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Thermal properties of poly(*N*-maleyl glycine), poly(*N*-maleyl glycine-*co*-acrylic acid), and their metal complexes

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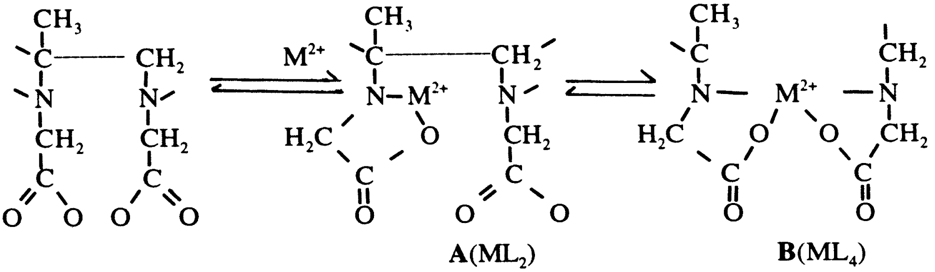
Abstract

The thermal properties of two water-soluble polymers; poly(N-maleyl glycine) and poly(N-maleyl glycine-*co*-acrylic acid) as well as their metal complexes with Co(II), Zn(II), Ni(II), Cu(II), Fe(III), Cd(II), Pb(II), and Hg(II) ions were investigated. The copolymer-metal ion complexes were obtained in aqueous phase by using the Liquid Phase Polymer-Based Retention (LPR) technique in conjunction with membrane filtration. The water-soluble P(MG) and P(MG-*co*-AA) are shown to be useful for the retention of different metal ions and their separation from elements not bound to the polymeric reagent. The thermal stability of the copolymer-metal ion complexes under nitrogen atmosphere at 20-500°C was also investigated. The complexes with different transition were characterized with FT-IR and thermogravimetry (TGA). From the TGA data the thermal decomposition temperature (TDT) and kinetic parameters such as activation energy (Ea) and reaction order (n) were determined.

Introduction

Amphoteric polyelectrolytes are capable of forming several types of complexes depending on the pH of the medium with participation of carboxy! or amino groups and also complexes of a mixed type (1). The binding of Ca(II), Mg(II), Co(II), Cu(II), and Zn(II) ions by polyampholytes based on N,N-dimethyl aminoethyl methacrylate and methacrylic acid has been investigated by the potentiometric method (2). For example, the Mg(II) ion formed a stable complex at pH> 9.7, while Co(II) was bound in the range 7.5< pH < 9.5. The formation of Cu(II) and Zn(II) complexes was observed in the region of 5.8 and 7.4, respectively. The dependence of the average coordination number on the pH of the medium shows, that the formation of the complex ML_2 is complexed at pH< 6.0, and ML_4 is formed at the range 6.0< pH < 10.0. A similar rearrangement of the coordination sphere of copper ions has been observed also for ternary polymer metal complexes, which have been examined in detail (3-5).

In particular, it was noted that two types of structures (A and B), differing in the structure of the coordination sphere of the central ion, are characteristic for the products of the interaction of poly(acrylic acid) (PAA), linear poly(ethylenimine) (PEI), and copper(II) ions. At high pH, the amino groups of PEI are not protonated and the $Cu(PEI)_2^{2+}$ complex with a type A structure is mainly formed. Thus, in this case the number and type of functional groups of the polyampholytes in the sphere of the metal



ion are determined by the pH of the medium (6). Complexes of metals with (meth)acrylates and acrylamides are used as examples for application of nontraditional methods for initiating polymerization of metal-containing monomers. It was concluded that Mn(II), Co(II), Ni(II), Zn(II), Cu(II), and Fe(III) nitrates in monomeric complexes with acrylamide are thermally unstable at above 130°C. However, these complexes, which are incorporated into the polymer matrix during polymerization, remain stable up to 200°C, i.e. the polymer matrix to a large extent prevents their decomposition (7). Usually, polymers based on metal chelates of monomers (MCM) are stable up to 473-573 K. Introduction of even a small amount of these monomers to copolymers of common monomers leads to crosslinked polymers with increased thermoplasticity and stability toward organic solvents (8).

