Polymer Bulletin

Complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate with heavy metals I. Preparation and properties

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Summary

The present paper studies the synthesis of complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate with aqueous solutions of of salts of $FeSO_4.2H_2O$; $CoCl_2.6H_2O$; $CuCl_2.2H_2O$; $VOSO_4.5H_2O$; $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$. The introduction of metal ions depends on the content of crosslinking agent and was in the range from 1.18 to 59.63 mg metal ion /g polymer carrier. The study of polymer complexes by IR and Moesbauer spectroscopy, as well as EPR, provides possibilities to suggest the probable co-ordination structure of the compounds.

Introduction

Recently, polymer metal complexes attracted great interest because of their valuable electrical, mechanical and thermal properties and the possibilities to use them as immobilized catalysts for various processes.

The use of polymer carrier provides possibilities to combine the properties of the matrix with the complex-forming abilities of the ligands and reveals new perspectives for preparation of heterogeneous catalysts.

Poly(2-*N,N*-dimethylaminoethyl) methacrylate (PDMAEM) and its copolymers are known for their versatility of the materials prepared from them. The presence of nitrogen containing functional groups leads to the formation of metal complexes when treated with solutions of salts of transition metals. The reactions of co-ordination of the polymer ligands with metal ion and the formation of new structures have been studied mainly by spectral methods [1-3]. The introduction of metal into polymer chains changes polymer behavior and its surface morphology. The complex structure depends on a number of factors: chemical nature of the ion, temperature, pH, etc. The new polymer materials synthesized on the basis of PDMAEM can be used as hydrogels [4,5], pH and thermosensitive systems for controlled release of medical preparates [6,7], membranes for retention of heavy metals [8,9] and conducting electrolytes [10]. Thermosensitive polymers were obtained on the basis of poly(*N*-isopropylmethacrylamide)[11].

The present paper is a continuation of our investigations on the preparation of polymer-metal complexes. It reports for the preparation of immobilized complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate with salts of $FeSO_4.2H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $VOSO_4.5H_2O$, $Na_2MoO_4.2H_2O$, $Na_2WO_4.2H_2O$, and discusses their structure.

Experimental Part

Chemicals

$FeSO_4.2H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $VOSO_4.5H_2O$, $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ were obtained from Fluka AG. 2-(*N,N*-dimethylaminoethyl) methacrylate and azobisisobutyronitrile were purchased from Aldrich. Divinylbenzene of 55 mass % content (it also contained 45 mass % 3- and 4-ethylvinylbenzene) was obtained from Merck. All other reagents used in these experiments were analytical grade.

Preparation of Poly(2-N,N-dimethylaminoethyl) methacrylate

Poly(2-*N,N*-dimethylaminoethyl) methacrylate was obtained by radical polymerization of the monomer 2-*N,N*-dimethylaminoethyl methacrylate (DMAEM) using initiator azobisisobutyronitrile (AIBN), as described in a previous publication [12]. Briefly AIBN(0.1g , $0.6×10^{-3}$) were dissolved in DMAEM (10g, 0.064M). After the complete dissolution of the initiator, the cross-linking agent divinylbenzene (DVB 1.0g, $7.5×10^{-3}$) were introduced into the reaction mixture. Then 20 ml toluene were also added to the reaction mixture and heated under vigorous agitation at 75°C for 1 h. The cross-linked polymer obtained was removed from the reaction medium, washed with toluene several times and dried in vacuum at 40°C.
The polymer with 10% cross-linking agent was obtained by the same procedure introducing 2.0g, $15×10^{-3}$ DVB.

Preparation of metal complexes of Poly(2-N,N-dimethylaminoethyl) methacrylate

The metal complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate were obtained by treating the polymer with 0.4 mass% aqueous solutions of $FeSO_4.2H_2O$; $CoCl_2.6H_2O$; $CuCl_2.2H_2O$; $VOSO_4.5H_2O$ for 24h at room temperature under continuous stirring. The complexes of Mo^{6+} and W^{6+} were prepared in aqueous-acid solutions at pH ~2.5. The treated polymers were dried under vacuum at 50°C to constant weight.

