{10}$–$10^{12}$.

As the pressure is lowered, the $I = f(P)$ curve does not retrace itself; instead, there is a smooth decrease in the conductivity, often all the way to $P = 0$. (The pressures we are talking about here are pressures over atmospheric.) These curves are shown by the dashed lines in Fig. 1. Shown in the same figure is the effect of the potential difference across the electrons on the pressure dependence of the conductivity.

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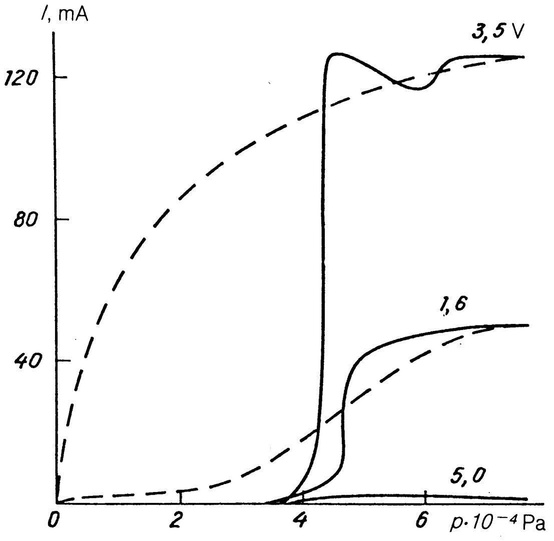

FIG. 1. Current through a polymer film 0.5 μm thick versus the uniaxial pressure.

The potential difference was varied over the interval 0.5–7 V. As the voltage is raised to 3 V, we see a negligible increase in the conductivity at pressures above the threshold. Above 3.3 V, the conductivity begins to decrease; above 5 V we do not observe the transition to a high-conductivity state.

The nature of the changes in the conductivity in PDP thin films under pressure at $P < P_c$ can be studied by examining the changes in the current-voltage characteristics. Figure 2 shows some characteristics recorded at various pressures. Curve *1* corresponds to the absence of a pressure. The shape of this curve is typical of bistable current-voltage characteristics, with an *S*-shaped region of a negative differential resistance, which cannot be controlled by the voltage. Similar curves were reported in Ref. 11 for thin films of various polymers. In the initial region, at low voltages, the characteristic is nonlinear and can be described best by a function $I \propto \exp(U^n)$, where n can take on values from 1 to 0.5. Such curves can be explained in terms of currents which are limited by space charge[12] or by a Schottky or Poole–Frenkel mechanism.[13]

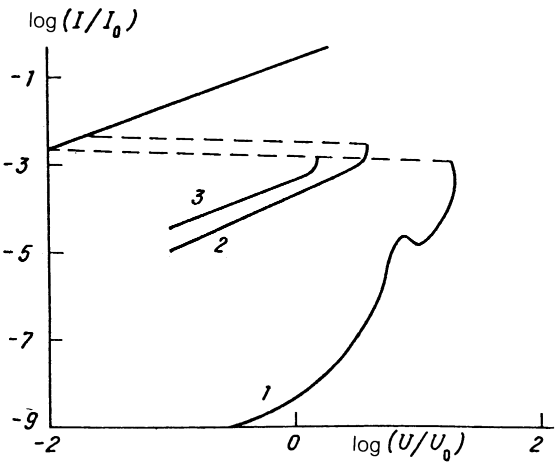

FIG. 2. Current-voltage characteristics of a thin polymer film. *1*—In the original insulating state; *2*—under a pressure of 0.4 MPa; *3*—in the "intermediate" state after a "switching off" by a current pulse.