Polymers of N-substituted maleimide is of considerable interest to achieve an excellent thermal stability because of their minimal number of oxidizable hydrogen atoms and the high extent of double bond conjugation. They are one of the most attractive classes of polymers because of their unusual chemical, thermal, and oxidative stability and especially their ease of processing to varnishes, films, adhesives, moldings, etc.

The purpose of this paper is to study the thermostability of polymers containing a maleimide moiety as well as the effect of the metal ion on their thermal stability.

Experimental

Reagents: Poly(N-maleyl glycine-*co*-acrylic acid), P(MG-*co*-AA) was synthesized by radical copolymerization with a 1:1 feed monomer composition in solution using 0.5 mol% of AIBN as the initiator (9). Prior to the polymer-metal interaction studies, the polymer was dissolved in water and purified by membrane filtration using a membrane with an exclusion limit of a molecular weight of 10.000 g/mol. All the salts were of analytical grade and used as received.

Equipment: The determination of the metal ion concentration was carried out with a Perkin-Elmer 1100 Atomic Absorption Spectrometer. For lyophilization, a continuous freeze dryer, model New Brunswich Scientific Co was used. The pH was determined with a Metrohm. pH-meter E 512. For purification of the copolymer-metal complex an ultrafiltration system was used. Details have been described previously (10, 11).

Complexation procedure with transition metals: It was carried out with the mixture of metals. To determine the complex binding capacity, the copolymer (200 mg) was dissolved in water (10 mL). The pH was adjusted by addition of diluted nitric acid or sodium hydroxide solution. The aqueous solutions (2 wt% with respect to the total metal ions) of the polymer and the metal nitrates or chlorides (20 ppm) were placed into the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water adjusted to the same pH of the cell solution. A membrane with an exclusion limit of 10 000 g/mol was used. The system was pressurized (300 kPa), the cell solution was stirred for 10 minutes and then washed with the reservoir fluid at a flow rate of 4-6 mL/min.

Complexation procedure with copper (II): The copolymer (200 mg) was dissolved in water (15 mL), and the pH was adjusted by addition of diluted nitric acid or sodium hydroxide solution. The polymers were saturated with an aqueous solution of copper nitrate (10 wt%), 1.2 mL, the pH was adjusted again. Subsequently, it was washed using the LPR technique. For the regeneration of P(MG) and P(MG-*co*-AA), protolysis with concentrated nitric acid was used (100 mg/mL). The concentration of released copper (II) ions was analyzed by absorption atomic spectrometry.

Measurement: Thermal analysis was performed in nitrogen atmosphere at a heating rate of 10°C/min. Thermogravimetric data were obtained by using a Perkin Elmer TGS-1 thermal analyzer. The molecular mass of the polymer was determined by a Knauer vapor pressure osmometer. FT-IR spectra were recorded on a Perkin Elmer model 1818.

Results and discussion

The complexes formed with different transition metal ions have been characterized by FT-IR, thermogravimetry (TGA), thermal decomposition temperature (TDT), and kinetic parameters such as activation energy (Ea) and reaction order (n).

The thermal stabilities of P(MG)-M^{n+}, P(MG)-Cu(II), P(MG-*co*-AA)-M^{n+}, and P(MG-*co*-AA)-Cu(II) have been analyzed by programmed thermogravimetric analysis over temperature range from 20 to 500 °C under nitrogen (see Table 1). The kinetic parameters pre-exponential factor (A), activation energy (Ea) and reaction order (n) were evaluated according to the following equation:

$$-d\alpha/dt = K_n (1 - \alpha)^n$$

where α is the fraction of the sample weight reacted at time t, *n* is the reaction order and K*n* is the specific rate which was obtained from the Arrhenius relationship $K_n = A_{exp} (-E_a/RT)$. The reaction rate $d\alpha/dt$ was calculated using a differential technique which includes the heating rate and uses temperature vs sample weight-fraction data (12-14).
The kinetic parameters were calculated according to the equation:

$$\beta = \ln \frac{-d\alpha/dt}{v(1 - \alpha)^n} = \ln A - E_a/RT$$

and using a linear multiple regression program by plotting β vs 1/T. v is the heating rate. Ea and A were determined from the slope and intercept, respectively.

