

# Synthesis, Characterization, and Properties of Polychelates of Poly(Styrene Sulfonic Acid-co-Maleic Acid) With Co(II), Cu(II), Ni(II), and Zn(II)

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Received 27 May 2001; accepted 1 December 2001

**ABSTRACT:** Polymer metal complexes of poly(styrene sulfonic acid-co-maleic acid) and Cu(II), Ni(II), Co(II), and Zn(II) were synthesized. The magnetic, spectral, and thermal properties, as well as the electrical conductivities, of the chelates were investigated, and possible structures were assigned to the polychelates. Semiempirical calculations at the AM1 level were carried out on the geometrical arrangement of the polychelates. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2546–2551, 2002

**Key words:** water-soluble polymers; metal ions; polychelates; semiempirical calculations

## INTRODUCTION

The investigation of copolymers of maleic acid in aqueous solutions has been a subject of growing interest.<sup>1–4</sup> One of these copolymers is poly(styrene sulfonic acid) and its copolymers.<sup>5–7</sup> These copolymers contain two different functional groups: –COOH and –SO<sub>3</sub>H. Carboxyl groups, two per each constitutional repeating unit, are bonded on two neighboring carbon atoms of the copolymer backbone, weakly dissociated in aqueous solution, unequal in strength but characterized by strong interactions. Sulfonate groups are located several bonds away from the copolymer backbone, and they are completely dissociated in aqueous solution. As both groups differ in hydration, they are surrounded by a different structure of water molecules.

A substitution of sulfonate group in the p-phenyl position of an alternating maleic acid/styrene (MA/Sty) copolymer does not change the structure and average chain length of the main chain, but the type and character of functionality, producing a marked modification in the physical properties. Dilute aqueous solutions of copolymers show typical polyelectrolyte behavior with some peculiar effects connected with the structural characteristics of alternating MA/St copolymers and the presence of easily dissociated sulfonate groups.<sup>8</sup>

The interactions of poly(maleic acid) and some of their copolymers in solid state with metal ions have been previously reported.<sup>9–11</sup> In these compounds, the metal ions are coordinated with two bidentate carboxylic groups. In contrast, poly(styrene sulfonate) forms a sodium salt with Zn(II).<sup>12</sup> Similar results have been reported by De et al.<sup>13–15</sup>

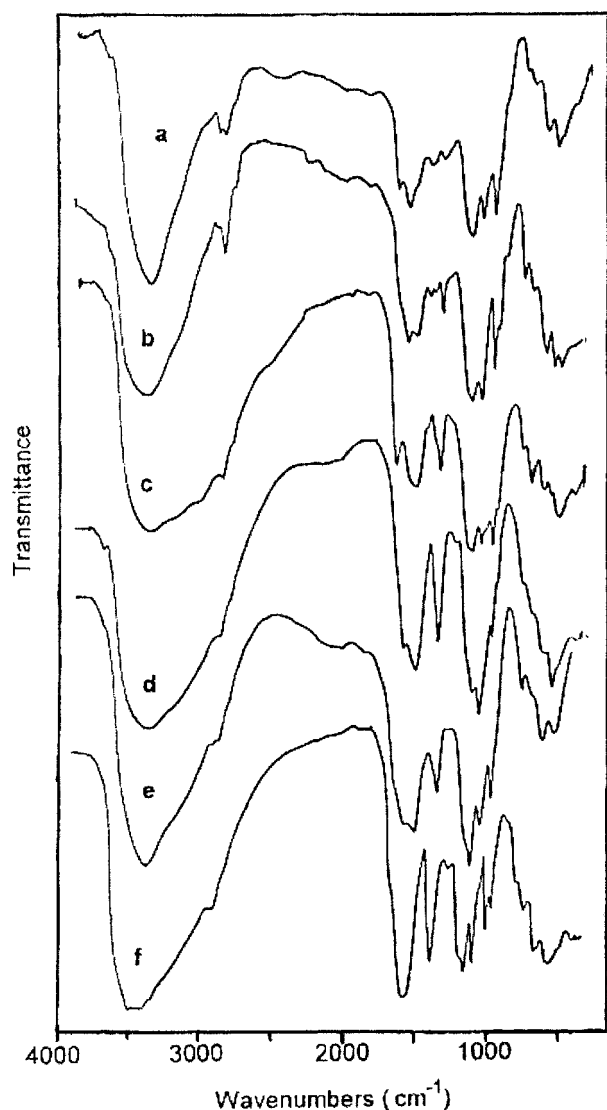
This article deals with the study of metal ion interaction with poly(styrene sulfonic acid-co-maleic acid) in the solid state.

