Maleic Anhydride Copolymers with Ability to Bind Metal Ions. 1. Polydentate Amine Derivatives for Cr (III) Ions' Removal

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ABSTRACT: New polymeric chelate structures derived from maleic anhydride–dicyclopentadiene copolymer (MA–DCPD) were synthesized by chemical modifications with triethylenetetramine (TETA), from Riedel De HaŠn AG Seelze, Hannover. Germany. Both amide and imide forms of these new polymers have been tested in the retention process of Cr (III) ions. Experimental results referring mainly to the retention capacity and retention efficiency, for different values of the working parameters: contact procedure, batch time, concentration of chelators, and pH, are presented. The polymer structures and their metal complexes were characterized by IR spectroscopy. IR spectra proved that the metal was coordinated by nitrogen from TETA. The thermal properties of modified polymers and polychelates were also examined. Based on these experimental results and literature data, we discuss a possible binding mechanism and suggest the polychelate structures. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1867–1874, 2011

Key words: polymer–metal complexes; wastewaters; Cr (III) removal; chelator

INTRODUCTION

Separation and removal of transitional metal ions from industrial wastewaters by means of chelators represent an actual research direction with applications in many fields such as tannery, textile manufacture, electroplating, hydrometallurgy.[1–4] Most commercial significant chelators are polystyrene anion-exchange matrixes.[5–9]

A particular interest was developing for chromium removal from industrial wastewaters. The US Office of Environmental Health Hazard Assessment from The Environmental Agency imposes a public health goal of 2.5 µg/L for total chromium ions, in the assumption that chromium (VI) does not exceed 7% of the total chromium content.[10]

Traditional removing technologies for Cr (VI) involve chemical reduction to Cr (III), followed by processes of concentration, precipitation/coagulation, and filtration.[11,12] These technologies are generally replaced by modern technologies such as membrane separation, electrodialysis, selective absorption, etc.[6,8,11,12]

Recent studies report a large number of polymer-bound chelating ligands, including polydentate amine, crown ethers, carboxylic derived, etc.[5,13,14]

The efficiency and the selectivity of the metal ions' separation can be improved by using polymeric reagents and membrane filtration. In this approach, a new technique, based on the retention on polymer in liquid phase was developed, using macromolecular materials with chelating groups (poly-chelatogens) characterized by solubility or wetting in water.[8,15,16]

In the case of retaining sieves with polymer matrix (such as ion exchangers), the access to the complexing sequences in the material bulk is limited. This problem disappears when the sieve is manufactured by crosslink graft on the surface of polymeric microspheres. In this case, the superficial area of the material increases, and the retention capability is imposed only by steric considerations[3,16,17]

The chelators binding the metal ions by means of multidentate amines or amine sequences that stabilize the ligand into a pseudoclosed conformation are the most stable forms of chelators.

