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Abstract

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Synthesis of Polymers Based on Ferrocene and Some of Their Electrophysical Properties

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V. V. Korshak and S. L. Sosin (^{1}), with collaborators, developed a reaction by which substances having no double bonds or corresponding functional groups can be converted into high-molecular-weight compounds (with molecular weight 1000–10,000–900,000) by treatment with peroxides. In this reaction, monomer molecules (diisopropylbenzene, diphenyl, ferrocene, etc.), splitting off hydrogen, form high-molecular-weight compounds.

The authors of the present work studied the polyrecombination of tert-butylferrocene, the joint polyrecombination of ferrocene with a series of aromatic compounds, and, in addition, obtained ferrocene-based polymers by the polycondensation reaction of acetylferrocene and ferrocene with acetone.

Joint polyrecombination of ferrocene with *p*-chlorobenzene. Ferrocene (m.p. 171–173°) was mixed with *p*-dichlorobenzene (m.p. 53°) in a molar ratio of 1:1; the mixture was heated to 200°, and with vigorous stirring under a layer of melt, tert-butyl peroxide was added over 4 hours in a ratio of 1.6:1. Separation of the reaction products was carried out in benzene, followed by precipitation of the soluble polymer with methanol.

The yield of soluble polymer was about 6% and of insoluble polymer 25%. The polymers obtained are dark-brown powders, infusible up to 500°. The molecular weight of the soluble polymer is about 1200. Elemental composition of the soluble polymer:

Found, %: C 62.92; H 5.21; Cl 11.65; Fe 20.22

of the insoluble polymer:

Found, %: C 60.83; H 4.82; Cl 11.10; Fe 23.28

Both polymers showed a signal in the EPR spectrum.

Joint polyrecombination of ferrocene with bromonaphthalene. Ferrocene was mixed with α-bromonaphthalene in a molar ratio of 1:2. The mixture was heated to 200° and, with vigorous stirring under a layer of solution, tert-butyl peroxide was added over 3–4 hours in a ratio of 1.36:1. The method for separating the polymers into soluble and insoluble fractions was the same as for *p*-chlorobenzene. The yield of soluble polymer was about 10% and of insoluble polymer, 23%. The polymers obtained are black powders, infusible up to 500°. The soluble polymers have a molecular weight lying between 2276 and 3034; the elemental composition is as follows:

Found, %: C 63.57; H 4.44; Br 19.96; Fe 12.03

For the insoluble polymers:

Found, %: C 62.56; H 4.83; Br 18.10; Fe 15.01

On the basis of the results obtained, the reaction of joint polyrecombination between ferrocene and α-bromonaphthalene can be represented by an equation with the proposed structure of the polymer:

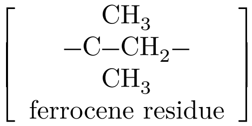
$$\text{Ferrocene+}\alpha\text{-bromonaphthalene} \xrightarrow{[(CH_3)_3CO]_2} [\text{ferrocene–}\alpha\text{-bromonaphthalene}]_x+(CH_3)_2CO+(CH_3)_3COH+$$

Investigation of the magnetic properties of the polymers obtained showed the presence of a signal in the EPR spectrum.

Polyrecombination of tert-butylferrocene.
11.5 g (0.05 mole) of tert-butylferrocene (b.p. 103–108°/4 mm Hg; n_D^{20} 1.5730; d_4^{20} 1.1852) was heated to 200°, and, with vigorous stirring, tert-butyl peroxide was introduced under a layer of the alkylate in a molar ratio of 2 : 1. As a result of the reaction, only a soluble polymer was obtained. The polymer, twice precipitated from benzene with methanol, was light brick-red in color, had a molecular weight of 2280, melted at 300°, and had the following elemental composition:

Found, %: C 68.42; H 6.8; Fe 24.76

This corresponds approximately to the formula of the polymer unit



$$\left[\begin{array}{c} \text{CH}_3 \\ \text{–C–CH}_2\text{–} \\ \text{CH}_3 \\ \text{ferrocene residue} \end{array}\right]$$

Found, %: C 70.0; H 6.67; Fe 23.33

In the EPR spectrum, poly-tert-butylferrocene showed no signal.

