

## **Anomalous ferromagnetism of oxidized polypropylene**

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The synthesis of an organic polymer ferromagnet on the basis of oxidized atactic polypropylene is reported. A fundamentally new phenomenon has been discovered: an abrupt transition of the material from a paramagnetic state to a ferromagnetic state, induced by a magnetic field.

In an analysis of the possible existence of a purely organic ferromagnet, Ovchinnikov<sup>1</sup> suggested a principle for the synthesis of polymer semiradicals with a spin proportional to the number of units in the polymer. This principle has been confirmed by the synthesis of a polymer ferromagnet with an electrically conducting polydiacetylene

chain and stable nitroxyl radicals as side substitutes.<sup>2</sup> It is believed that the ferromagnetism in such a structure stems from an ordering of the spin magnetic moments of the side groups.

To what extent this principle is a natural one for organic ferromagnets is not clear, however. Since it is obvious that a ferromagnetism would be impossible without a collective interaction of electrons, potential places to look for ferromagnets of a fundamentally different structure are polymers which exhibit any hint of a delocalization of at least some of the electrons. Of interest in this regard is polypropylene, thin films of which have exhibited an anomalously high local *n*-type conductivity,<sup>3,4</sup> which indicates the formation of domains with a high density of free electrons in the polymer. It was shown theoretically in Ref. 5 that the formation of such domains should be favored from the thermodynamic standpoint for slightly polar polymers in a highly elastic state—the state of polypropylene at room temperature. Since after its synthesis the original polypropylene is a nonpolar saturated hydrocarbon (i.e., should be an insulator and a weak diamagnet), it must be rendered polar in order to induce electrically conducting (and potentially magnetically active) domains. It can be rendered polar by oxidation.

In the present study we have accordingly examined the changes in the magnetic properties of polypropylene which result from its oxidation during heating and UV illumination in air.

The magnetic susceptibility  $\kappa$  is measured at room temperature by the Faraday method, by measuring the force which acts on a sample as a nonuniform magnetic field  $B$  is turned on and off. For the force measurements, we use a highly sensitive balance with<sup>6</sup>  $\text{grad}B \sim B$ . The induction  $B$  ranged from 0.01 to 0.2 T; the time constant of the balance was  $\approx 3$  s. The samples were films of easily oxidized atactic polypropylene with a thickness of 20–200  $\mu\text{m}$  and a weight of 1–10 mg, which were deposited from a heptane solution onto a nonmagnetic substrate made of copper foil.

In the original, unoxidized state, the samples exhibited a weak diamagnetism with  $\kappa \approx -10^{-6}$  cgs over the entire range of  $B$ . After a first oxidation, heating the samples in air (for 2–3 h at 370 K) converted the polypropylene into a weak paramagnet with  $\kappa \approx 10^{-6}$ . The magnetization of these samples satisfied  $J \sim B$  over the entire range of  $B$ . With a further oxidation in air for 1–2 h, exposure to unfiltered UV light from a DRK-120 lamp caused  $\kappa$  to increase to  $10^{-5}$ , while the plot of  $J(B)$  acquired the saturation characteristic of ferromagnets at  $B_0 \approx 0.16$  T (Fig. 1). An additional UV illumination in air for 4–6 h resulted in a decrease in  $\kappa$  in fields  $B < 0.01$ –0.1 T, to values of  $10^{-6}$ – $10^{-7}$ , indicating a paramagnetic state of the polypropylene. When the critical field  $B_{\text{cr}} = 0.12$ –0.2 T was reached, however, there was an abrupt increase in  $J$ , which the balance detected as an abrupt increase in the force acting on the sample. This jump, which occurred in a constant field, corresponded to an increase in  $\kappa$  by two or three orders of magnitude, to  $\kappa \sim 10^{-4}$ . With a further increase in the field, there was essentially no increase in  $J$ ; this result, combined with the high value of  $\kappa$ , indicates a transition of the polypropylene to a ferromagnetic state.