For the new designed polymeric structures, we wish to generate a special conformation of ligand by
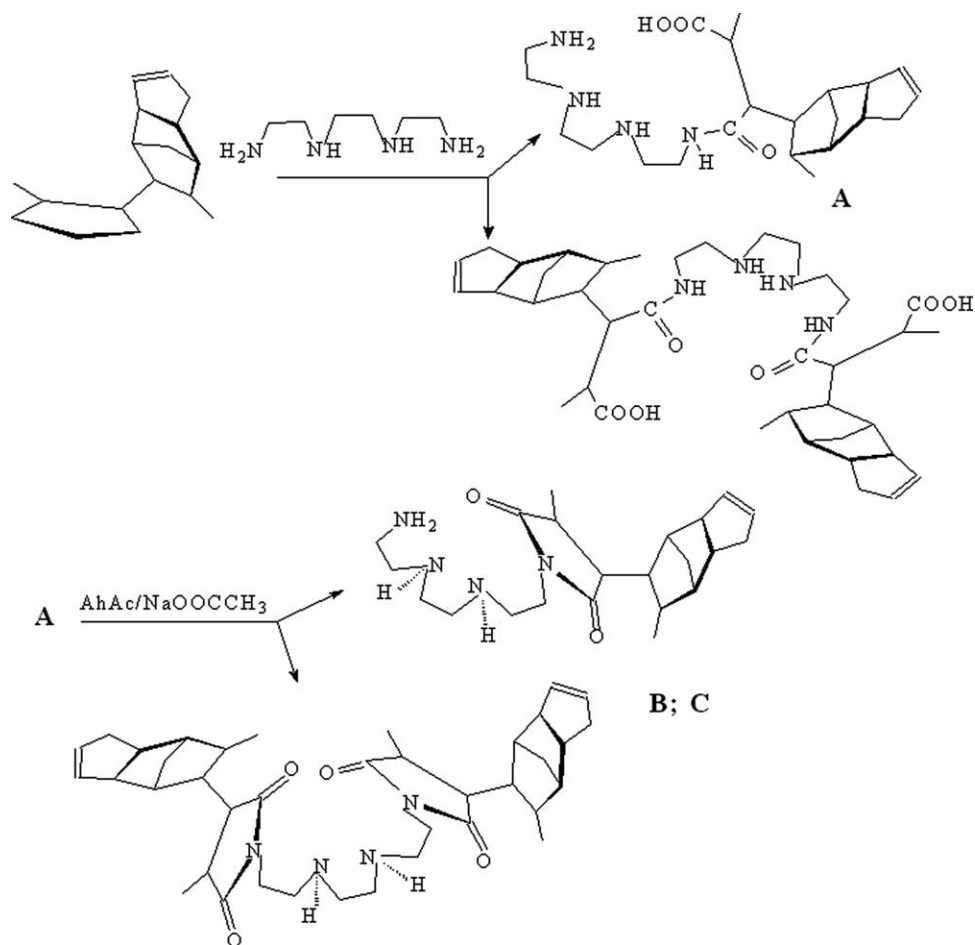
Scheme 1 Synthesis of polymeric structures.

superficial crosslinking of maleic anhydride–dicyclo-pentadiene (MA-DCPD) copolymer. The choice of MA copolymers as starting substrates is justified by the fact that they are commonly used for the synthesis of water soluble or strong wetting materials, such as thickeners in paints and coatings, industrial emulsifier and flocculating agents,[18–20] and carriers of biological substances.[21]

The aim of this research study was the assay of new polymer materials, derived from MA, in the retention process of chromium ions (III). In this preliminary study, we use the analytical solution of Cr (III). We intend to demonstrate the ability of Cr retention and the potential mechanism of retention in these cases. Further, another study which used the industrial waters is in progress.

EXPERIMENTAL

Materials

The starting substrate for the new materials was maleic MA–DCPD copolymer, synthesized and characterized in our laboratory (64.65 mol % MA, $M_n = 2860$, ID = 7).[22–25] The reagent used for the

chemical transformations was triethylenetetramine (TETA), from Riedel De Haën AG Seelze, Hannover. Germany; N,N-dimethyl formamide (DMF) and hexane (H), from Fluka, Switzerland, diglicoldibutylether (DGBE), from Merck, Darmstadt Germany diethyl ether (EE), from Reactivul Bucharest, Romania, were used as solvents or nonsolvents. Acetic anhydride (AcAh) and sodium acetate, from Reactivul Bucharest, were used as anhydrization agents in the imidization step. Chromium chloride, from Fluka, was used to prepare the metal ion solutions. The pH was adjusted with NaOH 1N solution from Reactivul Bucharest Romania.

Synthesis of polymer structures. Condensation of TETA with MA–DCPD copolymer

A, B, and C copolymers are the result of the chemical transformation of the MA–DCPD copolymer with TETA through an original technique of superficial graft on AM-DCPD pearls (Scheme 1).

The experimental procedure followed was: 16 mL of hexane was added in drops, under stirring to the solution obtained by dissolving 5 g of MA–DCPD copolymer in DMF. To the resulted homogeneous suspension, a solution of TETA (3.24 mL TETA
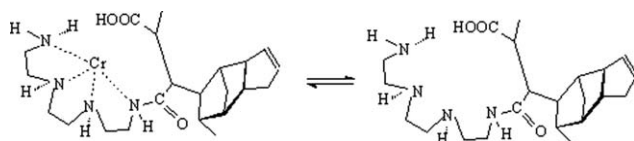
Scheme 2 Chelatization process of chromium.

diluted in 123 mL DMF) was added in drops. The reaction develops for 2 h at room temperature. The product was filtered, washed with DGBE, and dried at 60°C under normal pressure. The semiamide form (see Scheme 1, A) is obtained in this step.

