Superconductivity at room temperature in oxidized polypropylene

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(Submitted 29 November 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, 56–61 (10 January 1990)

It is shown that the electrical conductivity of a narrow channel formed in thin films of oxidized polypropylene exceeds $10^{11}\ \Omega^{-1}\cdot\text{cm}^{-1}$ at 300 K and $10^{14}\ \Omega^{-1}\cdot\text{cm}^{-1}$ at 2 K. These estimates are limited only by the instrumental capabilities.

It was previously reported[1–3] that thin films of atactic polypropylene deposited on metal substrates and then subjected to oxidation and UV irradiation have a high conductivity and that they are possibly superconducting. The conductivity appeared under the action of an electric field and mechanical stress, which were directed at right angles to the plane of the oxidized polypropylene film (OPF). The average resistance of the samples, obtained by oxidizing polypropylene on copper substrates, was $\sim 1\ \Omega$. There was no relationship between the resistance R of the sample, thickness of the film, and area of the electrodes. In our experiments, which are described in Ref. 3, the film thickness ranged from 5 μm to 50 μm, and the area of the upper clamping electrode ranged from 4×10^{-6} to 4×10^{-2} cm^2. The absence of a corrleation between the magnitude of R and the geometry of the sample indicates that OPF as such is not a conducting material and that the current flows along a channel that runs through the film. The total resistance in this case is apparently concentrated in the contact regions.

The purpose of the present work was to measure the electrical conductivity of the channel being formed. To this end, we first worked out a special design of the sample that made it possible to incorporate two microprobes into a film 15–20 μm thick, and to carry out the conductivity measurements at room temperature using the four-probe method. Secondly plates of superconducting metal (tin) were used as electrodes in the other samples. The temperature dependence of the conductivity of these samples was measured to 1.2 K.

The sample used for the four-probe measurements was prepared as follows. A layer of atactic polypropylene 15–20 μm thick was deposited on a substrate of polished copper from a 10% solution in heptane. In the interior of the OPF layer were two platinum wires 1.9 μm in diameter, arranged in mutually perpendicular directions in planes parallel to the substrate and at respective distances of 5 μm and 10 μm from it. Thus the distance between the lower electrode and the lower probe, between the probes, and also between the upper probe and the free surface of the film amounted to 5 μm each. The samples were subjected to oxidation and bombarded with UV light, as described in Ref. 3. Both before and after the treatment, the absence of shorting between the probes and also between any of the probes and the substrate was checked. As the upper electrode we used an indium-faced steel needle, which was clamped against the OPF film with a pressure exceeding the yield point of indium (2 MPa). Under action of the clamping force, the indium facing was deformed, since indium is more pliable than OPF. As a result, the area of the upper electrode had a transverse size ~ 20 μm. The OPF film was also slightly deformed. The location of the clamping was chosen above the cross lines of the two microprobes. This point was checked visually under the microscope.

Between the upper electrode and substrate was applied a field of 1–10^3 V/cm, which was substantially lower than the breakdown field for polypropylene ($\sim 10^6$ V/cm). The current was limited by a ballast resistance, and the voltage drop was measured between all the electrode pairs. It should be noted that after the first electrode had been lowered onto the polymer layer, the current in the circuit appeared, not immediately, but after a few seconds.

When the current passed through the probes, all three voltmeters recorded a voltage drop. A negligible part (10^{-4}) of the total voltage drop was measured across the structure between the probes. For example, at a current of 10 mA, the total voltage drop was 10 mV, with 3 mV between the upper electrode and upper probe, 7 mV between the lower probe and substrate, and only 1–2 μV between the probes. Most of the voltage drop thus occurred near the contacts.