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*Journal of Applied Polymer Science*, Vol. 85, 2546–2551 (2002)  
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**Table I Analytical Data of Polychelates of Poly(styrene Sulfonic Acid-co-Maleic Acid), L, and Its Polychelates With the Metal Ions Cu(II), Ni(II), Co(II), and Zn(II)**

Compound	M : L Ratio	Color
[CuL] · n(H <sub>2</sub> O)	1 : 1	Green
[Ni <sub>3</sub> L <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] · n(H <sub>2</sub> O)	3 : 2	Green
[Co <sub>3</sub> L <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] · n(H <sub>2</sub> O)	3 : 2	Violet
[Zn <sub>3</sub> L <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] · n(H <sub>2</sub> O)	3 : 2	White

**Figure 1** Fourier transform infrared (KBr) spectra of (a) poly(styrene sulfonic acid-co-maleic acid), (b) poly(styrene sulfonic acid-co-maleic acid) sodium salt, and the polychelates of poly(styrene sulfonic acid-co-maleic acid) with (c) Cu(II), (d) Ni(II), (e) Co(II), and (f) Zn(II).**Table II Thermal Stability of Poly(styrene Sulfonic Acid-co-Maleic Acid), L, and Its Polychelates With Cu(II), Ni(II), Co(II), and Zn(II)**

Sample	Temperature (°C) corresponding to weight loss (%)				Char % at 500°C
	10	20	30	40	
Cu(II)-L	200	300	380	450	58
Ni(II)-L	100	300	410	500	60
Co(II)-L	180	400	430	—	64
Zn(II)-L	200	430	450	—	62

## EXPERIMENTAL

### Reagents

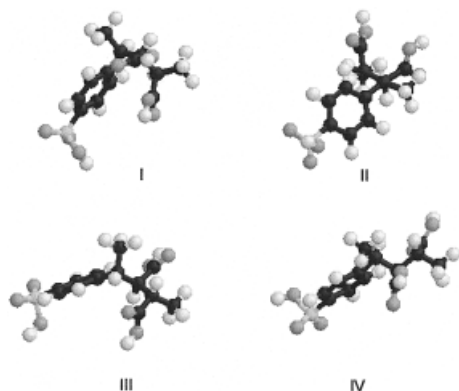
Poly(styrene sulfonic acid-co-maleic acid) sodium salt (1 : 1 styrene/maleic acid mole ratio) was purchased from Aldrich (Milwaukee, WI, USA) (MW = 20,000 g mol<sup>-1</sup>) and treated with 1M HCl. The metal salts were analytical grade (Merck, Darmstadt, Germany) CuCl<sub>2</sub> · 2H<sub>2</sub>O, NiCl<sub>2</sub> · 6H<sub>2</sub>O, CoCl<sub>2</sub> · 6H<sub>2</sub>O, and ZnCl<sub>2</sub>.

### Synthesis of Polychelates

The polychelates were synthesized by adding an aqueous solution of the copolymer to the metal salt, MCl<sub>2</sub> · nH<sub>2</sub>O. The solution was stirred and the pH adjusted with 0.1M HCl or 0.1M NaOH. The polychelates were precipitated by adding an ethanol/acetone mixture, and then the pH was adjusted to 4.5. The compounds are insoluble in water and in organic solvents such as methanol or acetone.

