Cu(II), Zn(II) and Mn(II) complexes of poly(methyl vinyl ether-*alt*-maleic anhydride). Synthesis, characterization and thermodynamic parameters

HIDAYET MAZI* and ALI GULPINAR

Department of Chemistry, Faculty of Science and Arts, University of Gaziantep, Gaziantep, Turkey
e-mail: mazi@gantep.edu.tr

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Abstract. The complexes of poly(methyl vinyl ether-*alt*-maleic anhydride) (poly(MVE-*alt*-MA)) with Zn(II), Mn(II) and Cu(II) ions were synthesized from the reaction of the aqueous solution of copolymer and metal(II) chlorides at different temperatures ranging from 25° to 40°C. Elemental analysis of the metal–polymer complexes suggests that the metal to ligand ratio is 1:1. The formation constants of each complex were determined by the mol-ratio method. UV–Vis studies showed that the complex formation tendency increased in the following order: Zn(II) > Cu(II) > Mn(II). This order was confirmed by the Irving–William series and Pearson’s classification. The IR spectral data indicated the metal ions to be coordinated through the hydroxyl groups of the hydrolysed maleic anhydride. The intrinsic viscosity and thermal properties of the copolymer and metal–polymer complexes and their thermal stability are discussed.

Keywords. Complex/maleic anhydride; polymer; UV-visible; viscosity.

1. Introduction

Polymer–metal complexes have been of interest to many researchers during the last three decades in the light of their potential applications¹ in varied fields such as organic synthesis,² waste water treatment,³ hydrometallurgy,⁴ polymer drug grafts and nuclear chemistry.⁵ They have also been used as models for enzymes.^{6,7} When metal ions form complexes with functional polymers, the activity of the metal polychelates changes due to the polymeric effect.^{8–12} Jiang and Zhu reported that poly(ester-anhydrides) exhibit better degradation ability as anti-infective polymeric prodrugs or matrices for drug delivery.¹³

Copolymers have available carboxylic acid functional groups, which can be used in further incorporation of drugs or other bioactive agents.^{14,15} Covalent linkages between polymer chains can be accomplished by the reaction of the functional groups with complementary reactive groups, such as amines, carboxylic acids or isocyanates.^{16–19} Poly(methyl vinyl ether-*alt*-maleic anhydride) P(MVE-*alt*-MA), its derivatives and complexes have many important applications such as in the capture of influenza A and B viruses,²⁰ nasal-sustained systems,²¹ capture of respiratory syncytial viruses,²² immune system activators,²³ isolation of nucleic acids²⁴ and generic capture of viruses.²⁵

Complexation of metal ions in solution is a significant process in several areas, for example, design of ligands as therapeutic reagents for the treatment of metal intoxication,^{26,27} design of antibiotics that owe their antibiotic action to specific metal complexation,²⁸ design of complexes to act as imaging agents,²⁹ design of functional groups for chelating ion-exchange materials,³⁰ and catalysts.³¹ The scope of applications of metal complexation of polymers has a tendency to increase considerably in the near future.

The present paper reports the synthesis and characterization of metal complexes between poly(MVE-*alt*-MA) and divalent metal ions (Cu(II), Zn(II) and Mn(II)). Compositions of metal complexes were studied by UV–Vis spectroscopy and the stability constants of the complexes were calculated according to the mol-ratio method. The interaction of transition metal ions with poly(MVE-*alt*-MA) in aqueous solutions was also studied by viscosimetric measurements, and the effects of the type and the concentration of the cation on the interaction mechanisms were investigated.

2. Experimental

2.1 Materials

Maleic anhydride (MA) (Aldrich) monomer was purified before use by recrystallization from anhydrous benzene and sublimation under vacuum at 40°C. Methyl

*For correspondence

vinyl ether (MVE) (Fluka) co-monomer was distilled under moderate vacuum before use. Benzoyl peroxide (BPO) (Fluka) was recrystallized twice from chloroform solution by methanol. Copper(II)chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, manganese(II)chloride MnCl_2 and zinc(II)acetate $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ were purchased from Sigma and used without purification.

