

Synthesis and Properties of Metal Complexes of Radiation Grafted Carboxyl Containing Copolymers

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Received 26 August 2005; accepted 22 December 2005

DOI 10.1002/app.24051

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Metal complexes of copolymers based on polyacrylic acid radiation grafted onto films of low density polyethylene were prepared by complex-forming with solutions of salts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and NH_4VO_3 . The introduction of metal ions was found to depend mainly on the degree of grafting of acrylic acid and was from 0.5 to 5.0 mass%. These complexes were characterized by IR, UV spectroscopy, and EPR. The moisture content of the materials obtained changed linearly with the degree of grafting of acrylic acid and was from 9.0 to 80.0%. The introduction of the MoO_2^{2+} and WO_2^{2+} towards carboxylic groups lead to increasing the thermal stability of the metal complexes of the copolymers compared to the

initial grafted films. The modified acrylate copolymers were studied in reactions of catalytic oxidation of cyclohexene. The activities of the complexes obtained towards cyclohexene epoxidation can be arranged in the following order: $\text{PAA-MoO}_2^{2+} > \text{PAA-VO}^{2+} > \text{PAA-VO}^+ > \text{PAA-WO}_2^{2+}$, while for the reaction of cyclohexene hydroxylation the order was $\text{PAA-Co}^{2+} > \text{PAA-Cu}^{2+} > \text{PAA-Fe}^{3+} > \text{PAA-Ni}^{2+}$. The contents of cyclohexene oxide and 2-cyclohexene-1-ol reached 38.5% and 7.5%, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1658–1665, 2006

Key words: radiation-grafted carboxylic copolymers; polyethylene; metal complexes; oxidation.

INTRODUCTION

The modification of polymeric materials by radiation grafted copolymerization has been rapidly developing in recent decades in the following directions: preparation of ion-exchange polymer membranes,¹ regulation of their hydrophilic–hydrophobic properties,^{2,3} preparation of metal complexes and increasing the adhesion to metals,⁴ electro-conductive materials,⁵ modification aimed at their use in medicine and biotechnology,⁶ preparation of polymer adsorbents and polymer carriers with catalytically active centers,^{7,8} etc. The radiation grafted copolymers synthesized can be used as ion-exchange membranes in the processes of electrodialysis for water freshening and purification of industrial waste waters.⁹

These are one of the most interesting types of deposited metal complexes in which the polymer acts both as carrier and specific ligand around the active metal center. The radiation grafted copolymers of acrylic acid (AA) and other vinyl monomers onto low density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) is important for the preparation of materials

with ion-exchange properties and metal complexes on their basis.^{10–15}

Studies devoted to preparation of new types of catalytically active complexes also attract much attention. For instance, the interest towards epoxidation rapidly increased when studies on preparation of propene oxide with hydroperoxides were published.¹⁶ Soluble complexes of Mo with ligands different in structure were used. Molybdenum naphthenates,¹⁷ acetylacetonates¹⁸ and carboxylates¹⁹ turned out to be quite effective catalysts for epoxidation.

Highly selective immobilized catalysts for epoxidation were obtained on the basis of copolymers of crosslinked poly(oxyethene) with 4-vinylpyridine, metacrylic acid, etc.^{20,21} It was found that the selectivity to the decomposed hydroperoxide depends on the type of ligands and the stoichiometry metal:ligand. Vanadium complexes based on poly(oxyethene) were obtained in organic solvents with different donor numbers.²² The activity of peroxocomplexes of tungsten (VI) in epoxidation of styrene with hydrogen peroxide under conditions of three-phase catalysis was studied.²³

The modern tendencies in the studies of immobilized metal complexes used as catalysts for epoxidation of alkenes were discussed by D. S. Sherrington.²⁴

Despite all the publications in this field so far, the problems related to finding the suitable conditions for synthesis of polymer carriers with catalytically active

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centers continue to attract the interest of researchers.^{7,8,10-15,25}

The aim of the present work is to prepare metal complexes on the basis of radiation grafted carboxyl containing copolymers (polyethene-grafted polyacrylic acid) with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NH_4VO_3 , and to study their catalytic activity in the reaction of oxidation of cyclohexene with *tert*-butylhydroperoxide.