### Measurements

Elemental analyses were obtained using a Series II CHNS 10 analyser 2400 Perkin Elmer. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Magna Nicolet 550 spectrophotometer. The diffuse reflectance spectra were measured on a Perkin Elmer Lambda 20 spectrophotometer coupled to a Labsphere reflectance diffuse attachment and using a Spectralon as reference. The thermogravimetric analysis of the polychelates were carried with a Polymer Laboratories STA 625 analyzer.



**Figure 2** MOPAC calculation for the configurations I, II, III, and IV of poly(styrenesulfonic acid-co-maleic acid).

### Quantum Chemical Calculations

The AM1 method does not allow calculations for Cu(II), Ni(II), and Co(II); their parameters are not available. AM1 semiempirical calculations were carried out using the related Zn(II) complex to study the different configurations of poly(styrene sulfonic acid-co-maleic acid)-Zn(II) with an ALCHEMY 2000 program. The geometries for different configurations of either the polymer or the polymer-Zn(II) complex were optimized without geometric restrictions, using a MOPAC program that is included in ALCHEMY 2000.

## RESULTS AND DISCUSSION

The polychelates from poly(styrene sulfonic acid-co-maleic acid) with several divalent cations were prepared and characterized. The analytical data are summarized in Tables I and II.

The polychelates of Ni(II), Co(II), and Zn(II) react with a M : P = 3 : 2 stoichiometric ratio; however, Cu(II) differs, having a 1 : 1 ratio.

### FTIR Spectroscopy

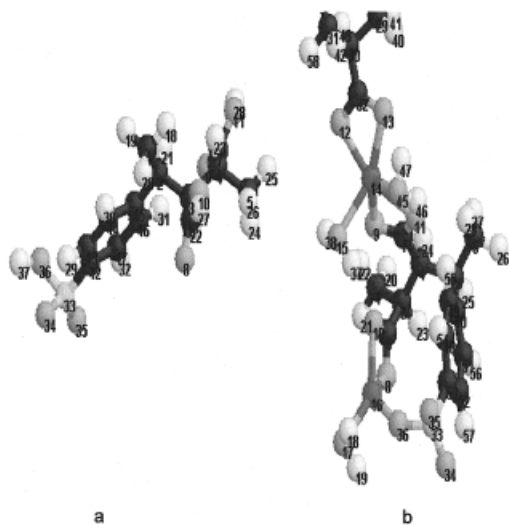
The FTIR spectrum of poly(styrenesulfonic acid-co-maleic acid) shows the characteristic absorption signals (see Fig. 1). Among the most relevant are those placed at (in  $\text{cm}^{-1}$ ) 1716 (C=O), 1404 (C-O), 1194, and 1042, attributed to asymmetric and symmetric absorption bands of  $\text{SO}_2$ , respectively. At 1644, 1489, and 1128  $\text{cm}^{-1}$ , those absorption signals can be attributed to the phenyl group. The FTIR spectrum of the sodium salt do not show the absorption signal at 1716  $\text{cm}^{-1}$ , but the bands at 1576 and 1409  $\text{cm}^{-1}$  corresponding to the carboxylate groups were recorded. It is well known that the bands of sulfonate were not changed after interactions with metal ions.<sup>16</sup>

The FTIR spectrum of the compound of Cu(II) shows an absorption band at 1716  $\text{cm}^{-1}$ , which is characteristic of the free carboxylic group. The absorption bands at 1576 and 1414  $\text{cm}^{-1}$  correspond to carboxylate groups coordinated with the metal ion. The band at 1576  $\text{cm}^{-1}$  is coupled with that at 1640  $\text{cm}^{-1}$  that is attributed to the phenyl group. The asymmetric band of  $\text{SO}_2$  is shifted to values around 20  $\text{cm}^{-1}$  with respect to the sulfonic acid and the sulfonate groups. Accordingly, it is possible to suggest a mechanism that involves both sulfonate and carboxylate groups for coordination of the metal ions.

