

# Possible superconductivity near 300 K in oxidized polypropylene

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As the temperature of oxidized polypropylene films is varied near 300 K, their resistance changes abruptly, by nine orders of magnitude. The resistance drops to the zero of the measuring instrument. The films also exhibit an anomalously strong diamagnetism, which can be destroyed by a magnetic field.

A quarter of a century ago, Little<sup>1</sup> predicted a superconductivity with  $T_c \sim 10^3$  K for macromolecules with a polyconjugated chain and highly polarizable side groups, but that superconductivity has not been realized. Our results show that the problem of high-temperature superconductivity of polymers can apparently be solved in a different class of macromolecules: weakly polar rubbers without polyconjugation in the main chain. A member of this class is oxidized atactic polypropylene, which we have studied.

Polypropylene films 0.3–100  $\mu\text{m}$  thick, deposited from solution on a copper or indium substrate, are good insulators before oxidation and have a slight diamagnetic susceptibility,  $\kappa \sim -10^{-6}$  (cgs unit). Samples of a first type (PP-1) were synthesized from polypropylene which had been oxidized in air for 3 yr at room temperature and in which about 10% of the functional groups were oxidized. The measurements of  $\kappa$  were carried out at 293 K by the Faraday method on a highly sensitive magnetic balance.<sup>2</sup> The local conductivity of the films was measured by the method of Ref. 3, by pressing an indium microelectrode against the film with an adjustable force  $\sim 1$  dyn and a maximum pressure of 3 MPa. This approach resulted in reliable contact over an area of 3–5  $\mu\text{m}^2$  and also prevented possible mechanical damage to the polymer (piercing). For films greater than 10  $\mu\text{m}$  thick, we also checked for a possible short-circuiting of the electrode to the substrate by observation through a microscope directly during the electrical measurements. The low voltage on the electrode,  $U \leq kT/e$ , ruled out dielectric breakdown. The contact resistance of the microelectrode,  $R_c \approx 1 \Omega$  (Fig. 1), was measured by a similar method, involving pressing an electrode against a part of the substrate free of the polymer.

In a PP-1 sample 0.3  $\mu\text{m}$  thick we observed a local conductivity: When we select points at random at which to press the electrode against the film, about 60% of the measurements yielded a resistance of less than  $10^5 \Omega$ , while the other  $\sim 40\%$  revealed essentially no conductivity (the resistance was more than  $10^9 \Omega$ ). A point which attracted interest was that the distribution of the conducting points with respect to the resistance at 293 K (Fig. 1) consists of two distinct groups, in one of which the average resistance is the same as  $R_c$ ; i.e., at these points the intrinsic resistance of the polymer is at the level of the zero of the measuring instrument.

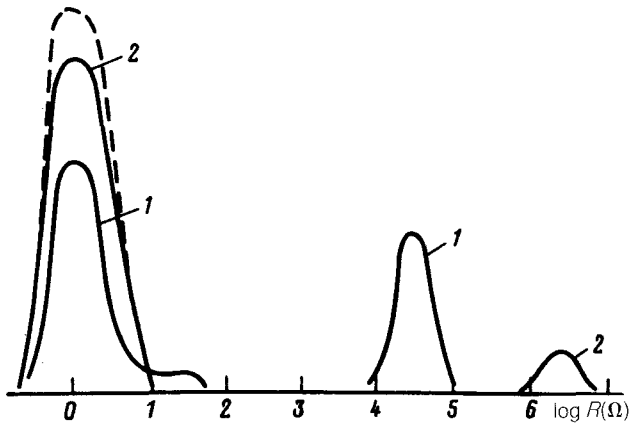


FIG. 1. Distribution of the logarithm of the resistance of the conducting regions in oxidized polypropylene of two thicknesses. 1— $0.3 \mu\text{m}$ ; 2— $50 \mu\text{m}$ . The dashed line is the distribution in the case in which the microprobe is in contact with the clean substrate. All the measurements were taken at 293 K.

As the thickness of the PP-1 films is increased, the relative number of conducting regions falls off sharply; at a film thickness of  $4\text{--}5 \mu\text{m}$  a significant electrical conductivity is observed only when the electrode area is increased to  $S \approx 0.1 \text{ cm}^2$ . A film of this type, between pieces of soft indium foil (at a clamping pressure of  $0.1 \text{ MPa}$ ), has a resistance  $\approx 0.3 \text{ G}\Omega$  at 293 K. Cooling the film rapidly from 293 K to 77 K (curve 1 in Fig. 2) causes simply a slight change in the resistance of the film, in the region 250–

