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Polymer-metal complexes: Synthesis, characterization, and properties of poly(maleic acid) metal complexes with Cu(II), Co(II), Ni(II), and Zn(II)

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SUMMARY

Polymer metal complexes of poly(maleic acid) and Cu(II), Co(II), Ni(II), and Zn(II) were synthesized. Elemental analysis, as well as magnetic, spectral and thermal properties, in addition to electrical conductivities of the chelates were investigated, and possible structures have been assigned to the polychelates. Semi-empirical calculations at the PM3 level were carried out on the geometrical arrangement of the polychelates.

INTRODUCTION

Polymer-metal complexes are attracting considerable attention for a variety of applications (1-5), like in organic synthesis, pollution control, hydrometallurgy, polymer grafts, *etc*. A number of polymer-bound chelating ligands, including polydentate amines, crown ethers, have been reported (6-7). The preparation of pendant type polymer-metal complexes having a uniform structure by the substitution reaction between a polymer ligand and a metal ion such as Co(III) or Cr(III) has also been studied (8). The polymer metal chelates were also found to act as electrochromic materials, since the colour of the polymer varies with the oxidation state of the metal ion present in the chelate (9-10). Poly(vinyl alcohol) with an aqueous solution of cupric ions shows a green coloration at pH 6.0 with a remarkable decrease of viscosity (11-12). It is attributed to the formation of stable mononuclear copper(II) complexes with hydroxyl groups of PVA. Poly(acrylic acid) (13-14) and poly(acrylic acid-co-maleic acid) (15) show a very interesting behavior to complex different metal ions.

This communication deals with the synthesis and characterization of poly(maleic acid)-metal complexes with Cu(II), Co(II), Ni(II), and Zn(II). The conductivity, magnetic properties, and the type of chelation with the metal ions are discussed. The present study, not only aims the synthesis and characterization of a new series of macromolecular metal chelates, but also demonstrates the simulation of FT IR spectra.

EXPERIMENTAL PART

Materials: Poly(maleic acid), Molecular weight: 1000 g/mol was purchased from Polysciences. Metal chlorides, analytical grade, from Merck were used as received.

Polymer-metal chelates: The polymer-metal chelates were prepared by dissolving the polymer in distilled water and by reaction with the metal halide under stirring. The

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resulting polychelates with Ni(II), Co(II), and Zn(II) were isolated at pH 6 and that of Cu(II) at pH 4. The polymer-metal chelates were completely insoluble in water and in organic solvents.

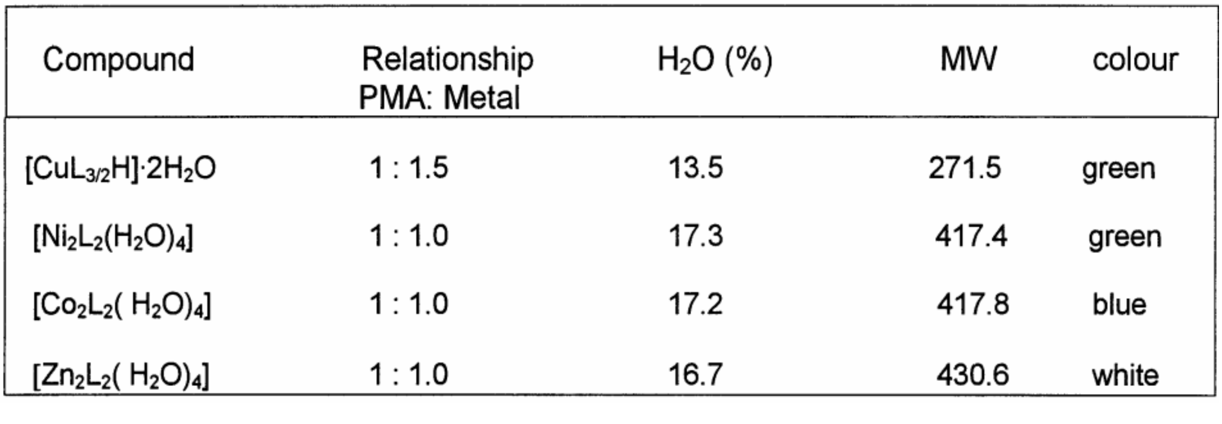
Measurements: Elemental analyses were done using a Series II CHNS 10 analyser 2400 Perkin Elmer. The FT IR spectra of the samples were recorded on a Magna Nicolet 550 spectrophotometer. The magnetic moments ($\mu_{eff} = 2.83 \sqrt{X_m T}$) were measured by the Gouy method and corrected for diamagnetism of the components using Pascal's constants. The diffuse reflectance spectra were measured on a Perkin Elmer Lambda 20 spectrophotometer coupled to Labsphere reflectance diffuse attachment and Spectralon as reference. The electrical conductivity of the polychelates were measured as pellets of 1.3 cm diameter and 0.07 cm thickness using an Analog Multimeter (Digital Kayton KT-2210). The thermogravimetric analysis of the polychelates were carried with a Polymer Laboratories STA 625 analyzer.