2.2 Methods

2.2a Copolymerization: Free radical copolymerization of MA and MVE were carried out in 1,4-dioxane with BPO as the initiator under nitrogen atmosphere. The reaction conditions are given in total monomer concentration $[\text{M}]_{\text{total}} = 3.0 \text{ mol.L}^{-1}$, $[\text{BPO}] = 5.58 \times 10^{-3} \text{ mol.L}^{-1}$ at 70°C . Copolymers were isolated by precipitation in methanol, then washed with benzene and dried under vacuum at 40°C up to a constant weight. The synthesized copolymer has the following characteristics: acid number (AN) = 729 mg KOH/g (by known nonaqueous titration method), for the copolymer synthesized using 1:1 monomer feed, monomer unit compositions determined by both methods are almost similar: $m_1 : m_2 = 47.95 : 52.05$ (by chemical analysis) and $m_1 : m_2 = 48.78 : 51.22$ (by ^1H NMR analysis), respectively.³¹ Weight average molecular weight (M_w) of the copolymer have been found to be 155.000 g/mol by light scattering method.

2.2b Preparation of polymer-metal complexes: Polymer-metal complexes were prepared according to the following procedure: Different amounts of the polymer (table 1) were added into 1.25 mM aqueous solutions (20 mL) of the salts (copper(II)chloride dihydrate, manganese(II)chloride or zinc(II)acetate dihydrate).

The solution was stirred for 24 h at different temperatures (25° and 40°C). Absorbance values of the solutions were measured and followed by precipitation of the polymer-metal complexes in diethyl ether. The precipitated complexes were washed with acetone and dried in vacuum at 40°C .

Table 1. Amounts of the polymer used in complexation.

Solution No.	[Metal] (mM)	Polymer (mg)	Concentration of repeating unit (mM)
1	1,25	1,872	0,600
2	1,25	2,810	0,900
3	1,25	3,750	1,200
4	1,25	7,450	2,400
5	1,25	9,360	3,000
6	1,25	11,700	3,750

2.2c Characterization techniques: Spectrophotometric measurements were performed on a PG Instruments T80+ UV-vis spectrophotometer. Infrared spectra were determined on a Perkin-Elmer Spectrum One ATR model FT-IR spectrometer. Thermal data were obtained using a DTA-60H Thermal Analyser in N_2 atmosphere. Elemental analyses was carried out using a Thermo Scientific Flash 2000 model auto microanalyser. Viscosimetric measurements of the copolymer and the complexes were carried out in water at 25°C by using an Ubbelohde-type capillary viscometer. Temperature of the thermostat was controlled within a range of $\pm 0.1^\circ\text{C}$ and the flow times were measured with a digital accuracy of $\pm 0.01 \text{ s}$. Concentration of poly(MVE-alt-MA) in solutions was varied between 1.872 and 11.700 mg/dL.

3. Results and discussion

3.1 FT-IR spectra

Figure 1 presents the FT-IR spectra of the poly(MVE-alt-MA) and its polychelates. An attempt to understand the mode of coordination of the metal ion with the ligand system from these spectra has been made. The shift and presence or absence of certain bands in the polychelate spectrums should in turn gives us an idea about the nature of coordination.