Determination of metal ions content in the polymer complexes

The amount of metal ions bonded to the polymer matrix was determined spectrophotometrically on a UV/VIS Spectrometer UNIGAN 8625 at the wavelengths (λmax, nm). After separation from the polymer matrix, the amount of Mo, Co and W, were determined spectropfotometrically by complexation with potassium rhodanide: Mo - λ=460 nm, Co - λ=620 nm and W – λ=405 nm, respectively. The amount of Fe, V and Cu, were determined spectrophotometrically by complexation with sulfosalicylic acid, hydrogen peroxide and ammonia at : λ=470 nm, λ=450 nm and λ=570 nm, respectively.

Analysis

IR analysis
Infrared (IR) spectra of the polymers and their metal complexes were taken by using a Specord IR 75 spectrophotometer (Carl Zeiss Jena, Germany), and the samples were prepared as KBr pellets.

EPR analysis
The electron paramagnetic resonance (EPR) spectra of the metal complexes were obtained at room temperature on a Bruker 200 DSRC spectrometer (Germany) operating in the X-range, at frequency of magnetic field modulation 100 KHz and rectangular resonator TE_{102}.

Moesbauer analysis
Moesbauer spectra of Fe^{3+} complexes were recorded on an electromechanical spectrometer (Wissenschaftliche Elektronik GmbH, Germany), at a regime of constant acceleration. The source used was ^{57}Co deposited on Cr matrix with activity of 20 mCi. The rate gauge was calibrated by using 25 μm thick α-Fe foil. The samples were studied at room temperature. The Moesbauer spectra obtained were computer processed by the least squares method using Lorents shaped curves and deconvolution.

The experimental spectra were mathematically worked out using a program based on the method of iteration optimization of initial approximations (least squares method). The parameters of the ultrafine interactions were determined : isomer shift (IS – the value of the isomer shift depends on the electronic density around the iron nucleus, i.e. it provides information on the type of the chemical bond, spin state and the co-ordination of the iron ions); quadruple split (QS – electric field gradient is initiated by deformations in the occupied nodes of the lattice whose symmetry is lower than the cubic one); effective internal magnetic field (H_{eff} – it is determined by the interaction between the magnetic moment of the atom and the magnetic field generated by the surrounding electrons, i.e. it is an indicator for the degree of arrangement of the magnetic structure); full-width at half-maximum of the lines (FWHM – universal spectroscopic value) and relative weight of the partial components (G) of the spectra (G – the content of iron ions in certain component was determined assuming the same Moesbauer-Lamb factor – f). An optimum processing was considered the one where the experimental and the theoretical spectra had the highest convergence (the sum of Lorents lines) in an optimum confidence interval.

Results and discussion

The results reported in the present paper are continuation of our studies on polymer complexes containing Fe^{3+}, Co^{2+}, Cu^{2+}, VO^{2+}, MoO_2^{2+} and WO_2^{2+} and determination of their structural and physico-chemical characteristics. The ternary aminogroup in poly(2-*N,N*-dimethylaminoethyl) methacrylate acts as chelate center for ions of transition metals. The formation of the metal complexes occurs by reaction between PDMAEM containing electron donor atoms(in this case, nitrogen atoms) and the metal ions.The mechanism of the formation of "polymer ions"by the reaction of molybdenyl and vanadyl ones with carboxyl groups, has been studied and reported in an earlier publication [13].

The contents of Fe^{3+}, Co^{2+}, Cu^{2+}, VO^{2+}, MoO_2^{2+} and WO_2^{2+} and in polymer complexes was determined spectrophotometrically.

