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SYNTHESIS AND SOME OPTICAL-MAGNETIC PROPERTIES OF POLYFERROCENES

In the present work, in studying the magnetic properties of various types of ferrocene derivatives—polyferrocenylene, polydiisopropylferrocene, polymethano- and polyethanopolyferrocenes—their unusual magnetic properties were discovered. Each of these types of ferrocene derivatives was synthesized in the following manner.

A. Polyrecombination reaction [1,2]. One mole of ferrocene (or, respectively, its diisopropyl homolog) was treated with 1–2 moles of tert-butyl peroxide at 200° in a nitrogen atmosphere. The formation of polyferrocenylene (and, respectively, polyisopropylferrocene) can apparently be represented in such a way that the tert-butoxy and methyl radicals arising upon decomposition of tert-butyl peroxide abstract hydrogen from ferrocene (or the α-hydrogen of the isopropyl substituent of ferrocene), and the radicals thereby formed recombine with the formation of linear polyferrocenylene (and, respectively, polydiisopropylferrocene). Simultaneously with the linear polymer, readily soluble in benzene, an insoluble polymer is obtained (samples Nos. 5–6), apparently possessing a two- or three-dimensionally cross-linked structure. These two polymeric forms of ferrocene were separated by treating the reaction mass with benzene. The linear polymer was isolated from the benzene solution by double reprecipitation with methanol. After distillation of benzene and methanol from the filtrate, a mixture of unreacted ferrocene and low-molecular products remained, from which ferrocene was isolated by sublimation in vacuum. The conversion of ferrocene into high-molecular products reached 25%. Their composition and structure were confirmed by elemental analysis and IR spectra, in which absorption bands are present in the region 1000–1100 cm^{-1}, characteristic of the free cyclopentadienyl ring. The polymers obtained are dark-red powders; the polydiisopropylferrocene samples are light yellow. Soluble polyferrocenylene samples (Nos. 1–4) were obtained with molecular weights from 370 to 7000 and a softening temperature of 290–300°. The molecular weight of samples Nos. 1–3 was determined cryoscopically in benzene, and of samples Nos. 4, 7 ebullioscopically. Insoluble polyferrocene (Nos. 5, 6) softens at about 400°, which apparently in-

dicates relatively rare cross-links between the chains.

B. Polyalkylenation of ferrocene with methylene chloride and 1,2-dichloroethane in the presence of aluminum chloride. To 40 g of ferrocene in 250 ml of dry dihaloalkane there was gradually added a solution of 20 g of anhydrous aluminum chloride in 50 ml of dry dihaloalkane. The mixture, with continuous stir—

was maintained at the boiling point of the solvent for 6 h. The next day a solution of 10 g of anhydrous aluminum chloride in 25 ml of digaloylalkane was added. Heating at the boiling point of the solvent and stirring were continued for another 6 h. The mixture was then decomposed with ice and 10% hydrochloric acid, treated with sodium sulfite, the digaloylalkane solution was separated, and the residue was extracted with ether and benzene. All solutions were washed with 5% sodium carbonate solution and with water, and dried over calcined calcium chloride. After removal of the solvents, the dry residue was extracted in a Soxhlet apparatus with methyl alcohol until a colorless solution ran off. Ferrocene was recovered from the solution. The residue in the thimble of the Soxhlet apparatus contained polyalkanoferrocenes, which differ in solubility in ether and benzene. The molecular weights (benzene, cryoscopy) of the polymers obtained are given in Table 1. All products are readily soluble in benzene,

Table 1

Polyferrocenylene and polyalkanopolyferrocenes

No.	Substance	Mol. weight	g-factor	Line width (Oe) at 300° K	Line width (Oe) at 78° K	Number N per 1 g	Number N per 1 unit	EPR signal in solution
1	Linear polyferrocenylene	370				no signal	no signal	
2	Same	1000	2.00	150	300	$9.8 \cdot 10^{21}$	3	no
3	» »	2500	2.00	120	300	$8.9 \cdot 10^{21}$	2.7	yes
4	» »	7000	2.00	120		$1.9 \cdot 10^{21}$	0.6	yes

No.	Substance	Mol. weight	g-factor	Line width (Oe) at 300° K	Line width (Oe) at 78° K	Number N per 1 g	Number N per 1 unit	EPR signal in solution
5	Insoluble polyferrocenylene		2.00	160	530	$3.9 \cdot 10^{22}$	12.3	
6	Same		2.00	150	460	$4.5 \cdot 10^{21}$	1.4	
7	Linear polydiisopropylferrocene	8000	—	—		no signal	no signal	—
8	Insoluble polydiisopropylferrocene		—	—		no signal	no signal	—
9	Products of condensation of ferrocene with di-1,2-chloroethane	500	—	—		no signal	no signal	—
10	Same	2300	2.00	6.4	7.5	$5.4 \cdot 10^{17}$	$0.2 \cdot 10^{-3}$	no
11	» »	1000	2.00	6.4	7.5	$1 \cdot 10^{18}$	$0.4 \cdot 10^{-3}$	no

No.	Substance	Mol. weight	g-factor	Line width (Oe) at 300° K	Line width (Oe) at 78° K	Number N per 1 g	Number N per 1 unit	EPR signal in solution
12	Products of condensation of ferrocene with methylene chloride	1000	—	—		no signal	no signal	—
13	Same	2000	2.00	6.4	7.5	$5.6 \cdot 10^{18}$	$1.7 \cdot 10^{-3}$	yes
14	Ferricinium cation	186	2.00	420	600			yes

have a decomposition temperature of about 115-120°. Compound No. 9 was purified by reprecipitation from ether with methanol. A light-yellow powder was obtained, yield 9.5% based on the ferrocene that entered into the reaction. Polymer No. 10 was reprecipitated from benzene with *n*-heptane; yield 2%, light-yellow powder. Polymer No. 11 was reprecipitated from benzene with methanol; dark gray-brown color, yield 2.65%. All the powders are amorphous.

