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PLASMA SURFACE MODIFIED POLYTETRAFLUOROETHYLENE GRAFTED NANOLAYERS AND COMPLEXES THEREFROM

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ABSTRACT

Metal complexes of copolymers based on poly(acrylic acid), poly(4-vinylpyridine) and poly(1-vinylimidazole) plasma grafted onto films of poly(tetrafluoroethene) were prepared by complex formation with solutions of salts of $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $VOSO_4.5H_2O$ *and* $Na_2MoO_4.2H_2O$ *at room temperature. The introduction of metal ions was found to depend mainly on the degree of grafting of acrylic acid, 4-vinylpyridine and 1-vinylimidazole and was from 1.1 to 6.5 mg metal ion/g polymer carrier. The studies carried out by IR spectroscopy, Moessbauer spectroscopy and electron paramagnetic resonance proved the preparation of metal complexes.*

Keywords: Plasma modification, Poly (Tetrafluoroethene), Poly (Acrylic acid), Poly (4-vinylpyridine), Poly (1-vinylimidazole) Grafted nanolayers, Complexes, Structure.

Contribution/ Originality

This study documents the investigation of surface modification on poly(tetrafluoroethene) films with argon plasma treatments, followed by graft polymerization. The copolymers with grafted nanolayers were obtained. The complexation was performed and the structures of the systems were suggested. The metal complexes can be used as catalytic centers in organic reactions.

1. INTRODUCTION

Plasma grafting of monomers on polymer films leads to obtaining perspective materials with modified surfaces and versatile application: ionomers for adsorption of metal ions from solutions, materials with biocontact properties and improved interaction with live cells, carriers for immobilization of biomolecules and other biomedical applications, as catalytic active centers, etc. [1-9]. Currently, surface modification of polytetrafluoroethylene is an object of intense investigation [10-14]. The wide range of applications of poly(tetrafluoroethene) (PTFE) is based on its outstanding bulk and surface properties, such as high thermal stability, excellent chemical inertness, low dielectric constant, low water sorption, extreme frictional resistance and low surface energy [7, 8]. However, the extremely hydrophobic and poor adhesive properties of this polymer limit its performance. The selection of carboxylic or nitrogen containing monomers for the grafting reaction was stipulated by the possibilities to introduce ligands different by nature. By grafting acrylic acid (AA) (well known for its ion-exchange properties and the ability to form stable complexes with metal ions), 4-vinylpyridine (4VP) and 1-vinylimidazole (1VI) onto polymer matrices, including PTFE ones, copolymers combining the valuable properties of the initial poly(tetrafluoroethene) and the functional groups of the grafted monomers can be obtained.

The aim of the present work is to prepare metal complexes on the basis of plasma grafted carboxyl (polytetrafluoroethene-grafted-polyacrylic acid) and nitrogen (polytetrafluoroethene-grafted-poly-4-vinylpyridine, polytetrafluoroethene-grafted-poly(1-vinylimidazole) containing copolymers with $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $VOSO_4.5H_2O$ and Na_2MoO_4 and study their structure and properties.

2. EXPERIMENTAL

2.1. Materials

Copolymers with grafted nanolayers of AA, 4VP and 1VI onto films (40 μm) PTFE (ONPO Plastpolymer, St.Peterburg, Russia) were used. All other reagents, such as $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $VOSO_4.5H_2O$, $Na_2MoO_4.2H_2O$ and HNO_3 (*Merck Germany*), were of analytical grade and were used as received. The carboxyl and nitrogen containing copolymers with different degrees of grafting were obtained by plasma grafted copolymerization of acrylic acid (BASF, Germany), 4-vinylpyridine and 1-vinylimidazole (Aldrich-Chemical Co. Ltd., Gillingham, England) onto PTFE films by argon plasma treatment followed by graft polymerization.

2.2. Preparation of Grafted Copolymer-Metal Complexes

The preparation of grafted copolymer-metal complexes was carried out by treatment either with 0.4 mass% aqueous solutions of $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$ and $VOSO_4.5H_2O$ under continuous stirring for 24 h at 296 K. The complexes of Mo^{6+} were prepared in aqueous-acid solutions with pH ~2.5. The treated films were dried under vacuum at 323 K to constant mass.

