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Abstract

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POLYMERS AND COPOLYMERS OF FERROCENE DERIVATIVES OBTAINED BY THE POLYRECOMBINATION METHOD

Studies related to the chemistry of ferrocene have for a number of years attracted the attention of many chemists. It also seemed of interest to introduce such a structural unit into polymer molecules. At present several types of ferrocene-based polymers are already known. The first polymers from a ferrocene derivative were obtained in 1955 by Arimoto ([1]) through the polymerization of vinylferrocene. Copolymers of vinylferrocene with such unsaturated monomers as methyl methacrylate, styrene, and chloroprene are also known ([1,2]). Interesting ferrocene polymers were obtained by Nesmeyanov and Kochetkova in 1959–1961 by polyalkylenation of ferrocene with 1,2-dichloroethane and methylene chloride in the presence of aluminum chloride at the boiling temperature of the dichloroalkane ([3–5]). Only quite recently, in 1961, Knobloch and Rauscher published a study on the preparation, by interfacial polycondensation, of polyamides and polyesters containing ferrocene, starting from 1,1-ferrocenedicarbonyl chloride and certain diamines and glycols ([6]).

There is a fundamental possibility of obtaining polymers whose structure contains ferrocene from disodium derivatives of α,ω-dicyclopentadienylalkanes with ferric chloride ([7,8]). By the polyrecombination reaction, a ferrocene-based polymer was first obtained in 1958 by Korshak, Sosin, and Chistyakova, starting from homoannular diisopropylferrocene ([9]). Later, the same authors studied polydiisopropylferrocene in detail ([10]).

The polyrecombination reaction was used to obtain polymers from ferrocene itself—polyferrocenylene ([11,12]). Soluble polyferrocenylenes were obtained with molecular weights from 370 to 115,000 and softening temperatures of about 300° for the high-molecular-weight samples; moreover, polyferrocenylene with a molecular weight of 115,000 was obtained at a consumption of 1.48 mol of peroxide per 1 mol of the initial ferrocene. Insoluble polyferrocenylenes decompose at about 400°.

In continuation of the above-mentioned work on obtaining ferrocene polymers by the polyrecombination reaction, in the present work the behavior of various alkyl derivatives of ferrocene in the polyrecombination reaction was investigated.

Polyrecombination of ferrocene derivatives was carried out according to the general procedure described in detail for the case of polyrecombination of ferrocene itself ([5]). The starting compounds used were isobutylferrocene, diisobutylferrocene, isoamylferrocene, and cyanoferrocene. In addition, copolymers of ferrocene with isobutylferrocene, with stilbene, and with the dimethyl ester of decamethylenedicarboxylic acid were obtained. The alkylferrocenes were kindly provided to us by Ya. M. Paushkin and T. P. Vishnyakova.

Polyrecombination was carried out at a temperature of 200°. The ratio of tert-butyl peroxide to the starting compound was taken as 1, 2, or more moles of peroxide per 1 mole of monomer. All the soluble polymers obtained were precipitated twice from benzene with methanol. As a result of the polyrecombination reaction, polymers were obtained from alkylferrocenes in the form of

Table 1

Starting compound	Molar ratio of tert-butyl hydroperoxide to starting compound	Soluble polymer: yield, % based on recovered starting material	Soluble polymer: mol. wt.	Soluble polymer: m.p., °C	Insoluble product: yield, % based on recovered starting material	Recovery of starting compound, %	Low-molecular-weight product: yield, % based on reacted starting material	Volatile reaction products: molar ratio tert-butyl alcohol to acetone	Found, % C	Found, % H	Found, % Fe	Calculated, % C	Calculated, % H	Calculated, % Fe	EPR signal N, g-free el. 1 g
Isobutylferrocene	2	59,3	4450	200 — 240[4]	—	29,5	31,4	75,85	6,33 : 1	68,95	6,83	20,98	69,98	6,70	23,32	No
Diisobutylferrocene	2	56,3	3900	190 — 240[4]	—	31,5	30	72,5	4,7 : 1	71,43	7,62	18,63	73,08	8,16	18,84	$2 \cdot 10^{20}$
Isoamylferrocene	2	50	7330	175 — 205	—	25	27,4	55,05	1,12 : 1	69,84	7,26	19,47	71,04	7,40	21,60	$2 \cdot 10^{20}$
Cyanoferrocene	0,66	72[3]	—	>300	—	73,5	—	—	—							—