The spectra of the compounds with Ni(II), Co(II), and Zn(II) show only the absorption corresponding to the carboxylate groups, indicating that all or the majority of those groups are coordinated. The asymmetric band of  $\text{SO}_2$  group is observed close to 1170  $\text{cm}^{-1}$ , indicating that the sulfonate group is also involved in the coordination. By analogy with other reported polychelates,<sup>9-11</sup> as the calculation of  $\Delta = [\nu_a(\text{CO}_2^-) - \nu_s(\text{CO}_2^-)]$  is very difficult to carry out because of the coupling of the phenyl group bands, it is possible to postulate a bidentate coordination of the carboxylate group.

**Table III** Physical Properties of the Configurations I, II, III, and IV

Configuration	Surface (Å <sup>2</sup> )	Volume (Å <sup>3</sup> )	Ovality	Formation Heat (KJ/mol)
I	320.399	260.581	1.624	-298.53
II	317.738	260.428	1.611	-298.27
III	317.802	259.724	1.614	-298.20
IV	317.027	259.414	1.612	-293.74



**Figure 3** AM1 calculated structure of (a) poly(styrene sulfonic acid-co-maleic acid) and (b) Zn(II) complex.

#### Diffuse Reflectance Electronic Spectra

The diffuse reflectance electronic spectra (DRES) of Cu(II) shows a band at 782 nm that may be

attributed to a pseudo-tetrahedral geometry. Those for the Ni(II) and Co(II) compounds present bands attributed to tetrahedral and octahedral geometry. In the tetrahedral geometry region, the Ni(II) compound shows a band at 677 nm with a shoulder at 750 nm, and the Co(II) species exhibit a band at 660 nm. In the octahedral geometry region, the Ni(II) and Co(II) compounds show bands at 426 and 464 nm, respectively.<sup>17,18</sup>

According to these results, it is possible to postulate that there are metal ions that coordinate only with carboxylate groups through an octahedral geometry, completing their coordination sphere with two water molecules, and that there are others that coordinate with one carboxylate and sulfonic group through a tetrahedral geometry, completing their coordination sphere with one water molecule. The presence of metal ions with different geometries in the same compound could explain the violet color of the Co(II) compound.

#### Configurational Analysis

The MOPAC calculation of the configurations I, II, III, and IV (see Fig. 2) are summarized in Table III.

**Table IV** Selected AM1 Structural Parameters of Poly(Styrene Sulfonic Acid-co-Maleic acid), L, and the Polychelate With Zn(II),  $[Zn_3L_2(H_2O)_3]$

Parameter	L	$[Zn_3L_2(H_2O)_3]$	$\Delta$	Atom $N^\circ$	Net Charge	
					L	$[Zn_3L_2(H_2O)_3]$
Bond length (Å°)						
				C (6)	0.3106	0.3637
C(3)–C(6)	1.505	1.482	–0.023	C (7)	0.3079	0.3802
C(4)–C(7)	1.506	1.485	–0.021	O (8)	–0.3427	–0.4365
C(6)–O(8)	1.233	1.299	0.066	O (9)	–0.3671	–0.4869
C(6)–O(10)	1.365	1.300	–0.065	O (10)	–0.3213	–0.4271
C(7)–O(9)	1.235	1.292	0.057	C (11)	–0.3089	–0.4412
C(7)–O(11)	1.361	1.292	–0.069	S (33)	2.8801	2.9343
S(33)–O(34)	1.386	1.388	0.002	O (34)	–0.9704	–0.9795
S(33)–O(35)	1.379	1.391	0.012	O (35)	–0.9261	–0.9797
S(33)–O(36)	1.661	1.562	–0.099	O (36)	–0.7662	–1.0432
Zn(14)–O(9)		2.244				
Zn(14)–O(11)		2.251				
Zn(16)–O(8)		2.212				
Zn(16)–O(10)		2.115				
Zn(16)–O(17)		2.192				
Zn(16)–O(36)		2.064				
Bond angle (°)						
O(8)–C(6)–O(10)	116.4	113.3				
O(9)–C(7)–O(11)	116.8	116.4				