2.3. Determination of Metal Ions Content in the Polymer Complexes

The amount of metal ions bound to the polymer matrix was determined spectrophotometrically, using *UV/VIS Spectrometer UNIGAN 8625* (*Germany*) at various wave lengths: λ_{max}=460 nm (Mo-rhodanide complex); λ_{max}=620 nm (Co-rhodanide); λ_{max}=470 nm (Fe-sulfosalicylic acid complex); λ_{max}=450 nm (V-hydrogen peroxide complex); and λ_{max}=570 nm (Cu by complexation with ammonia).

2.4. Analyses

Infrared (FT-IR) spectra of metal complexes were obtained by using spectrophotometer produced by Bruker (Germany) in the interval 4,000–400 cm^{-1} with Tensor 27.

The UV-VIS characteristics of sample films were measured on a Specord UV-VIS (*Carl Zeiss Jena, Germany*).

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

The Moessbauer spectra of Fe^{3+} complexes were recorded on an electromechanical spectrometer (*Wissenschaftliche Elektronik GmbH, Germany*), at constant acceleration mode. The irradiation source used was ^{57}Co with activity of 20 *mCi* deposited on Cr-matrix. The rate gauge was calibrated by using a 25-μm thick α-Fe foil. The samples were analyzed at room temperature. The Moessbauer spectra obtained were subjected to computer-aided processing by employing the least squares method with Lorentz-shaped curves and deconvolution.

3. RESULTS AND DISCUSSION

Surface modification on polytetrafluoroethene films was performed with argon plasma treatments and followed by graft polymerization. Peroxide groups were introduced on the surface of poly(tetrafluoroethene) films after plasma treatment and the consequent contact with air when the films were taken out of the reactor. Grafting polymerization initiated by the surface peroxide (hydroxide) groups was performed on the poly(tetrafluoroethene) film surface by using acrylic acid, 4-vinylpyridine and 1-vinylimidazole as monomers. Copolymers were obtained with grafting yield from 0.436 to 0.457 mg/cm^2 for poly(acrylic acid), from 0.299 to 0.390 mg/cm^2 for poly(4-vinylpyridine) and from 0.212 to 0.256 mg/cm^2 for poly(1-vinylimidazole), respectively.

Aiming to prepare metal complexes, part of these carboxyl and nitrogen containing copolymers were treated with aqueous solutions of $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $VOSO_4.5H_2O$ and $Na_2MoO_4.2H_2O$. The polyacrylic acid, poly-4-vinylpyridine and poly(1-vinylimidazole) grafted onto PTFE films act as chelate center for some ions of transition metals (Fe^{3+}, Cu^{2+}, Co^{2+}) and higher valency ions (VO^{2+} and MoO_2^{2+}). The formation of metal complexes was performed by bonding the polymer ligands with metal ions through reaction between the copolymer containing groups with donor atoms (-N and -O) and metal ions (Fe^{3+}, Cu^{2+}, Co^{2+}, VO^{2+} and MoO_2^{2+}). The mechanism of the formation of the corresponding "polymer ions" with molybdenyl and vanadyl moieties with carboxyl groups-containing polymer carriers was described in a previous publication [15]. The content of Fe^{3+}, Cu^{2+}, Co^{2+}, VO^{2+} and MoO_2^{2+} in plasma grafted copolymer films was determined spectrofotometrically by the UV-Vis method. The results show that vanadyl cations have the highest tendencies to coordination. The metal ions content is in the range from 1.1 to 6.5 mg metal ion/g polymer carrier. Cu^{2+} have a higher tendency to coordination with nitrogen ligands (P4VP and P1VI) than with oxygen ones (COOH groups of PAA). To clarify the formation of the metal complexes and their co-ordination structure, they were studied by IR–FT, Moessbauer spectroscopy and EPR. The IR spectra of plasma treated PTFE grafted copolymers and their metal complexes were investigated and the results are presented in Figures 1 and 2, and Table 1. The characteristics bands of different bonds are similar to those of grafted copolymers and proved the formation of metal polymer complexes.

