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ORIGINAL PAPER

Study of iron(III) polymer complexes using Moessbauer spectroscopy

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Abstract Metal complexes were prepared on the basis of polymer ligands with carboxylic and nitrogen-containing functionalities by complexation with iron ions in aqueous solutions of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 2H_2O$. The degree of introduction of iron ions into the polymer matrices depended on the relative content of the functional groups in the polymers studied such as polyacrylic acid, poly-4-vinylpyridine, and poly(2-*N,N*-dimethylaminoethyl) methacrylate. The metal content in the polymer complexes was found to vary between 9.0 and 30.0 (for acrylic acid-based copolymers); 0.1 and 5.3 (for copolymers of 4-vinylpyridine), and 19.7 and 34.4 (for poly(2-*N,N*-dimethylaminoethyl) methacrylate) mg metal ions per gram of polymer carrier, respectively. An attempt was made to evaluate the structure of the Fe-containing polymeric materials by Moessbauer spectroscopy. The parameters of the Moessbauer spectra such as the isomer shift, quadrupole splitting, effective internal magnetic field, and relative weight of the partial components were consequently determined for the complexes studied at different temperatures. The results obtained proved the existence of high-spin Fe^{3+} ions in oxygen- or nitrogen-containing ligand environment.

Keywords Polymer synthesis · Moessbauer spectroscopy · Iron-containing polymers · Metal complexes · Properties

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Introduction

The preparation and characterization of metal complexes based on polymer carriers with appropriate functional groups is one of the promising and interesting research fields in the polymer chemistry and extends significantly the possibilities for the practical usage of these materials. The development in the field of coordination polymers or metal–organic coordination networks, (metal–organic frameworks) is assessed in terms of property investigations in the areas of catalysis, chirality, conductivity, luminescence, magnetism, spin-transition (spin-crossover), nonlinear optics and porosity or zeolitic behavior upon which potential applications could be based [1]. The search for new perspectives of using these complexes as polymer-supported immobilized catalysts is associated with studies on the structural properties of the ionic phases in the polymers. The reactions of co-ordination of polymer ligands with metal ions and the formation of new structures of the resulting metal complexes have mainly been studied by employing spectral methods [2–4]. The introduction of a metal into polymer macromolecules leads to changes in the polymer behavior and its surface morphology. The formation and structure of the polymer complex depend on factors such as the chemical nature of the ion, temperature, and pH of the medium, etc. Interesting possibilities for structural studies of polymer–metal complexes are known to be presented by the use of Moessbauer spectroscopy. For example, the nuclear γ-resonance (effect of Moessbauer) and magnetic structure of iron in the complexes were studied. Moreover, the particles dispersion, the atoms regrouping by structural transformations and transitions during chemical reactions, as well the phase compositions of the intermediates and the end products, their structures before and after chemical reaction can be also evaluated by this sophisticated method. These studies are quite interesting when the polymer–metal complexes are used as nano-structured catalysts for various reactions in the organic sythesis. Rie Haruki et al. have studied *Nafion*-type perfluorinated ion-exchange membranes by Moessbauer spectroscopy at room temperature. As a result, the intrinsic dynamics of the cations inside the spherical regions surrounded by the sulfonic acid groups of *Nafion* have been evaluated [5]**.** Moessbauer spectral studies of Fe^{2+} and Eu^{3+} in *Nafion* polymer membranes at the temperature range between 90 and 250 K have also been performed [6]. According to the publication [7], the pattern of interaction of iron with the water-soluble polymer chitosan and D-glucosamine was investigated by Moessbauer spectroscopy. The 4.2 K Moessbauer spectrum of the product, the Fe–water-soluble chitosan complex indicated the presence of a magnetic pattern and a quadrupole doublet, and the consequent analysis of the spectral data led to the conclusion that the Fe(II) electronic state were partially stabilized in this system [7]. A number of complexes of $FeCl_2$ and $FeBr_2$ with amides, ureas, aniline, and benzothiazole were prepared and characterized by means of Moessbauer and IR spectroscopy as well as by magnetic measurements. The stoichiometries of metal complexes such as FeX_2L, FeX_2L_2, FeX_2L_3, FeX_2L_4, and FeX_2L_6 were established, involving six-coordinated iron. With the exception of the isobutyramide complex of overall molecular formula $[Fe(BUA)_6][FeCl_4]$, complexes of the first three types were found to be polymeric by nature, with bridging halogens, while FeX_2L_4 was monomeric complex, and FeX_2L_6 was characterized as $[FeL_6]Cl_2$ [8]. The formation of metallic clusters in the polymer matrices was also reported. The effect of the clusters on the structure of polymers was examined and examples for the dependence of the electrophysical and magnetic properties of the metal-containing polymers on the concentration of metallic clusters were provided [9]. Copolymers of 4-vinylpyridine (4-VP) and divinylbenzene with various degrees of crosslinking were obtained [10, 11] as polymeric precursors for the preparation of ionic polymers. Copolymers of 4-vinylpyridine/8% divinylbenzene were prepared and chemically modified by monochloracetic and acrylic acids. Studies on determining the iron(III) electronic states in the modified copolymer phase were performed by using both the Moessbauer and IR spectroscopy methods. The sorption of iron(III) ions from $Fe(NO_3)_3$ solutions was achieved by complexation of the cations with the carboxylic groups of the copolymer. The sorption of iron(III) ions from $Fe_2(SO_4)_3$ solutions was, on the other hand, caused by both the complexation of the cations with carboxylic groups and formation of the jarosite-type compound such as $R_4N[Fe_3(SO_4)_2(OH)_6]$. On boiling in an aqueous medium, the latter was transformed into highly dispersed particles of β-FeOOH. In the course of three of the so-called "sorption–boiling in aqueous medium" experimental cycles, a portion of the β-FeOOH particles became agglomerated (massive) and magnetically ordered, however, another portion remained in the highly dispersed superparamagnetic state, distributed within the narrow pores of the modified copolymer. Other authors [12] reported for gamma-resonance investigation of the structure of iron-containing polyacrylic acid

