

Poly(styrene-*alt*-maleic acid)–Metal Complexes with Divalent Metal Ions. Synthesis, Characterization, and Physical Properties

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ABSTRACT: Polymer–metal complexes of the alternating copolymer styrene and maleic acid with Cu(II), Co(II), Ni(II), and Zn(II) were synthesized and characterized by elemental analysis, infrared and electronic spectra, and thermogravimetry. In addition, magnetic measurements were performed and the electrical conductivity was studied at different temperatures. Semiempirical calculations at the PM 3 level were carried out to elucidate the geometrical arrangement of the polychelates. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1310–1315, 2001

Key words: metal ions; poly(styrene); polychelates; semiempirical calculations

INTRODUCTION

Homo- and copolymers of maleic acid and their modified products are used as auxiliary agents (scale inhibitors, dispersing agents, adhesives, etc).¹ Copolymers of maleic acid with hydrophobic monomers have been found to undergo a conformational transition from the compact to extended form upon the ionization of the primary carboxyl groups, and the two-state character of the transition has been assumed.^{2,3}

Ohno and Sugai^{4,5} have found the compact to coil transition in an alternating copolymer of maleic acid and styrene, in aqueous solution. The optical data and other physicochemical results

showed that in the compact form the phenyl groups are buried in the interior of the molecule, and hydrophobic interaction between the phenyl groups play an important role in stabilizing the compact form.

The behavior of aqueous solutions of alternating copolymers of maleic acid and styrene [100 NaMA/St; 50 NaMA/St, (mass %)] in the presence of salts of divalent metals (MgCl₂, CaCl₂, and BaCl₂), is generally similar to the behavior of solutions of other synthetic polyelectrolytes. The tendency of divalent cations to precipitate the copolymer follows the order Ba²⁺ > Ca²⁺ > Mg²⁺. The binding of divalent cations to polyanions causes their contraction, dehydration, decrease in solubility, and precipitation. The stability of solutions depends on the neutralization degree, concentration of copolymer, ionic strength, and on temperature.⁶

The aim of this article is to report the synthesis and characterization of the polychelates of poly(styrene-*alt*-maleic acid) with divalent ions as

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Table I Analytical Data of Polychelates of Poly(styrene-*alt*-maleic acid), L, with Cu(II), Co(II), Ni(II), and Zn(II)

Compound	Relationship M : L	Color
(CuL ₂ (H ₂ O) ₂ · nH ₂ O	1:2	blue
(NiL ₂ (H ₂ O) ₂ · nH ₂ O	1:2	green
(CoL ₂ (H ₂ O) ₂ · nH ₂ O	1:2	pink
(ZnL ₂ (H ₂ O) ₂ · nH ₂ O	1:2	white

well as to investigate their magnetic and electrical properties.

EXPERIMENTAL

Reagents

Metal chlorides (Merck p.a.) and solvents (Merck) were used as received. Poly(styrene-*alt*-maleic acid) (Aldrich, MW = 120,000 g mol⁻¹) was used without further purification.

Polychelates

The four polychelates were synthesized by reacting the polymer (L) with MCl₂ · nH₂O, M, (L : M mol ratio: 2 : 1) under stirring. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH. Polychelate with Cu(II) precipitates in water at pH = 4, and the complexes with Ni(II), Co(II), and Zn(II) could be precipitated in ethanol/acetonitrile. The polychelates were then filtered and dried under vacuum up to constant weight. All the compounds are insoluble in water and organic solvents as methanol, ethanol, acetone, and ether.

Measurements

Elemental analyses were performed using a Perkin-Elmer Series II CHNS 10 Analyser 2400. The

FTIR spectra of the samples were recorded on a Magna Nicolet 550 spectrophotometer. The magnetic moments were measured by the Gouy method and corrected for diamagnetism of the components using Pascal 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 was measured in the form of pellets (1.3 cm diameter, 0.07 cm thickness) using an analog multimeter (Digital Kayton KT-2210). The thermogravimetric analysis of the polychelates was carried out with a Polymer Laboratories STA 625 Analyzer.