The IR spectra of PTFE-*graft*-PAA contain absorption bands at 1,700 cm^{-1}, characteristic for the valent vibrations of ν(C=O), at 1,230 cm^{-1} corresponding to the valent vibrations of ν(C–O) and a band at 1,440 cm^{-1} which can be attributed to the deformation vibrations of δ(–CH_2–) groups (Fig. 1). In IR spectra PTFE-*graft*-P4VP, the 1,430 and 1,470 cm^{-1} bands were assigned to the skeletal vibration of (C=C) in pyridine and the band at 1,600 cm^{-1} was assigned to the skeletal vibrations of (C=N) in pyridine. After 1-vinylimidazole grafting, two new peaks were observed at 1,650 and 1,220 cm^{-1} and they were assigned to the C=N and C–N modes, respectively, of the imidazole [16]. All IR spectra of the grafted copolymer films showed absorption bands at 1,300–1,100 cm^{-1} for ν (>CF_2), 620 cm^{-1} for ν_w (>CF_2) and 500 cm-1 for ν_r (>CF_2) [17] characteristics for PTFE. Figure 2 shows the spectra of the initial PTFE-*graft*-P4VP copolymers with degrees of grafting 8.1% and their complexes with VO^{2+} and MoO_2^{2+}. The IR spectra showed absorption bands at 1,600 cm^{-1} ν(C=C) and ν(C-N) confirming the presence of pyridine ring and band at 990-810 cm^{-1}, corresponding to the out-of-plane vibrations of the ν(=CH) groups.

For the metal complexes, the band at 1,600 cm^{-1} for the asymmetric vibrations $\square_{as}$(-C-N-) of the pyridine ring was shifted towards higher frequencies (1,630 cm^{-1}).

Table-1. Absorption bands in the IR spectra and their assignment for plasma treatment of PTFE-*graft*-PAA, PTFE-*graft*-P4VP, PTFE-*graft*-P1VI

PTFE complex	ν_{as}(C-N)	ν_s(-COO-M)	ν(=CH)	ν(-N-M)	ν(M=O)	ν(-C=O)
PTFE-*graft*-PAA-VO^{2+}	-	1,600-1,620		-	980	1,720; 1,240; 1,190
PTFE-*graft*-PAA-MoO_2^{2+}	-	1,600-1,620		-	918	1,720; 1,240; 1,190
PTFE-*graft*-P4VP-VO^{2+}	1,630 1,600	-	990-810	1510-1490	1,000	-
PTFE-*graft*-P4VP-MoO_2^{2+}	1,630 1,600	-	990-810	1510-1490	780, 920	-
PTFE-*graft*-P1VI-VO^{2+}	1,220	-	3,124 2,851	-	968 1,112	-
PTFE-*graft*-P1VI-MoO_2^{2+}	1,220	-	3,124 2,851	1493	914 952	-

The shift is indicative of the formation of metal-nitrogen bonds with their ionic and donor-acceptor components, since it only appears after the formation of the metal-polymer complexes of PTFE-*graft*-P4VP with Fe^{3+}, Cu^{2+}, Co^{2+}, VO^{2+} and MoO_2^{2+}. The absorption bands at 1,490 cm^{-1} were, in turn, shifted to 1,510 cm^{-1}, which suggests a disturbed conjugated system of double bonds in the aromatic ring. After bonding the vanadyl ions to the grafted copolymer support, new bands for V=O at 1,000 cm^{-1} were observed (Fig. 2). The interaction with molybdenyl ions gave new bands for Mo=O at 780 and 920 cm^{-1} (PTFE-*graft*-P4VP) (Fig. 2), which also prove the formation of the corresponding complexes. Moreover, IR spectra of the copolymers of PTFE-*graft*-P4VP with $VO^{2+}$and MoO_2^{2+} (Fig. 2) showed absorption bands within $1{,}300^{-1}$ and 100 cm^{-1}, which are characteristic of PTFE support ν (>CF_2) (620 cm^{-1}); ν_w (>CF_2) and at 500 cm^{-1} ν_r (>CF_2). Again, absorption bands which can be assigned to a pyridine ring were observed, similarly to the IR spectrum of PE-*graft*-P4VP. Other bands discussed above which indicate changes in the electron densities associated with the formation of the –C–N-metal bonds were also observed.

