Organic polymer ferromagnet

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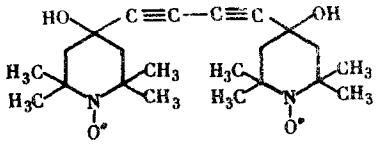
A purely organic polymer ferromagnet based on polydiacetylene has been synthesized. The Curie temperature (150–190 °C) and the magnetization of a powdered sample have been measured. Ferromagnetic particles with a remanent magnetization above 1 G have been obtained from the polymer material by separation in the field of a permanent magnet.

Many low-dimensionality organic substances having semiconducting, metallic, and superconducting properties have now been synthesized and studied. The possibility of synthesizing purely organic ferromagnets was raised in Ref. 1, and a principle was proposed for constructing polymer polyradicals having a ground-state spin proportional to the number of monomers in the polymer. The question of the organization of such molecules into a three-dimensional object having a spontaneous magnetization was discussed in Ref. 2. Note should also be taken of several attempts to synthesize organic ferromagnets from single crystals of stable radicals.[3–6]

In the present letter we report a study of the properties of an organic polymer ferromagnet.

The first step in the synthesis is the production of stable nitroxyl biradicals on the basis of diacetylenes with the chemical structure[7]



T_m = 145° C

	Calculated	Found
% C	67.66	67.30
% H	8.77	9.02
% N	7.17	7.16

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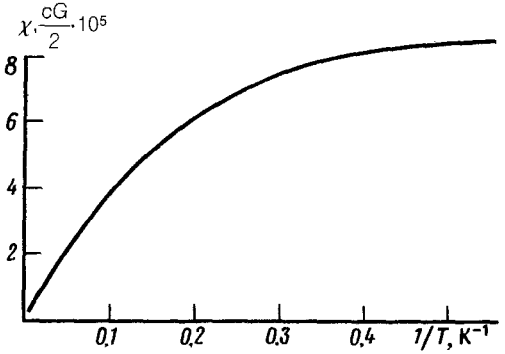

FIG. 1. Temperature dependence of the magnetic susceptibility of BIPO.

[1,4-bis-(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxyl)-butadiene (BIPO)].

The resulting diacetylene forms good single crystals, which undergo polymerization when illuminated or at elevated temperatures (80–100 °C), converting into single-crystal and polycrystalline polymers. We will skip over the purely chemical problems here, simply noting that this program was carried out. We produced both monomer and polymer polycrystalline samples. The latter have a spontaneous magnetization.

Atomic-absorption analysis of the polydiacetylene samples revealed no transition metals (Fe, Ni, Co). The sensitivity of the analysis method for these elements was $1.5\times10^{-3}\%$.

The initial monomer is a red powder with 1.2×10^{21} spins/cm^3. Figure 1 shows the magnetic susceptibility as a function of the temperature. The behavior is described well by

$$\chi_M(T) = \frac{C}{T+\Theta_a}, \qquad (1)$$

where $C = 7.7\times10^{-4}$ deg·cm^3/g and $\Theta_a \approx 2$ K. The susceptibility thus corresponds to an antiferromagnetic behavior of the sample with a Néel temperature near 1 K. The measurements were carried out on a Faraday balance from a temperature of 1.7 K.

During the polymerization of a sample by illumination, the sample converts into a black powder. We recorded magnetization curves of these polymer samples over a broad temperature range. Figure 2 shows curves of the magnetization at temperatures of 1.7, 4.2, 25, and 90 K; the diamagnetic component has been subtracted from the magnetic moment of the sample at 25 K and 90 K. At low temperatures (1.7 K and 4.2 K) the paramagnetic component is extremely large, corresponding to 0.5×10^{19} spins/cm^3. Consequently, curves 3 and 4, which have the shape typical of ferromagnets, are quite representative of the measurements of the spontaneous magnetization. The spontaneous magnetization is $I_s = 0.022$ G. The theoretical value of this magnetization reaches I_s(theo) = 24 G. This sample thus exhibits only 0.1% of the theoretical magnetization. This result implies that only an insignificant fraction of the crystallites have ferromagnetic properties. The magnetization varies markedly from one sample to