After drying, the product undergoes the imidization process. Sodium acetate (1 mol) is added under stirring to the solution of A in DMF/AcAh (1 : 1 vol.; 4% wt. copolymer). The temperature is increased to 60°C. The whole reaction takes 5 h. C form was obtained (Scheme 1).

Intermediary B form was obtained after 2 h of imidization at 60°C. Separation of the modified structure supposed precipitation in EE, filtering and drying. It was further purified by DMF-EE reprecipitation system.

The global yield was 63–65% in all steps; the resulted polymers were of a light brown color. Chemical modification processes of polymer materials, by grafting reactive functional groups, are generally accompanied by apparition of some insoluble fractions (gels), as a consequence of chemical interchains' processes (Schemes 1 and 2 and Table I).

The synthesis of polymer–metal ion complexes

The polymer–Cr (III) ions' complexes were obtained by contacting a suspension of polymer in DMF with aqueous solutions with precise concentrations of metal ions (1% polymer in DMF and 2.9 g/L metal ion in water).

The experiments were carried out in batch equipment provided with a reactor with mechanical stirring and thermostat. The working temperature was maintained at $22 \pm 0.5°C$,and the pH range was 29. The volumetric ratio of polymer solution/ metal ion solution was 0.6, which is equivalent to a weight ratio of polymer/Cr^{3+} ions of 2 : 1, as recommended in Ref. 3.

The precipitated complex was separated by filtering at ordinary pressure, was washed with warm water and ethanol, and dried at 60° C under reduced pressure to avoid the destruction of the support material.

MEASUREMENTS AND CHARACTERIZATION

The amount of Cr (III) ions adsorbed on the polymer support was calculated starting from the ions' residual concentration that was measured by atomic absorption technique, using a Spectrophotometer Perkin Elmer AAS3-1988.
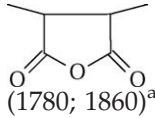
The polymer supports and their chelates were characterized by IR spectroscopy, Shimadzu FTIR 8000, by differential thermal analysis using a Shimadzu DTG-TA-51H apparatus and by porosity analysis, using a Pascal 240/140 apparatus. The efficiency of the employed materials as well as the discussions regarding the complexing–chelating mechanisms is based on the following parameters: the retention efficiency (r), the retention capacity (Q_e), and the distribution coefficient of the metal ion into the polymer matrix (K_d).[14] These parameters are defined by the following equations:

$$\eta_r = \frac{\Delta C}{C_0} = \frac{C_0 - C_f}{C_0} 100 \ (\%) \tag{1}$$

TABLE I
Physical Characteristics of Polymeric Substrate

Chelator groups	Polymer	Transf. degree	Crosslink. degree
	A	–	14
	B	63.74	50.1
	C	97.40	52.3

TABLE II
IR Spectral Data for Polymers

	—COO (1680)[a]		—NH— (820)[a]		(1780; 1860)[a]			
	h	A	h	A	h	A	h	A
B	1683		808.11		1775.4		1868	
	1.52	37.95	1.229	162.61	1.46	33.72	1.25	31.16
C	1685.6		804.26		1772.4		1868	
	1.40	34.68	1.169	158.34	1.30	29.8	1.25	31.16

h and A are the height and specific area of the peak, respectively.
[a] Theoretical values.

$$Q_e = \frac{C_0 - C_f}{E_{Me} m_p} \; mE_{Me}/gpolym \qquad (2)$$

$$K_d = \frac{m_c V}{m_{Cu} m_p} \; mL/g \qquad (3)$$

where C_0 is the initial metal ion concentration (g/L); C_f is the metal ion concentration in the effluent (g/L); m_p is the polymer weight (g); V is the volume of the polymeric solution in the reactor (mL), m_c is the amount of metal ion on the polymer (mg); and m_{Cr} is the amount of metal ion in solution (mg).

RESULTS AND DISCUSSION

The adsorption capacity is highly affected by some few working parameters, such as pH, microstructure and chemical nature of adsorbent support (due to the interface phenomena which govern the complexing process), and the nature of ligands (amide and/or imide forms).

The structural-constitutive difference for the three polymer proposed structures (A, B, C) regard only the crosslinking degree (Table I).