EXPERIMENTAL

Materials

Copolymers with different degrees of grafting of AA onto films (40 μm) LDPE grade Ropoten T FV 03-223, commercial product of Lukoil Neftochim Bourgas (Bulgaria). All other reagents used ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, NH_4VO_3 , HNO_3 , HClO_4 , cyclohexene, $(\text{CH}_3)_3\text{COOH}$ (Fluka, Switzerland), glacial CH_3COOH , KJ, $\text{Na}_2\text{S}_2\text{O}_3$, $\text{C}_6\text{H}_5\text{CH}_3$, starch (Chimnab, Bulgaria) were analytical grade. *Tert*-butylhydroperoxide was purified by vacuum distillation. Cyclohexene was distilled prior to use. Toluene was dried with molecular sieve 5A and used as solvent.

The carboxyl containing copolymers were obtained by radiation grafted copolymerization of acrylic acid (BASF, Germany) onto LDPE films using the direct method of multiple irradiation with γ -rays from ^{60}Co source at dose rate 5 kGy/h and doses from 1 to 20 kGy.²⁶

Synthesis of grafted copolymer-metal complexes

The preparation of grafted copolymer-metal complexes was carried out by treatment under continuous stirring either with 0.5 mass% aqueous solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for 2 h at 373 K²⁷; or with 0.4 mass% aqueous solutions of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, NH_4VO_3 for 12 h at 296 K. The complexes of Mo (VI), W (VI), and V (V) were prepared in aqueous-acid solutions with pH \sim 2.5.

The treated films were dried under vacuum at 323 K to constant mass before being introduced into the reaction mixture as catalysts. This was considered to be inevitable since the water molecules present in undried copolymers are inhibitors of catalytic reaction (water deactivated the active center). The metal polymer complexes were introduced into the reaction medium as white powder particle size 200-300 μm . The grinding was performed in a special vibrating sphere in liquid N_2 medium.

Oxidation of cyclohexene

Cyclohexene was oxidized with *tert*-butylhydroperoxide (*t*-BHP) in a thermostated glass reactor (batch pro-

cess) equipped with magnetic stirrer at 358 K for 90 min.

The following reagents were introduced into the reaction vessel:

- Copolymer containing 5.10^{-3} mmol/L;
- 0.1 mL *t*-BHP (0.081 g, $8.79 \cdot 10^{-4}$ M);
- 1.0 mL cyclohexene (0.8 g, $9.8 \cdot 10^{-3}$ M);
- 4.0 mL toluene.

The reaction occurs under continuous stirring and the initial sample was taken immediately after thermostating the reaction mixture. Then, samples for analyses of hydroperoxide and products were taken at certain time intervals.

Analyses

Infrared (IR) spectra of carboxyl copolymers and their metal complexes were taken by using a Specord IR 75 spectrophotometer (Jena, Germany). The UV characteristics of sample films were measured on a Specord UV-vis (Jena, Germany). The thermal properties of the grafted copolymers and their metal complexes were determined on a derivatograph type OD-102, system F. Paulik-J. Paulik-L. Erdey (MOM, Budapest, Hungary), following conditions: temperature from 293 to 823 K, sample mass 100 mg, rate of heating 6 K min^{-1} , static air atmosphere.

The electron paramagnetic resonance (EPR) spectra of the metal complexes studied were taken at room temperatures on a spectrometer Bruker 200 DSRC working in the X-range, at frequency of magnetic field modulation 100 k $\dot{\text{z}}$ and rectangular resonator TE₁₀₂.

The analysis of the reaction products resulting from the cyclohexene oxidation reaction was carried out on a gas chromatograph "Sigma 2000" (Perkin-Elmer, USA) equipped with computer system "Chromatographics." The components of the samples studied were separated using quartz capillary column (50 m \times 0.25 mm).²⁸ The grafting of degree of PAA (P,%) was determined by the formula:

$$P = \frac{W_g - W_i}{W_i} \times 100$$

where W_g and W_i are the weights of grafted and initial films, respectively (g).