Program for Modeling

PM3 semiempirical calculations were carried out using a MOPAC program that is included in AL-CHEMY 2000. The geometries were optimized without geometric restrictions.

RESULTS AND DISCUSSION

The polychelates from poly(styrene-*alt*-maleic acid), L, and Cu(II), Co(II), Ni(II), and Zn(II) are colored solids, which were insoluble in water. The elemental analyses showed that the metal-ligand ratio varied according to the metal.

The analytical data of the polychelates are summarized in Table I.

FTIR Spectra

FTIR spectrum of poly(styrene-*alt*-maleic acid) shows the characteristic absorption bands of the carbonylic groups at 1714 cm⁻¹ (C=O) and at 1409 cm⁻¹ (C—O). Two additional bands at 1642

Table II Thermal Stability of Poly(styrene-*alt*-maleic acid), L, and Its Polychelates with Cu(II), Ni(II), Co(II), and Zn(II)

Compound	Weight Loss (%) at Different Temperatures (°C)				
	100	200	300	400	500
L	6.5	11.9	17.5	38.9	58.0
(CuL ₂ (H ₂ O) ₂ · nH ₂ O	8.3	16.7	28.7	56.3	66.5
(NiL ₂ (H ₂ O) ₂ · nH ₂ O	8.8	20.9	26.9	66.1	75.3
(CoL ₂ (H ₂ O) ₂ · nH ₂ O	1.5	9.6	13.0	30.6	68.9
(ZnL ₂ (H ₂ O) ₂ · nH ₂ O	5.2	13.4	15.9	36.9	61.6

Table III Magnetic Measurements and Electronic Spectra of Polychelates of Poly(styrene-*alt*-maleic acid), L

Compound	λ máx (cm^{-1})	Assignment	Field Ligand Parameters (cm^{-1})	μ_{ef} (BM)
[CuL ₂ (H ₂ O) ₂]	1256	${}^2T_{2g} \leftarrow {}^2E_g$	10Dq = 12,560	1.81
[NiL ₂ (H ₂ O) ₂]	8928 (calc)	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	10Dq = 8928	2.76
	13,333	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	B = 911	
	14,577	${}^1E_g \leftarrow {}^3A_{2g}(F)$	$\beta = 0876$	
	25,300	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$		
[CoL ₂ (H ₂ O) ₂]	8836 (calc)	${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$	10Dq = 10,344	4.13
	19,180	${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$	B = 1027	
	21,200	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	$\beta = 0.92$	

cm^{-1} and 1448 cm^{-1} , assigned to aromatic group, are also present.

The FTIR spectra of the polychelates show the characteristic bands corresponding to the carboxylic groups without coordination, due to excess functional groups, and at 1560 cm^{-1} attributed to asymmetric vibration stretching of the carboxylate group coordinated with the metal ion. This band is coupled with that of the aromatic ring. The vibration frequency of the symmetric vibra-

tion frequency is difficult to assign with certainty, as the spectra show several bands in a very close region with coupling of signals. However, it is possible to suggest that the carboxylate group is coordinating as a bidentate ligand, which is in accord with data of poly(maleic acid) in literature.⁷

Thermal Properties

The polymer show a high thermal stability with a weight loss lower than 20% at 300°C . The polychelates showed a similar thermal behavior up to

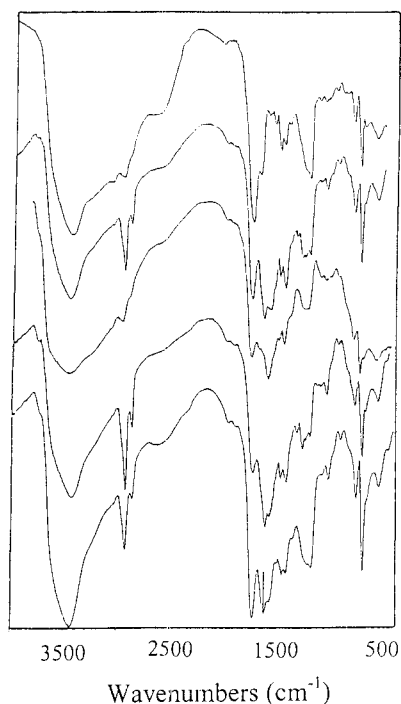


Figure 1 FTIR spectra (KBr) of poly(styrene-*alt*-maleic acid) (a), and its polychelates with Cu(II) (b), Ni(II) (c), Co(II) (d), and Zn(II) (e).