IR spectra provide qualitative and quantitative data regarding the structure of the polymeric supports. Thus, the conversion of the anhydride group to the semiamide and imide form can be evaluated.[21] It is known that the anhydride unity is characterized by theoretical adsorptions at 1780 and 1860 cm^{-1}. In the case of copolymer AM-DCPD, they undergo a shift to 1782 cm^{-1} and 1865 cm^{-1}. Following the reaction with the amine derivative, the peaks corresponding to amide I band (1655 cm^{-1}) and amide II (1550 cm^{-1}) are observed together with the peak specific for the carboxylic group (1705 cm^{-1}). The evaluation of the cycling degree and subsequently the imidization process is possible by measuring the specific surface under the semiamide peak, which narrows[21] (Table II and Fig. 1).

Thermal measurements offer data regarding the thermal stability of the polymer structures (Fig. 2). We remark in all cases an intermediary degradation transition comparing with the copolymer structure. Polymer B exhibits the best thermal resistance in the A, B, and C series. Porosity analysis put forward data concerning microstructure of polymeric materials, thus for polymer B, the maximum distribution of pores is rather large, with an average dimension of 11.96 μm and a specific area 3.151 m^2/g; for polymer C, the maximum of the distribution shifts to 7.62 μm, the specific area is 2.998 m^2/g and the density is four times bigger than that of polymer B.

Contact procedure and adsorbent substrate

The contact procedure established the order of mixing up for the polymer and the metal ion solution. In all experiments, an important parameter was the stirring regime to assure a uniform distribution of the two phases (polymer solution vs. metal ion solution).

When Cr (III) ions' solution was added to the polymer solution, the polymer undergoes a collapse phenomenon, which determines the decrease of adsorbed Cr (III) ions. In this case, the adsorption process develops by trapping and superficial adsorption of the metal ions precipitated on the polymer substrate.

The best results were obtained when the polymer solution was added in drops under stirring to the metal ion solution. In this way, the fast contact of the polymer material with water is assured, and the collapse of organic macromolecules from the total or partial crosslinking structure is avoided.

Batch time

Heterogeneous reactions involving low wetting material structures have the disadvantage of long contact times due to the diffusion control of the complexation process. The most important parameters, in this case, are the diffusion and the
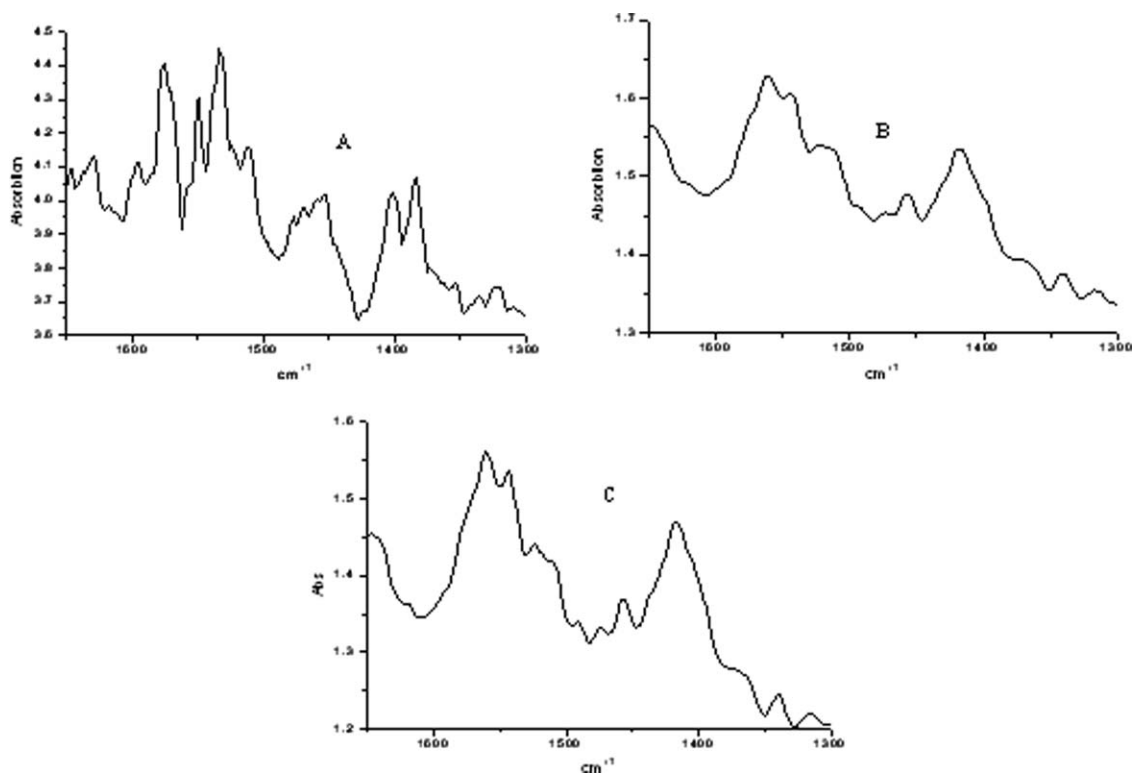
Figure 1 IR spectra for polymers A, B, and C.