The water content (W , %) of the carboxyl containing copolymers and the corresponding metal complexes was determined in distilled water for 24 h at room temperature and calculated by the formula:

$$W = \frac{W_s - W_g}{W_g} \times 100$$

TABLE I
Contents of Metal Ions in PE-graft-PAA Copolymers

Degree of grafting (%)	Content, mass (%)						
	Cu ²⁺	Ni ²⁺	Co ²⁺	VO ²⁺	VO ₂ ⁺	MoO ₂ ²⁺	WO ₂ ²⁺
27.6	2.11	1.60	1.90	0.92	1.45	0.55	0.78
42.8	3.24	2.79	1.97	1.35	1.56	0.97	1.15
52.4	3.55	2.96	2.03	1.67	1.93	1.77	1.98
64.2	3.67	4.21	2.36	1.98	2.05	1.96	2.78
73.4	4.21	4.65	2.93	2.77	2.66	2.55	2.48
95.2	4.50	4.94	3.91	3.90	3.78	3.47	3.56

where W_s and W_g are weights of wet and dry samples, respectively (g).

The removal of excess water for determination of polymer films water content was carried out by a technique described in Ref. ²⁹

The *t*-BHP concentration ($C_{t\text{-bhp}}$, M) was determined iodometrically while conversion (X , %) was calculated using:

$$X = \frac{C_{0t\text{-bhp}} - C_{1t\text{-bhp}}}{C_{0t\text{-bhp}}} \times 100$$

where $\tilde{C}_{0t\text{-bhp}}$ and $\tilde{C}_{1t\text{-bhp}}$ are initial and final concentrations of *t*-BHP, respectively.

RESULTS AND DISCUSSION

Using direct irradiation with γ -rays from a ⁶⁰Co source, carboxyl containing copolymers were synthesized on the basis of PE-graft-PAA with degrees of grafting of PA from 27.6 to 95.2%. Aqueous solutions of PA with concentration of 40 mass% and homopolymerization inhibitor Mohr's salt with concentration 1.5 mass% versus aqueous-acidic solution were used.

The basic characteristics of the copolymers synthesized as ion-exchange membranes were reported in previous papers.³⁰

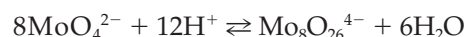
Aiming to prepare metal acrylate complexes, part of the carboxyl containing copolymers were treated with aqueous solutions of FeCl₃·6H₂O, CuCl₂·2H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, VOSO₄·5H₂O, Na₂MoO₄·2H₂O, Na₂WO₄·2H₂O, and NH₄VO₃.

The polyacrylic acid grafted onto PE films acts as chelate center for some ions of transition metals (Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺) and higher valency ions (VO²⁺, VO₂⁺, MoO₂²⁺ and WO₂²⁺). The formation of metal complexes was performed by bonding the polymer ligands with metal ion through reaction between the copolymer containing donor groups (in this case, —COOH groups) and metal ions (Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, VO²⁺, VO₂⁺, MoO₂²⁺, and WO₂²⁺).

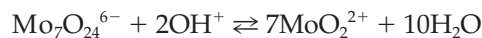
The solution of Na₂MoO₄·2H₂O in aqueous solution gives molybdenyl Mo (VI) anions according to the equation:



By acidic hydrolysis of the molybdenyl ions, "polymer" anions formed following the reactions:³¹



In acidic solutions, the "polymer anions" depolymerize to form molybdenyl cation MoO₂²⁺ along the reaction:



The solution of Na₂WO₄·2H₂O in acidic aqueous solutions lead to formation of tungstenate cations (WO₂²⁺) according to similar reactions.

It is well known that vanadium ions form complex compounds with donor atoms like nitrogen, oxygen or sulfur. In aqueous solutions of vanadylsulfate, vanadium exists in the form of vanadyl (VO²⁺) cation.³²



In most cases, the co-ordination number of vanadium is five or six. Many complex compounds containing VO²⁺ are blue or purple colored and most often, the bidentant ligands form complexes in ratio 2:1 with VO²⁺.