Table 1. Contents of metal ions in PDMAEM, mg metal ion /g polymer carrier

Polymer carrier	Co^{2+}	Fe^{3+}	Cu^{2+}	MoO_2^{2+}	VO^{2+}	WO_2^{2+}
PDMAEM 5%	4.89	34.40	5.45	6.49	59.63	2.07
PDMAEM 10%	1.65	19.71	2.05	2.85	31.15	1.18

As can be seen from the results presented in Table 1, the strongest affinity to co-ordination showed the vanadyl ions. The experimental data suggest that, beside ion nature, the content of cross-linking agent also exerts influence on the formation of the complex. The samples with 5% content of cross-linking agent had higher content of mg metal ions per g of polymer carrier. This can be explained with the fact that the transport of metal ions to the nitrogen containing groups is disturbed by the more cross-linked PDMAEM which impedes the formation of a co-ordination bond.
The co-ordination structure of the metal complexes was studied by different spectral analyses – IR, Moesbauer and EPR.
The analyses of the IR spectra of the complexes of PDMAEM with Fe^{3+}, Co^{2+}, Cu^{2+}, VO^{2+}, MoO_2^{2+} and WO_2^{2+} provide information about their structure (Table 2).

Table 2. Absorption bands in the IR spectra of metal ions with poly(2-N,N-dimethylaminoethyl) methacrylate and their assignments

Polymer complex	$v_{as}(C-N)$	$v_s(C-N)$	$v(N-M)$	$v(M=O)$	$v(C=O)$
PDMAEM- VO^{2+}	840	755	430	880	1710
PDMAEM- MoO_2^{2+}	840	750	450	900	1710
PDMAEM- WO_2^{2+}	840	750	450	910	1710
PDMAEM- Cu^{2+}	850	750	450	-	1710
PDMAEM- Co^{2+}	840	760	450	-	1710
PDMAEM- Fe^{3+}	850	755	450	-	1710
PDMAEM	825	780	-	-	1710

Absorption bands at 825 cm^{-1} – from asymmetric valent vibrations of $v(C-N-)$ and at 780 cm^{-1} – from the symmetric vibrations of the $v(C-N-)$ groups were observed in both spectra. Simultaneously, bands at 1710 cm^{-1}, characteristic for the valent vibrations of the $v(C=O)$ groups in PDMAEM were also registered. In the IR spectra of the metal complexes, the bands at 825 and 780 cm^{-1} were shifted and a new band was observed at 450 cm^{-1}. The latter corresponds to the vibrations of the bond $v(-N-M)$ indicates for the interaction between the nitrogen atom of the polymer macromolecules with the metal ions [14]. It should be noted that the band at 1710 cm^{-1} in the spectra of the polymer metal complexes was not shifted which was considered enough to suggest the bonding of the metal ions proceed towards the nitrogen atom rather than towards the oxygen atom. After bonding of PDMAEM with vanadyl, molybdenyl and tungstenate cations, new bands were registered, characterizing the vibrations of the bond $v(M=O)$

- at 880 cm^{-1} for (V=O) [15], at 900 cm^{-1} for (Mo=O) [16] and at 910 cm^{-1} for (W=O)[17].

The electron configuration of the vanadyl ions in the metal complexes of PDMAEM was studied by EPR (Figure 1). A typical spectrum of disordered system containing oxovanadium ions VO^{2+} (V^{4+}) with configuration ($3d^1$) – (d^1 – single uncoupled electron on d-level of vanadium electron cloud at this degree of oxidation) was registered, characterized by axial symmetry. Due to the interaction of this uncoupled electron with the magnetic moment of the nucleus of the isotope ^{51}V (which is 100% of the natural isotope mixture of vanadium and has nuclear spin (I)=7/2), each line (in this case, $g_{\parallel}$ and $g_{\perp}$) in the EPR spectrum splits into 8 lines with parallel and 8 lines with perpendicular orientation. Because of the overlapping of some lines, the EPR spectrum had 13 instead of 16 lines. The EPR parameters of the spectrum before the catalytic reaction were $A_{\parallel}$ = 17.7 +_ 0.3 mT and $g_{\parallel}$ = 1.925.

