Synthesis, characterization, and properties of polychelates of poly(maleic acid-co-olefin) with Cu(II), Co(II), Ni(II), and Zn(II)

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SUMMARY

Polychelates of poly(maleic acid-*co*-olefin) with Cu(II), Co(II), Ni(II), and Zn(II) metal ions are synthesized. These compounds are characterized by FT IR, UV-vis spectroscopy, and thermal analysis. The electrical conductivity measurements are carried out. These demonstrate that at temperature close to 130°C the electrical conductivity increased to values near to the semiconductor range. The PM3 calculations are also carried to study the geometry of the polychelates.

INTRODUCTION

Copolymers of maleic acid always exhibits a two- step dissociation and anomalies in the range of dissociation of primary carboxyl group. Such behaviors are referred to the conformational chain transition from compact globule to an extended coil (1-6). In hydrolyzed form they are polyelectrolytes, and their solution properties are governed mainly by electrostatic interactions between the fixed charges of polyions and mobile charges of counter ions (7). Structural characteristic of maleic acid polymers (8), enables a variation of charge density along the chain, strong nearest-neighbor interactions, formation of hydrogen bonds and hydrophobic effect of alternative units. As all these effects influence the conformation of polyions and the balance of hydrophobic-hydrophilic interactions within the chains, they, in fact, influence the behavior and properties of polymer solutions. The investigation of homopolymers and alternating copolymers of maleic acid in solution has been subject of many papers and still remains a topic of considerable interest.

Wang, reported the synthesis of a cross-linked poly[(maleic acid)-co-styrene]-platinum complex, an active and stable catalyst in the hydrogenation of methyl formate under mild conditions (25°C, 1 atm) (9).

Poly(maleic acid) has a higher density of carboxylic group at the backbone.To the polychelates of poly(maleic acid) with Ni(II), Co(II), and Zn(II) all the carboxylic groups are coordinated with the metal ion but for Cu(II) only the 66% of them are coordinated (10). It was different to the poly(acrylic acid-*co*-maleic acid) (11) and poly(styrene-*alt*-maleic acid) (12) were only one carboxylic acid is involved in the complexation.

The aim of this paper is to prepare polychelates of poly(maleic acid-*co*-olefin) with Cu(II), Co(II), Ni(II), and Zn(II) ions as well as to investigate their nature in order to ascertain stereochemistry, geometry and their thermal and semiconducting behavior.

EXPERIMENTAL

Reagents.
Poly(maleic acid-*co*-olefin) sodium salt was purchased from Aldrich (MW = 12.000) and was treated with 1M HCl. The metal salts were analytical grade (Merck) $CuCl_2$ x $2H_2O$, $NiCl_2$ x $6H_2O$, $CoCl_2$ x $6H_2O$, and $ZnCl_2$.

Synthesis of polychelates.
The polychelates were synthesized by reaction of an aqueous solution of the copolymer with the metal salt, $MCl_2 \cdot nH_2O$. The solution was stirred and the pH adjusted with 0.1M HCl or 0.1M NaOH. The polychelates were precipitated by adding etanol/acetone and adjusting at pH 4. The compounds are completely insoluble in water and in organic solvents like methanol, acetone.

Measurements.
The FT IR spectra and UV Vis were recorded with a Magna Nicolet 550 and Perkin Elmer Lambda 20 spectrophotometers respectively. Electrical conductivities were carried out with an Analog Multimeter Digital Kayton KT-2210.

RESULTS AND DISCUSSION

The polychelates from poly(maleic acid-*co*-olefin) with divalent cations were obtained and characterized. The analytical properties are summarized in Table 1.

Table 1. Analytical data of the polychelates, poly(maleic acid-*co*-olefin), L.

Compound	M-L Ratio	H_2O(%)	Colour
$CuL_5 \cdot 8H_2O$	1:5	12.7	Sky blue
$NiL_3 \cdot 10H_2O$	1:3	22.6	Green
$CoL_5 \cdot 3H_2O$	1:5	5.5	Pink
$ZnL_5 \cdot 6H_2O$	1:5	9.8	White

The polychelates of Cu(II), Co(II), and Zn(II) react with a M:P = 1:5 stoichiometric ratio, but Ni(II) with 1:3.

FT-IR spectroscopy.
The figure 1 shows the FTIR spectra of the polymer ligand and their polychelates. The FT-IR spectrum of poly(maleic acid-*co*-olefin) shows the characteristic absorption bands corresponding to C=0 from free carboxylic acid at 1720 cm^{-1} and at 1776 cm^{-1} assigned to carboxylic groups with hydrogen bridge between two carboxylic groups (13).