According to analysis, substances Nos. 10 and 11 are close to pentaethanodiferrocene No. 9 ([3]) and, possibly, represent two and four molecules similar to it, joined by ethane bridges. The structure of substances No. 12 and No. 13 is being studied. According to analysis, for two ferrocene residues in the molecule of polymers No. 12 and No. 13 there are 4-5 methylenes. All the substances contain no halide. The IR spectra of compounds Nos. 9-13 have frequencies in the region 1000-1100 cm^{-1}.

Investigation of the EPR spectra showed that polyferrocenylenes possessing π-conjugation between the ferrocene units, as well as

as do polyaromatic hydrocarbons ([5]), give an EPR signal (see Table 1).*

From Table 1 it is seen that an EPR signal is also given by polymers in which the

Fig. 1. Absorption spectra of *n*-octane solutions. 1 –ferrocene, 2 – polyferrocenylene with mol. weight 1000, 3 –polydiisopropylferrocene, 4 – absorption spectrum of ferrocene in CCl4 (7)

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ferrocene units are separated by the group $-CH_2-CH_2-$([4]). In this connection it is interesting to note that, in a study of the dibenzyl anion ([6]), it was found that the $-CH_2-CH_2-$group does not prevent delocalization of the unpaired electron between the two phenyl rings. In the substances described by us that give an EPR signal, the signal is the smaller the smaller the number of ferrocene units. In polydiisopropylferrocene this signal disappears within the limits of measurement accuracy.

Polymers with low molecular weight do not give an EPR signal in solution (benzene) but do give it in the solid state. This result, as in the case of polyaromatic hydrocarbons ([5]), can be explained by the fact that in the solid state intermolecular interactions lead to the appearance of conjugation between neighboring polymer molecules, which in turn leads to the appearance of an EPR signal.

Fig. 1. Absorption spectra of *n*-octane solutions. 1 –ferrocene, 2 –polyferrocenylene with mol. weight 1000, 3 –polydiisopropylferrocene, 4 –absorption spectrum of ferrocene in CCl_4 ([7])

All the polymers in which this signal is observed give a single symmetrical EPR line of Lorentzian form. Polyferrocenylene obtained by a polyrecombination reaction gives a broad EPR line from 120 to 160 oersteds, the line width depending on the structure of the polymer. When the measurement temperature is lowered the line broadens; the line width changes most strongly in low-molecular-weight polymers. Polyalkanoferrocenes give a comparatively narrow EPR line with a width of 6.4 oersteds, the width of which depends only weakly on temperature. The *g*-factor of all the substances described that give an EPR signal is the same and is equal to 2.00.

Determination of the concentration of unpaired electrons is usually carried out by comparing the signal under study with a standard, for which dilute paramagnetics are used. However, in the present case the nature of the signal is not clear, and we cannot consider that the numbers of unpaired electrons obtained by the method indicated above correspond to their true number. Nevertheless, this quantity may serve as a certain characteristic of the magnetic properties of the system. From Table 1 it is seen that, for separate fractions of polyferrocenylene with different molecular weight (see Nos. 2, 3, 4), the "number of unpaired electrons" (N) per unit has different values. In insoluble polyferrocenylene (see No. 5) the "number of unpaired electrons" per unit reaches an anomalously large value. Apparently this is connected with some collective effect of a ferromagnetic

type.

In studying the UV spectra of polyferrocenylene dissolved in *n*-octane, it was found that the spectra of polyferrocenylene that gives an EPR signal in the solid state and of polyferrocenylene that has no EPR signal in the solid state differ from one another. In the case of polyferrocenylene that gives an EPR signal, the UV spectrum completely coincides with the UV spectrum of ferrocene dissolved in CCl_4, in which, as was shown ([7]), charge transfer takes place with formation of the ion pair $Fer^+CCl_4^-$; whereas in the case of polyferrocenylene that has no EPR signal, the UV–

* The presence of an EPR signal in the systems studied cannot be explained by the presence of the corresponding amount of the oxidized form of the ferricinium cation. This follows both from the method of synthesis (oxidizing products are insoluble in ether and benzene) and from comparison of the data obtained (see Table 1) with the results of studying the EPR spectra of the ferricinium cation.

the spectrum is close to the spectrum of ferrocene recorded in a neutral solvent (*n*-octane), i.e., under conditions in which charge transfer is absent.

L. A. Blumenfeld, A. A. Berlin, and others recently [5], in studying polynucleotides and polyaromatic hydrocarbons, discovered magnetic properties unusual for organic compounds; subsequently, in [8] it was proposed that the anomalous magnetic properties of a number of ordered organic macromolecular structures, called by the authors "pseudoferromagnetism," are associated with the formation of intramolecular (or intermolecular) charge-transfer complexes between valence-saturated particles. The collective interaction between the unpaired electrons that arise in this process leads to the appearance of anomalous magnetic properties. The results set forth above on the UV spectra may, to a certain extent, be regarded as confirming this assumption.

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