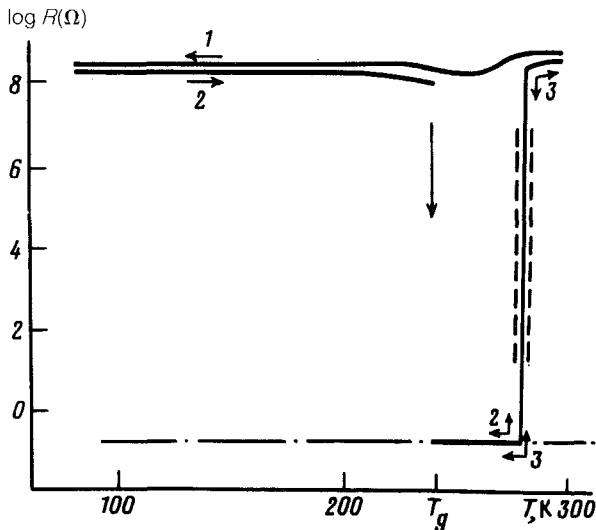


FIG. 2. Temperature dependence of the resistance of a PP-1 film  $4\text{--}5 \mu\text{m}$  thick between pieces of indium foil with an area of  $0.1 \text{ cm}^2$  at a clamping pressure of  $0.1 \text{ MPa}$ . 1—Cooling at a rate of  $1 \text{ K/s}$ ; 2—heating at a rate of  $1 \text{ K/min}$ ; 3—cyclic cooling and heating over the interval  $240\text{--}293 \text{ K}$  at a rate of  $1 \text{ K/min}$ . The dashed lines show the temperature interval in which the abrupt changes in the resistance are observed during the cyclic temperature changes. The dot-dashed line is the zero of the measuring instrument ( $0.1 \Omega$ ). The arrows near the curves show the directions in which the temperature and the resistance changed.

280 K. During a subsequent slow heating (curve 2 in Fig. 2) the resistance initially falls off smoothly, but in the vicinity of the glass transition temperature ( $T_g \approx 240$  K) it falls abruptly to the zero of the measuring instrument and remains there up to 280 K, where it abruptly returns to  $\sim 10^8 \Omega$ .

If the cooling from 293 K is instead carried out slowly (1 K/min), the abrupt decrease in the resistance to zero occurs near 280 K, and from that point on the resistance remains the same down to 77 K. If the temperature is varied slowly, the transition near 280 K is completely reversible; we observe it an unlimited number of times as we scan over the interval 293–240 K (curve 3 in Fig. 2). The reproducibility of the transition temperature is  $\pm 3$  K. We were not able to measure the width of the transition, since the abrupt change in the resistance occurs in a time of less than 1 s.

Since the results of the measurements of the electrical properties of PP-1 indicate a possible superconductivity near room temperature, we are very interested in the magnetic properties of this polymer. For the PP-1 samples, the curve of  $\kappa(B)$  at 293 K is a typical ferromagnetic curve with saturation at  $B = 0.05$ – $0.1$  T, both for the electrically conducting thin films and for large pieces of the polymer (1–2 mm) which did not exhibit a high conductivity. Repeated measurements taken from the same samples over a period of several months showed that the values of  $\kappa$  for all of the samples fluctuate markedly in time (over the range  $5 \times 10^{-5}$ – $5 \times 10^{-4}$ ). At 293 K, we repeatedly observed a spontaneous transition of these samples to an anomalously strong diamagnetic state with  $\kappa \sim -10^{-4}$ , which is unstable and which undergoes an equally spontaneous transition to a ferromagnetic state. The impression one gets is that the PP-1 samples the critical temperature can fluctuate around 300 K, rising slightly above room temperature at certain times and falling slightly below it at others.

Since a further, and close, study of the effect which we discovered would have been held up by the slow procedure of spontaneous oxidation of the polypropylene at room temperature, we developed an accelerated procedure,<sup>2</sup> in which the samples (PP-2) were synthesized as films of unoxidized polypropylene and then heated in air and exposed to UV light. We found as a result that both the electrical and magnetic properties characteristic of the PP-1 films were also exhibited by the PP-2 films and were substantially more obvious in the latter case. For example, the local electrical conductivity of PP-2 can easily be found with a small-area microprobe, even at film thicknesses up to 100  $\mu\text{m}$ . A significant increase in the film thickness does not alter the resistance of the points falling in the low-resistance group, which remains equal to  $R_c$  (curve 2 in Fig. 1). This result agrees with the suggestion that these points are in a superconducting state at 293 K. The resistance of the points in the high-resistance group, on the other hand, increases significantly, roughly in proportional to the film thickness, indicating that these points have a normal conductivity.

Since the resistance of the PP-2 films corresponds to the zero of the measuring instrument even at room temperature, there is no abrupt change in the resistance as they are cooled, and the resistance itself corresponds to  $R_c$  down to liquid-helium temperatures. (We are deeply indebted to N. B. Brandt and Ya. G. Ponomarev for carrying out the low-temperature measurements of the electrical properties of the PP-2 films which we synthesized.) When PP-2 is cooled below  $T_g$ , the measured resistance becomes stable (over time), while at  $T > T_g$  it can fluctuate by a factor of a few units

(similar fluctuations have been observed previously<sup>4</sup> in ultrathin films of isotactic polypropylene).