For PTFE-*g*-P1VI, the intensity of the bands at 3,124-2,851 cm^{-1} characteristic of (ν (NH) Imidazoll + νCH + νNH_3 +) after complexation substantially decreased and new bands at 968 and 1,112 cm^{-1} which could be attributed to the ν (V=O) were observed [18] For the molybdenum complex with imidazole nucleus, bands at 914 and 952 cm^{-1}, corresponding to ν (Mo–O) bond were observed [19, 20].

The electron configuration of the V ions in the metal complexes of the grafted copolymers was studied by EPR (Fig. 3). The values of the EPR parameters calculated from the spectrum were as follows: g_{II} = 1.941; $g_{\square}$ =1.996 ; A_{II} = 18.8 mT (188 Gauss); $A_{\square}$ = 7.04 mT (70.4 G). The spectrum of VO^{2+} is typical of a complex with axial symmetry. V^{+4} has a d 1 configuration with 8 parallel and 8 perpendicular lines. Due to overlapping of some of the lines, the spectrum displays 13 lines instead of 16. For paramagnetic objects containing one unpaired electron and with axial spectra, two lines are usually registered. The location of these lines is determined by *g*-factors which, in the case of axial symmetry, are called *g*-parallel and *g*-perpendicular factors. Since the V atom has nuclear spin of 7/2, then each of the two lines splits into 8 components (the so-called superfine components) due to the interaction between the nuclear spin of the electron and that of the vanadium nucleus.

Comparing the values of the constants of superfine interaction and the *g*-factors with literary data, the co-ordination of VO^{2+} with nitrogen donors can be proved.

The experimental spectrum of PTFE-*graft*-P1V-Fe^{3+} obtained by Moessbauer spectroscopy was a quadruple doublet. The corresponding calculations gave the following results: *IS*=0.38 mm/s, *QS*=0.65 mm/s, *FWHM*=0.50 mm/s (Table 2). 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 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. The broadened spectral lines for a single component might account for the 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 an X-ray amorphous one. Similar results were obtained for the Moessbauer parameters of the PTFE-*graft*-P4VP-Fe^{3+} complex.

Based on the results obtained from the authors and literary data [21], the architectural structures may be suggested in the following Scheme 1.

Table-2. Parameters of the Moessbauer spectra

Polymer complexes	Measuring temperature T, K	Components	IS, mm/s	QS, mm/s	FWHM, mm/s
PTFE-*g*-P1VI-Fe^{3+}	300	Db Fe^{3+} octa	0.38	0.65	0.50

4. CONCLUSIONS

Selected part of carboxyl and nitrogen-containing copolymers with grafted nanolayers, synthesized by plasma graft copolymerization of AA, 4-VP and 1-VI onto PTFE films were used for complexation with different metal ions. The FT-IR, EPR and Moessbauer spectroscopy confirm the obtaining of copolymer complexes. Based on the analysis methods used, the possible co-ordination structures of the complex systems were suggested. Finally, these metal complexes can be successfully used for different applications as catalytic active centers, etc.

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Figure-1. FT-IR spectra of the PTFE films (a) non-treated, (b) treated in Ar plasma (c) PTFE-*graft*-P1VI, (d) PTFE-*graft*-P4VP, and (e) PTFE-*graft*-PAA.

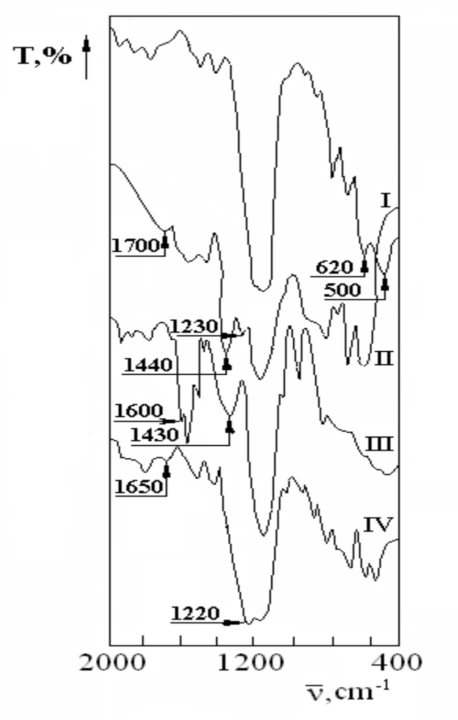


Figure-2. IR spectra of PTFE-*graft*-P4VP copolymer (1), PTFE-*graft*-P4VP-VO^{2+} (2) and PTFE-*graft*-P4VP-MoO$_2$$^{2+}$ (3) complexes.