Polycondensation of ferrocene with acetone. It is known that aldehydes and ketones react with aromatic compounds in the presence of hydrogen chloride to form alkylchloro derivatives of aromatic hydrocarbons (chloromethylation reaction). As we established in the case of ferrocene and acetone, in the presence of zinc chloride and hydrogen chloride a polycondensation reaction occurs, with the formation of soluble polymers having molecular weights in the range 2500–3500. It is interesting to note that the polycondensation reaction of aromatic hydrocarbons with acetone ends with the formation of low-molecular compounds with molecular weights not exceeding 250–350.

With ferrocene this reaction is carried out as follows. Into a flask fitted with a reflux condenser were placed 2 moles of acetone (116 g), 0.1 mole of ferrocene (18.6 g), and 0.036 mole of zinc chloride (4.8 g) was added to the solution. Hydrogen chloride was passed into the solution at the boiling temperature of acetone until complete saturation. Then the acetone that had not entered into the reaction was distilled off, and the solid reaction products were dissolved in benzene; to separate zinc chloride, the reaction products were precipitated from the benzene solution with methanol. The precipitate was washed with aqueous ammonia and again reprecipitated from benzene solution with methanol. After purification, 22.6 g of a light-brown powder was obtained, with m.p. 320–360°; the molecular weight, determined by the cryoscopic method, gave values lying between 3050 and 3180.

In the infrared spectrum of this polymer, frequencies of 1000 and 1100 cm^{-1} are observed, corresponding to the free cyclopentadienyl ring of ferrocene. Investigation of the magnetic properties showed the presence of a signal in the EPR spectrum.

Polycondensation of acetylferrocene. Acetylation of ferrocene with acetic anhydride in the presence of the molecular compound of ethyl acetate with boron fluoride readily gives acetylferrocene in 80–85% yield (5). Acetylferrocene was used by us to obtain polyferrocenylvinylene by the reaction discovered for aliphatic ketones by V. A. Kargin and co-workers (6). For this purpose, 22.8 g (0.036 mole) of acetylferrocene was heated in an autoclave at 200° for 20 h with 4.8 g of zinc chloride (0.036 mole). The reaction products were removed from the autoclave and washed with aqueous ammonia solution to remove zinc chloride.

21 g of a dark-brown powder was obtained, representing polyferrocenylvinylene; polymer yield 94.3%. The reaction may presumably be represented by the equation:

$$\mathrm{x}\ [\text{acetylferrocene}] \xrightarrow[-\mathrm{xH_2O}]{\mathrm{ZnCl_2}} [-\mathrm{C{=}CH}-(\text{ferrocenyl})-]_{\mathrm{x}}$$

Elemental composition:

$$\text{Found, \%:}\quad C\ 69.9;\quad H\ 5.0;\quad Fe\ 25.1$$
$$\text{Calculated, \%:}\quad C\ 68.61;\quad H\ 4.8;\quad Fe\ 26.59$$

The main portion of the polymer is insoluble, 74.5%; the soluble polymer (in benzene) amounts to 19.8% and melts at 260-270°. Investigation of the magnetic properties of the obtained polymers showed the presence of signals in the EPR spectrum.

For the polymers obtained, the electrophysical properties were determined. The dependence of electrical conductivity on temperature was determined. All samples have a positive temperature coefficient of conductivity and, in the temperature range studied, obey the exponential dependence of conductivity on temperature

$$\sigma = \sigma_0 \cdot e^{-E/kT},$$

which is also found for ordinary semiconductors; from this the activation energy of these semiconductor materials is determined.

To measure the dependence of electrical conductivity on temperature, the polymer powders were pressed into pellets 6 mm in diameter and 1-2 mm thick in the temperature interval 50–150° at a pressure of 15,000 atm; the contacting surfaces were vacuum-deposited with copper, with a layer thickness of 2–3 μ. The measurement of the dependence $\sigma = \sigma(T)$ was carried out in a vacuum of $1 \cdot 10^{-4}$ mm Hg by the compensation method in the temperature range 20–200°. The method of measuring electrical resistance ensured an accuracy of ±7%.

Before each measurement, the prepared pellets were kept in a vacuum of $1 \cdot 10^{-4}$ mm Hg for 3 h at a temperature of 50° in order to remove from the surface and from the bulk readily desorbed substances adsorbed during the processing of the powder.