RESULTS AND DISCUSSION

Poly(maleic acid) has a higher density of carboxylic groups at the backbone with a titration curve in two steps, that 50% of protonated groups may be stabilized in a pair of pH units (16-18).

The polychelates from poly(maleic acid), L, and Cu(II), Co(II), Ni(II), and Zn(II) are colored solids, insoluble in water. The elemental analysis shows that the metal ligand ratio varies according to the metal $[CuL_{3/2}H]$; $[Ni_2L_2(H_2O)_4]$; $[CoL_2(H_2O)_4]$, and $[Zn_2L_2(H_2O)_4]$ (see Table 1).

Table 1. Analytical data of PMA, L, and its polychelates with Cu(II), Co(II), Ni(II), and Zn(II).



Compound	Relationship PMA: Metal	H_2O (%)	MW	colour
$[CuL_{3/2}H]\cdot 2H_2O$	1 : 1.5	13.5	271.5	green
$[Ni_2L_2(H_2O)_4]$	1 : 1.0	17.3	417.4	green
$[Co_2L_2(H_2O)_4]$	1 : 1.0	17.2	417.8	blue
$[Zn_2L_2(H_2O)_4]$	1 : 1.0	16.7	430.6	white

Thermal properties

The polychelates lost lower than 18% of weight up to 100°C, at 300°C polychelate with Cu(II) showed the higher weight lost and therefore it increases only up to 63%, but the polychelate with Ni(II) showed a high weight lost at 400°C (56%) and particularly at 500°C (73.3%). The polychelate with Zn(II) was the most stable with a weight lost lower than 50% at 500°C (see Table 2).

Table 2. Thermal stability of PMA and its polychelates with Cu(II), Co(II), Ni(II), and Zn(II).

	Weight-loss (%) at different temperatures (°C)				
Compound	100	200	300	400	500
$[CuL_{3/2}H]\cdot 2H_2O$	12.2	18.7	50.9	56.2	63.9
$[Ni_2L_2(H_2O)_4]$	14.1	28.2	31.3	56.0	73.3
$[Co_2L_2(H_2O)_4]$	17.5	27.0	32.2	54.5	58.8
$[Zn_2L_2(H_2O)_4]$	13.7	19.1	21.0	33.3	49.3

FT IR spectra

The IR spectral studies of the polychelates provide important clues regarding the complexation of the metal ion with the polymer. The ligand stretching frequency of the carboxylate groups involved in coordination undergo shift which can be taken as an evidence of coordination. The FT IR spectrum of poly(maleic acid) shows characteristic absorption bands of the carboxylic groups at 1708 cm^{-1} ($\nu_{C=O}$) and at 1418 cm^{-1} (νC-O). The FT IR of the polychelate with Cu(II) shows the characteristic absorption signals of carboxylate without coordinate and the two stretching signals at 1611 cm^{-1} and 1560 cm^{-1} attributed to symmetric and asymmetric bands of carboxylate groups coordinated to the Cu(II) ions. However, for the polychelates of Ni(II), Co(II), and Zn(II) these signals are placed at 1560 cm^{-1} and 1408 cm^{-1} respectively (see Figure 1).