The contents of Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, VO²⁺, VO₂⁺, MoO₂²⁺, and WO₂²⁺ in copolymer films was determined by the weight method. The results showed that the amount of metal ions introduced varied from 0.5 to 5.0% and increased with the increase of the grafting degree of AA (Table I).

To clarify the formation of the metal complexes and their co-ordination structure, they were studied by UV- and IR-spectroscopy and EPR.

The analysis of IR spectra of the acrylate complexes with Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, VO²⁺, VO₂⁺, MoO₂²⁺,

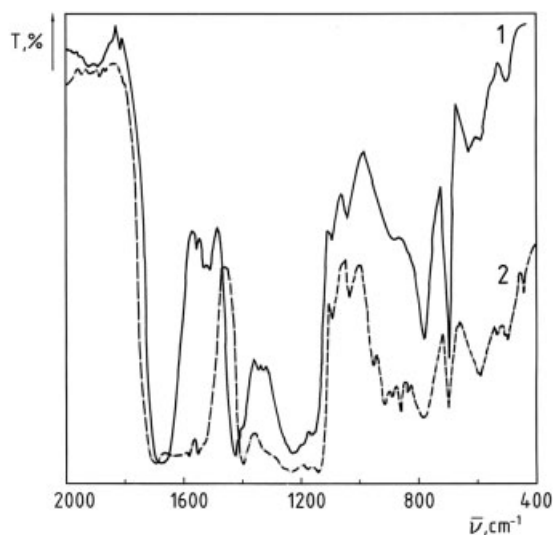


Figure 1 IR spectra of PE-graft-PAA copolymer (1) and PE-graft-PAA-VO²⁺ (2) complexes.

and WO₂²⁺ with degree of grafting 95.2% provided information on their structure. Figures 1 and 2 show the spectra of the initial PE-graft-PAA copolymer with grafting degree of PA 95.2% and the corresponding metal complexes with VO²⁺ and MoO₂²⁺. Absorption bands were registered at 1720, 1240, and 1190 cm⁻¹, characteristic for the carboxyl groups in PAA. The existence of a new band at 1620–1600 cm⁻¹ corresponds to asymmetric vibrations [$\gamma_s(-COO-)$] of the bond in the carboxyl group.³³ This band characterizes the ionization of the bond —C—ME since it is created during the complex forming of the carboxyl groups of PE-graft-PAA with Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, VO²⁺, VO₂⁺, MoO₂²⁺, and WO₂²⁺. After the

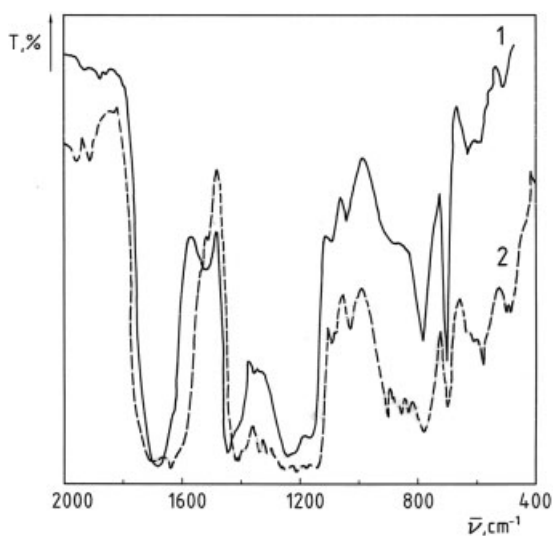


Figure 2 IR spectra of PE-graft-PAA copolymer (1) and PE-graft-PAA-MoO₂²⁺ (2) complexes.

