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New polymer materials - new prospects

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ABSTRACT

The present paper discusses experimental results obtained during the investigations of electron instabilities in the thin films of poly(3,3'-phthalidylidene-4,4'-biphenylene) (PPB). A common feature for all these phenomena is that they are characterized by the dielectric-metal phase transition which is initiated by external effects of abnormally low values. The latter include uniaxial pressure, electric field, and temperature. Possible mechanisms of electron instabilities in thin polymer films are discussed.

INTRODUCTION

A highly conductive state (HCS) detected recently in pristine non-conjugated polymers of the polypropylene (1) and PPB (2) types is of great interest.

Results reported in (1,2) as well as in (3,4) indicate that there are probably other ways avoiding doping and conjugation of valence electrons and ensuring considerably higher conductivity of organic systems. For example, in (3), the reported value of conductivity is no less than 10^5 (Ohm cm)⁻¹ and in (4) it is even 10^{12} (Ohm cm)⁻¹ while the reported conductivity of doped conjugated polymers never exceeds $5 \cdot 10^3$ (Ohm cm)⁻¹.

The nature of this abnormally high conductivity is still vague. It may result from a so-called electron switching effect (3) or occurs in cases when the electric field of about $5 \cdot 10^2$ V/cm and the uniaxial pressure of about 10^5 Pa are applied to the polymer film simultaneously (5). Note please the abnormally low value of the critical pressure which is much lower than that measured for polyacetylene $P_c \sim 2 \cdot 10^{10}$ Pa (6).

In this paper we consider the possibility of inducing of HCS in thin films of non-conjugated organic polymers.

EXPERIMENTAL

The PPB has a molecular weight of $(50 - 80) \cdot 10^3$ depending on the conditions of the synthesis. The softening temperature is 440°C , the temperature of decomposition (TGA, 1% weight loss, air) is 450°C . The polymer is soluble in conventional organic solvents, such as chloroform, methylenedichloride, 1,1,2,2-tetrachloroethane. The high solubility of PPBs makes it possible to purify them effectively, make films and study their various properties.

In the present work, samples of the metal/polymer/metal sandwich type structure were used. Polymer films less than 2000 nm thick were prepared by spin coating glass substrates with the polymer solution, whereupon a Cu electrode was deposited by thermal vaporation in vacuum. Top electrodes of Cu, Cr, Al, or Au were deposited on the film surface in the same way or were pressed upon it. No effect of the electrode material on the sample properties has been detected. The samples were put into a vacuum chamber, which allowed us to perform measurements in the 77 - 430 K temperature range. Measurements were performed as described in (5).

RESULTS

Electric-Field

In a high electric field (more than 10^5 V/cm), the effect of switching with memory was discovered in thin PPB films. In the "off" state, the polymer is a dielectric with a conductivity of less than 10^{-14} (Ohm cm) $^{-1}$ at room temperature and an exponential I-V characteristic. The time of switching from the "off" to "on" state never exceeds 100 ns. In the "on" state, the I-V characteristic is ohmic, and the sample reveals metal-like temperature dependence of conductivity, its value at room temperature being about 10^{-3} (Ohm cm) $^{-1}$.

Uniaxial-Pressure

Fig.1 shows current passing through the 300 nm thick sample as a

Fig. 1. Dependence of the current passing through the sample on pressure at different voltages applied to the sample. Solid curves reflect the growth of pressure and dashed curves correspond to the decrease of pressure.

function of a uniaxial pressure P . Originally, the polymer film conductivity is less than 10^{-14} (Ohm cm) $^{-1}$. When the critical pressure is achieved, which is $P \sim 5 \cdot 10^8$ Pa in this case, conductivity abruptly increases and reaches 10^{-3} (Ohm cm) $^{-1}$. The phase transition induces metal-like conductivity in the polymer film. Dashed lines indicate the route of the $I(P)$ curve under the decreasing pressure. As the pressure decreases, the current often does not drop abruptly, but smoothly goes down to zero.

Temperature

Fig. 2 shows the current versus temperature plot for PPB films of different thicknesses. Measurements were carried out during heating. Below $T_c \sim 265$ K, the PPB is a dielectric, its conductivity being less than 10^{-12} (Ohm cm) $^{-1}$ and almost independent of the temperature. Near T_c , thermostimulated currents are observed so that in films less than 500 nm thick, a transition to a metal-like states similar to those described above occurs. The conductivity of such films rises up to 10^{-3} (Ohm cm) $^{-1}$ and its temperature dependence is metal-like type. In thicker samples, the metal-like state has never been observed. When cooled, the metal-like state persists down to 140 K.

Fig. 2. Thermostimulated currents in PPB films of various thickness. Heating rate 3 K/min. Film thickness: 1 - 1000 nm (left axis); 2 - 1500 nm (right axis); 3 - 400 nm (right axis).

DISCUSSION

As indicated by the experiments described above, the electric field, uniaxial pressure and heating can change the sample conductivity. All these effects induce states with similar properties so that it is impossible to define the origin of the state achieved. Let us consider some of these properties.

The "on" state possesses the anisotropy of conductivity of $\sigma_{\perp}/\sigma_{\parallel} \sim 10^{10-12}$, where $\sigma_{\perp}$ and $\sigma_{\parallel}$ are conductivities across and along the polymer film respectively. This anisotropy is due to the formation of highly conducting channels oriented across the polymer film (3).

In the "off" state, the conductivity of the PPB film is $\sigma \sim f^s$, where $2 \text{ Hz} < f < 10^7 \text{ Hz}$ is the frequency and $s \approx 1$, which confirms the hopping

mechanism of charge transport (7). In the "on" state the sample conductivity does not depend on frequency.

The I-V characteristic of a sample in the "on" state under the bipolar sawtooth voltage has the shape of a symmetric "butterfly" (5).

Let us consider instabilities observed in PPB from the point of view of the polaron or bipolaron lattice theory supposed to explain the transition to the metal state in polyacetylene (8), polyaniline (9) and other polymers with nondegenerate ground state (10). Trapping states, whose concentration in the PPB films according to the available results is sufficiently high, can form a subband in the polymer band gap. The electron-phonon interaction is very strong in such systems and hence, the charging of these states can result in the formation of polaron-like states. When their concentration is sufficiently high, the half filled polaron subband can appear. Alternatively, one of the bipolaron bands can merge with the valence or conducting bands.

In each case, the dominating mechanism of the charge generation is probably different. Thus, thermostimulated processes it can be ionization of specific traps. When switching is induced by the electric field, charges can be injected from electrodes. This is incidentally confirmed by experiments on electrical luminescence (11). When uniaxial pressure is applied, changes in the surface conditions are important.

In the majority of the above mentioned cases switching is evidently the result of a combination of different mechanisms.

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