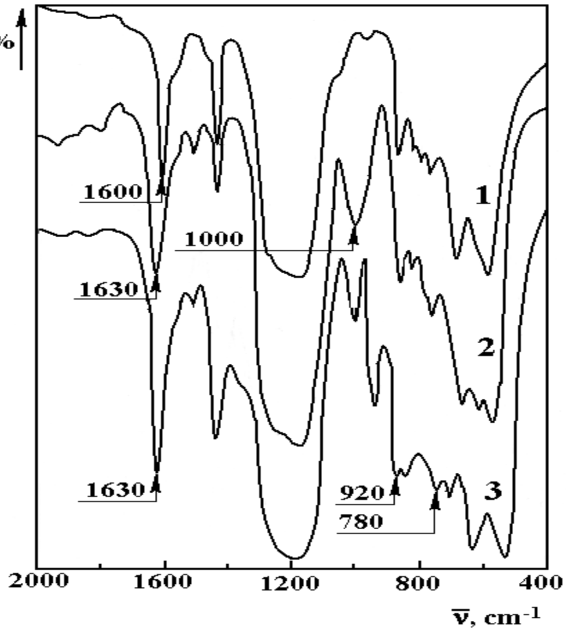
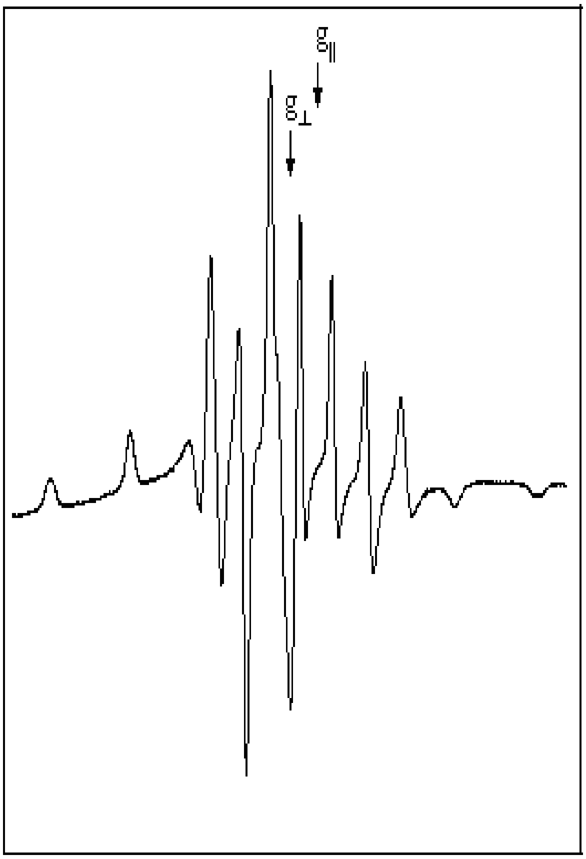
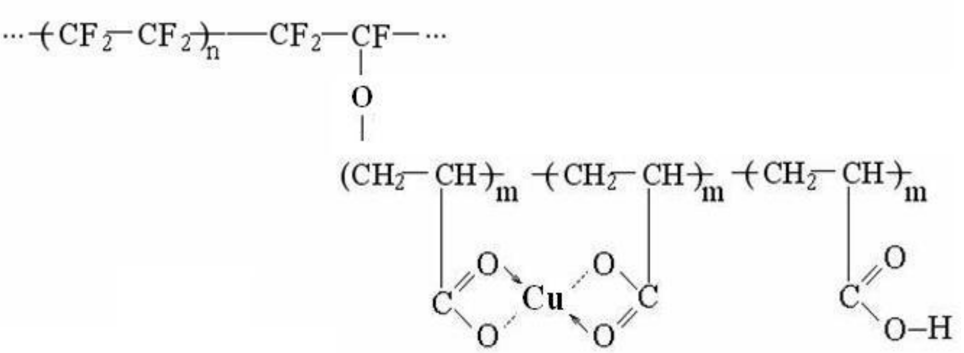


Figure-3. EPR spectrum of PTFE-*graft*-P4VP-VO^{2+} complex.