Magnetic measurements and diffuse reflectance spectra

Table 3 shows the magnetic susceptibility values, electronic transitions and ligand field parameters of paramagnetic polychelates. For the PMA-Cu(II) is suggested a pseudo tetrahedral geometry, however, all the other PMA-metal ion show a distorted octahedral geometry incorporating water molecules to the coordination sphere.

For the electronic spectrum of PMA-Ni(II) was not observed the calculated electronic transition ν_1 (8680cm^{-1}) (19) but a weak absorption at 11400 cm^{-1} was observed which was assigned to the forbidden transition by the multiplicity of the spin. The absorption at 17099 cm^{-1} is splitted with a shoulder at 16051cm^{-1} which can be attributed to distorted tetragonal coming from the different nature of the ligands.

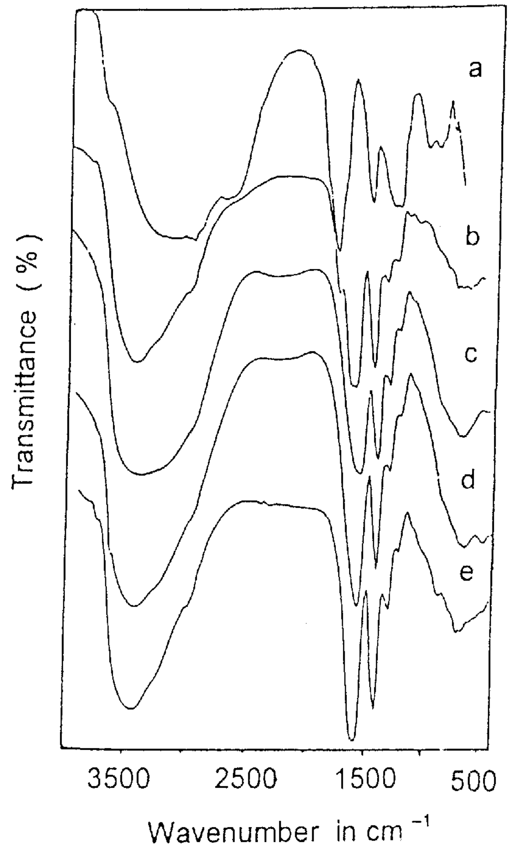


Figure 1. FTIR spectra of the a) poly(maleic acid) and its polychelates b) PMA-Cu(II), c) PMA-Ni(II), d) PMA-Co(II), and e) PMA-Zn(II).

Table 3. Magnetic measurements and electronic spectra of polychelates of poly(maleic acid),L.

Compound	λ máx (cm^{-1})	Assignment	Field ligand parameters(cm^{-1})	μ_{ef} (M.B.)
$[CuL_{3/2}H)\cdot 2H_2O$	14044	${}^2T_{2g} \rightarrow {}^2E_g$		1.74
$[Ni_2L_2(H_2O)_4]$	8680(calc.) 14577 25316	${}^2A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3Ag_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3Ag_{2g}(F) \rightarrow {}^3T_{1g}(P)$	10Dq = 8680 B = 923 β = 0.89	2.69
$[Co_2L_2(H_2O)_4]$	9765 11049 16059(sh) 17099 20202	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^2E_g$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ ${}^4T_{2g}(F) \rightarrow {}^4T_{1g}(P)$	10Dq = 7334 B = 533 β = 0.55	4.43