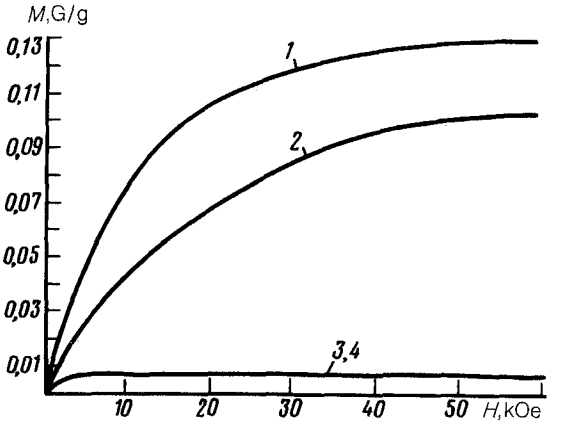

FIG. 2. Magnetization of polyBIPO versus the magnetic field at various temperatures: 1—1.7; 2—4.2; 3—25; 4—90 K.

another, because of the poorly controllable crystallite growth conditions during the polymerization. However, magnetic separation made it possible to obtain particles with a magnetization above 1 G, which respond noticeably to the field of a permanent magnet.

In the ESR spectra ($\nu = 3$ cm), there are two broad peaks, at $H_1 = 1800$ and $H_2 = 5000$ Oe, which are reproducible quite well in the different samples. This behavior corresponds to a ferromagnetic resonance in an easy-axis ferromagnet with an anisotropy field $H_A \sim 2400$ Oe. We should point out that in analyzing the curves (Fig. 3) we ignored demagnetizing factors and the porosity of the sample. The field $H_A \sim 2400$ Oe corresponds well to zero fields in stable organic biradicals or in organic molecules in a triplet state.[8] The polydiacetylene samples have a strong magnetic anisotropy (cf. curves 1 and 2 in Fig. 3).

Measurements of the magnetization with a vibration magnetometer with a field of 0.04 T at temperatures from 0 to 200 °C showed that the magnetization disappears at temperatures in the interval 150–190 °C. The Curie temperature is thus[1)] $T_C = 420$–460 K. A temperature of the same order of magnitude could be found by noting that

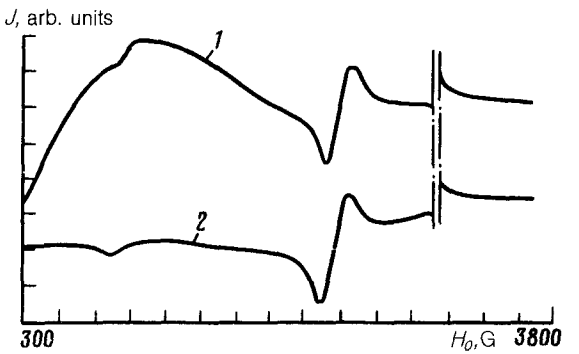

FIG. 3. ESR spectra of polyBIPO in two arrangements. 1—Parallel to the field; 2—perpendicular to the field.

we are dealing with quasi-one-dimensional, highly anisotropic Heisenberg ferromagnet. The scale value of the transverse exchange integrals can be found from the value of Θ_a for the monomer ($J_\perp \sim 2$ K). The exchange integrals along a chain are $J_\parallel \sim 1$ eV. In the spin-wave approximation we would have

$$T_c \sim 2\sqrt{J_\perp J_\parallel} \sim 280 \text{ K}. \tag{2}$$

These values are of course offered as order-of-magnitude estimates.

We obtained a diffraction pattern of a polymer sample, finding that the material is characterized by the absence of a long-range order and by a high packing anisotropy ($S'_{h/2}:S''_{h/2} = 0.3$).

In summary, the polydiacetylene crystal—polyBIPO—is a quasi-one-dimensional organic easy-axis ferromagnet with a Curie temperature in the region 420–460 K.

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[1)]In some of the samples, the magnetization persists up to 515 K.

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