The temperature curves of the voltage between the probes were also recorded (Fig. 1). It is evident that as the temperature is lowered, the resistance decreases linearly, with a coefficient matching within 10% the temperature resistance coefficient of the probe material (platinum). During the heating, a typical situation is observed:

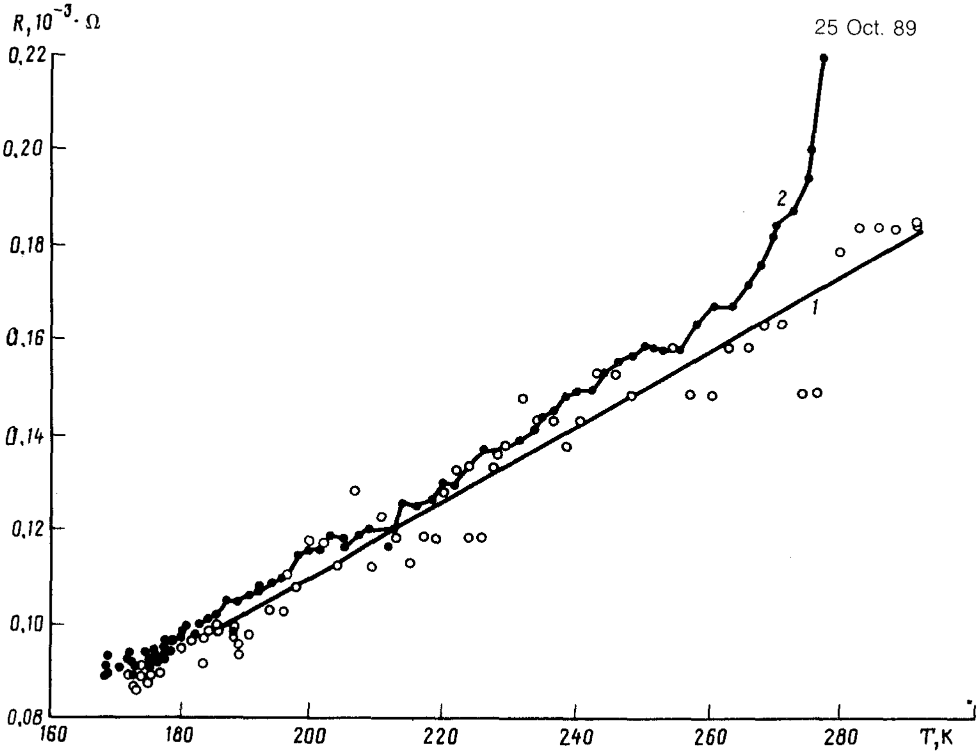

FIG. 1. Temperature dependence of the resistance of the interprobe gap of a sample with platinum probes. 1—Cooling; 1—heating.

Above the glass transition temperature of polypropylene (250 K) the resistance of the entire structure increases abruptly as does the voltage between the probes, which changes at 270 K to an avalanche-type transition to a dielectric state with $R > 10^9\ \Omega$. After holding at room temperature for several minutes, the conducting state was then restored.

The conducting state is also preserved when the structure is heated above room temperature (in our experiments, the samples were heated to 190 °C, since at higher temperature the solder of the joint holding the measuring wires would melt).

Thus the results of conductivity measurements by the four-probe method show that the conductivity of the OPF film takes place in a narrow channel, and almost the entire voltage drop is concentrated in the contact regions.

The concentration of the resistance near the contact may occur, for example, because of the presence of a potential barrier at the OPF-metal electrode boundary, which must be overcome by the above-the-barrier or tunnel method. Accordingly, the temperature dependence of the resistance should either be of an activation nature or there should be no temperature dependence at all, which would contradict the experimental data. Another possible cause of contact resistance is the spreading resistance which occurs when the flux lines enter the opening of the conducting channel. In this case the temperature dependence of the resistance of the structure should be determined by the temperature dependence of the resistivity ρ_m of the metal electrode, as has been observed experimentally.[3]

The spreading resistance in the case of a narrow channel between two massive electrodes is determined from the expression $R \approx \rho_m / d$, where d is the channel diameter. For the metals which we used, ρ_m at 300 K was less than $10^{-5}\ \Omega \cdot \mathrm{cm}$, and the resistance of the entire structure was of the order of $1\ \Omega$; hence, $d < 10^{-5}$ cm. This makes it possible to estimate the conductivity in the channel from the resistance of the interprobe gap, $10^{-4}\ \Omega$, and from the channel geometry: length $l \approx 5 \times 10^{-4}$ cm, and cross section $S < 10^{-10}\ \mathrm{cm}^2$. Hence, $\sigma > 5 \times 10^{10}$–$10^{11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which is more than five orders of magnitude above the conductivity of the best metals. Actually, the channel conductivity is even higher, since the residual resistance between the probes probably stems from the fact that the current travels a certain microscopic part of the path through the probe electrodes. This is also indicated by the temperature dependence of the interprobe resistance, which is consistent with the dependence of the resistivity of platinum (Fig. 1).