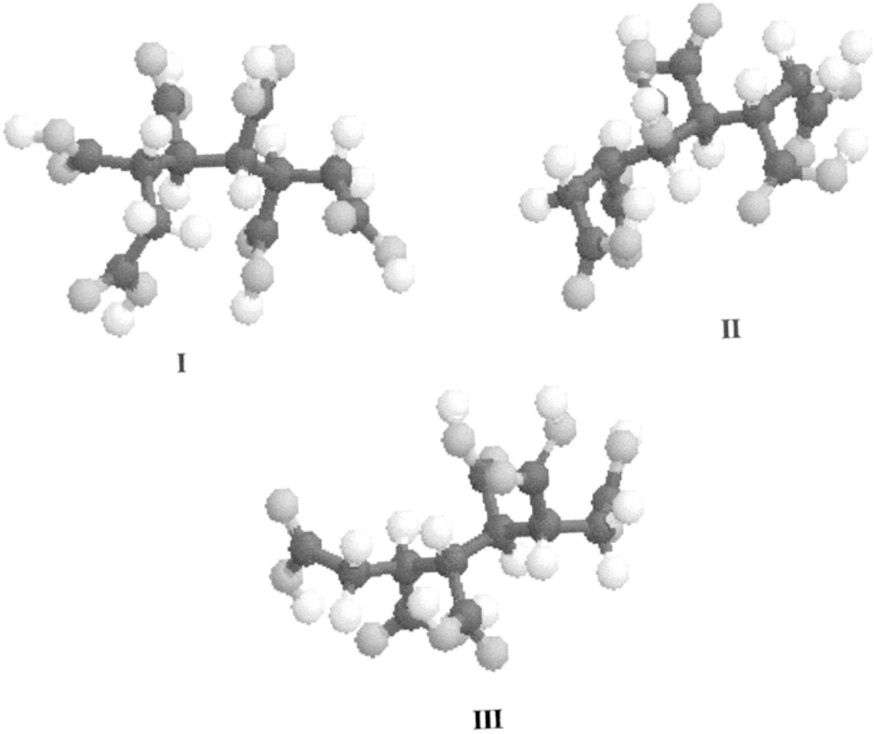


Figure 2. PM3 calculation for the configurations of poly(maleic acid).

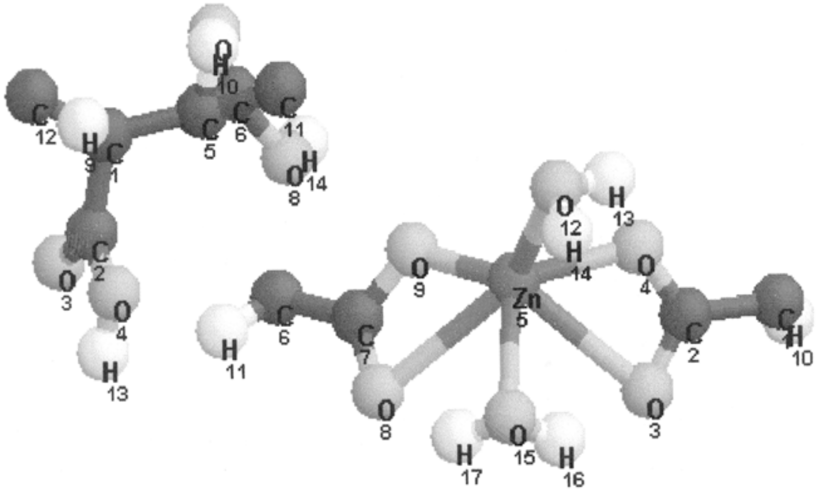


Figure 3. PM3 calculation of the polychelate with Zn(II).

The PM3 calculations of the Zn-O lenght bonds are in range to those calculated for poly(acrylic acid-*co*-maleic acid) (15).

Moreover, the semi-empirical calculations of the vibration frequency of PMA and PMA-Zn(II) were carried out. The difference between the experimental and calculated vibrational frequencies is due to that the well known that the quantic semiempirical

The ligand field parameters were calculated from Orgel diagrams considering the configuration interaction (20). For the PMA-Ni(II) and PMA-Co(II) was calculated β by using the B values corresponding to the free ion at 1041 cm^{-1} and 971 cm^{-1} (21). From the β value it is possible infer that the polychelate with Ni(II) has a high ionic character but not for that with Co(II).