For all the polymers, the program was run for n=0 and n=1, except for copolymer-Cu(II) n=2. The linear relationship obtained indicated that the thermal decomposition reaction has a n=0. It means that, d ‡/dt is constant at a specified temperature so that if the sample mass is increased the rate of decrease in mass remains unchanged at that temperature. This can only happen if a constant concentration of volatile material is maintained at the sample surface; this implies that the sample geometry is such that diffusion and evaporation on the surface of the sample are the rate-controlling factors.

The coefficients of linear correlation vary from 0.991 to 0.998. The thermal decomposition temperature and weight loss are summarized in Table 1. The kinetic parameters Ea and n calculated from these plots are shown in Tables 2 and 3. The thermal studies indicate that the homopolymer and copolymer degraded between 320 and 260 °C (TDT) respectively. The latter temperature is higher than that of the PAA (200°C), and lower than that of P(MG) (see Table 1).

Table 1.- Thermal decomposition temperature (TDT) and weight loss percentage (%) at the 20 to 500°C range of the polymers and polymer-metal complexes.

Polymers	TDT (°C)	Weight loss (%)
P(MG)	320	60
P(AA)	200	82
P(MG-*co*-AA)	260	75
P(MG)-M^{n+} (pH 3)	290	50
P(MG)-M^{n+} (pH 5)	290	48
P(MG)-Cu^{2+} (pH 3)	290	40
P(MG)-Cu^{2+} (pH 5)	300	55
P(MG)-Cu^{2+} (pH 7)	290	65
P(MG-*co*-AA)-M^{n+} (pH 3)	290	60
P(MG-*co*-AA)-M^{n+} (pH 5)	300	38
P(MG-*co*-AA)-Cu^{2+} (pH 3)	290	50
P(MG-*co*-AA)-Cu^{2+} (pH 5)	290	45

The thermal decomposition temperature for P(MG)-M^{n+}, where M^{n+} represents metals such as Cr(III), Fe(III), Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) (20 ppm in the feed), was analyzed at pH 3 and 5. The weight loss decreases slowly up to 290°C, but strongly between 290°C and 400°C. The thermal temperature decomposition for P(MG)-Cu(II) at different pH was increased at pH 5 and decreased at pH 7 being the latter value the same that of pH 3. This behavior may be attributed to that the polymer-metal interaction is less favored at the pH 7, but TDT varies non linearly as a function of pH (see Table 1 and Fig. 1).

Table 2.-Thermal decomposition temperatures and kinetic parameters for poly(maleyl glycine-*co*-acrylic acid) and its complexes. Stirring time of cell solution 10 min. Heating rate: 10°X•min^{-1}.

	TDT (°C)	Ea (kJ/mol)	n	pH	Correlation Factor
P(MG-*co*-AA)-M^{n+} [a)]	290	50.3	0	3	0.999
	300	67.0	0	5	0.996
P(MG-*co*-AA)-Cu^{2+}	290	57.8	0	3	0.995
	310	73.7	0	5	0.991
P(MG-*co*-AA)-Cu^{2+} Different reaction order	290	57.8	0	3	0.993
	290	54.5	1	3	0.994
	300	67.0	0	5	0.991
	290	63.7	1	5	0.998
	290	111.5	2	5	0.998

a) It corresponds to complex of the polymer with a mixture of metal ions.

The thermal decomposition of the P(MG)-Cu(II) saturated to precipitation shows a lower value than that of the TDT of P(MG) (see Table 1), but with a lower weight loss percentage. Therefore, it is suggested that the thermal stability of the polymer-copper complex is the highest. The Ea increases up to 92.2 kJ/mol at pH 3, and up to 103.0 kJ/mol at pH 5, but at pH 7 decreases at 86.7 kJ/mol. This suggest that the copolymer-metal interaction is less favored at pH 7 (see Table 3).