The magnetic properties of PP-2 change in the course of the oxidation (Fig. 3). For most of the samples (~90% of them) which reach a highly conducting state, these changes in magnetic properties stop in a stage of anomalous ferromagnetism.<sup>5</sup> For ~10% of the samples, on the other hand, the evolution of the magnetic properties continues, and the films go into an anomalously strong diamagnetic state which is stable at room temperature. Distinguishing features of this state are not only a strong dependence  $\kappa(B)$ , with values reaching  $\kappa = -3 \times 10^{-4}$  in weak fields, but also an abrupt destruction of the diamagnetism at  $B > B_{cr}$ , accompanied by a transition of the sample to a ferromagnetic state. In a zero magnetic field the destroyed diamagnetism is usually restored over a time which ranges from tens of seconds to several days for the various samples. This situation is characteristic of the spectrum of relaxation times of polymers. We can therefore suggest that the changes in the magnetic properties are somehow related to a restructuring of the polymer matrix.

Combined with the zero resistance, this anomalously strong diamagnetism of PP-2, which can be destroyed by a magnetic field, indicates the possibility of superconductivity at room temperature.

Our results show that the conductivity of the oxidized polypropylene is electronic, rather than ionic. Evidence for this conclusion comes from the fact that the resistance remains constant as a current of 20 mA is passed through the microelectrode for many hours. Further evidence for this conclusion is that the highly conducting state persists when the sample is cooled to liquid-helium temperatures.

If the effect which has been discovered here is indeed superconductivity, we have

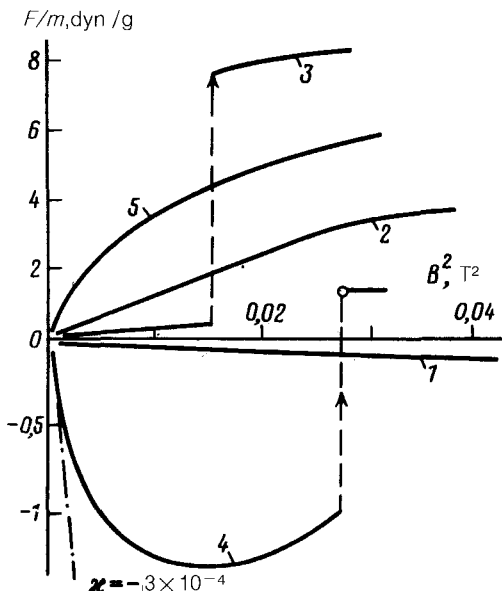


FIG. 3. Force per unit mass of the interaction of the PP-2 samples with the magnetic field of the balance, during various stages of the oxidation of the polypropylene. 1—Initial state; 2—weak ferromagnetism; 3—anomalous ferromagnetism<sup>5</sup>; 4—anomalous diamagnetism which can be destroyed by a magnetic field; 5—typical behavior after the destruction of diamagnetism of the samples for which the restoration of the diamagnetism in a zero field takes a day or more. All the measurements were taken at 293 K.

not yet been able to accurately determine the critical parameters: the critical temperature and the critical current. We can, on the other hand, estimate some lower limits on these parameters. For example, in measurements in which we use an indium microelectrode the highly conducting state of thick PP-2 films persists until, at a current of 0.5 A, the sharp tip of the electrode—in contact with the polymer and at the same temperature—melts. It can thus be concluded that for PP-2 the critical temperature is at any rate no longer than the melting point of indium, i.e., 429 K.

In experiments in which the indium electrode was replaced by an extremely sharp copper needle (the diameter of the contact with the surface of the PP-2 film was  $\approx 10 \mu\text{m}$ , and the film thickness was about  $100 \mu\text{m}$ ), we were able to raise the current through the film to 2–3 A, at which point the copper conductor, 0.06–0.1 mm in diameter, supplying current to the needle melted. Even a microscopic analysis revealed no indication of damage to the polymer at the point at which it made contact with the needle. Since atactic polypropylene, like most polymers, is thermally unstable to an extreme degree, these results show that even at  $j \gtrsim 3 \times 10^6 \text{ A/cm}^2$  there is essentially no heat evolution in the polymer. This result is further support for the suggestion that these films are in a superconducting state.

For samples with a stable diamagnetism which have been stored in air for more than a year, no significant changes have been observed in electrical or magnetic properties.

<sup>1</sup>W. A. Little, *Phys. Rev.* **134**, A1416 (1964).

<sup>2</sup>L. N. Grigorov and S. G. Smirnova, Deposited article No. 2381-V 88, All-Union Institute for Scientific and Technological Information, 1988, p. 45.

<sup>3</sup>N. S. Enikolopyan, S. G. Gruzdeva (Smirnova), N. M. Galashina, *et al.*, *Dokl. Akad. Nauk SSSR* **283**, 1404 (1985).

<sup>4</sup>S. G. Smirnova, L. N. Grigorov, N. M. Galashina, and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR* **288**, 176 (1986).

<sup>5</sup>S. G. Smirnova, O. V. Demicheva, and L. N. Grigorov, *Pis'ma Zh. Eksp. Teor. Fiz.* **48**, 212 (1988) [*JETP Lett.* **48**, 231 (1988)].

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