Table 1

Electrophysical characteristics of the polymers studied

Starting materials	Polymer	Mol. wt.	E, eV	σ_{50°, ohm^{-1} · cm^{-1}*	σ_0, ohm^{-1} · cm^{-1}
Ferrocene + bromonaphthalene (soluble)	Polyferrocenylbromonaphthylene	3094	1.74	$1.35 \cdot 10^{-20}$	$2.3 \cdot 10^{-7}$
Same (insoluble)	Same	–	0.54	$2.5 \cdot 10^{-13}$	$7.5 \cdot 10^{-5}$

Starting materials	Polymer	Mol. wt.	E, eV	σ_{50°, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$*	σ_0, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$
Ferrocene + acetone	Condensation products of ferrocene with acetone	3050	0.67	$1.23 \cdot 10^{-12}$	$4.8 \cdot 10^{-2}$
Ferracenyl acetate	Polyvinyleneferrocenylene	–	1.45	$2.8 \cdot 10^{-10}$	$1.5 \cdot 10^{-11}$
Ferrocene + *p*-chlorobenzene (insoluble)	Polyferrocenyl-*p*-chlorophenylene	–	0.47	$2.83 \cdot 10^{-10}$	$5.7 \cdot 10^{-3}$
tert-Butylferrocene	Polyisobutylferrocenylene	2280	0.34	$1.5 \cdot 10^{-15}$	$1.5 \cdot 10^{-1}$

* Electrical conductivity of inorganic semiconductors at ordinary temperature is 10^3–10^{-10}; for organic semiconductors, 10^{-8}–10^{-10} (7).

Table 1 gives the electrophysical characteristics of the polymers studied. As can be seen from the data in this table, the semiconductor materials we investigated, under the indicated measurement conditions, have an activation energy from 1.74 to 0.47 eV and a specific electrical conductivity at a temperature of 50° from $1 \cdot 10^{-20}$ to $1 \cdot 10^{-10}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. The rather steep course of the conductivity curve and the high melting temperatures of almost all the investigated

of the samples give grounds to suppose that these polymers can be used under high-temperature conditions for operation in circuits requiring semiconductor elements with high resistances.

It should be noted that the electrical conductivity of ferrocene + insoluble bromonaphthalene is 7 orders of magnitude greater, and the activation energy 3 times smaller, than for ferrocene + soluble bromonaphthalene. As a rule, insoluble polymer samples have a higher molecular weight than soluble ones, or crosslinked chains. It is possible that the electrical conductivity and the width of the forbidden band of these polymers are basically connected with "contacts" between macromolecules, which is manifested in the influence of molecular weight on the electrophysical properties.

All the polymers studied have very high resistances; the best electrophysical properties are possessed by ferrocene + paradichlorobenzene (insoluble). It also seemed of interest to determine the influence of surface adsorption on the measured electrophysical properties, in connection with the possible catalytic properties of the polymers studied.

For this purpose, polymer samples were heated in a high vacuum for 3-5 hr for desorption from their surface of vapors of various contaminants, after which adsorption of air was again carried out.

Table 2

Influence of conditioning and measurement conditions on σ and E

Starting materials	Conditioning (treatment) τ, hr	Conditioning (treatment) Temp., °C	Conditioning (treatment) P, mm Hg	Measurement conditions P, mm Hg	σ_{50°, $\mathrm{ohm}^{-1}\cdot\mathrm{cm}^{-1}$	E, eV
Ferrocene + bromonaphthalene (insoluble)	3	50	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$2.5 \cdot 10^{-13}$	3.62*0.54
Ferrocene + bromonaphthalene (insoluble)	3	200	$1 \cdot 10^{-4}$	760	$5.4 \cdot 10^{-8}$	0.32
Ferrocene + acetone	3	50	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1.23 \cdot 10^{-12}$	0.67
Ferrocene + acetone	3	200	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$6.2 \cdot 10^{-14}$	1.13
Ferrocene + acetone	3	200	$1 \cdot 10^{-4}$	760	$9.2 \cdot 10^{-11}$	0.68
Ferrocenyl acetate	3	50	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$2.85 \cdot 10^{-10}$	1.45*0.47
Ferrocenyl acetate	3	200	$1 \cdot 10^{-4}$	760	$1.01 \cdot 10^{-9}$	0.47*0.31

* The curve $\sigma = \sigma(T)$ has a break with the corresponding E.

Table 2 gives the values of σ_{50° and E for the semiconductor substances we investigated as a function of the measurement and conditioning (treatment) conditions. As can be seen from the data of Table 2, adsorption from air increases the electrical conductivity and decreases the width of the forbidden band. The greatest effect was found for the polymer obtained from ferrocene + bromonaphthalene (insoluble), whose electrical conductivity changed by 5 orders of magnitude.

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