20 mT
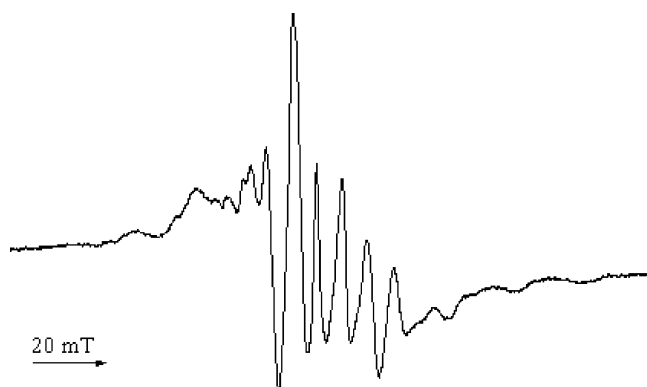
Figure 1. EPR-spectra of PDMAEM-VO^{2+} complex

Taking into account the constants of superfine interaction and g-factors, the comparison with literary data [18] proved the co-ordination of VO^{2+} with nitrogen donors.

In metal complexes, the substitution of oxygen atoms with nitrogen donor atoms leads to increase of the degree of covalence of the bond metal-ligand. With VO^{2+}, it is manifested by a change in the values of g-factor and A – the constant of superfine interaction the values of which can be established easier. These changes were observed mostly by the change of the values of g_{II} (parallel) increased while A_{II} decreased with the transition from oxygen to nitrogen (for the VO^{2+} complexes).

Comparing g_{II} and A_{II} for PDMAEM-VO^{2+} complexes with our previous studies on polyethene - graft- polyacrylic acid-VO^{2+}, this tendency was the same. The value of $A_{\perp}$ in PDMAEM-VO^{2+} sample was also lower than that of polyethene - graft-polyacrylic acid-VO^{2+} [13].

The experimental Moesbauer spectra (Figure 2) 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.

Table 3. Parameters of the Moesbauer spectra

| Polymer complexes	Compo-nents	IS, mm/s	QS, mm/s	H_{eff}, T	FWHM, mm/s	G, %
Poly(2-*N,N*-dimethy-laminoethyl)metha-crylate - Fe^{3+}	Sx	0.44	-0.08	33.8	1.19	31
	Db	0.37	0.56	-	0.31	69

The values of the parameters established (mainly IS) for both spectral components showed that all iron ions were in third degree of oxidation. These Fe^{3+} ions are with high spin, i.e. low degree of coupling of valent electrons and octahedron co-ordination. The presence of electric gradient around iron nucleus (comparatively high value of QS) indicates for disturbed symmetry of its surrounding charge. This may be due also to placement of the iron nucleus in polyhedrons built from ligands of different chemical nature.

The sextet component has parameters which can be attributed to iron ions included in a system with antiferromagnetic arrangement. The significantly wider lines (about 3 times vs. the reference) are probably due to multiple lorentsians (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 average ones. The initial ferrous salt used was $FeSO_4$, i.e. the ferrous ions were with second degree of oxidation - Fe^{2+} . The Moesbauer spectrum did not contain component with such parameters but only Fe^{3+}-ions. All these facts showed that the iron ions were fully oxidized during the process of complex synthesis.

As it is well known, that $FeSO_4.2H_2O$ is also used in the synthesis of soft and hard ferrites. Their preparation is carried out in liquid medium (aqueous solutions) at pH=4.5 – 9. The process is known as oxidative hydrolysis because the iron ions are oxidized and hydrolyzed. Depending on ferrous salt concentration, solution pH and temperature of the synthesis, the products obtained are different polymorphic forms of iron hydroxides (goethite FeOOH; lepidokrokit, γ-FeOOH; ferrihydrid, $Fe_5OH_8.4H_2O$). At room temperature of hydrolysis and higher concentration of the ferrous salt, the phase α-FeOOH will be most probably obtained.