This work is a continuation of our research on the synthesis of polymers, containing functional groups, and their metal complexes [13–17]. It reports the preparation and characterization of iron complexes with carboxyl- and nitrogen-containing polymers. Moessbauer spectroscopy was employed to study the iron state, magnetic structure and to estimate the microstructure characteristics of the ionic phases of these polymers, aiming at their use as polymer-supported nano-structured catalysts in some organic synthetic reactions.

Experimental

Materials

$FeSO_4 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ (Fluka, Switzerland); poly(2-*N,N*-dimethylamino-ethyl) methacrylate (PDMAEM); copolymers with different degrees of grafting of 4-VP and acrylic acid (AA) onto films (40 μm) of low-density polyethene (LDPE) ("Ropoten T" trade FV 03-223, commercial product of Lukoil Neftochim Co, Bourgas, Bulgaria); and poly(tetrafluoroethene) (PTFE) "Ftoroplast-4P", product of ONPO "Plastpolymer", Russia) were used as starting materials in this study.

Preparation of graft copolymers

The poly-4-vinylpyridine (P4VP) (LDPE-*graft*-P4VP and PTFE-*graft*-P4VP) and the polyacrylic acid (PAA) copolymers (LDPE-*graft*-PAA and PTFE-*graft*-PAA) were obtained by radiation-induced graft-copolymerization of 4-vinylpyridine or acrylic acid (BASF, Germany) onto polyethene and polytetrafluoroethene films, using the direct method of batch irradiation. The irradiation was carried out with γ-rays from ^{60}Co source at the dose rate from 3.5 to 5.0 kGy/h and doses from 1 to 35 kGy [13, 14]. The polymer films were immersed into 240 cm^3 of 40% methanol or water solutions of the corresponding monomers (4-vinylpyridine or acrylic acid), placed in 250 cm^3 glass reactor. The graft copolymerization was carried out in an inert medium. The graft copolymerization time and temperature were 2 h and 288 K, respectively. Mohr's salt of 1.5% mass concentration with respect to the monomer solutions was used as inhibitor of homopolymerization. Following the irradiation procedure, the films were washed with methanol or hot water and, consequently, subjected to continuous extraction with methanol or water for 24 h in order to remove the unreacted 4-vinylpyridine or acrylic acid and their possible homopolymers. The copolymers thus obtained were dried in vacuum at 343 K to constant weight. The resulting nitrogen- and carboxylic acid-containing copolymers used for the preparation of iron complexes had grafting degrees with respect to 4-VP within 17.1–74.5 mass% for polyethene and within 0.7–13.4 mass% for polytetrafluoroethene. Concerning the degree of grafting of AA, these values varied from 30.0 to 96.7 mass% for polyethene and from 15.0 to 50.5 mass% for polytetrafluoroethene, respectively. Parts of the hydrophilic carboxylic acid-containing copolymers were transformed to ionomers in K-, Na-, and H-forms, respectively, which were studied by our group previously [14, 18].