Absorption bands (figure 1a) between 2950 and 3100 cm^{-1} are assigned to symmetrical and asymmetrical C-H stretching vibration of CH (MA unit), CH_2 and CH_3 (MVE unit); absorption bands at 1858 and 1777 cm^{-1} have been assigned to the symmetrical and asymmetrical C=O stretching vibration of MA unit, respectively.³² Absorption bands at 1221 and 1092 cm^{-1} are related to C-O-C stretching vibration of MVE and MA units respectively.^{33,34} Comparative analysis of FTIR spectra of the poly(MVE-alt-MA) (figure 1a) and its polychelates (figure 1b,c,d) reveal the intensity of the distinguishing symmetric and antisymmetric stretching bands for the C=O group and C-O-C bond of the MA unit at 1858 , 1777 and 1092 cm^{-1} to decrease. Other bands seen at 1729 and 1650 cm^{-1} , are characteristic for the C=O group of COOH and metal-O-C groups (b,c), respectively in relation with the bands seen at 3420 (O-H stretching of COOH), 1390 (O-H bending), 1510 (Zn-O-C).³⁵ Appearance of an O-H stretching (3420), O-H bending (1390) and C=O (1729) bands of COOH group in poly(MVE-alt-MA)/Mn(II) and poly(MVE-alt-MA)/Cu(II) spectra and disappearance of these bands with appearance of new

Figure 1. FT-IR spectra of (a) poly(MVE-alt-MA), (b) poly(MVE-alt-MA)/Mn(II), (c) poly(MVE-alt-MA)/Cu(II) and (d) poly(MVE-alt-MA)/Zn(II).

C=O (1510) band in poly(MVE-alt-MA)/Zn(II) spectrum confirmed the proposed mechanism (figure 2) for the complexation.³⁶

In complexation of Cu(II) and Mn(II), only one of the carboxylate groups coordinates whereas for Zn(II), MA acts as a bidentate ligand.

Figure 2. Proposed mechanism for the complexation of poly(MVE-alt-MA) with Zn(II), Cu(II) and Mn(II) ions.

3.2 Effect of metal ions on the absorption spectrum of poly(MVE-alt-MA)

Complex formation is a reaction between a donating group such as -COOH of polymeric ligand and a metal ion. Absorption spectra of poly(MVE-alt-MA), its chelates and metal ions are shown in figure 3 and the λ_{max} values are given in table 2.

The λ_{max} values of Cu(II), poly(MVE-alt-MA) and poly(MVE-alt-MA)/Cu(II) complex were obtained at 196, 216 and 200 nm, respectively. The λ_{max} value of poly(MVE-alt-MA) represents the $n \rightarrow \pi^*$ transition of the -C=O groups on the copolymer. According to figure 3(a), the addition of Cu(II) ions to the poly(MVE-alt-MA) solution, resulted in the λ_{max} value of poly(MVE-alt-MA) (216 nm) shifting to a shorter wavelength (200 nm) due to the decrease in the electron density of the -COOH group. Figure 3(b), (c) and (d) represents the absorption spectra of Mn(II) and Zn(II) ions, polymer complexes of these ions and the comparative spectrum of the complexes with the copolymer, respectively. The λ_{max} value of poly(MVE-alt-MA) also shifted to shorter wavelengths in the presence of Mn(II) (202 nm) and Zn(II) (196 nm) ions proving the complexation reaction between poly(MVE-alt-MA) and these metal ions. From figure 3(d), it is possible to establish the following order for the metal ions in terms of increasing complex stability with poly(MVE-alt-MA): Zn(II) > Cu(II) > Mn(II), also confirmed by the order of chelating stability of metal ions.³⁷

3.3 Equilibrium constants

The mol ratio method³⁸ is the most common technique used in complex-ion studies. To obtain the equilibrium constants, a series of solutions were prepared in which the analytical concentration of metal ions were held constant, and that of others varied. Plots of absorbance versus mol ratio of the reactants (ratio of the molar concentration of repeating unit in polymer to molar concentration of the metal ion used) were then prepared and two lines with different slopes were obtained (figure 4).

The two lines intercepted at a mol-ratio that corresponded to the combining ratio in the complex. Coordination numbers of poly(MVE-alt-MA)-Mn, poly(MVE-alt-MA)-Cu and poly(MVE-alt-MA)-Zn complexes appeared as 1 from figure 4, that is, one metal ion is coordinated by one repeating unit in the copolymer. It can be concluded that the complexation reaction is the result of covalent bonding and Zn is coordinated by two chelating groups (carboxyl), whereas Cu and Mn are coordinated by one chelating group.