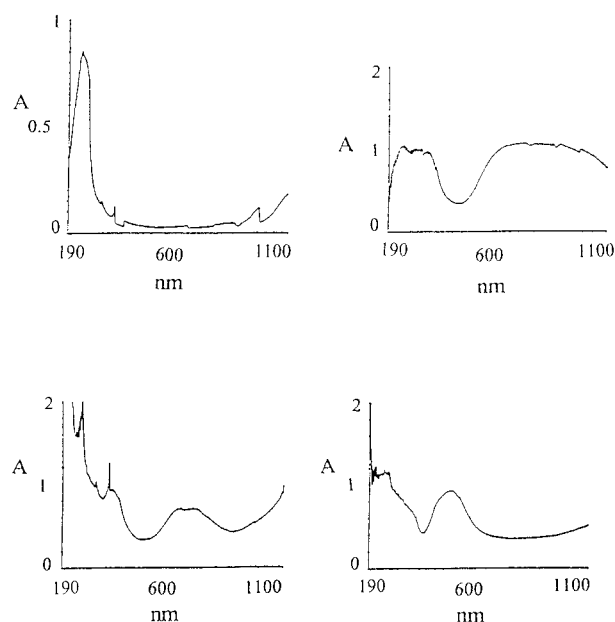


Figure 2 Electronic spectra of poly(styrene-*alt*-maleic acid) (a), and its polychelates with Cu(II) (b), Ni(II) (c), and Co(II) (d).

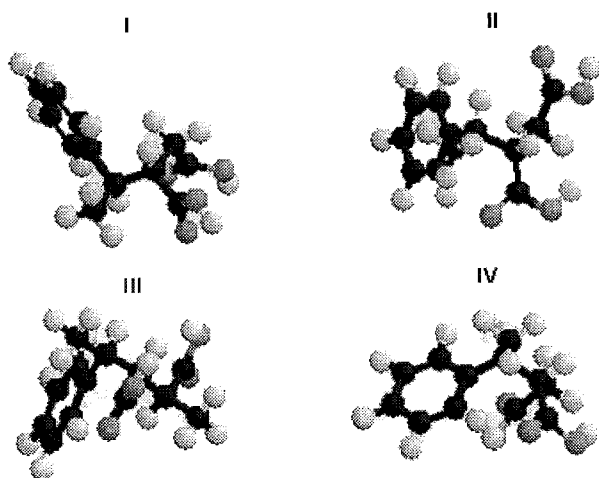


Figure 3 Configurations of poly(styrene-*alt*-maleic acid).

300°C. At higher temperatures, however, the polychelates of Cu(II) and Co(II) lost more weight, particularly at 400°C, when compared to the polychelate. This is attributed to the higher incorporation of the metal ion.

Magnetic Measurements and Diffuse Reflectance Spectra

Table III shows the magnetic susceptibility, electronic transitions, and ligand field parameters of the paramagnetic polychelates. According to the electronic spectra, it is possible to postulate a distorted octahedral geometry with the water molecules for completion of the coordination sphere. The electronic transition ν_1 was not observed for the polychelates with Ni(II) and Co(II) and, therefore, calculation was necessary.⁸

The ligand field parameters were calculated from the Orgel Diagram⁹ considering the configuration interaction. β was calculated for the polychelates with Ni(II) and Co(II) by using the B values for the free ion at 1041 cm⁻¹ and 971 cm⁻¹,

respectively.¹⁰ The β value indicates that the compounds with Ni(II) and Co(II) have a high ionic character.