**Table V** Calculations of Some Stretching Vibrations of Poly(Styrene Sulfonic Acid-co-Maleic Acid) and the Polychelate With Zn (II)

Sample, $V_i$ ( $\text{cm}^{-1}$ )	PED (%)	$V_{\text{exp}}$ ( $\text{cm}^{-1}$ )
Poly(styrenesulfonic acid-co-maleic acid):		
2085	97.3(C <sub>6</sub> -O <sub>8</sub> )	1715
1543	78.6 (C <sub>6</sub> -O <sub>10</sub> )	1402
1189	58.4(S <sub>33</sub> -O <sub>34</sub> (19.7) + S <sub>33</sub> -O <sub>35</sub> (18.2))	1193
953	62.2(S <sub>33</sub> -O <sub>34</sub> (15.4) + S <sub>33</sub> -O <sub>35</sub> (10.7))	1042
789	81.4 (S <sub>33</sub> -O <sub>36</sub> )	—
Polychelate of Zn(II):		
1808	84.9 (C <sub>6</sub> -O <sub>10</sub> )	1590
1736	97.7 (C <sub>6</sub> -O <sub>8</sub> )	1412
1138	77.2(S <sub>33</sub> -O <sub>34</sub> (30.9) + S <sub>33</sub> -O <sub>35</sub> (30.7))	1176
967	67.1(S <sub>33</sub> -O <sub>35</sub> (10.3) + S <sub>33</sub> -O <sub>35</sub> (10.7))	1038
778	86.2(S <sub>33</sub> -O <sub>36</sub> )	—

**Calculated Structures to the Poly(Styrene Sulfonic Acid-co-Maleic Acid), L, and Its Polychelate with Zn(II)**

The AM1 calculations for poly(styrenesulfonic acid-co-maleic acid) and the polychelate only with Zn(II) were performed because the parameters for Ni(II), Co(II), and Cu(II) were not available. The structure of poly(styrenesulfonic acid-co-maleic acid) and the polychelate with Zn(II) are shown in Figure 3, and the calculations are summarized in Table IV.

In the structure calculated for the polychelate of Zn(II), the Zn(II) ions coordinate with two carboxylate groups with a distorted octahedral geometry. However, Zn(II) ions that coordinate with one carboxylate and another sulfonate group show a tetrahedral geometry. In both cases the carboxylate groups present a symmetric coordination, and the Zn-O bond lengths are in the reported range for similar compounds.<sup>19</sup>

Semiempirical calculations of the vibration frequencies of poly(styrenesulfonic acid-co-maleic acid) and the Zn(II) polychelate were also carried out. The differences observed between those experimental and calculated values probably may be attributed to the fact that quantic semiempirical methods overestimate the calculation of these frequencies.<sup>20</sup>

Some of these vibration frequencies are included in Table V. Nevertheless, it is possible to correlate these values with the assignment of the infrared absorption bands. In the spectrum calculated for the polychelate, a shift of the asymmetric stretching band of SO<sub>2</sub> (1189  $\text{cm}^{-1}$ ) to the sulfonic acid moiety (1138  $\text{cm}^{-1}$ ) was also observed.

**CONCLUSIONS**

The copolymer poly(styrenesulfonic acid-co-maleic acid) containing carboxylic acid and sulfonic acid groups was found to coordinate with several metal ions, and the polychelates with Cu(II), Co(II), Ni(II), and Zn(II) were prepared. According to the FTIR spectroscopic analysis with a shift of the band of the SO<sub>2</sub> groups at 1194  $\text{cm}^{-1}$ , an active role of the sulfonate group in the polymer-metal ion coordination is postulated. In the polychelate-Cu, the Cu(II) ions are coordinated exclusively through only one carboxylate group and the sulfonate group. However, the polychelate with Ni(II), Co(II), and Zn(II) showed a different coordination behavior.

We thank FONDECYT (Grant 8990011) and Dirección de Investigación, Universidad de Concepción (Grant 99.021.10-1.0).

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