repartition coefficients into the two phases: solution and "solid–polymer." Our polychelates are characterized by the existence of two components: a soluble phase and a gel phase. We expected higher metal ion retention for longer contact periods. Experimentally, we found that for a contact period of 2 h (Fig. 3), the maximum retention efficiency was realized. Beyond this period, the retention efficiency diminished, probably determined by a change of the complexation equilibrium.
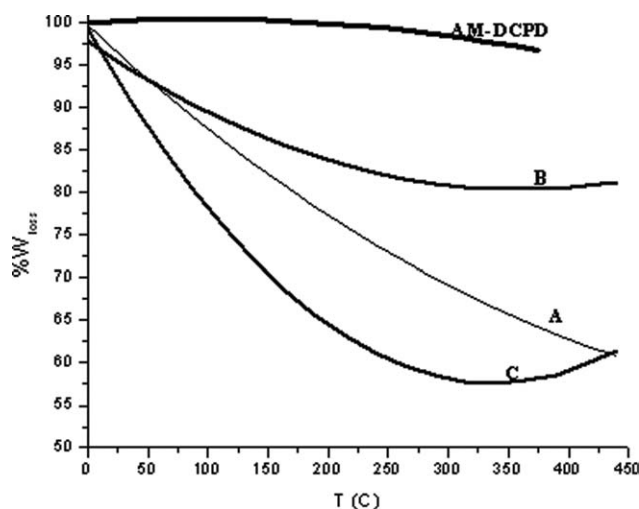
pH value and micromolecular structure of polymer substrate

Generally, pH is the most important working parameter. So, for this parameter should be careful monitoring to avoid precipitating metal hydroxides before contacting the polymer with metal ion solution. In addition, it modifies the swelling degree of the polymer structure by favoring the hydrolization of unreacted anhydride groups. There is a mutual relationship between the pH value and the local micromolecular structure of the polymer. In this relationship, the degree of macroligand ionization is important for the conformational change of the linear segment in the gel fraction.
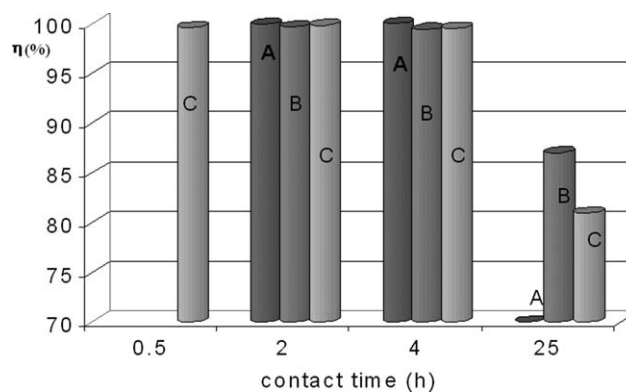

Figure 2 Thermal analysis data for polymer materials.

