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Abstract

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CHEMISTRY

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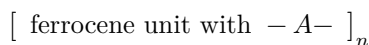
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STUDY OF FERROCENE COPOLYMERS BY MEANS OF THE MÖSSBAUER EFFECT

The study of unusual "sandwich" structures, which include ferrocene derivatives, is of great theoretical importance for understanding the nature of the chemical bond ⁽¹⁾. In addition, the study of ferrocene copolymers is also of definite practical interest, since these compounds belong to the class of organic semiconductors. Mössbauer spectroscopy ⁽²⁾ makes it possible to obtain information both on the electronic state of the iron atoms contained in the polymer and on the general structure of the polymer. We studied the dependence of the resonant absorption of γ -quanta on the relative velocity of motion of the source and absorber. The source of gamma radiation was Co^{57} , diffused into a stainless-steel matrix, and the absorbers were samples of copolymers.

Polyvinylferrocene and a copolymer of ferrocene with acetone were obtained by the condensation reaction in the presence of $ZnCl_2$ ⁽³⁾; the remaining copolymers were obtained by the method of polyrecombination in the presence of an organic peroxide ⁽⁴⁾.

Data on the spectra of the copolymers studied are summarized in Table 1. Among the samples investigated there were both soluble (for example, in benzene) and completely insoluble (without destruction of the structure) polymers of the general formula



A —copolymer component (in the case of polyferrocenes A is absent).

Soluble copolymers

As is seen from Table 1, for all soluble copolymers at the temperature of liquid nitrogen the presence of a doublet structure of the velocity spectra is characteristic. The observed effect amounts to $\sim 10\%$.

The values of the quadrupole splitting lie within the range 2.2-2.4 mm/sec, and the values of the chemical shift relative to iron in stainless steel within 0.4-0.55 mm/sec. Thus, the spectra of soluble copolymers are close to the velocity spectrum of ferrocene itself and its derivatives ⁽⁵⁾, which is quite natural for the linear structure of copolymers assumed, for example, in ⁽⁶⁾. In such a polymer molecule, neighboring units may be regarded as homoannular substituents in the given ferrocenylene group of the copolymer. With such a polymer structure, the iron does not participate in the conjugation chain, and the electronic structure characteristic of iron in ferrocene is largely preserved in soluble copolymers as well.

At room temperature in soluble copolymers the observed effect is very small (less than 1%)—much smaller than in ferrocene itself. In light of the assumed linear structure of such polymers, the sharp decrease in the observed effect should apparently be explained by the presence of

Table 1

Data of Mössbauer spectra for ferrocene copolymers

No.	Polymer	T, °K	Soluble frac- tion: δ	Soluble frac- tion: Δ	Soluble frac- tion: $\bar{\eta}$	Soluble frac- tion: T'_a	Insoluble frac- tion: δ	Insoluble frac- tion: Δ	Insoluble frac- tion: $\bar{\eta}$	Insoluble frac- tion: T'_a	ξ
1	Polyferrocene (soluble)	300	0,45*	2,4*	1%	0,02	—	—	—	0	0
1	»	80	0,55	2,3	9%	0,23	—	—	—	—	—
2	Polyferrocene (insoluble)	300	—	—	—	—	0,40	0,85	2,5	0,042	—
2	»	80	0,55	2,4	7,5	0,11	0,45	0,80	5	0,072	40
3	Polyvinylferrocene (soluble)	300	Observed effect less than 1%				—	—	—	0	0
3	»	80	0,55	2,25	4%	0,075	—	—	—	—	—

No.	Polymer	T, K	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	ξ
			frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	
4	Polyvinyl (in- sol- u- ble)	300	0,55	2,40	1%	0,009	0,70*	0,86*	1%	0,01	—
4	»	80	0,60	2,25	3,5	0,067	0,50	0,65	2,5	0,021	25
5	Copolymer of fer- rocene with ace- tone	300	Observed				—	—	—	—	0
5	»	80	0,50	2,40	11%	0,15	—	—	—	—	—
6	Copolymer of fer- rocene with naph- tha- lene (sol- u- ble)	300	Observed				—	—	—	—	0
6	» »	80	0,55	2,40	15%	0,17	—	—	—	—	—
7	Copolymer of fer- rocene with naph- tha- lene (in- sol- u- ble)	300	0,50	2,4	15%	0,02	0,40	0,65	4,5	0,075	—