When the voltage reaches a certain level, which usually corresponds to a field of 10^4–10^6 V/cm, a region with a negative differential resistance appears on the characteristics. This negative resistance cannot be controlled by the voltage. In the high-conductivity state, into which the polymer film switches, the characteristic obeys Ohm's law, and the conductivity has a metallic temperature dependence. As was shown in Ref. 5, conducting channels perpendicular to the surface arise in the interior of the film upon this "switching." The concentration of these channels is about 10^5 cm^{-2}. The switch to the original low-conductivity state is made by the standard method for this effect: by applying a short voltage pulse, with a length of 0.1–1 μm and a height of 15–20 V. In certain cases, however, the conductivity is not completely "turned off": The sample retains a residual conductivity. In other words, there is an "intermediate" state in the sample, with a semiconducting conductivity. The current-voltage characteristics in this state obey a power law $I \propto U^n$, where n takes on values from 1 to 2 (see curve *3* in Fig. 2).

The application of pressure to the polymer film results in a change in the original current-voltage characteristic (curve *2* in Fig. 2). At $P < P_c$, the characteristic takes the form corresponding to the intermediate state. As the pressure is raised, the initial conductivity also rises, and the exponent n approaches one. An increase in the pressure has essentially no effect on the threshold voltage for switching, $U_{\rm thr}$. An effect is seen only when the pressure reaches values just below P_c. At $P > P_c$ the current-voltage characteristic of the polymer film is linear.

DISCUSSION AND CONCLUSIONS

The low pressure (~ 0.1 MPa) at which the transition to the metallic state occurs and the small film thickness (< 300 nm) suggest at least two trivial explanations for this effect (in addition to the nontrivial explanation based on a phase transition): (1) a mechanical breakdown of the film caused by the electrodes and a short-circuiting of these electrodes and (2) an increase in the probability for a field-induced switching near electrode irregularities, as a result of a decrease in the film thickness as the film is compressed.

The film was inspected for irregularities in an ÉMMA-100 electron microscope by a replica method, and the free film was examined in transmitted light. It was established that, at the resolution of this microscope, there are absolutely no holes running completely through the PDP films, either before or after the application of the pressure. In this regard the PDP films differ from polypropylene films.[14] The films used in this study ranged in thickness from 500 to 3000 Å. However, the conclusion that there are no holes running completely through the film is not iron-clad, since holes may "heal" when the pressure is withdrawn, even though these films are fairly hard (their elastic modulus is ~ 3000 MPa). We accordingly carried out some additional experiments to learn about the properties of the polymer films in their high-conductivity state, i.e., when the samples were subjected to a uniaxial pressure $P > P_c$.

Figure 3 shows a current-voltage characteristic of a polymer film under a pressure of 0.2 MPa. A bipolar sawtooth voltage with an amplitude of ± 10 V and a frequency of 10^{-3} Hz was applied to the sample. In this case, the

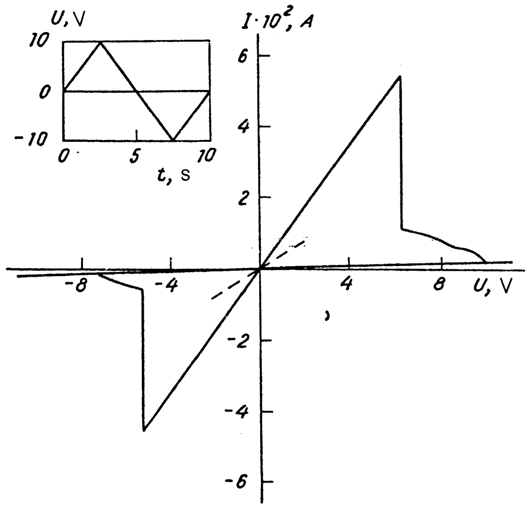

FIG. 3. Current-voltage characteristic of a polymer film under a uniaxial pressure of 0.1 MPa. A bipolar sawtooth voltage with a frequency of 0.1 Hz and an amplitude of ± 10 V is applied to the sample. The dashed line separates regions corresponding to the half-period of increasing voltage and the half-period of decreasing voltage. The inset shows the voltage waveform applied to the sample.

