ON THE MAGNETIC PROPERTIES OF FERROCENE POLYMERS

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ON THE MAGNETIC PROPERTIES OF FERROCENE POLYMERS

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In papers ([1,2]) it was found that, in polymeric compounds obtained from diamagnetic ferrocene, signals of electron paramagnetic resonance and a positive static magnetic susceptibility were observed. It turned out that polyethanopolyferrocenes, in which the ferrocene molecules are joined to one another through CH_2 groups, give narrow e.p.r. lines and possess comparatively small paramagnetism, whereas linear polyferrocenylene, in which the ferrocene molecules are linked directly to one another, gives broad e.p.r. lines and has a large positive static susceptibility.

Detailed measurements of the magnetic susceptibility of these two classes of ferrocene polymers, carried out by us on the same specimens as were used in papers ([1,2]), in the temperature range from 295° to 1.35°K and in the field range from 0 to 13 kOe, showed that in specimens of polyethanopolyferrocene with different molecular weight, i.e., with different numbers of units in the polymer molecule, the magnetic moment is proportional to the field and the paramagnetic susceptibility in the indicated temperature range obeys the Curie law, whereas in specimens of linear polyferrocenylene the magnetic moment depends nonlinearly on the field, indicating the presence of ferromagnetism. It also turned out that the number of unpaired spins per gram of substance, which was calculated in the first case from the measured value of the susceptibility and in the second from the magnitude of the saturation moment, agrees neither with the number of polymer molecules nor with the number of units in each molecule.

There therefore arose the supposition that the observed effects are connected with the possible presence of some magnetic impurities, especially since a study of nuclear magnetic resonance in these substances showed us that the proton lines do not undergo noticeable paramagnetic shifts. A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova pointed out to us that, in the synthesis of ferrocene polymers, the final product was analytically pure, but that no special measures were taken to purify it from magnetic impurities, and they proposed carrying out repeated measurements on specially purified specimens. The specimens of polyethanopolyferrocene were purified by them by repeated reprecipitation from freshly distilled absolute ether into absolute methyl alcohol, the entire purification being carried out in glassware that had previously been etched with nitric acid. On the other hand, A. N. Nesmeyanov, V. A.

Sazonova, N. V. Drozd, and others ([3]) carried out the synthesis of linear and polyferrocenylene by the Ullmann reaction, undertaking a thorough purification of the final product. Purified specimens of polyethanopolyferrocene with molecular weight 1000, i.e., with approximately five units in the polymer molecule, and of linear polyferrocenylene with a number of units in the molecule greater than three were kindly placed at our disposal, and we measured their magnetic susceptibility in the same range of temperatures and fields.

The results of measurements of the temperature dependence of the specific susceptibility of two specimens of polyethanopolyferrocene with molecular weight 1000, the original specimen and the specimen subjected to special purification, are given in Fig. 1. In contrast to the original specimen, the specially purified specimen

at room temperature is diamagnetic, and its specific susceptibility is $\chi = -0.75 \pm 0.1 \cdot 10^{-6}$. Let us note that the specific susceptibility of the monomer

[Fig. 1 and Fig. 2 graphs]

Fig. 1. Temperature dependence of the specific susceptibility. Polyethanopolyferrocene, molecular weight 1000. *a*—initial sample, *b*—specially purified sample

Fig. 2. Dependence of the magnetic moment on the field at $T = 4.2^\circ$ K. Linear polyferrocene. *a*—initial sample, *b*—specially purified sample

ferrocene at room temperature, according to our measurements, is $-0.55 \pm 0.05 \cdot 10^{-6}$, so that upon polymerization the diamagnetic susceptibility not only does not decrease, but even increases somewhat. At a temperature of 77°K the specially purified sample remains diamagnetic, and only at the temperature of liquid helium does it become slightly paramagnetic; moreover, its specific susceptibility proves to be approximately 40 times smaller than the susceptibility of the initial analytically pure sample.

The same practically complete absence of paramagnetism was found in a sample of linear polyferrocenylene with more than three units in the molecule, synthesized by A. N. Nesmeyanov, V. P. Sazonova, V. N. Drozd, and others. At room temperature this sample is diamagnetic with $\chi = -0.5 \pm 0.2 \cdot 10^{-6}$ and becomes slightly paramagnetic only at helium temperatures. In Fig. 2 we give, for illustration, the results of measurements of the dependence of the magnetic moment on the field at a temperature of 4.2°K in this sample and in the sample used in works ([1,2]). The magnetic moments of these samples differ from each other by approximately a factor of one hundred, so that it is difficult to depict them together on one graph.

Thus, it may be regarded as established that the anomalous magnetic properties of ferrocene polymers found in works ([1,2]) were entirely due to the presence of paramagnetic or ferromagnetic impurities*. The small paramagnetism observed in specially purified samples at helium temperatures is apparently also due in origin to the presence of a very small amount of magnetic impurities.

In conclusion, we express our deep gratitude to P. L. Kapitsa for his constant attention to the work and his support, to A. N. Nesmeyanov, V. A. Sazonova, N. S. Kochetkova, R. B. Materikova, and V. N. Drozd for providing samples and for useful discussions, and also to V. M. Chibrikin and A. S. Borovik-Romanov for useful discussions.

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1. A. N. Nesmeyanov, V. O. Korshak et al., *DAN*, **137**, 1370 (1961).
2. A. N. Nesmeyanov, A. M. Rubinshtein et al., *DAN*, **138**, 125 (1961).
3. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, V. I. Romanenko, A. K. Prokof' ev, L. A. Nikonova, *Izv. AN SSSR, OKhN* (in press).

* As N. M. Bazhin and V. M. Chibrikin informed us, in purified samples of ferrocene polymers the EPR signal is also absent.

Note: Figure translations are in progress. See original paper for figures.