Preparation of poly(2-*N,N*-dimethylaminoethyl) methacrylate

Poly(2-*N,N*-dimethylaminoethyl) methacrylate was prepared by radical polymerization of 2-*N,N*-dimethylaminoethyl methacrylate (DMAEM) in the presence of azobisisobutyronitrile (AIBN) as initiator as described in our previous publication [15]. Briefly, AIBN (0.1 g, 0.6×10^{-3} M) were dissolved in DMAEM (10 g, 0.064 M). After the complete dissolution of the initiator, divinylbenzene (DVB 1.0 g, 7.5×10^{-3} M) was introduced as cross-linking agent into the reaction mixture. Then 20 mL of toluene were added, and the resulting mixture was heated under vigorous agitation at 75 °C for 1 h. The cross-linked polymer thus obtained was removed from the reaction medium, washed several times with toluene and dried in vacuum at 40 °C. The polymer sample containing 10% cross-linking agent was obtained by the same procedure by introducing 2.0 g, (15×10^{-3} M) DVB into the reaction mixture.

Synthesis of polymer–iron complexes

The preparation of polymer–iron complexes was carried out by treatment with 0.4% aqueous solutions of $FeCl_3\cdot6H_2O$ or $FeSO_4\cdot2H_2O$. The treated polymer materials were dried under vacuum at 323 K to constant weight.

Determination of the metal ions content in the polymer complexes

1 cm^3 of standard solution, containing 0.1 mg Fe^{3+} was first prepared with the dissolution of 0.49 g $FeCl_36H_2O$ in 1,000 cm^3 H_2O. The molar extinctions of 8–10

samples, containing different amounts of iron were measured at $\lambda_{max} = 470$ nm in order to obtain the calibration curve, necessary for the following analytical procedure.The iron was extracted from the polymer complex by using HCl. Accurately weighed sample was treated with 10 cm^3 aqueous solution of HCl (1:3); then 5 cm^3 of solution of sulfosalicylic acid $C_7H_6O_6S2H_2O$ (10%) was added, followed by 5 cm^3 buffer ($2NH_3$:$3H_2O$), in order to stabilize the solution, so that Fe^{3+} was determined as iron bis-disalycate complex. Consequently, the solution volume was increased to 50 cm^3 by adding distilled water and vigorous agitation. The intensity of solution coloring as a measure for the absorbance was determined at $\lambda_{max} = 470$ nm, according to procedure described previously [17]. The amount of different metal ions bound to the polymer matrix has principally been determined spectrophotometrically on a UV/VIS Spectrometer *UNIGAN 8625* at the corresponding characteristic wavelengths ($\lambda_{max} = 470$ nm).

Moessbauer spectroscopy

Moessbauer spectra of polymer samples, containing Fe ions were obtained in air at room temperature (RT) or at liquid nitrogen temperature (LNT) with a "Wissel" (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A ^{57}Co/Cr (activity ≅ 20 mCi) source and an α-Fe standard were used. The spectra were accumulated using 1,024 channels. The experimentally obtained spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H_{eff}) as well as the line widths (FWHM) and the relative area (G) of the partial components of the spectra were determined.

Results and discussion

In this work, the procedures of interaction between part of the polymer materials synthesized and aqueous solutions of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 2H_2O$ were carried out to obtain iron-containing polymer complexes. The basic characteristics of the copolymers prepared as ion-exchange films and their complexes with transition metals have been reported in our previous papers [13–17, 19]. The nitrogen- and carboxyl group functionalities of poly-4-vinylpyridine and acrylic acid, when grafted onto LDPE and PTFE films as well as the nitrogen atoms from poly(2-*N,N*-dimethylaminoethyl) methacrylate were found to act as a chelate centers for complexation of Fe^{3+}. The metal complexes were formed by bonding the polymer ligands with the metal ions through interaction between the copolymers, containing electron donor (N– or O–) atoms and Fe^{3+} during the formation of the polymeric coordination complexes. The amount of Fe^{3+} in the polymer complexes was determined spectrophotometrically, and the corresponding results are presented in Table 1. As can be seen, the content of iron incorporated into the polymer matrices ranged from 0.1 to 34.4 mg metal/g polymer. The amount of the metal ions bound to the nitrogen- or oxygen-containing ligands of the grafted polymers was naturally