When the measurements of the dependence  $J(B)$  of a given sample are repeated many times, the critical field  $B_{\text{cr}}$  varies from measurement to measurement in a fluctu-

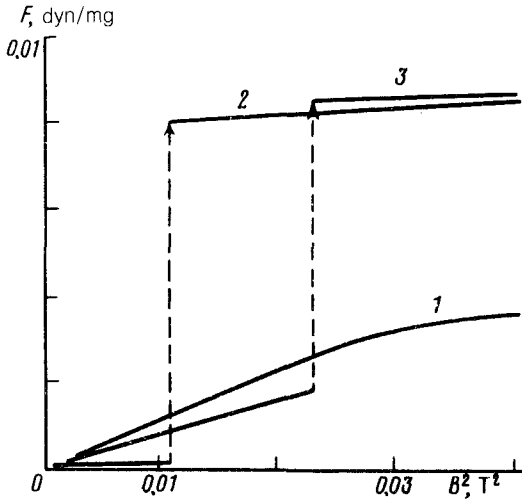


FIG. 1. The force (per unit mass) of the interaction of a sample with a nonuniform magnetic field versus the square of the magnetic induction. 1—after heating and UV illumination for 1–2 h; 2 and 3—after an additional UV illumination for 4–6 h (for various samples).

ating way, remaining in the interval 0.12–0.2 T. The values of  $B_{cr}$  found for the various samples fall in the same interval. The time evolution  $J(t)$  in a constant field  $B$  (Fig. 2) may differ slightly from sample to sample and also when measurements are repeated on the same sample, although the general behavior remains the same in all cases. It is interesting to note the example of a two-stage time evolution, which proves that the change in  $J$  is actually abrupt.

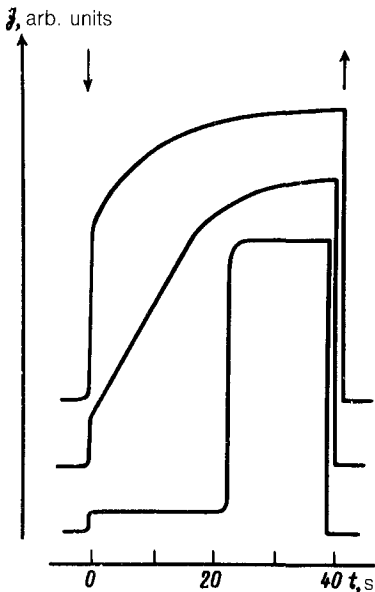


FIG. 2. Time evolution of the abrupt change in the magnetization in a static field  $B > B_{cr} = 0.12\text{--}0.2$  T. The arrows indicate the times at which the magnetic field is applied and removed.

The nature of the anomalous ferromagnetism which has been observed is not yet clear. However, if one assumes that the ferromagnetic domains in the polypropylene are not interacting with each other, one can estimate the average number of magnetically ordered electrons in a single domain  $n$ , from the field  $B_0$  at which  $J$  reaches saturation:

$$n \approx kT / \mu_B B_0 \quad ,$$

where  $\mu_B$  is the Bohr magneton, and  $kT = 4 \times 10^{-14}$  erg. An estimate for the initial stage of the appearance of a ferromagnetism (line 1 in Fig. 1) yields  $n = 3 \times 10^3$ ; combining this figure with the value  $\kappa = 10^{-5}$ , we find an average domain density  $\sim 3 \times 10^{14} \text{ cm}^{-3}$ . It can be seen from lines 2 and 3 in Fig. 1 that in the state corresponding to an abrupt transition to a ferromagnetic state we have  $B_0 \ll B_{cr}$ , i.e.,  $n \gg 5 \times 10^{-3}$ . The density of domains is  $\sim 2 \times 10^{15} \text{ cm}^{-3}$ . This result shows that the oxidation of polypropylene is accompanied by an enlargement of individual domains and also an increase in their density.

In conclusion we should point out that the magnetic-field-induced abrupt transition of oxidized atactic polypropylene from a paramagnetic state to a ferromagnetic state has no analogs among known ferromagnets. This fundamentally new behavior, which is manifested only as a result of a modification of the structure of the polymer by oxygen, provides convincing proof that the ferromagnetism of oxidized polypropylene is not a consequence of some foreign impurity but a property of the polymer itself.

<sup>1</sup>A. A. Ovchinnikov, Dokl. Akad. Nauk SSSR **236**, 928 (1977) (Sic.).

<sup>2</sup>Yu. V. Korshak, A. A. Ovchinnikov, A. M. Shapiro *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 309 (1986) [JETP Lett. **43**, 399 (1986)].

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

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

<sup>5</sup>L. N. Grigorov and V. M. Andreev, Vysokomol. Soedin **B30**, 589 (1988).

<sup>6</sup>L. N. Grigorov and S. G. Smirnova, Deposited Article No. 2381-V88, All-Union Institute of Scientific and Technological Information, 28 March 1988.

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