The magnetic moment of the polychelate with Cu(II), 1.81 M.B., is in agreement with those data reported in the literature at room temperature.¹¹ The polychelates of Ni(II) and Co(II) show a magnetic moment of 2.76 M.B. and 4.13 B.M., respectively, which are attributed to a distorted octahedral geometry. The polychelate with Ni(II) is very near to the value of spin-only value, and it is lower than expected, which can be attributed to the electronic delocalization t_{2g} .

Configurational Analysis

To determine the most stable configuration an analysis of the four configurations (I to IV) was carried out. The PM3 calculations to the four configurations are shown in Figure 3, and the respective calculations are summarized in Table IV.

From the formation heat values it is possible to postulate that the configuration I is the most stable. It also shows a higher surface, volume, and ovality.

PM3 Calculations

The structures of poly(styrene-*alt*-maleic acid) and the poly(styrene-*alt*-maleic acid)-Zn(II) were calculated using PM3 calculations. They are shown in Figure 4, and the results of the calculations are compiled in Table V. The parameters for the polychelates with Cu(II), Ni(II), and Co(II) were not available.

The distribution charge of the copolymer present a higher delocalization than that in poly(maleic acid),⁷ which can be attributed to the influence of the aromatic ring.

Additionally, the semiempirical calculations of the vibration frequencies of poly(maleic acid) and its Zn(II) complex were carried out.

Table IV Physical Properties of the Different Configurations of the Poly(styrene-*alt*-maleic acid)

Configuration	Surface (Å ²)	Volume (Å ³)	Ovality	Heat Formation (KJ/mol)
I	257.21	203.929	1.535	-712.38
II	249.63	202.198	1.498	-692.76
III	247.62	202.478	1.485	-682.22
IV	243.48	202.496	1.460	-667.82

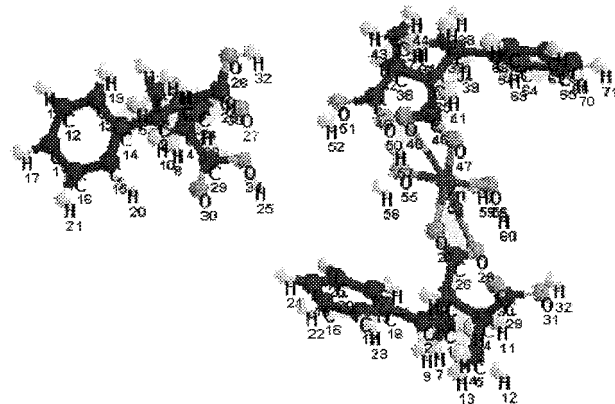


Figure 4 PM3 calculations of the polychelate with Zn(II).

The polychelate of Zn(II) showed a distorted octahedral geometry where the carboxylate group exhibited an asymmetric chelation with a longest Zn—O bond. The bond lengths of the Zn—O bond with the oxygen atoms from the carboxylate group are 1.978 and 2.861 Å. The last value is very high for a Zn—O bond but is lower than that of the sum of the van der Waals radii.¹²

The differences between the observed and calculated values are attributed to the well-known fact that the quantum and semiempirical methods overestimate the calculation of these frequencies. Some of them are included in Table III. Nev-

Table VI Calculation of Some Stretching Vibrations of Poly(styrene-*alt*-maleic acid) (L) and Its Complex with Zn(II) (L-Zn)

	ν_1 (cm^{-1})	PED (%)	ν_{exp} (cm^{-1})
Poly(styrene- <i>alt</i> -maleic acid)	3851	100.0 (O ₂₈ —H ₃₃)	3434
	1977	97.3 (C ₂₆ —O ₂₇)	1714
	1442	82.1 (C ₂₆ —O ₂₈)	1409
Polychelate of Zn(II)	3852	99.0 (O ₃₁ —H ₃₂)	3446
	1978	92.0 (C ₂₉ —O ₃₀)	1746
	1820	89.0 (C ₂₆ —O ₂₈)	1542
	1540	82.7 (C ₂₆ —O ₂₇)	—
	1447	49.7 (C ₂₉ —O ₃₁)	14

ertheless, these differences, the calculated vibration frequencies, and their assignment are correlated with the experimental FTIR spectra data.