P(MG-*co*-AA)-M^{n+} was analyzed at pH 3 and 5. An increase of the TDT and thermal stability is observed with an increase on the weight loss percentage at pH 3 and 5 (see Fig. 2). The kinetic parameter values are summarized in Table 2. The P(MG-*co*-AA)-M^{n+} shows a TDT of 290 °C at pH 3 and 300 °C at pH 5, higher than that of the copolymer and with the lowest weight loss at 300 °C (see Table 1).

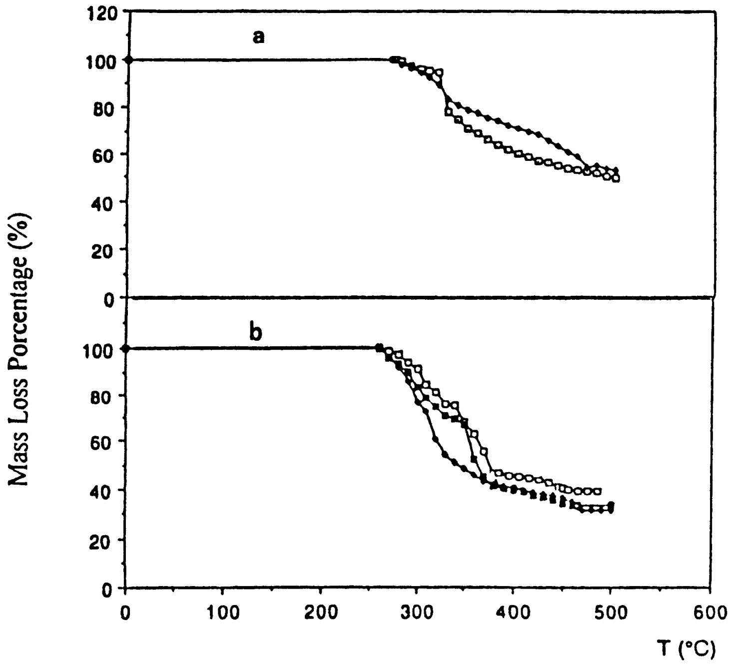


Figure 1.- Thermal decomposition of the poly(N-maleyl glycine)-M^{n+} complex at pH 3 (□) and 5 (◆), a), poly(N-maleyl glycine)-Cu(II) at pH 3 (□), 5 (◆), and 7 (■), b). Heating rate 10°C/min under N_2.

The E_a increases at pH 5, this suggests that the probable copolymer-metal interaction is more stable at this pH. The P(MG-*co*-AA)-Cu^{2+} were analyzed at pH 3 and 5. An increase of the TDT and thermal stability is observed with an increase on the weight loss percentage at pH 3 and 5 but it is lower than that of the copolymer (see Table 2). Ea increases also at pH 3 and 5 compared with the copolymer and it is higher at pH 5 corroborating the higher stability of the complex at this pH. It may be attributed to the important contribution of the carboxylate groups of the acrylic acid moiety.

All the thermal degradation reaction of the complex formed have a n = 0, except for copolymer-Cu(II) with n=2 with an excellent correlation (0.998) and a Ea= 111.4 kJ/mol, (see Table 3). This Ea value is higher than that for other reaction order (see Table 2). A variation of the method to complex formation reaction with P(MG) was also done. The metal ion solution was added to the polymer solution in water and subsequently the pH was adjusted to working pH. In this case, the TDT was decreased by the Ea increased such as the weight loss percentage is the highest. This behavior is attributed to a stable of the interaction of the polymer with the metal, where not weakening of the intramolecular hydrogen binding attraction forces of the polymer chain at acid pH<1 (see Table 3). The thermal decomposition values of Ea suggest a higher thermal stability for the complex formed at pH< 1.

