

Charge instability in thin films of organic semiconductors

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The topology of an electrically conducting structure which arises spontaneously in thin polymer films has been studied experimentally. The anomalously high conductivity results from conducting channels which run perpendicular to the surface. Experiments reveal that these channels are associated with a charge instability in polymer semiconductors.

The high conductivity of polymers is presently attributed to the formation and kinetics of charge carriers of a polaron type (solitons, polarons, bipolarons), which form as a result of the effect of acceptor-donor impurities, a light wave, or other external agent on a polymer molecule.¹

There are, however, apparently some other mechanisms by which charge carriers would be generated in polymers, according to reports of a high conductivity which arises spontaneously as the thickness of the polymer films decreases.² It has been suggested in several places^{3,4} that a high- T_c superconductivity occurs in such films.

The conditions under which the experiments yielding conclusions of this sort have been carried out and, in particular, the test samples (the thickness of the films has been less than 100 nm) have been such that it has not been possible to determine the topology of the conducting structure or the conditions under which it is formed. In the absence of this information, it is difficult to pursue the interpretation of the results.

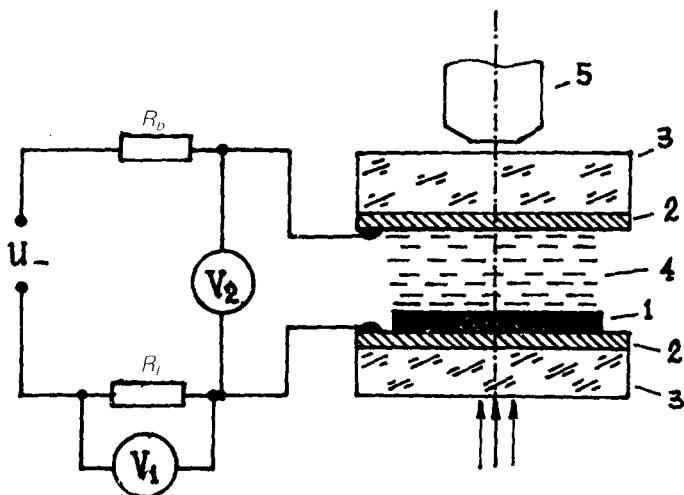


FIG. 1. Layout of the experimental cell and circuit for measuring the current-voltage characteristics. 1—Polymer film; 2—transparent conducting coating of SnO_2 ; 3—glass plates; 4—liquid crystal; 5—microscope; R_b —ballast resistance; R_l —load resistance [$R_b > R_l$ (sample) $> R_l$]; V_1 —meter which measures the voltage drop across R_l ; V_2 —meter which measures the voltage drop across the sample.

In this letter we are reporting a study of the topology of the conducting structure in polymer films and the dynamics of this topology in an electric field.

The problem was solved by the method of a "virtual" cathode, which in this case was a layer of a homeotropically oriented nematic liquid crystal, and by the technique of electronic switching. The idea underlying the experiment can be summarized by saying that as the potential at the surface of the polymer is varied a change should occur in the orientation of the molecules in the layer of liquid crystal (methoxybenzylidenebutylaniline) in contact with the polymer, as a result of, for example, a reorienting effect of the electric field.

The polymer used in the present experiment was polydiphenylenephthalide. We used R EM-200 and  EMMA-100 electron microscopes for quality control of the polymer film. The number of mechanical defects did not exceed two per square centimeter. For the measurements we used polarized-optics methods with an Amplival Pol U polarizing microscope. The experimental layout is shown in Fig. 1. The polymer film (1) is deposited from solution in a centrifuge on a glass plate with a transparent conducting coating of SnO_2 (2). The measurement cell contains two such plates (3), separated by a gap $\sim 20 \mu\text{m}$, which is filled with the liquid crystal (4). Figure 1 shows current-voltage characteristics recorded in this arrangement. In the case in which we measured the current-voltage characteristic of a polymer without the liquid crystal, the In upper electrode was deposited directly on the film. The field was applied in the direction perpendicular to the surface of the sample. Analysis of the current-voltage characteristics revealed that there is apparently a potential drop at the polymer-(liquid crystal) interface, as can be seen from the slight change in the slope of the current-

voltage characteristics upon a reversal of the voltage polarity, when the polymer is in a poorly conducting state. This circumstance is not reflected in the orientation behavior of the liquid crystal.

Polymer films less than 250 nm thick were synthesized as initially highly conducting films with a conductivity less than 10 S/cm. The observation of thin films by the technique described above, involving the nematic liquid crystal, revealed that the electrical conductivity is dominated by conducting channels surrounded by nonconducting polymer regions. This conclusion follows from the circumstance that the application of an electric field to the measurement cell results in the appearance of spherulites in the liquid crystal [Fig. 2(a)]. As the field is increased in the region where a channel emerges at the surface of the film, a local electrohydrodynamic instability occurs. We observe the convection of the liquid crystal which is characteristic of the regime of charge injection into the volume of a nematic liquid crystal [Fig. 2(b)]. The transition of the liquid crystal to an electrohydrodynamic instability confirms the conclusion