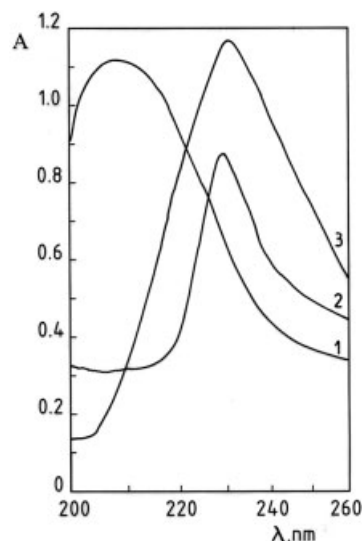


Figure 3 UV spectra of PE-graft-PAA (1), PE-graft-PAA-MoO₂²⁺ (2), and PE-graft-PAA-VO²⁺ (3) complexes.

bonding of vanadyl cations, new absorption bands appear at 610 (V—O) and 980 cm⁻¹ (V=O).³⁴ The bands observed at 1740–1700 and 3250–3550 cm⁻¹ correspond to the valent vibrations of C=O and —O—H bonds in the —COOH groups. It means that not all functional groups were co-ordinated with metal ions.

The UV-spectra of the metal complexes obtained showed maximal absorptions at a wave length (λ , nm) corresponding to the maximal absorption of the corresponding ion, Fe³⁺, (460) Cu²⁺, (800) Co²⁺, (520) Ni²⁺, (390) VO²⁺ (230) and MoO₂²⁺ (228), Figures 3 and 4. Figure 4 shows vis spectra of PE-graft-PAA after the formation of a complex with cuprous anions. The

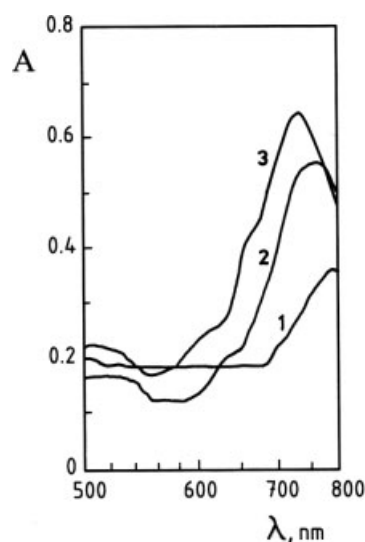
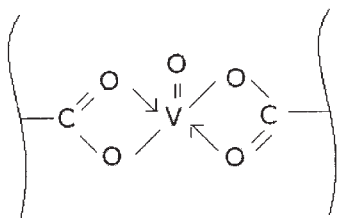


Figure 4 UV spectra of PE-graft-PAA-Cu²⁺ complexes with different degrees of grafting of AA (%): 27.6 (1), 64.2 (2), and 95.2 (3).

TABLE II
Thermal Properties of PE-graft-PAA Copolymers and Their Metalcomplexes with Grafting Degree of 52.4%

Metal complex	$T_{\text{start of destruction}}$ (K)	T_{10} mass% loss (K)	T_{50} mass% loss (K)	$T_{\text{first exothermal peak}}$ (K)
PE-graft-PAA	425	531	723	503
PE-graft-PAA-VO ²⁺	423	539	718	481
PE-graft-PAA-Fe ³⁺	468	533	728	488
PE-graft-PAA-VO ²⁺	426	529	726	491
PE-graft-PAA-MoO ₂ ²⁺	439	542	741	497
PE-graft-PAA-Ni ²⁺	468	528	718	503
PE-graft-PAA-WO ₂ ²⁺	451	560	749	509
PE-graft-PAA-Co ²⁺	458	548	723	513

color of the copolymers changed from light blue to blue with the increase of the content of carboxyl groups. As can be seen in Figure 4, the absorption increased with the carboxyl groups content and the absorption maximum (λ_{max}) was shifted to lower wave lengths. For the copolymers with 27.6% grafting degree, λ_{max} was at 790 cm⁻¹ while for these with 95.2% λ_{max} was shifted to 730 cm⁻¹. Similar results were obtained when the complex-forming properties of poly(propylene imine) dendrimers having 8, 32, and 64 primary amine end groups with Cu (II)³⁵ was studied.

