Chemistry

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Abstract

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Investigation of the Magnetic Susceptibility of Polyalkanopolyferrocenes and Polyferrocenylenes

In connection with recently discovered features ([1–5]) of the magnetic and other properties of polymers whose molecules possess a large number of conjugated multiple bonds, it was of interest to study polyalkanopolyferrocenes, in which between each two residues of ferrocene molecules there are 4-5 CH_2- (or $-CH_2—CH_2-$) groups. In addition to these polymers, obtained by a condensation reaction ([6,7]), polyferrocenylene* formed as a result of a recombination reaction ([10]) was taken for comparison.

The degree of polymerization of the polymers was low, but nevertheless it was possible to obtain different molecular weights for each type of polymer. For all these polymers the static magnetic susceptibility was measured in the range of magnetic-field strengths from 3500 to 4500 oersteds and temperatures from 20 to 120°. The measurements were carried out by the Faraday method on magnetic balances with a sensitivity of $1 \cdot 10^{-5}$ g. In addition to measurements in the solid state, the magnetic susceptibility was also determined for solutions of these polymers in benzene (by Gouy' s method in the field-strength range from 4400 to 6100 oersteds). Some results of the measurements are given in Table 1.

Table 1

No.	Substance	Mol. weight	Specific magnetic susceptibility
I	Ferrocene	186	$-0.65 \cdot 10^{-6}$
II	Diferrocenyl* ([8,9])	370	$-0.25 \cdot 10^{-6}$
III	Pentaethanodiferrocene	502	$-0.05 \cdot 10^{-6}$
IV	Polymethanopolyferrocene	1000	$+1.4 \cdot 10^{-6}$
V	Polymethanopolyferrocene	2000	$+0.7 \cdot 10^{-6}$
VI	Polyethanopolyferrocene	1000	$+0.6 \cdot 10^{-6}$
VII	Polyethanopolyferrocene	2000	$-0.1 \cdot 10^{-6}$
VIII	Polyferrocenylene	2500	$+43.0 \cdot 10^{-6}$

* Diferrocenyl was kindly provided to us by V. A. Sazonova and V. N. Drozd, to whom the authors express their gratitude.

The values of the specific magnetic susceptibility given in Table 1 are given without correction for diamagnetism and, consequently, after correction will become more positive. In particular, polyethanopolyferrocene VII, after correction for the diamagnetism of ferrocene itself, has a positive susceptibility value equal to $+0.55 \cdot 10^{-6}$.

* Polyferrocenylene was kindly provided to us by S. L. Sosin, to whom we express our deep gratitude.

Thus, in contrast to the initial diamagnetic products from which the polymers were synthesized, the latter are paramagnetic.* From the data in Table 1 it follows that the closer the ferrocene residues are to one another in the molecule, the greater the paramagnetism that arises. Specially performed measurements showed that the values of the specific magnetic susceptibility of these polymers in solutions are the same as those obtained in measurements on the solid polymers.

From all these facts it follows that the paramagnetic properties of amorphous polyalkanopolyferrocenes and polyferrocenylene are determined by the electronic structure of their molecules; moreover, the magnitude of the magnetic susceptibility depends on the nature of the bond between the ferrocene residues. An interesting fact is the distinct interaction of ferrocene residues even in polyethanopolyferrocenes, despite the considerable distance between them. The data from EPR spectra are in complete agreement with the data we have obtained ([11]).

Very interesting questions arising as a result of the investigations carried out are those concerning the mechanism by which paramagnetism appears in the transition from ferrocene to polymers based on it, and concerning the temperature dependence of the magnetic susceptibility of such polymers. It should be noted that upon heating to 120° we observed a considerable irreversible increase in the values of magnetic susceptibility without the appearance of ferromagnetism. On the basis of the data obtained it is not yet possible to establish whether this phenomenon is connected with the oxidation process of the polymers or proceeds independently of it.

Comprehensive investigations of polyalkanopolyferrocenes will be continued by us.

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* The value of the magnetic susceptibility does not depend on the field strength, which indicates the absence of ferromagnetism.

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