No.	Polymer	T, K	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	ξ
			frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	
7	» »	80	0,50	2,30	10%	0,125	0,50	0,75	6,5	0,090	40
8	Copolymer of fer- rocene with α - Br- naphthalene (sol- u- ble)	80	0,55*	2,5*	2%	0,19	—	—	—	—	0
9	Copolymer of fer- rocene with α - Br- naphthalene (in- sol- u- ble copoly- mer No. 1)	80	0,55*	2,5*	2,5%	0,21	0,60*	0,80*	1%	0,05	20
10	(insoluble) copoly- mer No. 2)	80	—	—	—	—	0,40	0,75	1,5%	0,16	—
10	» »	80	0,5	2,2	2%	0,11	0,50	0,75	2,2%	0,14	55

No.	Polymer	T, K	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	ξ
			frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	frac- tion: δ	frac- tion: Δ	frac- tion: $\bar{\eta}$	frac- tion: T'_a	
11	Copolymer with p-dichlorobenzene (insoluble)	300	—	—	—	0,015	0,40	0,75	5%	0,09	—
11	» » »	80	0,5	2,15	5,5%	0,095	0,50	0,70	5,5	0,095	50
12	Copolymer with salicylaldehyde (insoluble)	300	—	—	—	0,035	0,45	1,2	2%	0,032	—
12	» » »	80	—	—	—	—	0,55	1,05	7,5%	0,011	75
13	Copolymer with benzaldehyde	80	0,55	2,2	3,5	0,031	0,60	0,80	2%	0,06	65
14	Copolymer with phthalic anhydride (see note 3)	300	1,3	2,65	—	0,096	1,35	1,0	—	0,02	—
14	» » »	80	1,35	2,9	—	0,22	1,24	0,80	—	0,06	—

Note. 1. δ is the chemical shift (mm/sec) relative to Fe in stainless steel; Δ is the quadrupole splitting (mm/sec); $\bar{\eta}$ is the mean magnitude of the observed effect (%); T_a is a quantity proportional to the effective thickness of the absorber; ξ is the degree of polymer cross-linking (%). 2. The accuracy of the values of δ and Δ is ± 0.05 mm/sec; values marked with an asterisk are given with an accuracy of ± 0.1 mm/sec. 3. The spectrum of the ferrocene copolymer with phthalic anhydride has an unusual magnitude of the asymmetry of the two peaks of the quadrupole splitting and values of the chemical shift and quadrupole splitting sharply different from those of the other polymers.

vibrational or rotational degrees of freedom of the ferrocenylene unit as a whole relative to the entire polymer molecule. At low temperature, and also in crystalline ferrocene, these degrees of freedom are strongly hindered. Indeed, the probabilities of the effect at the temperature of liquid nitrogen for soluble copolymers (including soluble polyferrocene) and crystalline ferrocene are very close.

Insoluble copolymers of ferrocene

The most important feature of the velocity spectra of insoluble copolymers of ferrocene is the decrease in quadrupole splitting in comparison with the value characteristic of ferrocene derivatives and its soluble copolymers (see Table 1). As follows from the literature data (⁶) and from our measurements, an analogous phenomenon is observed in the velocity spectra of ferricinium salts, i.e., upon removal of an electron from the iron atom in ferrocene with formation of the ferricinium cation.

In insoluble copolymers a three-dimensional network structure is formed. In this case, for some of the ferrocene molecules both cyclopentadienyl rings are incorporated into the macromolecule, and the degrees of freedom for vibration of the ferrocenylene unit as a whole, which existed in soluble copolymers, are hindered; this accounts (see Table 1) for the observability of the Mössbauer effect at room temperature. The iron atoms located in such ferrocenylene units participate in the conjugation chain, and it is precisely for these iron atoms that a rearrangement of the electron shell is observed, apparently similar to that which occurs in the transition to ferricinium salts.