Table 1 Content of Fe^{3+} ions in polymer complexes, mg metal/g polymer carrier

Polymer carrier											
LDPE-*graft*-P4VP						PTFE-*graft*-P4VP				PDMAEM, content of DVB	
Degree of grafting *P* (%)						Degree of grafting *P* (%)					
17.1	35.1	39.2	66.2	69.0	74.5	0.7	6.5	8.2	13.4	5%	10%
Fe^{3+}											
2.45	3.13	3.98	4.56	4.88	5.30	0.03	0.14	0.45	0.72	34.40	19.71
LDPE-*graft*-PAA						PTFE-*graft*-PAA				–	–
Degree of grafting *P* (%)						Degree of grafting *P* (%)					
26.5	41.9	50.5	65.9	75.9	96.7	8.3	23.4	30.3	45.7	–	–
Fe^{3+}											
9.0	11.2	19.8	24.4	26.5	30.2	0.52	1.95	2.11	2.84	–	–

found to increase with the increase of the grafting degree. However, for poly(2-*N,N*-dimethylaminoethyl) methacrylate used as polymer support, this amount depended also on the degree of cross-linking with DVB. The co-ordination structure of various metal complexes has already been analyzed by using IR and EPR methods in some of our previous publications [15, 16]. Based on these studies as well as other literature data [2, 20], the assumed probable co-ordination structure of part of the products obtained is shown in Fig. 1a–f.

The parameters derived from the Moessbauer spectroscopy studies were used to obtain information on the character of the chemical bond and the valency of the Moessbauer atom, Iron ligand environment (isomer shift IS) or the symmetry of the charge distribution around Fe atom (quadrupole splitting QS), hyperfine interactions (IS, QS, effective magnetic field H_{eff}) were also discussed. The polymer complexes, studied by Moessbauer spectroscopy are presented in Table 2.

LDPE-graft-PAA and PTFE-graft-PAA

All spectra obtained at room temperature were associated with the existence of quadruple doublets with slight asymmetry (Figs. 2, 3, 4, 5, 6) and parameters shown in Table 3.

The Moessbauer parameters indicated that the main component in the spectra contained high-spin Fe^{3+} ions in distorted co-ordinated ligand field. The parameters obtained were the same as those, characteristic for oxygen environment of iron ions. Notable differences in the pattern of the spectra for the Na- and H-forms of the copolymer complexes were not observed. The slightly higher values of IS in the spectra of the H-form, compared to these of the Na-form probably were caused by the fact, that the electron density around the iron nucleus involved the electron donor function of the alkali ion, associated with the typical electronic characteristics of alkali metals. This fact can be regarded as the indication of the introduction of these ions in or around the second co-ordination sphere of iron. The values of line widths (FWHM) were found to be significant and they were considered to be due to