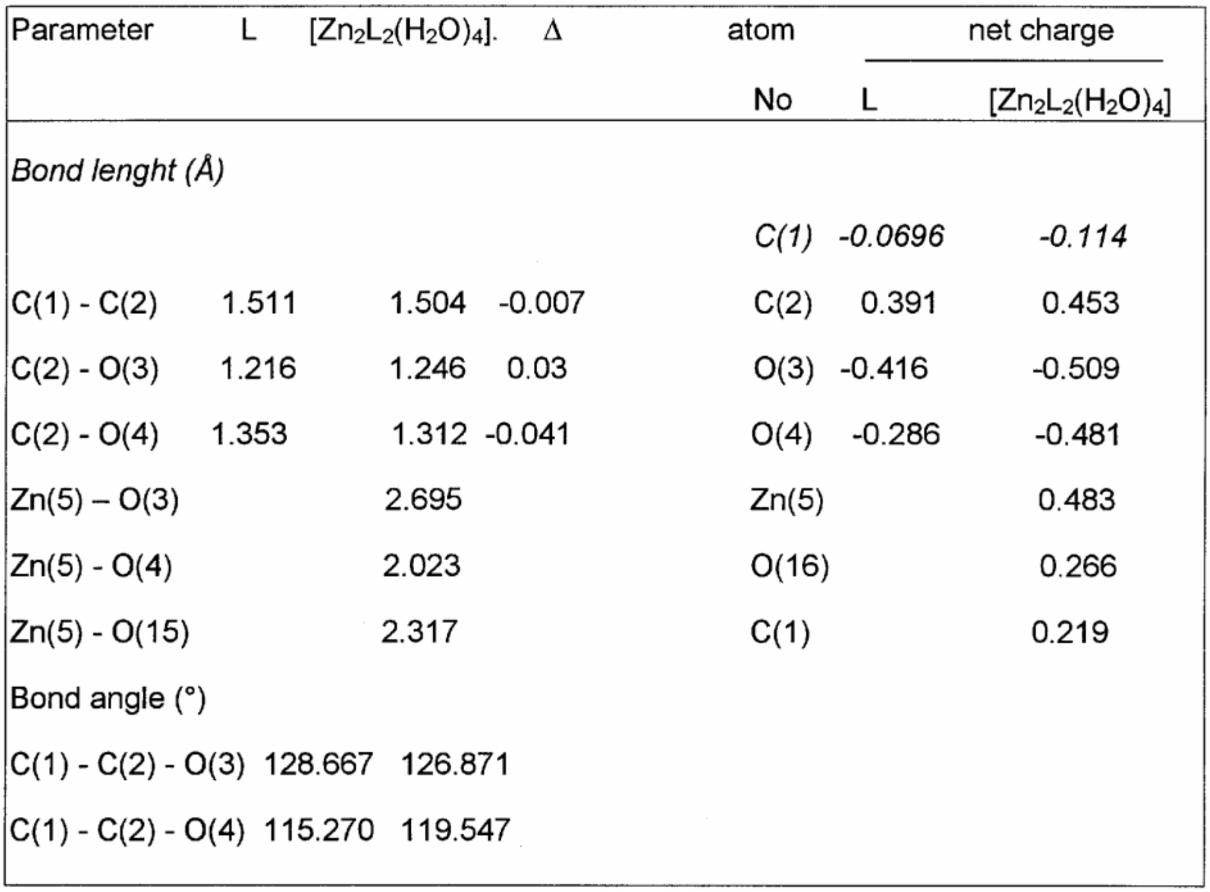
The magnetic moment of PMA-Cu(II) is 1.74 M.B. which is common to compounds with covalent bonds. The PMA-Ni(II) and PMA-Co(II) show a magnetic moment of 2.7 M.B. and 4.4.M.B. respectively which correspond to a distorted octahedral geometry.

Calculated structures to the poly(maleic acid) and poly(maleic acid)-Zn(II).

The values of heat formation for configurations I, II, and III by PM3 calculations were -542.79 Kcal mol^{-1}, -526.41 Kcal mol^{-1}, and -532.99 Kcal mol^{-1} respectively indicate that the configuration I is the most stable. It is in agree with ^{13}C NMR studies carried out by J.de Grot et al.(22). The calculations were carried out to the PMA-Zn(II) due to the parameters to Cu(II), Co(II), Ni(II) are not available.

