NOTES

Mössbauer Spectroscopic Studies of Complexes of Fe(III) with Nitrogen Containing Polymers

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Coordination polymer compounds have been successfully used in various catalytic processes such as hydrogenation, oxidation, hydroformylation, polymerization, isomerization, etc.¹ Nitrogen containing polymers are interesting polymer ligands that function as supports in catalysis.

Complex formation ability of nitrogen containing polymers in relation to the transition metal ions is due to the presence of primary, secondary and tertiary aminogroups which are able to form donor–acceptor bonds.^{2–7} The structures of coordination compounds influence on the catalytic activity of polymer–metal complexes.

In the present paper the results of an investigation of solid complexes of poly(2-vinylpyridine) (P2VPy), poly(2-methyl-5-vinylpyridine) (P2M5VPy), poly(4-vinylpyridine) (P4VPy), copolymers of vinylimidazole (VI), and vinylpyrrolidone (VP) with Fe(III) by Mössbauer and IR spectroscopy are presented in order to elucidate the influence of the polymeric ligand nature on the structures of polymer–metal complexes.

EXPERIMENTAL

P2VPy, P2M5VPy, and P4VPy were synthesized by the radical polymerization of monomers in methanol at 333 K in presence of azobisisobutyronitrile (AIBN) as initiator.⁸ Copolymers based on VI and VP were synthesized by radical copolymerization in ethanol at 333 K in the presence of AIBN. All polymers and copolymers were purified by fractional precipitation. The compositions of copolymers were determined by IR spectroscopy⁹ and by elemental analysis. PVI with molecular weight 16×10^3 and commercial sample of PVP with molecular weight 5.6×10^5 were used.

Intrinsic viscosities of VI–VP copolymers determined in ethanol solution are 0.34, 0.43, and 0.62 dl g^{-1} for 0.63VI: 0.37VP; 0.41VI: 0.59VP; and 0.21VI: 0.79VP, respectively.

The complexes of nitrogen containing polymers with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained by mixing the ethanol solutions of the initial components. The precipitated complexes were filtered, washed with ethanol, then dried at room temperature under vacuum.

The Mössbauer spectra of the complexes

were taken with a nuclear gamma resonance spectrometer CMTE of an electrodynamic source type at room temperature in the constant acceleration regime. The source of γ -rays were $^{57}\text{Co(Pd)}$ with an activity of 3 mCi. Absorbers were the complexes of polymers with Fe(III). The Mössbauer parameters, the isomeric shift (ΔE_I) and quadrupole splitting (δE_Q) were calibrated with respect to the standard absorber $\text{Na}_2^{57}\text{Fe(CN)}_5\text{NO}$.

The Mössbauer parameters were calculated by the computer MERA-60. IR spectra of complexes were obtained with the help of the spectrophotometer "UR-20" (DDR) using

KCl pellets.

RESULTS AND DISCUSSION

It was established that during interactions of PVI and VI-VP copolymers with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ the polymer-metal complexes yield reached 95%. The composition of polymer-metal complexes depends on the molar ratio of initial components and distribution of ligend groups in the case of VI-VP copolymers. Some characteristics of polymer-Fe(III) complexes are shown below.

Ligand	Molar ratio of initial components L : FeCl_3	Cl % found	Cl % calculated	Composition of complexes
PVI	2 : 1	22, 20	22, 17	$(\text{PVI})_3\text{FeCl}_3$
0.41VI : 0.59VP	2 : 1	11, 93	11, 74	$(0.41\text{VI} : 0.59\text{VP})_3\text{FeCl}_3$
0.63VI : 0.37VP	2 : 1	34, 11	23, 63	$(0.63\text{VI} : 0.37\text{VP})_{2.5}\text{FeCl}_3$

The composition of poly(vinylpyridine)-Fe(III) complexes does not depend on the molar ratio of initial components, which is equal to 2 : 1.

Complexation of poly(vinylpyridine)s with transition metal ions is often accompanied by the increase of the stretching frequency on the C=N bond.¹⁰⁻¹² This can be used for the elucidation of the complexation ability of polyligands and for the determination of the stability of the coordination compounds.