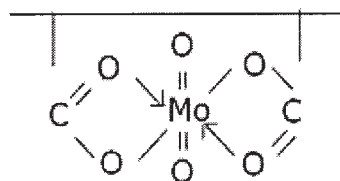


The data from the DTA analysis of the grafted copolymers with grafting degree of AA 52.4% and their metal complexes showed that all the samples had similar melting temperatures (385–388 K) (Table II). The decomposition of the metal complexes with W and Co began at a temperature 14–16 K higher than that of the initial carboxyl-containing copolymers with the same degree of grafting of AA. The same was observed also for $T_{10\text{mass\%}}$ and $T_{50\text{mass\%}}$ weight loss – the corresponding temperatures were higher by 10–30 and 18–26 K than these of the initial copolymers. For the complexes with Mo and W, the first exothermal peak was shifted to higher temperatures, 509–513 K. It means that the thermostability of the complexes was slightly better due to the additional “crosslinking” of the metal ions.

For the complexes with Fe³⁺, Co²⁺, Ni²⁺, VO²⁺, and VO₂⁺, such changes were not observed. The results obtained confirmed that only the introduction of MoO₂²⁺ and WO₂²⁺ in the grafted chains and

The electron configuration of V ions in the metal complexes of the grafted copolymers was studied by EPR (Fig. 5). The spectrum of VO²⁺ was typical for a complex with axial symmetry. V(IV) was with d1 configuration. For paramagnetic objects containing one single (uncoupled) electron and axial symmetry, two lines are present in the spectrum. The position of these lines is given by g-factors called g-parallel and g-transverse in the case of axial symmetry. Since the V atom has nuclear spin of 7/2, then each of the two lines would split into 8 components (or so called ultrafine components) because of interaction between the nuclear spin of the electron and that of vanadium nucleus. In Figure 5, the middle of each group of eight lines lies at the corresponding g-factor and the average distance between the lines for certain direction is the constant of the ultrafine interaction. Using the constants of ultrafine interaction and the g-factors obtained, a comparison with literary data shows the co-ordination of VO²⁺ with oxygen donors. The EPR spectrum is characterized by a singlet with g-factor value of 1.934.

Based on the results obtained from UV, IR, and EPR analyses and literary data, the following structures may be suggested:



the formation of a complex leads to positive changes in the thermal stability of these materials.

The content of —COOH groups in the grafted copolymers determines their swelling in water under opera-

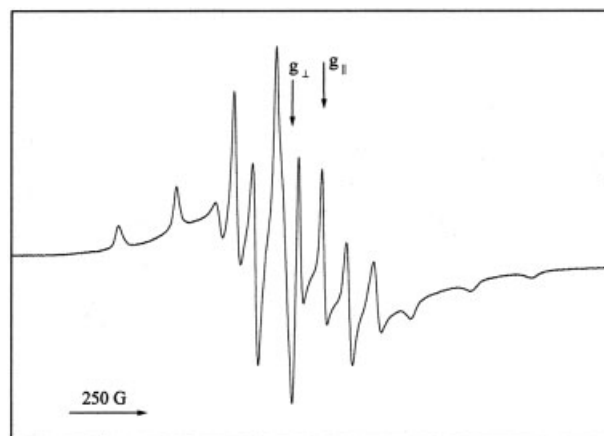


Figure 5 EPR spectrum of PE-graft-PAA-VO²⁺ complex.

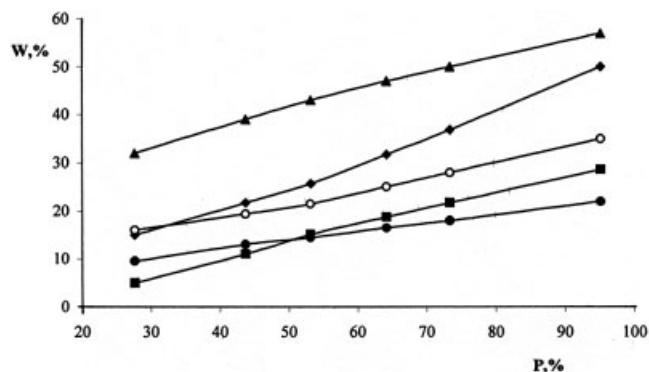


Figure 6 Dependence of the water content in PE-*graft*-PAA copolymers in H-form (■) and their metal complexes with: Cu²⁺(○), Fe³⁺ (▲), Ni²⁺ (●), and Co²⁺(◆).