The structure of poly(maleic acid) and its polychelate with Zn(II) are shown in figures 2 and 3, and the calculations in table 4.

Table 4. Selected PM3 structural parameters of PMA, L, and PMA-Zn(II), $[Zn_2L_2(H_2O)_4]$.



Parameter	L	$[Zn_2L_2(H_2O)_4]$.	Δ	atom	net charge	
				No	L	$[Zn_2L_2(H_2O)_4]$
Bond lenght (Å)						
				C(1)	*-0.0696*	*-0.114*
C(1) - C(2)	1.511	1.504	-0.007	C(2)	0.391	0.453
C(2) - O(3)	1.216	1.246	0.03	O(3)	-0.416	-0.509
C(2) - O(4)	1.353	1.312	-0.041	O(4)	-0.286	-0.481
Zn(5) – O(3)		2.695		Zn(5)		0.483
Zn(5) - O(4)		2.023		O(16)		0.266
Zn(5) - O(15)		2.317		C(1)		0.219
Bond angle (°)						
C(1) - C(2) - O(3)	128.667	126.871				
C(1) - C(2) - O(4)	115.270	119.547				

methods overestimate the value of these frequencies. With a higher set of experimental data to polymeric ligand should be possible re-parametrize the PM3 method to do it more exact respect the frequencies values. Some vibration frequencies and the potential energy distribution (PED) values are shown in Table 5. Neverthless these differences, the calculated vibrational frequencies and their assignment are correlated with the experimental FT IR spectrum.

Table 5. Calculations of some stretching vibrations of PMA and PMA-Zn(II).

Compound	$\nu(cm^{-1})$	PED (%)	ν_{exp} (cm^{-1})
PMA			
	3853.8	99.8 $(O_{12} - H_{13})$	3550
	1982-5	86.1 $(C_2 - O_3)$	1707
	1445.7	79.1 $(C_2 - O_4)$	1418
PMA-Zn (II)			
	3800.2	68.5 $(O_{15} – H_{16})$	3710
	1821.4	88.2 $(C_2 - O_3)$	1585
	1551.1	83.9 $(C_2 - O_4)$	1410

Electrical conductivity

At room temperature the polychelates with Cu(II), Co(II), and Zn(II) show a very low conductivity, appr. 10^{-11} (ohm cm^{-1}) but with Ni(II) 10^{-9} (ohm cm^{-1}). Increasing the temperature over 100°C, were the polychelate loss the water molecules, the electrical conductivity increases to 10^{-6} (ohm cm^{-1}). These polychelates behave as semiconductors in a wide temperature range considering the variation of σ in function of the temperature (see figure 4). The higher electrical conductivity was observed for the polychelate with Ni(II). It can be attributed to the higher ionic character between the metal ion and the functional groups of the polymer.