Another experiment was carried out with structures in which superconducting metals were used as the electrodes. In particular, tin ($T_c \approx 3.6$ K) was used. The

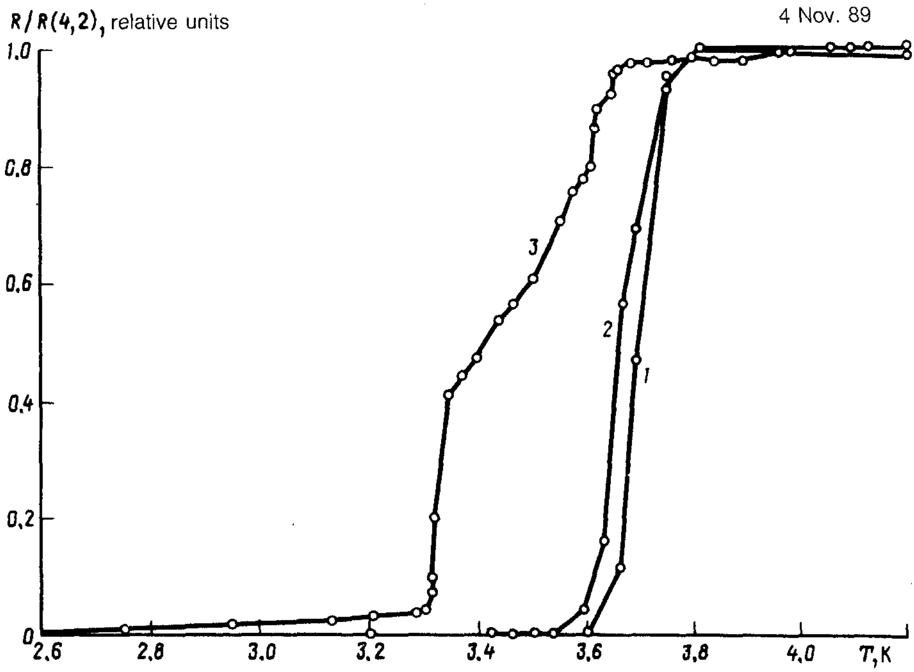

FIG. 2. Temperature dependence of the resistance of samples with a sandwich structure and tin electrodes. 1—With no OPF layer; 2, 3—with an OPF layer 20 μm thick. Current through the structure: 2—1 mA; 3—5 mA.

sample was made in the shape of a sandwich,[3] which precluded direct contact between two tin electrodes. The two halves of the structure, each of which consisted of a massive polished tin substrate with an OPF layer 10 μm thick, were connected by an insulating strip of Teflon or Dacron, 5–10 μm thick, to several holes 0.3 mm in diameter. Under slight compression, the polypropylene was pressed through these holes, shorting out the tin electrodes. The resistance of the structure at 300 K was 0.7 Ω. On cooling, the resistance decreased in accordance with the temperature dependence of the resistivity of tin, and at $T < T_c$ it dropped abruptly to the instrumental zero (Fig. 2). It is also apparent from the figure that the T_c of the system depends on the magnitude of the current: As the current passed through the structure is increased, T_c shifts down the temperature scale. This result becomes understandable if one considers that the contact between two superconducting tin electrodes is accomplished through a narrow channel, in which the current density is very high and can easily exceed the critical parameters for tin. At the point of entry of the narrow channel into the electrode, the superconductivity of tin can then be stopped even by small currents.

The results of the experiment make it possible to estimate the magnitude of channel conductivity in the OPF. It is evident from Fig. 3 that at the current $I = 100$ mA, the voltmeter recorded the instrumental zero, i.e., $U < 10^{-8}$ V. This means that the resistance of the structure is $R < 10^{-7}$ Ω, and for a certain geometry of the channel ($l = 20$ μm, $S = 10^{-10}$ cm^2), corresponds to a conductivity $\sigma > 10^{14}$ Ω^{-1} cm^{-1}, i.e., the connecting neck is essentially superconducting.