IR spectra of poly(vinylpyridine) complexes of iron(III) are shown in Figure 1. It is seen that for all complexes ν_{CN} shifted to higher frequency. Analogous shifts are also observed for the out-of-plane vibration of the pyridine ring ($\nu = 550\text{ cm}^{-1}$).¹³ The complexing ability of poly(vinylpyridine)s in relation to Fe(III) determined as $\Delta\nu = \nu_{\text{CN}}^{\text{coord.}} - \nu_{\text{CN}}^{\text{free}}$ (where $\nu_{\text{CN}}^{\text{coord.}}$ and $\nu_{\text{CN}}^{\text{free}}$ are the frequencies of coordinated and free CN groups respectively) varies as follows: $\text{P2M5VPy} > \text{P4VPy} > \text{P2VPy}$.

Mössbauer spectroscopic data of poly-

(vinylpyridine) complexes of Fe(III) are summarized in Table I. The Mössbauer spectra of the complexes represent asymmetric doublets except for P2VPy-Fe(III) which contains only one doublet (Figure 2).

Similar values of isomeric shift and quadrupole splitting for all poly(vinylpyridine) complexes probably indicate similar coordinate

Figure 1. IR spectra of Poly(vinylpyridine) complexes of Fe(III). 1, P2M5VPy/Fe(III); 2, P4VPy/Fe(III); 3, P2VPy/Fe(III).

Table I. Mössbauer parameters of poly(vinylpyridine) complexes of Fe(III)

Poly(vinylpyridine)s	ΔE_I	δE_Q	ε
	mm s ⁻¹	mm s ⁻¹	%
P2M5VPy	0.34	0.51	6.0
	0.47	0.52	
P2VPy	0.41	0.50	2.7
P4VPy	0.47	0.56	1.4
	0.35	0.51

Figure 2. Mössbauer spectra of poly(vinylpyridine) complexes of Fe(III). 1, P2VPy/Fe(III); 2, P4VPy/Fe(III); 3, P2M5VPy/Fe(III).

surrounding of the irons. The Mössbauer parameters of the complexes are typical of high-spin compounds of Fe(III). The maximal value of the resonance effect (ε) for P2M5Py-Fe(III) is accounted for by the formation of a strong coordination bond in this system. This is probably connected with the increase of electron density in the pyridine ring owing to the donor ability of methyl groups.

For iron(III) complexes of VI-VP copolymers the stretching frequency of C=C and C=N bonds at 1493 and 1503 cm⁻¹ shifted to 1515 cm⁻¹. Spectral changes are also observed for the lactam cycle of VP. The band at 1672 cm⁻¹ corresponding to C=O vibrations

Figure 3. Mössbauer spectra of complexes of Fe(III) with VI-VP copolymers. 1, PVI/Fe(III); 2, 0.63VI:0.37VP/Fe(III); 3, 0.41VI:0.59VP/Fe(III); 4, 0.21VI:0.79VP/Fe(III); 5, PVP/Fe(III).**Table II.** Mössbauer parameters of complexes of Fe(III) with VI-VP copolymers

Copolymers	ΔE_I	δE_Q	ε
	mm s ⁻¹	mm s ⁻¹	%
PVI	0.50	0.67	1.0
0.63VI:0.37VP	0.51	0.67	1.5
0.41VI:0.59VP	0.51	0.71	2.6
0.21VI:0.79VP	0.54	0.66	5.0
PVP	0.55	0.66	4.0

is shifted to lower frequency at 1630 cm⁻¹. These data indicate the interactions of both nitrogen atoms of the imidazole ring and the carbonyl groups of the lactam cycle with Fe(III) ions. Earlier^{2,13} it was shown by NMR

^{13}C and IR spectroscopy that PVP interact with cupric(II) ions only through the carbonyl oxygen of *N*-vinylpyrrolidone groups. Mössbauer spectroscopic data of complexes of Fe(III) with VI-VP copolymers are presented in Figure 3 and Table II.

As seen from Table II the increase of VP content in copolymers leads to growth of the isomeric shift. From these data the preferential coordination of iron(III) ions with VP units although the nitrogen atom in the VI ring may possibly have more electron donating ability than that of oxygen. This is explained by the fact that the lone pair electrons of nitrogen atoms in VI are conjugated with π -electrons of the imidazole ring whereas the lone pair electrons of the oxygen atoms in the lactam ring are free and interact more easily with Fe(III). This is confirmed by the increase in the resonance effect (ϵ).

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