Starting compound	Molar ratio of tert-butyl hydroperoxide to starting compound	Soluble polymer: yield, % based on recovered starting material	Soluble polymer: mol. wt.	Soluble polymer: m.p., °C	Insoluble product: yield, % based on recovered starting material	Recovery of starting compound, %	Low-molecular-weight product: yield, % based on recovered starting material	Volatile reaction products: yield, % of theory	Volatile reaction products: molar ratio tert-butyl alcohol to acetone	Found, % C	Found, % H	Found, % Fe	Calculated, % C	Calculated, % H	Calculated, % Fe	EPR signal N, g-free el.	
Ferrocene and isobutylferrocene	1,57	48,3	4780	250 — 320	0,207	32,9	21,4	73,2	1,78 : 1	67,58	6,78	23,59	72,94	7,45	19,61	26,34	No
Ferrocene and stilbene	2	51,5	4500	180 — 205	0,149	27,2	34,5	74,9	0,9 : 1	84,62	7,02	4,97	85,94	6,38	7,69		No
Ferrocene and stilbene	2,36	58,2	9660	230 — 290	0,71	23,4	25,5	70,3	0,8 : 1								No
Ferrocene and dimethyl ester of decamethylenedicarboxylic acid	0,9	41,7	—	>360	1,23	34,5	—	60,1	6,33 : 1	64,68	7,34	12,86	65,57	7,28	12,65		No

[1] —Recovery of a mixture of starting compounds; [2] —molecular weights were

determined ebulliometrically in benzene; [3] –polymer not reprecipitated; [4] –m.p. determined in a sealed capillary; [5] –the elementary unit of the polymer contains one ferrocene residue and one isobutylferrocene residue; [6] –the elementary unit of the polymer contains three stilbene residues and one ferrocene residue; [7] –the elementary unit of the polymer contains one ferrocene residue and one residue of dimethyl ester of decamethylenedicarboxylic acid.

dark-yellow, brown powders, molecular weight from 3000 to 9000. The experimental data and characteristics of the products obtained are summarized in Table 1.

On the thermomechanical curves recorded for the polymers and copolymers obtained, no elasticity plateaus are present.

IR spectra were recorded for all the polymers studied. For the soluble polymers, in all cases absorption maxima at 1000 cm^{-1} and 1100 cm^{-1}, characteristic of free cyclopentadienyl rings, were observed. Consequently, in the formation of the polymer in the listed samples, in each case only one cyclopentadienyl ring takes part, and the structure of the resulting polymer may be represented, for example in the case of polyisobutylferrocene, as follows:

$$\left[\begin{array}{c}\text{(ferrocene unit with one substituted cyclopentadienyl ring)}\\ \text{and a } C(CH_3)_2CH_2\text{– substituent}\end{array}\right]_n$$
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In contrast to polyferrocenylene, for which intense EPR signals were obtained ([4,5]), in none of the ferrocene copolymers studied was an EPR signal detected, just as in the case of polyisobutylferrocene and the previously described ([4,5,9,10]) polymer from *n*-diisopropylferrocene, which is apparently explained by disruption of conjugation in the polymer chain due to the alkyl groups. Exceptions are the polymers from diisobutylferrocene and isoamylferrocene, which give an EPR signal. Evidently, in these cases polyrecombination proceeds through the hydrogens of the cyclopentadienyl ring, while the alkyl substituents do not enter into the reaction.

Thus, by the method of polyrecombination, polymers have been obtained from ferrocene with molecular weight 115,000; isobutylferrocene, diisobutylferrocene, isoamylferrocene, cyanoferrocene, and copolymers of ferrocene with isobutylferrocene, with stilbene, and with dimethyl decamethylenedicarboxylate. The properties of the polymers and copolymers obtained have been investigated.

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