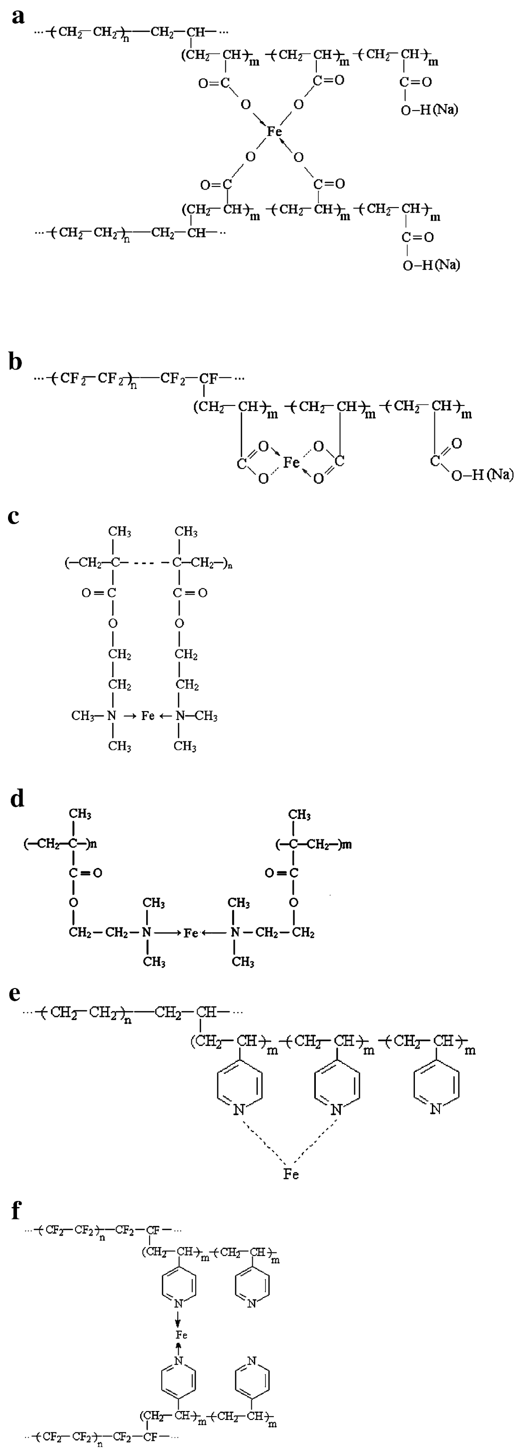

Fig. 1 **a** Intermolecular co-ordination structure of LDPE-*graft*-PAA-Fe. **b** Intramolecular co-ordination structure of PTFE-graft-PAA-Fe. **c** Intramolecular co-ordination structure of PDMAEM-Fe. **d** Intermolecular co-ordination structure of PDMAEM-Fe. **e** Intramolecular co-ordination structure of PE-*graft*-P4VP-Fe. **f** Intermolecular co-ordination structure of PTFE-*graft*-P4VP-Fe

Table 2 Polymer metal complexes used for Moessbauer spectroscopy

No	Polymer complexes	Degree of grafting or content of cross-linking agent (%)	Form
1.	LDPE-*graft*-polyacrylic acid–Fe^{3+}	41.9	H
2.	LDPE-*graft*-polyacrylic acid–Fe^{3+}	75.9	H
3.	LDPE-*graft*-polyacrylic acid–Fe^{3+}	75.9	Na
4.	PTFE-*graft*-polyacrylic acid–Fe^{3+}	23.4	H
5.	PTFE-*graft*-polyacrylic acid–Fe^{3+}	45.7	Na
6.	LDPE-*graft*-poly-4-vinylpyridine–Fe^{3+}	74.5	–
7.	Poly-*N,N*-dimethylaminoethyl methacrylate–Fe^{3+}	5.0	–

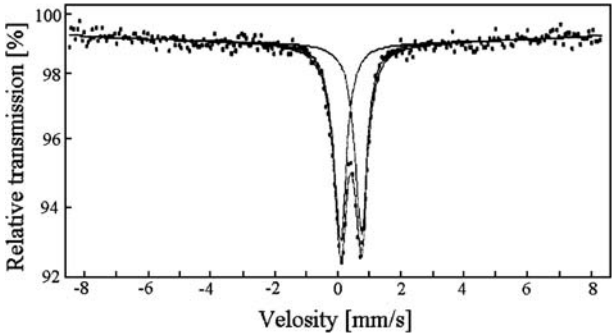

Fig. 2 Moessbauer spectra (RT) of LDPE-*graft*-PAA–Fe^{3+} complexes with grafting degree 41.9% in H-form

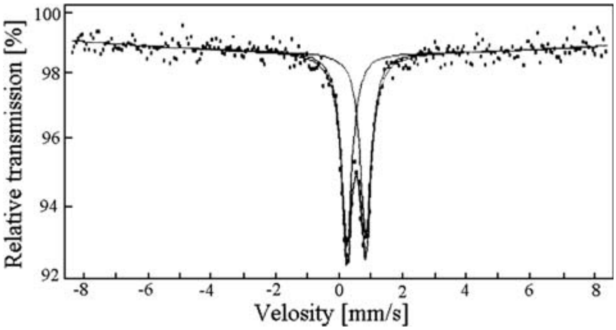

Fig. 3 Moessbauer spectra (RT) of LDPE-*graft*-PAA–Fe^{3+} complexes with grafting degree 75.9% in H-form

superposition of individual doublet lines with small differences in QS. The deconvolution procedure which was carried out showed that the value of the quadruple splitting was distributed from 0.59 to 0.69 mm/s. There is no simple explanation of the discrete character of the lines. Generally, it might mean that the iron ions were incorporated as non-repeating fragments (or clusters) of various sizes