changes in the conductivity occur in the following way. In the high-conductivity state, the behavior is linear up to a threshold voltage U_{thr}, above which the conductivity drops sharply, and an N-shaped region forms on the current-voltage characteristic. The steepness of this region depends on such factors as the voltage sweep rate and the ballast resistance. A further change in the voltage results in the appearance of a lower branch of the characteristic, which corresponds to a low-conductivity state with $R_{\text{low}}/R_{\text{high}} \sim 10^2$–$10^3$, where R_{high} and R_{low} are the resistances of the film in its high-conductivity and low-conductivity states, respectively (Fig. 3). As the voltage is lowered, the working point moves along the lower branch to the origin of coordinates. The sample switches to its low-conductivity state in this manner. When the voltage crosses zero, however, the the sample is forced to "turn on" again, and the working point moves onto the high-conductivity region of the characteristic. Here the changes in the signs of I and U are being taken into account. Further on, the characteristic duplicates symmetrically the same shape as during the positive half-period: When U_{thr} is reached, an N-shaped region appears, and the sample turns off to the low-conductivity state. As zero is crossed, the sample turns on again. We thus obtain a symmetric butterfly-shaped characteristic. We should add that this shape is characteristic of both the high-conductivity state reached under pressure and that reached through switching the film by an electric field.

We will not go into the mechanism responsible for this current-voltage characteristic in the present paper. We simply note that the symmetric pattern which arises upon a change in polarity is evidence that the N-shaped region is not a consequence of a possible thermal destruction of metallic conducting channels or of simply metal bridges (the existence of such bridges was discussed in Ref. 6). It is instead due to a redistribution of space charge. This conclusion is supported by the fact that the change in slope at the origin on the current-voltage characteristic is observed only when the decrease in the voltage and the change in polarity occur past the N-shaped region. If the sample is in the high-conductivity state, this slope change is not at the origin. When the characteristic is scanned repeatedly, there is a gradual decrease in the threshold voltage for the N-shaped region. After 10 to 100 cycles, the conductivity in the intermediate state stabilizes. If the ballast resistance and the internal resistance of the power supply are chosen correctly, weakly damped oscillations of the current occur in the circuit.

Analyzing the experimental results, we conclude that it is difficult to attribute them all just to puncturing of the film. More plausible is the explanation based on a pressure-facilitated switching caused by a variation of the field, since most of the electrical properties of the high-conductivity state are very nearly the same in the two cases. However, this explanation is contradicted by at least two facts: The switching induced by a variation of the pressure is suppressed by an electric field above a certain value (Fig. 1), and we do not find the expected effect of the pressure on the threshold voltage for a switching induced by a variation of the field.

Summarizing these experimental results, we can thus assert the following. The anomalously strong effect of the pressure on the conductivity of the thin polymer film, which results in a sharp change in the conductivity, from an insulating behavior to a metallic behavior, seems to be a new version of the so-called electronic switching effect. The transition to a metallic state is accompanied by the formation of high-conductivity longitudinal domains in the interior of the film. The properties of these domains are similar to those of the domains which arise in the case of an S-shaped electronic instability in an electric field. Electronic instabilities of these domains apparently determine the distinctive features in the electrical properties of PDP films.

The nature of the high-conductivity domains (or conducting channels, as they are called in some other papers) is not yet clear. All we can do is offer some general suggestions, which are based on the following experiential facts: 1) The effect is observed at thicknesses below a certain critical value. 2) As the thickness decreases, there is a sharp increase in the concentration of trapping states (there are substantial increases in the height of peaks in the thermally stimulated current and the thermoluminescence[15,16]). In addition, we know that the role of charged surface states increases with decreasing thickness. The regions in which the domains form are apparently regions of a maximum concentration of trapping centers. The ionization of these centers, promoted by the electric field or the pressure, gives rise to charged states in a certain region. The concentration of these states must be sufficient to set the stage for the formation of a polaron lattice and, according to Ref. 17, a metallic subband. However, further experimental and theoretical research will be required to determine how well this mechanism corresponds to the actual events.

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