There is the danger that this superconducting neck may be the result of the

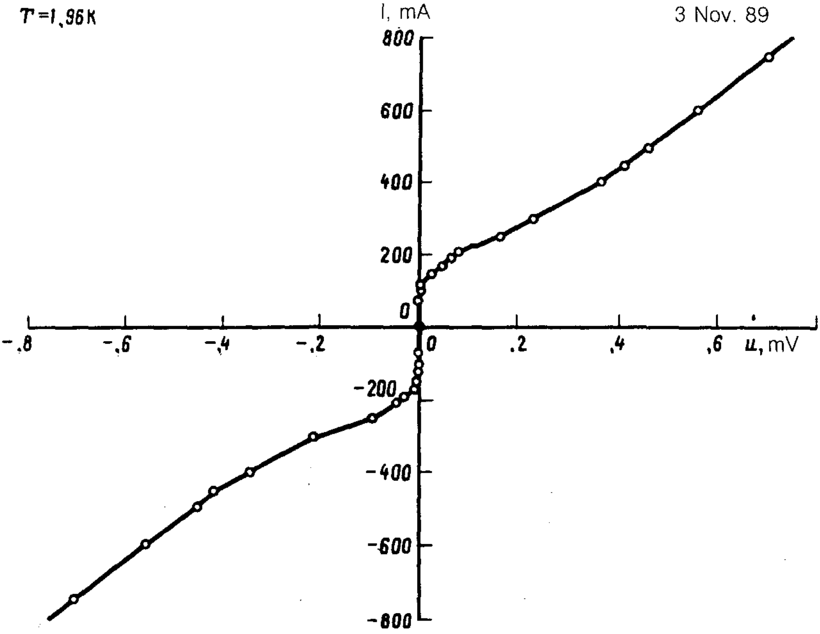

FIG. 3. The current-voltage characteristic of a sandwich-type sample at $T = 1.96$ K.

growth through the thin polymer film during the preparation of the structure (oxidation, UV irradiation) of a "wire" or even a dendrite-type branched structure of the electrode material, in this case, tin. This process could qualitatively account for the temperature dependence of the resistance R of the structure down to the lowest temperatures, including the transition to the superconducting state.

It can be shown that this hypothesis contradicts the fact that when currents up to 1–2 A were passed for a long time through a structure with $R = 1\ \Omega$ at room temperature, the value of R did not change, and only a slight heating of the electrodes was observed. In fact, if the electrodes are shorted by a connector of the same metal, the observed resistance R is that of the connector, in which the total Joule heating should occur. Since the thermal conductivity (λ) of polymers is three orders of magnitude lower than that of metals, the released power (1–4 W) should be dissipated through the end contacts of the connector. For any geometry of the connector (wire or pyramid with a point), the following simple relation should then exist between the thermal resistance R_T and electrical resistance R: $R_t = (R/\rho_m \lambda)$. For metals at 20 C we have $\lambda < 5$ W/cm °C; hence, $R_T > 2 \times 10^4$ °C/W; i.e., the release of 1 W will melt a connector of any material.

According to our interpretation, a channel in OPF at 300 K as 2 super-high conductivity, and R is the spreading resistance which is concentrated in the massive electrode. This circumstance accounts for the fact that current can be passed through the structure for a long time.

Thus the model of a metallic connector made of the electrode material is unsound. We thus conclude that the channel being formed, which is superconducting in the entire range of temperatures from liquid-helium temperature to $+190$ °C, is directly connected to the polymer.

The criterion of superconductivity is, as we know, the combination of zero resistance and absolute diamagnetism. However, OPF is not a homogeneous superconducting material; this material forms only under certain conditions narrow channels with superhigh conductivity and with a diameter that does not exceed the depth of the skin layer in ordinary superconductors ($< 10^{-5}$ cm). The Meissner effect in such systems is obviously difficult, if possible at all, to observe. The superhigh conductivity detected in oxidized polypropylene may thus be regarded as a kind of superconductivity.

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[3] V. M. Arkhangorodskii *et al.*, Dokl. Akad. Nauk SSSR **309**, 603 (1989) [Sov. Phys. Dokl. **34**, 252 (1989)].

Translated by A. Peiperl