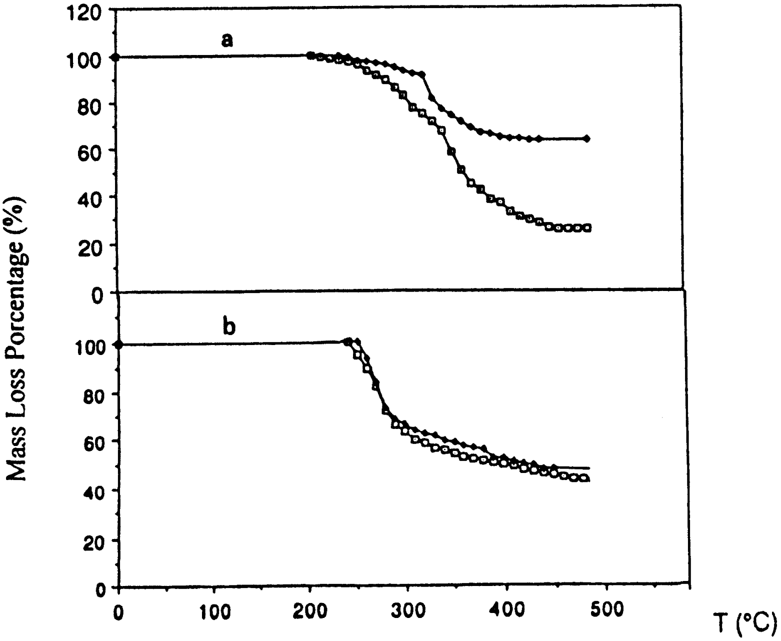


Figure 2. Thermal decomposition of the poly(N-maleyl glycine-*co*-acrylic acid)-Mn^{n+} complex a) at pH 3 (□) and 5 (◆), and b) poly(N-maleyl glycine-*co*-acrylic acid)-Cu^{2+} at pH 3 (□) and 5 (◆). Heating rate 10°C/min, in nitrogen atmosphere.

Different time periods for the polymer-metal contact were also tested and it was observed that the TDT does not increase with an increase of the interaction time before of the filtration process, but the Ea increases from 103.0 to 115.6 kJ/mol.

Table 3.-Thermal decomposition temperatures and kinetic parameters of the polymers.

Polymer sample	Ea (kJ/mol)	n	pH	Time a) (min)
P(MG)	84.0	0		
P(AA)	21.3	0		
P(MG-*co*-AA)	53.7	0		
P(MG)-M^{n+} b)	90.5	0	3	10
	97.2	0	5	10
P(MG)-Cu^{2+}	92.2	0	3	10
	103.0	0	5	10
	86.7	0	7	10
P(MG)+Cu^{2+}+ pH	87.7	0	5	10
P(MG)+pH+ Cu^{2+}	103.0	0	5	10
Different method of complex reaction				
P(MG)-Cu^{2+}	103.0	0	5	10
	115.6	0	5	120

a) Time of stirring of cell solution.

b) Corresponds to complex of the polymer with a mixture of metal ions.

The FT-IR spectra of the complexes in comparison with the spectra of the homo- and copolymers give information on the binding site of the ligand groups to the central metal ions. The FT-IR spectrum of the homopolymer shows the characteristic absorption bands, a strong absorption at 3527 cm^{-1} (-OH of -COOH), at 2949 cm^{-1} (-CH, of the

CH_2), at 1710 cm^{-1} (-C=O, of the imide and -COOH), at 1439 cm^{-1} (-C-N, of the imide ring). Compared these signals with the complex-signals at pH 3 and 5, the following differences were observed: a strong increase and broadening of the absorption band of the functional group -COOH; a little band of the group $-CH_2$, a splitting in two signals of the imide-signal at 1710 cm^{-1} to 1699 and 1620 cm^{-1} of the carboxylic groups and of the signal at 1439 cm^{-1} (characteristic features of the group -C-N in the imide ring), in two signals at 1427 cm^{-1} and 1384 cm^{-1}.