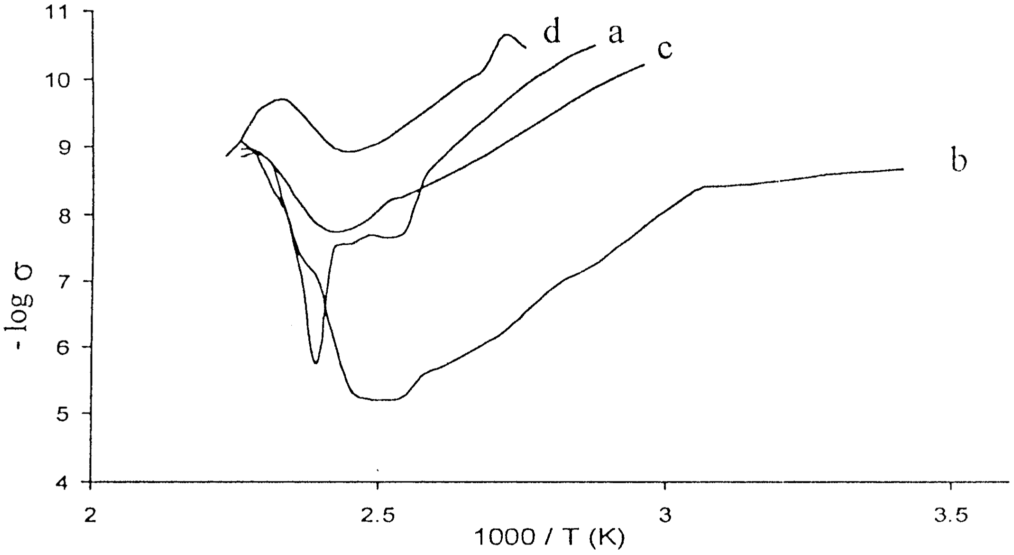


Figure 4. Electrical conductivity of polychelates with a) Cu(II), b) Ni(II), c) Co(II), and d) Zn(II).

Conclusions

Polychelates of poly(maleic acid) with Cu(II), Co(II), Ni(II), and Zn(II) from an aqueous solution were synthesized. They were completely insoluble in water. According to the results, the involved functional groups in the coordination with the different metal ions coming from the different polymer chains. To the polychelates with Ni(II), Co(II), and Zn(II) all the carboxylic groups are coordinating with the metal ion, but for Cu(II) only the 66% of them are coordinated. It was different to the poly(acrylic acid-*co*-maleic acid) (15) where only one carboxylic acid is involved in the complexation. The electrical conductivity increased with the temperature. The higher electrical conductivity of poly(maleic acid)-Ni(II) is attributed to the higher ionic character of the metal ion -carboxylate bond.

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REFERENCES

1. C.H.Chen, J.Shi, Coord.Chem.Rew. **171**, 161 (1998).
2. H.Shirai, T.Koyama, Y.An. K.Hanabusa, Macromol.Symp. **105**, 217 (1996).
3. M.Biswas, A.Mukherjee, Adv.Polym.Sci. **115**, 91 (1994).
4. Y.An, T.Ushida, M. Sizuki, T. Koyama, K.Hanabusa, H.Shirai, Polymer, **37**, 3097 (1996).
5. L.A.Linden, J.F.Rabek, H.Kaczmarek, Mol.Cryst.Liq.Cryst.Sci.Technol.Sect.A **240**, 143 (1994).
6. C.J.Pedersen, H.K.Frensdroft, Angew.Makromol.Chem.Int.Edn.Engn. **11**, 16 (1973).
7. L.D.Rollman, J.Am.Chem.Soc. **97**, 2132 (1975).
8. Y.Osada, Makromol.Chem. **176**, 1983 (1974).
9. H.P.Abruna, P.Denisevich, M.Umana, T.J.Meyer, R.Murray, J.Am.Chem.Soc. **103**, 1 (1981).
10. C.M.Elliot, J.C.Redopeming, E.M.Balt, J.Am.Chem.Soc. **107**, 8032 (1985).
11. N.Hoyo, H.Shirai, S.Hayashi, J.Polym.Sci. **C47**, 299 (1974).
12. N.Hoyo, H.Shirai, J.Chem.Soc.Jpn. **96**, 1316 (172).
13. F.T.Wall, S.J.Gill, J.Phys.Chem. **58**, 1128 (1954).
14. H.P.Gregorm, L.B.Luttinger, E.M.Loebl, J.Phys.Chem. **59**, 34 (1955).
15. B.L.Rivas, G.V.Seguel, Polyhedron **18/19**, 2511 (1999).
16. T.Kitano, S.Sawaguchi, K.Ito, Macromolecules **20**, 1598 (1987).
17. J.de Groot, J.G.Hollander, J. De Bleijer, Macromolecules **31**, 4182 (1998).
18. S. Kawaguchi, T.Kitano, K.Ito, Macromolecules **25**, 1294 (1992).
19. B.N. Figgis, Introduction to Ligand Fields. 2*nd* Ed. J. Wiley, New York, p.220(1967)
20. D. Sutton, Espectros electrónicos de los complejos de los metales de transición.Ed.Reverté,España,p. 119 (1975).
21. E. König, Stucture and Bonding **9**,175 (1971)
22. J. de Grot, J.G. Hollander, J.de Bleijser, Macromolecules **30**, 6884 (1997).