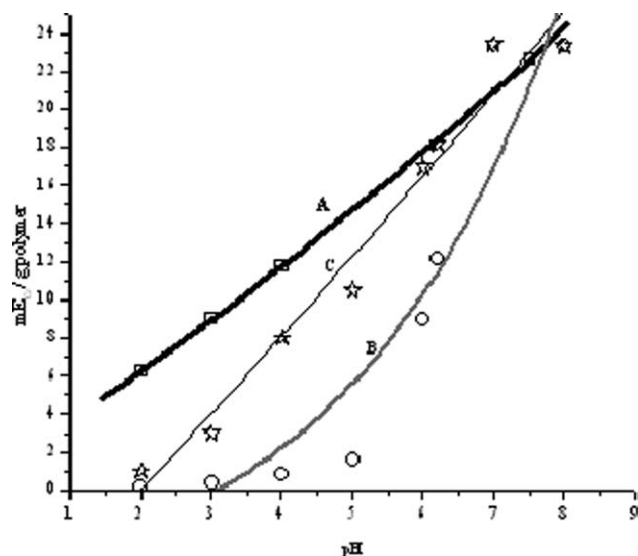**Figure 3** Retention efficiency versus contact time.

Figure 4 Global retention profile evolution for the three-polymer structure.

Figure 4 shows the retention profile of Cr (III) ions on A, B, and C polymer substrates. Polymer–metal ions interaction is highly affected by the working pH. For strong acid solutions, the complexing process is insignificant. The maximum complexing ability is obtained, in all cases, for pH = 7. This evolution can be explained by the total protonation of amide groups in acidic medium. That determines the electrostatic repulsion of Cr (III) ions. Therefore, there is a kinetic competition between the protonation and complexation processes influenced by the pH value. The increase of pH diminishes the electrostatic barrier of metal ions and increases the wettability of the polymer skeleton by favoring the hydrolysis of the unreacted anhydride.
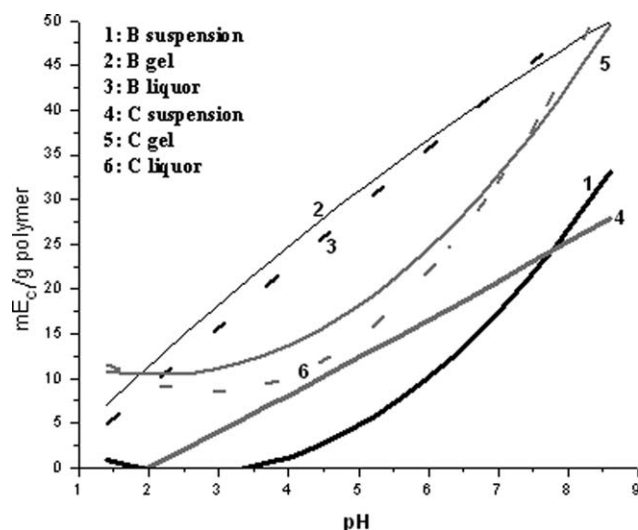

Figure 5 Retention of Cr (III) profile of gelous, liquor, and suspension form of tested polymer supports.
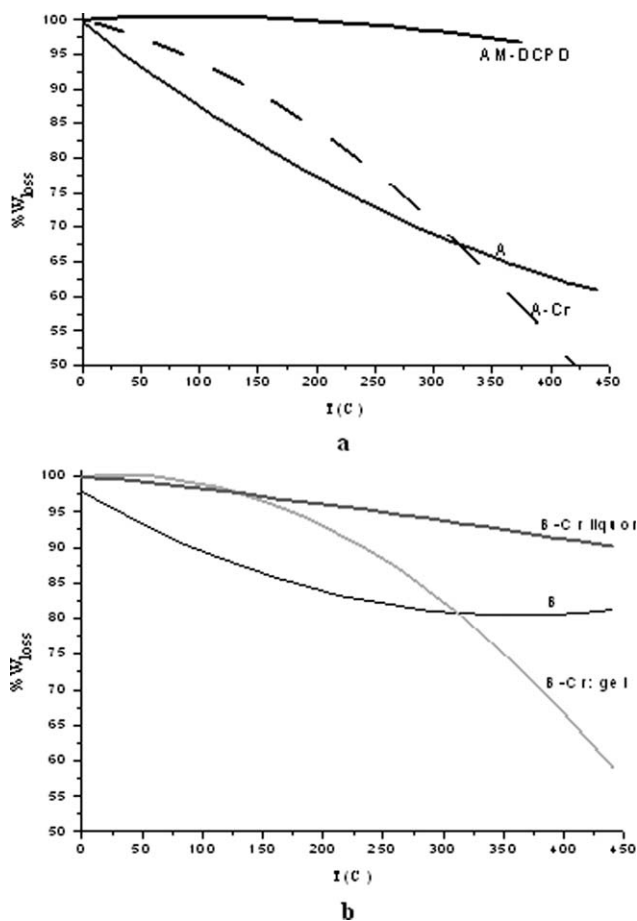
Figure 6 Thermal curves of AM-DCPD modified with TETA.