The FT-IR spectrum of the copolymer shows the characteristic feature, a strong absorption at 3500 cm^{-1} (-OH of the functional group -COOH), at 2955 cm^{-1} (-CH, of the CH_2), at 1770 cm^{-1} (-C=O, of the imide), at 1422 cm^{-1} (-C-N, of the imide ring). Comparing these signals with those of the complex at pH 3 and 5, a strong increase, broadening, and a splitting of the absorption band of the functional group -COOH. It is also observed that a little band of the group $-CH_2$, a splitting of two signals of the imide-signal at 1770 cm^{-1} to 1698 cm^{-1} and 1604 of the carboxylic groups a splitting of the signal at 1439 cm^{-1} in two signals of the imide-signal to 1424 cm^{-1} and 1343 cm^{-1}, characteristic features of the group -C-N of imide ring. The splitting and broadening of the bands observed suggest that those functional groups have an active participation in the complex process.

Conclusions

The polymer metal ion complexes obtained by using the Liquid Phase Polymer-Based retention technique (LPR) were studied by thermogravimetric analysis under dynamic conditions and by FT-IR spectroscopy. The thermal decomposition temperature (TDT) of the P(MG)-M^{n+} complexes and polymer-Cu(II) saturated to precipitation showed a lower TDT than that the respective polymers, but with a lower weight loss. For example, the P(MG) has an Ea = 84.0 kJ/mol and the P(MG)-Cu(II) has an Ea increases to 92.2 kJ/mol at pH 3, and to 103.0 kJ/mol at pH 5, but at pH 7 decreases at 86.7 kJ/mol, this suggest that the interaction copolymer-metal is less favored at pH 7. The P(MG-*co*-AA)-M^{n+} and polymer-Cu(II) complex showed a higher TDT than that the copolymer and a lower weight loss percentage. Therefore, it is suggested that the thermal stability of the polymer metal ion complex is higher.

The FT-IR spectrum of the homopolymer shows the characteristic features and strong absorption bands. The comparison of the FT-IR absorption of the polymers with those of the complexes at pH 3 and 5 shows the following differences: a strong increase and broadening of the absorption band of the functional group -COOH; a small band of the group $-CH_2$, a splitting into two signals of the imide-signal, of the carboxylic groups was also observed. This suggests an active role of these functional groups in the polymer-metal ion complex formation process.

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References

1. Bekturov EA, Kudaibergenov SE, Khamzamulina RE (1986) Cationic Polymers, Nauka, Alma-Ata, p 160
2. Zezin AB, Izumrudov VA, Kabanov VA (1989) Makromol Chem Macromol Symp 26: 249

3. Philipp B, Dautzenberg H, Linow K-J, et al. (1989) Prog Polym Sci 14: 91
4. Bekturov EA, Kudaibergenov SE (1989) Makromol Chem Macromol Symp 26: 281
5. Kudaibergenov SE, Shaaikhutdinov EM, Bekturov EA (1989) Novosti Nauki Kazakhstana (4): 25
6. Bekturov EA, Kudaibergenov SE Rafikov SR (1991) Russian Chem Rev 60: 410
7. Pomogailo AD, Savostyanov VS(1991) Russian Chem Rev 60: 762
8. Uflyand IE, Pomogailo AD (1991) Russian Chem Rev 60: 772
9. Pizarro G del C, Rivas BL, Geckeler KE (1997) J Macromol Sci Pure Appl Chem A34: 681
10. Geckeler KE (1993) Polym J 25: 115
11. Pizarro Gdel C, Rivas BL, Geckeler KE (1996) Polym Bull 37: 525
12. Rivas BL, Pizarro G del C, Tagle LH (1991) Thermochim Acta 184: 183
13. Rivas BL, Pizarro G del C, Catalán RE, Tagle LH (1991) Thermochim Acta 188: 163
14. Pizarro G del C, Rivas BL, Geckeler KE (1996) Bol Soc Chil Quim 41: 181