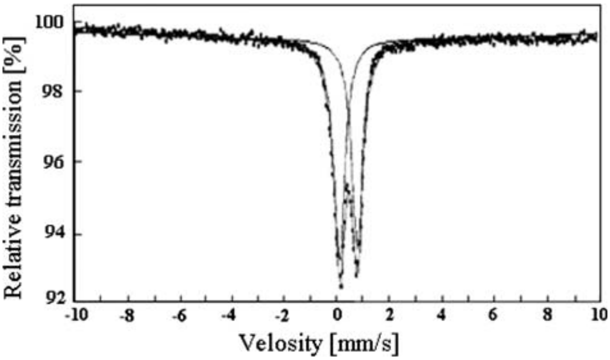

Fig. 4 Moessbauer spectra (RT) of LDPE-*graft*-PAA–Fe^{3+} complexes with grafting degree 75.9% in Na-form

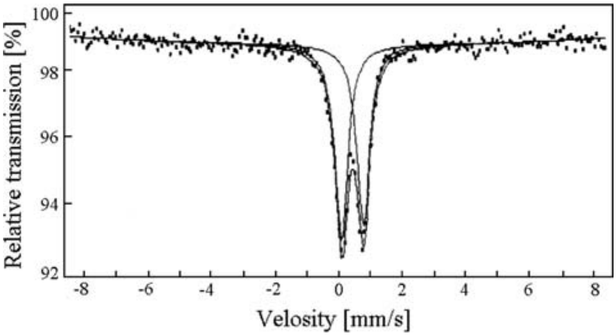

Fig. 5 Moessbauer spectra (RT) of PTFE-*graft*-PAA–Fe^{3+} complexes with grafting degree 45.7% in Na-form

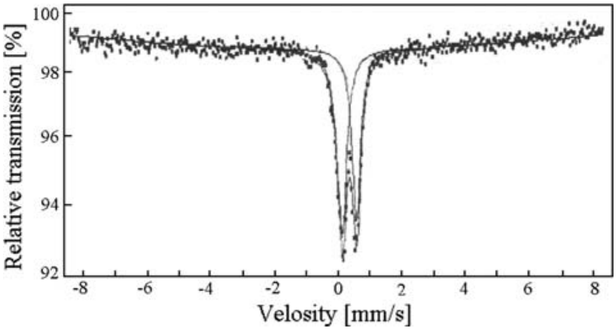

Fig. 6 Moessbauer spectra (RT) of PTFE-*graft*-PAA–Fe^{3+} complexes with grafting degree 23.4% in H-form

and compositions, which is characteristic for amorphous or partially amorphous substances. The different intensities of the lines in some spectra could be regarded as a confirmation for this structural pattern.

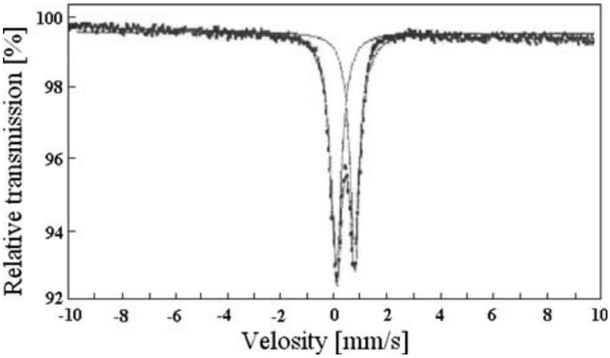

Fig. 7 Moessbauer spectra (LNT) of LDPE-*graft*-PAA–Fe^{3+} complexes with grafting degree 75.9% in Na-form

Two spectra were registered at the liquid nitrogen temperature: PTFE-*graft*-PAA with grafting degree of 23.4% (H-form) (Fig. 8), and LDPE-*graft*-PAA with grafting degree of 75.9% in Na-form, with different contents of Fe^{3+} (Fig. 7). The RT and LNT Moessbauer spectra of the copolymer LDPE-*graft*-PAA with 75.9% and in Na-form have doublet character. Moreover, except for the expected changes in IS, depending on temperature, no other differences were observed.

The spectrum of the grafted copolymer PTFE-*graft*-PAA in H-form was evaluated, following its mathematical processing, as being composed of a sextet and doublet with partial spectra areas ration 3:2. The relative weights of these components of the spectrum were $G_{\mathrm{sxt}} = 40\%$ and $G_{\mathrm{dbl}} = 60\%$, respectively. The co-existence of sextet and doublet for a sample which has doublet spectrum at room temperature, as well as the broad and asymmetric sextet lines, make the explanation of this phenomenon with superparamagnetism more probable [21, 22]. This reveals a possibility to estimate the size of the particles by taking temperature-scanned spectra at different temperatures. Analyzing once again the spectrum of the copolymer PTFE-*graft*-PAA in H-form of 23.4% degree of grafting, it could be also stated that the sextet component with relative weight of 38% is stipulated by particles, for which the changes in the spectrum recording temperature had resulted in collapse of the sextet and its gradual transformation into a paramagnetic doublet. The sextet lines were broad and asymmetric, even at the temperature of liquid nitrogen.