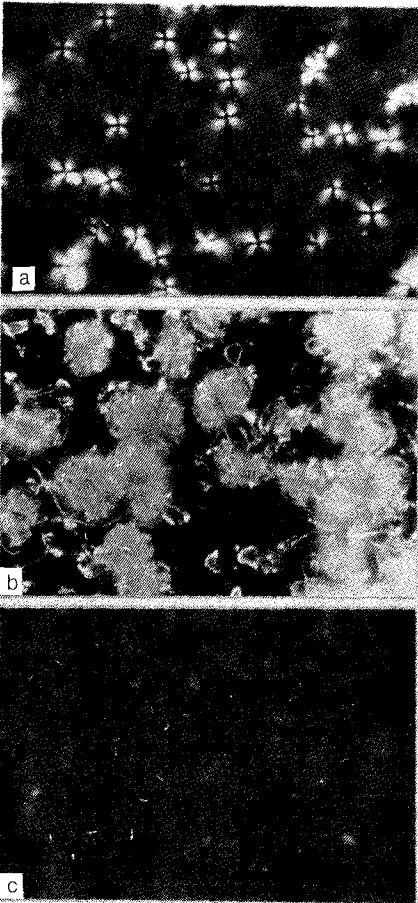


FIG. 2. Polarized-optics pattern of the layer of nematic liquid crystal after the application of an electric field. *a*—System of spherulites; *b*—pattern of dynamic scattering by liquid-crystal layer; *c*—form of liquid-crystal layer when the polymer is in a nonconducting state.

that spherulites arise and localize near the ends of current channels in the polymer film.

Conducting channels are known to be a consequence of a charge instability of the *S* type.⁵ It was accordingly suggested that the high conductivity is a consequence of an instability of this sort, and an attempt was made to arrange the charge instability in a polymer film and to visualize the process, step by step, with the help of a nematic liquid crystal. It was found that a film could be "switched" from a "highly conducting" state to a poorly conducting state by applying a constant voltage above a certain value to the film.

Figure 3 shows current-voltage characteristics of the polymer samples. On these curves we can distinguish a threshold voltage U_t above which there is a region of an *S*-type negative differential resistance, which cannot be controlled by the voltage. The inverse "switching" also occurs during the flow of a direct current. In principle, switching events of this type have been observed previously; it was stated in Ref. 6 that the number of switching cycles reached 1.5×10^5 .

Let us examine the process by which a switch to the conducting state is visualized. In the nonconducting state, the total resistance of the system consisting of the liquid crystal and the polymer is $R_0 \sim 10^{10} \Omega$, the resistance of the liquid crystal is $R_{LC} \sim 10^7 \Omega$, and the average conductivity over the area of the sample is $\sigma \sim 10^{-13} \text{ S/cm}$. Because of the high resistance of the polymer, $R_{\text{pol}} \gg R_{LC}$, essentially the entire voltage drops across the polymer, so no electrooptic effects occur. This situation is in

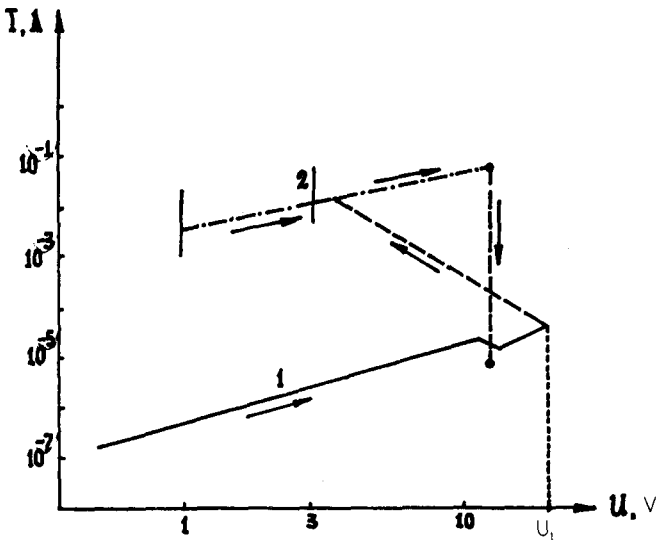


FIG. 3. Current-voltage characteristic of a thin polymer film. The arrows show the direction in which the voltage drop across the sample is changed. 1—Poorly conducting state; 2—conducting state. The vertical lines bound the region in which spherulites form in the nematic liquid crystal.

accordance with the dark visual field [Fig. 2(c)]. On the current-voltage characteristic, this state is illustrated by a region 1 in Fig. 3. When the threshold voltage U_t is reached (this voltage corresponds to a field $\sim 10^5$ V/cm), the film becomes conducting, and when the voltage is subsequently reduced (branch 2 of the current-voltage characteristic in Fig. 3, the liquid crystal passes in succession through the states shown in Fig. 2(b) and 2(a). In other words, after the switching a local electrohydrodynamic instability occurs and then gives way to a system of spherulites. The different dimensions of the spherulites and the different degrees of bleaching of the nematic liquid crystal near the current "filaments" are a consequence of differences in the conductivity of the conducting channels in the following film, which varies over the range 10^2 – 10^4 S/cm according to numerical estimates. The cross-sectional area of the channels is less than 10^{-10} cm².

The presence of highly conducting channels explains the large scatter⁷ in the values of the resistance measured by a microprobe on various parts of polymer films.⁷ A spontaneous appearance of highly conducting channels apparently stems from a structural instability of the samples. This instability may be associated with a condensation of impurities around certain or—apparently a more likely explanation—the presence of internal over stresses which lead to large local deformations, which are known to arise during the formation of films. In principle, processes of this sort were modeled in Ref. 8 in thicker films, which were subjected to uniaxial pressure. The properties of conducting channels of this sort are identical to those which arise as a result of electronic switching during an S-shaped instability.

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