Figure 3. Absorption spectra of (a) poly(MVE-*alt*-MA), Cu(II) and poly(MVE-*alt*-MA)/Cu(II); (b) poly(MVE-*alt*-MA), Mn(II) and poly(MVE-*alt*-MA)/Mn(II); (c) poly(MVE-*alt*-MA), Zn(II) and poly(MVE-*alt*-MA)/Zn(II); (d) poly(MVE-*alt*-MA), poly(MVE-*alt*-MA)/Cu(II), poly(MVE-*alt*-MA)/Mn(II) and poly(MVE-*alt*-MA)/Zn(II) complexes at 40°C in which the concentration of all metal ions and the polymer repeating unit is 1.25 mM.

The carboxyl group acts as a mono and bidentate ligand, depending on the pH value.³⁹ The complex formation reaction can be expressed as:

where M represents the metal, PL is the chelating unit of the polymer ligand and n is the coordination number

Table 2. $\lambda_{\max}$ values of poly(MVE-*alt*-MA), metal ions (Me^{+2}) and poly(MVE-*alt*-MA)/ Me^{+2} complexes.

Sample	$\lambda_{\max}$ (nm)
Cu(II)	232
Mn(II)	196
Zn(II)	192
poly(MVE- <i>alt</i> -MA)	216
poly(MVE- <i>alt</i> -MA)/Mn(II)	202
poly(MVE- <i>alt</i> -MA)/Cu(II)	200
poly(MVE- <i>alt</i> -MA)/Zn(II)	196

of the metallic ion. The formation constant K_f can be expressed by the following equation.^{40,41}

$$K_f = (1 - \alpha)/\alpha(\alpha n C)^n, \quad (1)$$

where C is the concentration of the complex and α is the dissociation constant, which is calculated by the ratio of the absorbance for a defined coordination number to the theoretical absorbance value for maximum coordination. Complex formation constants from Eq. (1) for the three metal ions are given in table 3.

K_f values of poly(MVE-*alt*-MA)/Zn(II), poly(MVE-*alt*-MA)/Cu(II) and poly(MVE-*alt*-MA)/Mn(II) complexes were obtained as 3.48×10^8 , 3.04×10^8 and 6.1×10^7 at 25°C and 1.1×10^8 , 10.8×10^8 and 15.5×10^8 at 40°C, respectively. The increasing order of the stability constants can be given in the order Zn(II) > Cu(II) > Mn(II). This was confirmed by the order of metal ion efficiency on the absorption spectrum of poly(MVE-*alt*-MA), which can be explained by Pearson's classification.^{42,43}

Figure 4. Absorption curves of poly(MVE-alt-MA)-Mn(II), poly(MVE-alt-MA)-Cu(II) and poly(MVE-alt-MA)-Zn(II) complexes (a) at 25°C and (b) at 40°C for the determination of equilibrium constants according to the 'mol-ratio' method.

3.4 Polyelectrolyte behaviour of poly(MVE-alt-MA) and effect of metal ions on the reduced viscosity of poly(MVE-alt-MA)

The isoionic dilution for polymer solutions in different salt solutions is given in figure 5. Water-soluble poly(MVE-alt-MA) shows typical polyelectrolyte behaviour, that is, a decrease in the reduced viscosity with an increase in polyelectrolyte concentration.^{44,45} This behaviour can be explained with the formation of an ionic atmosphere greater than the diameter of the polymer coil, with decreasing polyelec-

trolyte concentration and increasing ionization degree. Repulsion among the ions raises the rigidity of the chain, expanding the polymeric coil, with a consequent increase of viscosity.⁴⁶

Viscosity, is a significant term which gives information about interaction in aqueous solutions.⁴³ Behaviour of the polymer and its complexes has been studied in understanding the interaction of the polymer with the metal ions. Figure 6 shows the alteration of the reduced viscosity with poly(MVE-alt-MA) concentration. At constant concentration, addition of metal ions to the solution results in a decrease in the reduced viscosity of the polymer due to contraction of the polymer coil with intrapolymer complex formation.⁴⁶