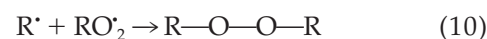
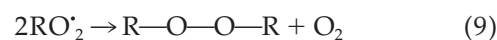
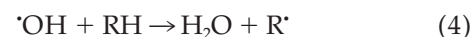
tion conditions. Figures 6 and 7 show the dependence of water content (*W*) of the initial copolymers and the complexes obtained on their basis on the grafting degree of AA (*P*). In the initial H-forms, *W* increased almost linearly with the increase of the grafting degree.

As can be seen, the introduction of transition metals affected water content (especially for the Fe³⁺-complexes) compared to that of the initial copolymers. The increasing the hydrophilicity of acrylic complexes of Fe³⁺ can be explained with the formation of hydroxy-complexes. For the metal complexes, *W* had values from 9.0 to 45.2% while the H-form from 5.1 to 27.2%.

The introduction of VO²⁺, VO₂⁺, MoO₂²⁺, and WO₂²⁺ also affected water content compared to that of the initial grafted copolymers. The change of the values of *W* for the different complexes can be explained with the affinity of each metal ion to formation of a complex. The latter changes the number of hydrophilic groups in the copolymers resulting in change of water content.³⁶ Therefore, the degree of swelling depends mainly on the number of hydrophilic groups in them (respectively, the degree of grafting) and, probably, the metal ion nature also exerts some effect.

The different metal complexes obtained and characterized were studied as catalysts in the oxidation of cyclohexene with *tert*-butylhydroperoxide. Metals like Mo, W and V, having small oxidation potential and high Lewis acidity, were the most active during the epoxidation of alkenes with organic hydroperoxides. Compared to hydrogen peroxide and peracids, the organic hydroperoxides are less susceptible to heterolytic breaking of the O—O bond. The rate of this breaking can be increased only ion presence of catalysts, salts and complexes of some transition metals, Fe, Co, Ni, Cu etc.²⁴ These metals have high oxidation potential and initiate homolytic decomposition of organic peroxides. These metals and complexes, however, do not have significant effect in the epoxidation reaction. Catalysts for the process were found to be the complexes of Mo, V, W, and Ti. These metals have high activity when they are in high valency state.³⁷

In homolytic systems, free radicals are formed as intermediate products where the metal takes part in a series of single-electron reactions of oxidation or reduction. The liquid phase homolytic oxidation occurs along a chain-radical mechanism where the metal does not necessarily take part in each stage. The reactions between the organic compounds and oxygen proceeding by free-radical mechanism can be described as a combination of several processes:



The key role of the metal is in the catalysis of the process of decomposition of the hydroperoxide (ROOH) and, to smaller extent, that of the peroxide. If compounds of the type shown in stages 7 or 9 and 10 are produced during the oxidation process, then the metal complexes may catalyze their decomposition and change the direction of the oxidation process.

Basically, the metal ion can take part in each stage.²⁴ For instance, the molybdenum complexes can possibly

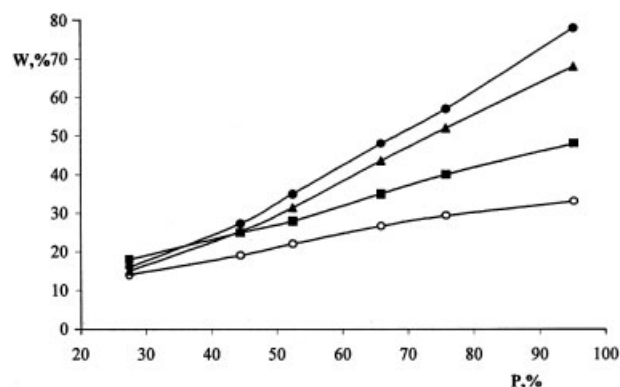


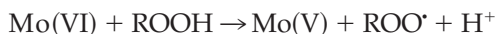
Figure 7 Dependence of water content in PE-*graft*-PAA metal complexes with: VO₂⁺(■), VO₂⁺ (○), MoO₂²⁺ (▲), and WO₂²⁺(●).