The signal placed at 1640 cm^{-1} corresponds to hydrogen bridge between COOH and COO^- groups (14). In the region of 1400 cm^{-1} two stretching vibrations (C-O of free carboxylic groups and the carboxylic groups with hydrogen bridge) are observed.
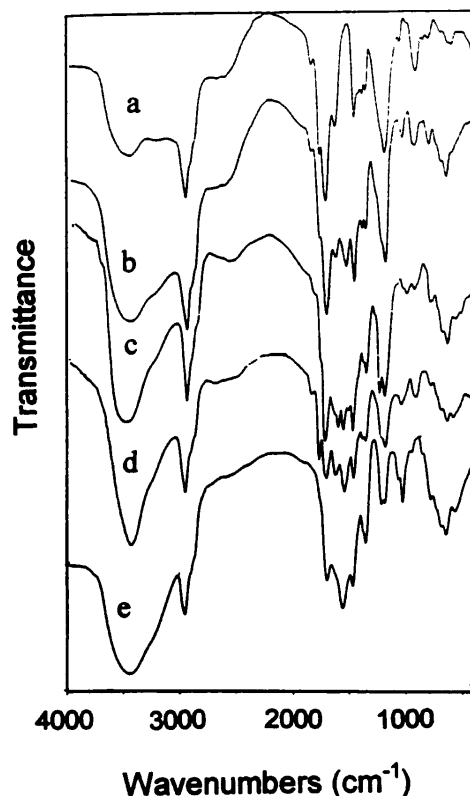

Figure 1. FT IR spectra (KBr) of a) poly(maleic acid-co-olefin) and its polychelates with b) Cu(II), c) Zn(II), d) Co(II), and e) Ni(II).

The polychelate of Co(II) shows a band of middle intensity at 1779 cm^{-1} which can be attributed to carboxylic groups with hydrogen bridge. This band is also observed for the polychelate with Cu(II) but very weak. The spectra of polychelates of Cu(II), Co(II), and Zn(II) present a band close to 1630 cm^{-1} which can be attributed to hydrogen bridge between carboxylic and carboxylate groups.

The spectra of the polychelates show also the bands at 1550 cm^{-1} and near to 1370 cm^{-1} corresponding to free carboxylic and metal ion coordinated carboxylate groups respectively.

The band at 1720 cm^{-1} (free carboxylic group) is very intense for the polychelates with Cu(II) and Zn(II) and that at 1550 cm^{-1} (metal ion-coordinated carboxylate groups) only of middle intensity. However, for the polychelates of Co(II) and Ni(II), the bands at

1720 cm^{-1} and 1550 cm^{-1} decreased and increased respectively. For the polychelate of Ni(II), the band at 1720 cm^{-1} is coupled with the band at 1640 cm^{-1}, therefore the intensity increased.

From the spectra it is possible postulate that metal ions coordinate with the carboxylate groups at different magnitud with the metal ion. It would be related with the size of metal ion and the lower density charge of the copolymer by comparison with poly(maleic acid) and the lower flexibility of the chain.

Diffuse reflectance electronic spectra.

These spectra show for the polychelate of Cu(II), Ni(II), and Co(II) bands at 797 nm and 724 nm, and 542 nm respectively. The polychelate of Ni(II) also shows a shoulder at 660 nm. These bands are placed in characteristic zones for octahedral geometries for each metal ion (15) and are relatively weak as the metal ion is in a small amount regarding the polymer ligand.

The compound of Co(II) has pink colour but by heating at 40°C it changes to blue-lilac, but without significative changes in the electronic spectra. In most cases one can establish that a 6-coordinate Co(II) complex is pink and a tetrahedral 4-coordinate one is blue, buth there are a number of exceptions. First of all, anhydrous $CoCl_2$ possesses a $CdCl_2$ structure, so that the Co(II) ion in its 6-coordinate. It is however, deep blue, still more strangely, when cooled with liquid air the colour of this compound changes into a dull pink without a structural change (16).

According to that, it is possible postulate that metal ions are surrounded of various polymer chains, but only two carboxylic groups (bidentate) are able to coordinate. It has been reported that the poly(carboxylic acids) coordinate completing their coordination sphere with water molecules. It is probable that these coordinated carboxylic groups belong to different chains due to the small flexibility of the polymer chains.

Regarding thermal stability the ligand losses a 15.7% of weight at 200ºC which increased up to 45.6% at 400°C. The weight-loss can be attributed basically to CO_2. The polychelates show a similar behavior up to 300°C, with a higher weight-loss than that ligand but at 400°C all the polychelates except Co(II)-L show a higher weight-loss. It is attributed to the presence of the metal ions (see Table 2).

Table 2. Thermal stability of poly(maleic acid-*co*-olefin) and their polychelates of Cu(II), Ni(II), Co(II), and Zn(II).

Compound	Weight-loss (%) at different temperatures (°C)			
	100	200	300	400
L	1.3	15.7	22.7	45.6
Cu (II) -L	11.4	18.6	45.1	78.5
Ni(II) - L	18.7	29.1	32.3	79.6
Co(II) - L	1.2	8.0	15.1	69.2
Zn(II) - L	15.6	22.1	25.1	76.8

Electrical conductivity.