The distinction between the total spectra of samples 3 and 4 measured at liquid nitrogen temperature (the former is just a doublet while the latter is a doublet and sextet) can be attributed to the different grafting degree and the type of the polymer matrix (LDPE or PTFE). We suggested that the lower grafting degrees (23.4 vs. 75.9%) allows the introduction of Fe^{3+} among the grafted chains. As a result, sample 4 shows that Fe can be found in another form which, after hydrolysis and drying, transform into β-FeOOH. It is proved by the sextet observed in the spectrum in Fig. 8. β-FeOOH is formed in a medium of chlorine ions and its Neel temperature is 295 K. For this reason, its room-temperature spectrum is a quadrupole doublet (paramagnetic state), while at liquid nitrogen temperature it is a sextet

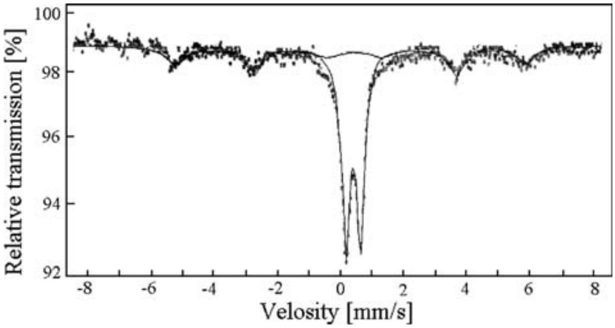

Fig. 8 Moessbauer spectra (LNT) of PTFE-*graft*-PAA–Fe^{3+} complexes with grafting degree 23.4% in H-form

(antiferromagnetic state). In the spectrum of sample 4 at room temperature. β-FeOOH cannot be observed because of its low content or due to superimposition with the spectrum of the chelate complex $(RCOO^{-})_xFe$.

LDPE-graft-P4VP and PTFE-graft-P4VP

The experimental spectrum of PE-*graft*-P4VP-Fe^{3+} obtained by Moessbauer spectroscopy was a quadruple doublet (Fig. 9). For the mathematical processing of the results, a model with one doublet was employed. The corresponding calculations gave the following results: IS = 0.38 mm/s, QS = 0.71 mm/s, FWHM = 0.43 mm/s (Table 3). The value of the isomer shift indicated the presence of Moessbauer-active iron ions of the third oxidation state and octahedralal co-ordination. The ions were found to exist in the high-spin state, characterized by low degree of coupling of 3d

Table 3 Moessbauer parameters of samples

Polymer complexes	Measuring temperature, T (K)	Components	IS (mm/s)	QS (mm/s)	FWHM (mm/s)	G (%)
1.	300	Db	0.40	0.67	0.47	100
2.	300	Db	0.40	0.60	0.40	100
3.	300	Db	0.34	0.68	0.50	100
	77	Db	0.43	0.69	0.48	100
4.	300	Db	0.40	0.61	0.45	100
	77	Db	0.51	0.63	0.44	60
	77	Sx*	0.53	0.09	0.67	40
5.	300	Db	0.33	0.69	0.48	100
6.	300	Db	0.38	0.71	0.43	100
7.	300	Sx**	0.44	−0.08	1.19	31
		Db	0.37	0.56	0.31	69

Sx* $H_{\mathrm{eff}} = 46.6$ T

Sx** $H_{\mathrm{eff}} = 33.8$ T

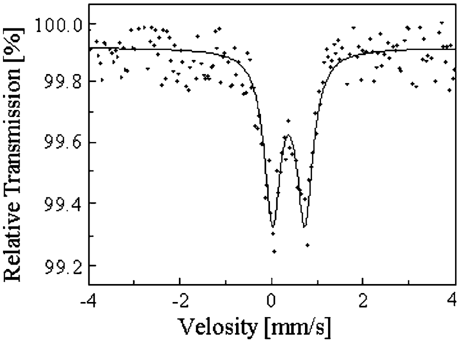

Fig. 9 Moessbauer spectra (RT) of LDPE-*graft*-P4VP–Fe^{3+} complexes with grafting degree 74.5%

electrons. The fairly high value of the quadruple splitting could be regarded as an indicator for a disturbed symmetry of the charge, surrounding the iron nucleus, located in the polyhedrons. In other words, the iron nucleus had a significant electric field gradient, most probably generated by the ligands of various chemical nature. Under the experimental conditions employed, the substance acted as paramagnetic-type one. The broadened spectral lines for a single component might account for the probable assumption that the substance was not structurally arranged in a regular and ordered solid-state pattern, except for the first co-ordination sphere; in general aspects, however, it could be considered as X-ray amorphous one. Similar results were obtained for the Moessbauer parameters of the PTFE-*graft*-P4VP-Fe^{3+} complex.