Reduced viscosity of the polymer and its complexes showed a decrease below the concentration of 0.015 g/dL. The complexes showed a higher degree of decrease in comparison to the polymer, indicating the complex formation to be preferentially intrachain. As seen in figure 5, Zn(II) showed the strongest relative decrease in reduced viscosity of poly(MVE-alt-MA). In other words, Zn(II) ion was the most effective ion in complex formation compared to all metals studied. Figure 6 showed that the reduced viscosity of poly(MVE-alt-MA) decreased in the following order: Zn(II) > Cu(II) > Mn(II).

3.5 Thermogravimetric analysis

Figure 7 represents the comparative Thermo Gravimetric Analysis (TGA) curves of the poly(MVE-alt-MA) and its complexes.

TGA curves of the poly(MVE-alt-MA)/Mn(II) and poly(MVE-alt-MA)/Cu(II) indicate a visible weight loss (the weight loss is about 7.5% in which the molecular weight of the repeating unit is 228 g/mol for Mn complexes and 236.5 g/mol for Cu complexes) starting at 134° and 152°C, respectively, which can be related to the thermal dehydration of carboxylic groups in the complexes. However, no change in the TGA curves of the copolymer and its Zn complexes can be observed at this temperature. These results are another confirmation of the complexation mechanism. TGA analysis of poly(MVE-alt-MA) and its complexes, show a

Table 3. Complex formation constant (K_f) for the poly(MVE-alt-MA)-metal chelates.

Sample	$K_f \times 10^{-8}$ (at 25°C)	$K_f \times 10^{-8}$ (at 40°C)
Poly(MVE-alt-MA)-Mn(II)	0.61	1.1
Poly(MVE-alt-MA)-Cu(II)	3.04	10.8
Poly(MVE-alt-MA)-Zn(II)	3.48	15.5

Figure 5. Variation of reduced viscosity versus concentration of poly(MVE-alt-MA) in water at 25°C.

Figure 6. Variation of reduced viscosity versus concentration of poly(MVE-alt-MA) in water at 25°C in the presence of 0.003 M Zn(II), Cu(II) and Mn(II) ions.

Figure 7. TGA curves of poly(MVE-alt-MA), poly(MVE-alt-MA)/Zn(II), poly(MVE-alt-MA)/Cu(II) and poly(MVE-alt-MA)/Mn(II).

two-step degradation reaction between 250–415°C (T_{d1}) and 415–500°C (T_{d2}). The first step of the degradation can be related to the decarboxylation reactions of carboxylic groups.³⁴ The second step of the degradation is associated with a thermal chain-degradation reaction of the copolymer and its complexes. These results indicate the complexes to be thermally more stable than the copolymer and the thermal stability of the complexes is in order of Zn(II) > Cu(II) > Mn(II).

4. Conclusion

Polyelectrolyte complexes of poly(MVE-alt-MA) with Zn(II), Cu(II) and Mn(II) ions were synthesized. The copolymer and its chelates were characterized by UV, FTIR, TGA and viscosimetric methods. The results showed a complexation reaction to occur between the copolymer and the metal ions and the tendency of the metals to form a complex with poly(MVE-alt-MA) was in the following order: Zn(II) > Cu(II) > Mn(II). This order was confirmed by Pearson's classification and Irving–Williams series. Stability constants of the complexes calculated by the mol-ratio method also confirmed the same order. Interactions of poly(MVE-alt-MA) with the metal ions were also studied using viscosimetric methods. Poly(MVE-alt-MA) and its complexes showed a polyelectrolyte behaviour. Thermal analysis of poly(MVE-alt-MA) and its chelates showed the complexes to be thermally more stable than the copolymer. TGA analysis also revealed the poly(MVE-alt-MA)/Zn(II) complex to have the highest thermal stability.

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