Electrical Conductivity

The polymers showed a low electrical conductivity at room temperature with values of about 10^{-9} S cm^{-1} for the polyligand and its Zn(II) complex, and about 10^{-10} S cm^{-1} for the polymeric Cu(II), Ni(II), and Co(II) complexes. The temperature-

Table V Selected PM3 Structural Parameters of Poly(styrene-*alt*-maleic acid) (L) and Its Complex with Zn(II)

Parameter	L	[ZnL ₂ (H ₂ O) ₂]	Δ	Atom No.	Net charge	
					L	[ZnL ₂ (H ₂ O) ₂]
Bond length (Å°)						
C(3)—C(26)	1.521	1.536	0.015	C(3)	-0.0654	-0.0696
C(3)—C(4)	1.544	1.542	-0.002	C(4)	-0.0715	-0.0751
C(4)—C(29)	1.520	1.519	-0.001	C(26)	0.3800	0.4553
C(26)—O(27)	1.217	1.304	0.087	O(27)	-0.3850	-0.4064
C(26)—O(28)	1.355	1.245	-0.110	O(28)	-0.3070	-0.5377
C(29)—O(30)	1.218	1.217	-0.001	C(29)	0.3824	0.3769
C(29)—O(31)	1.352	1.354	0.002	O(30)	-0.3964	-0.3837
Zn(53)—O(27)		1.978		O(31)	-0.2960	-0.3024
Zn(53)—O(28)		2.861				
Zn(53)—O(56)		2.205				
Zn(53)—O(55)		2.232				
Bond angle (°)						
C(3)—C(26)—O(27)	130.07	118.07				
C(3)—C(26)—O(28)	114.57	125.11				

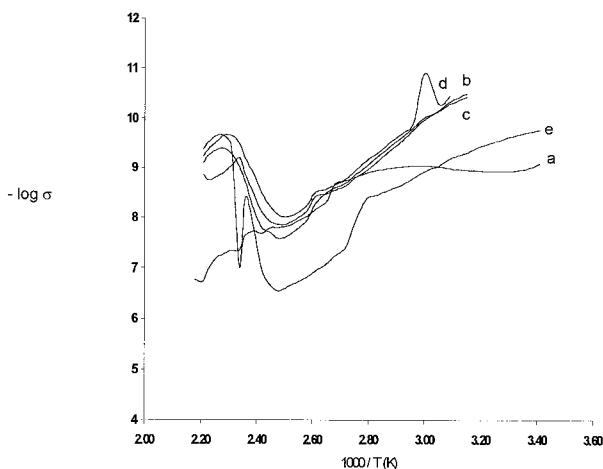


Figure 5 Electrical conductivity of poly(styrene-*alt*-maleic acid) (a), and its complexes with Cu(II) (b), Ni(II) (c), Co(II) (d), and Zn(II) (e).

dependent curve of polychelate shows a break point at $\sim 130^\circ\text{C}$ due to dehydration. The highest value (appr. $10^{-7} \text{ S cm}^{-1}$) was observed at 130°C for the polychelate of Zn(II) (see Fig. 5).

CONCLUSIONS

From the characterization results obtained it is postulated that poly(styrene-*alt*-maleic acid) is able to coordinate with two carboxylic groups pertaining to different polymer chains, indicating intermolecular complexation. A fraction of 50% remained unchanged and without coordination. The charge distribution of the copolymer showed a higher delocalization than that of poly(maleic

acid), which is attributed to the influence of the aromatic ring. The Zn(II) complex of the copolymer was characterized by different bond lengths of the Zn—O bond; however, the longest was shorter than that the sum of the van der Waals radii. The electrical conductivity of these polychelates studied is based on ionic conductivity.

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