Poly(2-*N,N*-dimethylaminoethyl) methacrylate

The corresponding experimental Moessbauer spectra (Fig. 10) were composed of paramagnetic component (doublet, Db) and a component with superfine magnetic structure (sextet, Sx). A model, including the lines of one doublet and one sextet was used for the mathematical processing. The parameters determined are presented in Table 3.

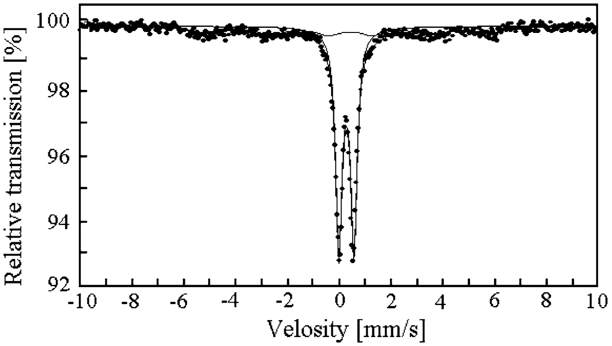

Fig. 10 Moessbauer spectra (RT) of PDMAEM–Fe^{3+} complexes

The values of the parameters established (mainly IS) for both spectral components showed that all iron ions existed in the third degree of oxidation [23, 24]. These Fe^{3+} ions were in high-spin state, which corresponded to low degree of coupling of the valent electrons and octahedron-type co-ordination [24]. The presence of electric gradient around the iron nucleus as indicated by the comparatively high value of QS suggested disturbed symmetry of its surrounding charge. This might be also due to the incorporation of the iron nuclei in polyhedrons, built from ligands of different chemical nature. The sextet component had parameters which could be attributed to iron ions, included in a system with anti-ferromagnetic arrangement. The significantly broadened lines (about three times as wide as the reference ones) could be probably due to multiple Lorentsians-type phenomena (superposition of lines), with parameters close to each other, i.e., lines of iron ions in similar (but not equivalent) surroundings. In this respect, the values of the effective magnetic field (H_{eff}) should be considered as average ones. The initial ferrous salt used was $FeSO_4$, i.e., the ferrous ions were of the second oxidation state (Fe^{2+}). The Moessbauer spectrum, however, did not contain any components, other than those, corresponding to Fe^{3+}-ions only. All these facts proved that the iron ions were fully oxidized during the process of the preparation of the metal–polymer complexes.

From the Moessbauer spectra only, it turned out to be difficult to determine how the iron ions, immobilized with nitrogen- or carboxyl-containing ligands in the polymer would be involved in exchange-type interactions in order to form an anti-ferromagnetic structure. Besides, one could not determine definitely what part of the paramagnetic iron ions are bound to the polymer carrier and what part are just mechanically incorporated. If there were other proofs for the presence of “built-in” iron ions in the polymer carrier, one explanation could be that the sextet part of the spectrum was associated with part of the iron ions (perhaps 31–32%), not chemically attached to the polymer functionalities and grouped as individual Fe-oxide phase with anti-ferromagnetic behavior [25]. The rest of the iron ions (the paramagnetic part of the spectra, 68–69%) could be those, which were structurally “built-in” (immobilized) in the polymer matrix, since their paramagnetic behavior did not contradict this statement.

Conclusions

Polymer complexes with Fe^{3+} ions are prepared on the basis of some carboxyl- and nitrogen-containing graft copolymers. The Moessbauer parameters of the complexes’ spectra correspond to high-spin Fe^{3+} ions in oxygen ligand surrounding. Depending on the nature of the ionogenic group, the Fe^{3+} ions can be retained in the polymer by two principal mechanisms. These mechanisms are associated with both the ion exchange and donor–acceptor interactions for the Na- and H- forms of the grafted copolymers with iron ions. The Moessbauer parameters indicate for well isolated Fe^{3+} ions situated in non-magnetically arranged structures.

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