TABLE III
Oxidation of Cyclohexene with *tert*-Butylhydroperoxide in Presence of Immobilized Catalysts

Catalyst	Conversion (%)	Yield ^a (%)		
		Cyclohexene oxide	2-cyclohexene-1-ol	2-cyclohexene-1-on
PAA-VO ²⁺	56.1	22.3	2.7	2.5
PAA-VO ₂ ⁺	6.1	10.1	2.6	2.4
PAA-MoO ₂ ²⁺	10.0	38.5	1.8	1.4
PAA-WO ₂ ²⁺	1.5	3.2	3.1	3.5
PAA-Co ²⁺	3.0	<1	7.5	1.5
PAA-Ni ²⁺	2.5	<1	3.5	<1
PAA-Cu ²⁺	13.0	<1	5.8	1.4
PAA-Fe ³⁺	1.6	<1	5.2	1.4

^aAccording to reaction shown in Experimental part and data from gas-chromatographic analysis.

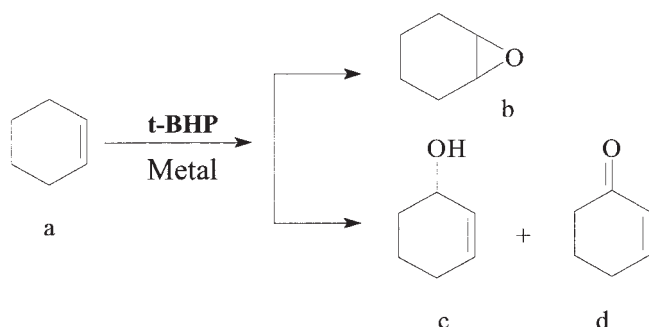
decompose organic hydroperoxides by the scheme of Haber-Weis:³⁷



If the metal ion is able to affect these reactions then the decomposition of the hydroperoxide would be stoichiometric rather than catalytic one.

The experimental results obtained from the iodometric titration and gas-chromatographic analysis are presented in Table III. Obviously, the highest conversion of *t*-BHP was achieved with PAA-VO²⁺ complex (56.1%) and the smallest, with the complexes of PAA with WO₂²⁺, Co²⁺, Ni²⁺, and Fe³⁺. Beside the aimed product cyclohexene oxide, the reaction gives some side products: 2-cyclohexene-1-ol and 2-cyclohexene-1-on. High yields of cyclohexene oxide were observed with immobilized catalysts PAA-MoO₂²⁺ and PAA-VO²⁺ while the use of complexes with Co²⁺, Ni²⁺, Cu²⁺, and Fe³⁺ gave cyclohexene oxide yields <1%. The results showed that different products were obtained depending on the initial valent state of the metal cation (VO²⁺, VO₂⁺).

On the basis of the products obtained, the following scheme of cyclohexene oxidation can be suggested:



Three products were obtained from the epoxidation of cyclohexene (a) in the presence of the immobilized catalysts of Mo, V, and W: cyclohexene oxide (b), 2-cyclohexene-1-ol (c) and 2-cyclohexene-1-on (d). Probably, cyclohexene was oxidized to cyclohexenylhydroperoxide and, after interaction with cyclohexene, cyclohexene oxide and 2-cyclohexene-1-ol formed. The latter interacted with cyclohexenylhydroperoxide to oxidize to 2-cyclohexene-1-on.

The probable reason for the lower yields observed using complexes based on radiation grafted carboxyl containing copolymers compared to the yields obtained with complexes based on poly(oxyethene),^{20,21} can be explained with (i) lower swelling of polyacrylic acid in toluene, (ii) mass transfer of the reactants, (iii) an internal diffusion.

CONCLUSIONS

Metal complexes of radiation grafted carboxyl containing copolymers were synthesized and characterized. One possibility was shown for their application as catalysts for the oxidation of cyclohexene with organic hydroperoxides. Good results from epoxidation were obtained using the metal complexes with VO²⁺ and MoO₂²⁺. In the future, new approaches should be sought for preparation of polymer carriers with suitable lyophilic properties.

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