At room temperature the compounds show a very low electrical conductivity, the polychelates of Cu(II), Co(II), and Zn(II) near to 10^{-11}(ohm cm) $^{-1}$ and of Ni(II) close to 10^{-10} (ohm cm)$^{-1}$. Above 100° C (~130°C), the polychelates show a break point, increasing the electrical conductivity, thus the polychelate of Zn(II) achieves a value of 10^{-7} (ohm cm)$^{-1}$.

Geometry calculations

PM3 calculations for poly(maleic acid-*co*-olefin) and polychelate of Zn(II) were carried out. It was not possible carry out these calculations for the polychelates of Cu(II) , Ni(II), and Co(II) as there are not available the corresponding values. The structure of poly(maleic acid-*co*-olefin) and polychelate of Zn(II) are shown in the figure 2 and the calculations are summarized in Table 3.

Table 3 : Selected PM3 structural calculations of poly(maleic acid-*co*-olefin) , L, and the [Zn L$_5$] nH$_2$O complex.

Parameter	L	[Zn L$_5$]nH$_2$O	Δ	Atom N°	Net charge L	[ZnL$_2$(H$_2$O)$_2$]
Length of bond (A°)						
				C(28)	-0.1002	-0.0752
C(28) - C(31)	1.540	1.542	0.002	C(31)	-0.0643	-0.0666
C(28) - C(44)	1.529	1.535	0.006	C(32)	-0.1102	-0.1066
C(31) - C(32)	1.533	1.533	0.000	C(44)	0.3514	0.4545
C(31) -O(45)	1.522	1.523	0.001	C(45)	0.3762	0.3780
C(44) -O(48)	1.212	1.245	0.033	O(48)	-0.3254	-0.5285
C(44) -O(52)	1.353	1.305	-0.048	O(49)	-0.3855	-0.3910
C(45) -O(49)	1.217	1.218	0.001	O(52)	-0.2664	-0.4235
Zn(111) – O(48)		2.832		O(53)	-0.3081	-0.3059
Zn(111) – O(52)		1.984		O(84)		0.3986
Zn(111) – O(84)		1.969		O(85)		-0.5378
Zn(111) – O(85)		2.833				
Zn(111) –O(112)		2.196				
Zn(111) - O(113)		2.212				

The polychelate of Zn(II) presents a distorted octahedral geometry where the other carboxylate presents an asymmetric chelation with one of the longest Zn - O bonds. The length of Zn -O with the oxygens of the carboxylate groups measure between 1.969 Å and 2.833 Å. The last value is enough high for a Zn - O bond but lower than that reported for the polychelate of poly(styrene-*alt*-maleic acid) with Zn(II) (12).

It is observed that the Zn - O(52) y Zn - O(85) bonds correspond to the longest M-O bonds in the polychelate and that the O(52) y O(85) present the higher charge density. This can be interpreted due to that the bonds have a high ionic character.

This can explain the $\Delta v = [v_a(CO_2^-) - v_s(CO_2^-)]$ values calculated from the FT IR spectra (between 175 cm^{-1} and 192 cm^{-1}). These values are higher than those reported (17) for ionic compounds and bidentate chelates but lower than those monodentate chelates.
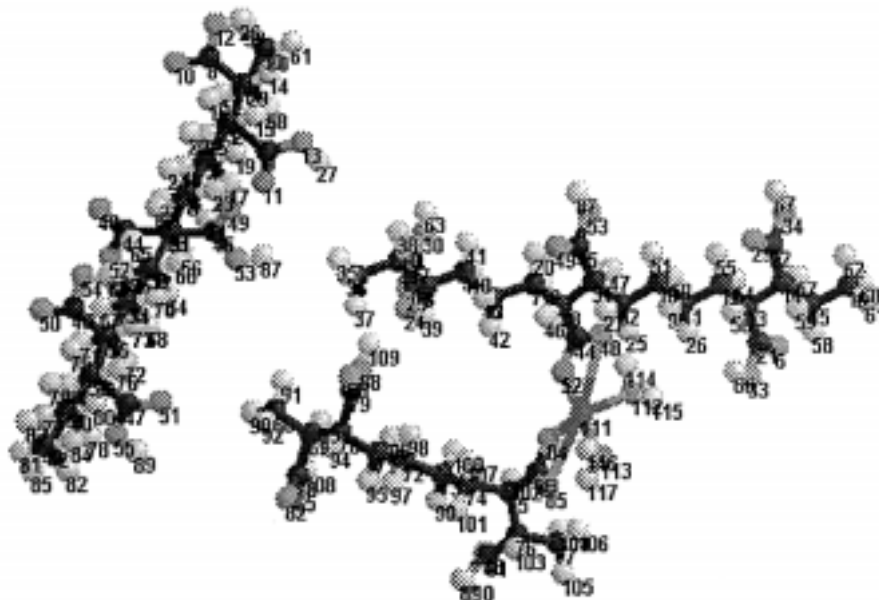

Figure 2. PM3 structures of poly(maleic acid-*co*-olefin) and polychelate of Zn(II).

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