At present it is accepted (⁷) that organic semiconductors, which include the copolymers of ferrocene, consist of regions with a conjugated chain possessing metallic conductivity, separated by regions that disrupt conjugation and cause a decrease in the conductivity of the entire conjugated-polymer chain. One of the electrons of the iron atom participating in the conjugation chain may, with some probability, be located in such a group orbital encompassing a number of monomer units. The probability of such an electron belonging to the iron atom then, naturally, decreases, and the electronic structure of the iron approaches the structure occurring in the ferricinium cation and corresponding to a decrease in quadrupole splitting.

However, not all ferrocenylene units in insoluble copolymers of ferrocene are

linked to the macromolecule by both cyclopentadienyl rings. From the form of the Mössbauer spectra of insoluble copolymers at the temperature of liquid nitrogen, the presence here of two doublet components is evident (as an example see Fig. 1,), one of which (the narrower doublet) corresponds to units sewn into the three-dimensional structure, and the other (the broader doublet) to linear portions of the copolymer. Thus, the narrower doublet corresponds to iron in the conjugation chain, and the broader one to iron in ordinary ferrocenylene groups.

At room temperature the component of the spectrum corresponding to the linear portions of the polymer, as we have already noted above, is not observed, and the spectrum consists only of one more weakly split doublet, due to portions of the polymer sewn into the three-dimensional structure. In soluble copolymers of ferrocene, apparently, there are no sewn-in portions, for in their velocity spectra only one doublet is observed both at room temperature (when the effect is very weakly expressed) and at the temperature of liquid nitrogen.

Since the sewn-in and unsewn portions of copolymers of ferrocene have different velocity spectra, analysis of these spectra makes it possible to determine the fraction of iron atoms located in ferrocenylene units linked to the macromolecule by both cyclopentadienyl rings (i.e., to estimate the degree of sewing of the polymer into a network structure). For this purpose we constructed a nomogram that makes it possible to determine from

experimental data in the presence of quadrupole splitting and broadening of the Mössbauer peaks, the quantity T'_a , proportional to T_a , to the product of the absolute probability of the Mössbauer effect f' and to the thickness of the absorber in iron. Using the example of insoluble copolymers of ferrocene with α -bromonaphthalene, having different degrees of cross-linking, it was established in this way that, despite the change in the contributions of the broad and narrow doublets, the total value T'_a remains unchanged. It follows from this that, at liquid-nitrogen temperature, the probabilities of the effect for the linear and cross-linked fractions of the polymer are approximately the same. Since, for identical f' , the quantity T'_{ai} is proportional to the number of iron atoms in the sample that are in the given state, the ratio characterizing the degree of cross-linking of the polymer is equal to

$$\xi = \frac{T'_{a_2}}{T'_{a_1} + T'_{a_2}} \cdot 100\%,$$

where index 1 refers to the linear fraction and index 2 to the cross-linked fraction of the polymer. Thus, Mössbauer spectroscopy provides a unique possibility for determining the degree of cross-linking of a polymer.

Fig. 1. Mössbauer spectra: *a* —ferrocene; *b* —soluble polyferrocene; *c* —insoluble polyferrocene (ordinate axis —channel count, in thousands; abscissa axis —absorber velocity, mm/sec)

Fig. 1. Mössbauer spectra: a —ferrocene; b —soluble polyferrocene; c — insoluble polyferrocene (ordinate axis —channel count, in thousands; abscissa axis —absorber velocity, mm/sec)

Figure 1: Fig. 1. Mössbauer spectra: a —ferrocene; b —soluble polyferrocene; c —insoluble polyferrocene (ordinate axis —channel count, in thousands; abscissa axis —absorber velocity, mm/sec)

The data given in Table 1 show that the value ξ varies within rather significant limits for different samples. The electrophysical properties of the polymer apparently depend substantially on the degree of its cross-linking; therefore it would be desirable to carry out a systematic comparison of the electrophysical properties of ferrocene copolymers and the values of the parameter ξ obtained by the method described above.

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