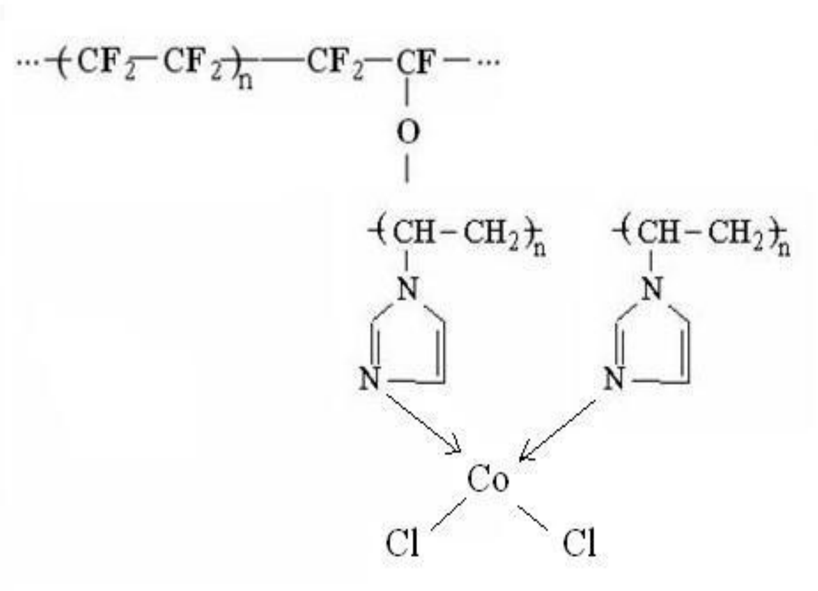


Scheme-1. The proposed structure of copolymer complexes.

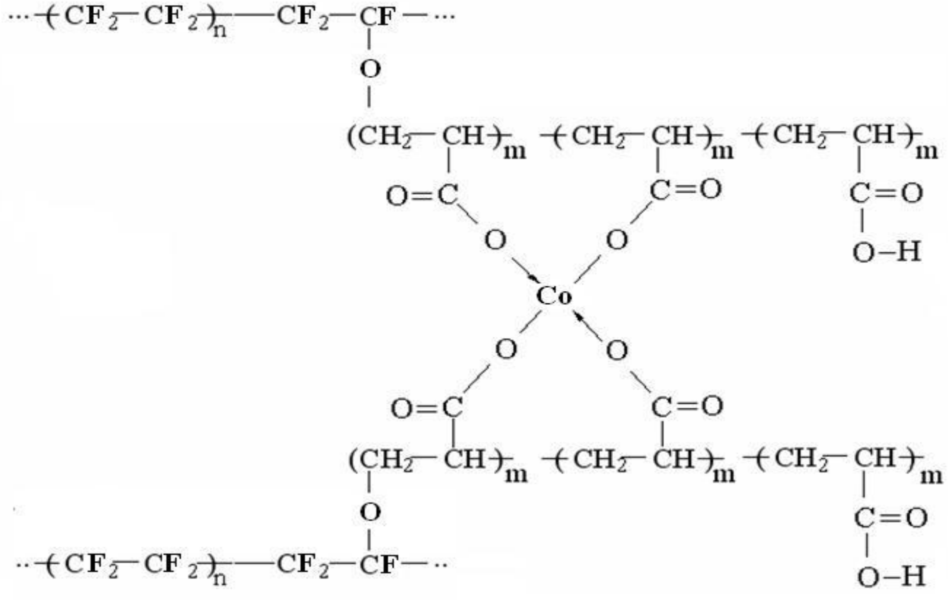
1.1. Intramolecular co-ordination structure of PTFE-graft-PAK-Cu^{2+}.



1.2. Intramolecular co-ordination structure of PTFE-graft-P1VI-Co^{2+}.



1.3. Intermolecular co-ordination structure of PTFE-graft-PAK-Co^{2+}.



1.4. Intermolecular co-ordination structure of PTFE-graft-P4VP-Fe^{2+}.