The spectra registered and the parameters of the sextet part determined are quite close to those of high dispersion goethite phase (D = 12-15 nm) in a state of collective magnetic excitation, i.e. at strong reduction of the magnetic field. The doublet component can be attributed to the other polymorphic form of iron hydroxide - γ-FeOOH which is paramagnetic at room temperature. Part of the doublet may also belong to α-FeOOH but, due to dimension effect, the particles have supermagnetic behavior. From the Moesbauer spectra only, it was difficult to determine how the iron ions immobilized with nitrogen-containing or hydroxylic ligands in polymeric medium would enter exchange interactions forming antiferromagnetic structure. One cannot also determine definitely what part of the paramagnetic iron ions are bonded to the carrier and what part are just mechanically mixed with it. If there are other proves for the presence of "built-in" iron ions in the polymer carrier, one explanation could be the following: the sextet part of the spectrum are iron ions (31-32%) not included in the polymer and grouped as individual ferrous oxide phase with antiferromagnetic behavior. The rest of the ferrous ions (the paramagnetic part of the spectra – 68-69%)

are those structurally "built-in" (immobilized) in the polymer, since their paramagnetic behavior does not contradict this statement.
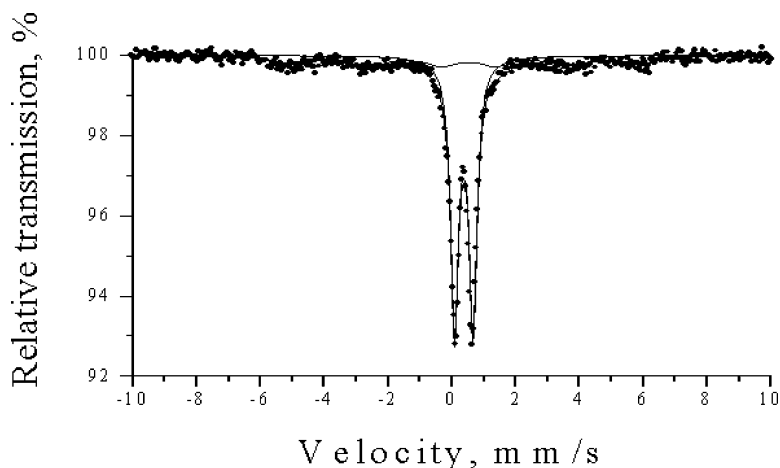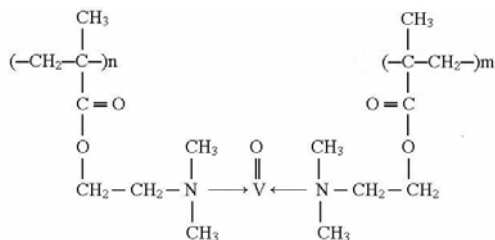

Figure 2. Moesbauer spectra of PDMAEM - Fe^{3+} complexes at room temperature

On the basis of the results obtained from the IR and EPR analyses, and from the literature[1,19], the following structures can be suggested: (Scheme 1)

a– Intramolecular co-ordination structure of PDMAEM - Fe
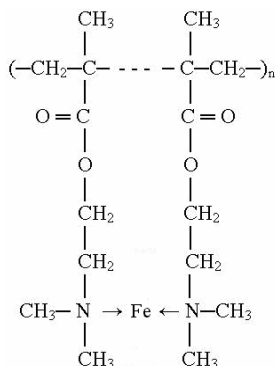
b –Intermolecular co-ordination structure of PDMAEM - VO^{2+}

Scheme 1

Conclusion

Complexes of poly(2-*N,N*-dimethylamioethyl) methacrylate with heavy metals were synthesized. The complexes were characterized and their co-ordination structure was established different analytical methods. These complexes will use as catalysts for the oxidation of cyclohexene using *tert*-butylhydroperoxide as an oxidant. The effect of metal ions on its catalytic activity towards epoxidation and hydroxylation will be investigate.

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