On the other hand, the existence of the crosslinking sequences diminishes the frequency of reversible binding, characteristic for the soluble fraction with a great number of free amine groups (Scheme 2). This is explained by trapping of metal ion into the functionalized molecular sieves' pores.

Distinct investigations of Cr (III) sorption on the gel and soluble (liquor) phases are shown in Figure 5. Variations of retention capacity confirm a different evolution with pH for the two phases.

The low starting value for the retention capacity at high crosslinking degrees can be explained by steric factors, and the coordination process are developed both at intermolecular and intramolecular level.

The curves' shape suggests two distinct complexing mechanisms. For all tested polymers, we remark the high retention values for the soluble fractions. For the suspension phases, the global complexing process is a pondered average of the processes developed in solution and gel phase.

At the same time, similar to hydrogels' behavior,[20] the increase of the swelling degree at high pH values may be explained by additional charge because of the ionization of unsubstituted carboxylic

TABLE III
Thermal Analysis Data for Polymer–Cr Complexes

Cod	Decomp. Temp. (°C)		Peak temp, T_s (°C)	Mass loss (%)	Remarks
B–Cr	29.17	61.07	49.52	0.375	Soluble phase
	61.06	148.99	90.00	1.253	
	148.99	248.50	219.44	2.006	
	248.5	300.77	268.81	0.906	
	300.77	344.01	329.88	0.249	
	31.33	99.71	53.66	3.050	Suspension 1%
	210.61	318.58	299.66	13.994	(soluble + gel)
	318.58	350.78	339.59	7.145	
A–Cr	31.33	82.33	64.24	3.112	Suspension 1%
	82.33	119.65	92.40	2.626	(soluble + gel)
	119.65	220.91	189.28	10.113	
	220.91	276.87	254.39	7.196	
	276.87	340.08	288.58	5.478	

groups or coordination process with amine, amide, or imide's groups of the ligand.

Generally, all structures bind the target ions by steric effect in the fixed cages formed at the crosslink sequence level. The retention differences are due to the dimensions and geometry of these cages and their density of distribution on the polymeric structure.

The rapid increase of the retention efficiency at pH values higher than 7, even for the imide form of the polymers (Figures 4 and 5), may be explained by the decrease of the surface potential of the gel form, which promotes easy penetration of metal ions inside the network.

We suppose that the capacity and the efficiency of the retention process were controlled by diffusion.

In this context, wettability, rather than the diameter and volume density of pores, are the major factors that determine evolution of complexation process. The thermal transitions registered for the complexes with Cr (III) are shown in Figure 6. The first mass loss interval (30–190°C) is assigned to loosing the adsorbed and/or coordinated water (0.3–14%). We remark the cases for which are present as absorbed water (the first loss peak) as coordinating water (the second loss peak) (Table III).

The interval of mass loss that comprises 190–245°C is specific for decarboxylation process. Values of mass loss, for that about 11–16%, denote a 20% decarboxylation (Table III). Subsequently mass loss, 245–350°C, suggests a total decarboxylation, similar to the start support.

CONCLUSIONS

The results showed that the retention efficiency is strongly influenced by the nature of the ligand groups. The higher values were obtaining for imide form C. This proves that the dominant complexing mechanism is the chemical binding in fixing cages in cooperation with the chelate groups from the neighboring chains.

The proposed polymer materials have a structural "heterogeneity": soluble and crosslinking fraction. Therefore, ion metallic–polymer reaction is due to the electrostatic forces forming coordination bonds and the trapping of metal ions in the bulk phase of the polymer, by sterical effects.

To describe the coordination of metal ions on the polymer supports by complexation theories, it will be necessary to consider some particular aspects. Therefore, for soluble sequences the binding of the metal ion is predominant interchain. For the crosslinking sequences, preserving the porous structure, the wettability of the skeleton, and the functionalization degree are responsible for the adsorption process.

Therefore, the crosslinking density is not the only parameter that determines the adsorption capacity of the crosslinking materials.

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