Thermal Properties of Poly(maleic anhydride-*alt*-acrylic acid) in the Presence of Certain Metal Chlorides

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ABSTRACT: Polychelates were synthesized by the addition of aqueous solutions of copper(II), cadmium(II), and nickel(II) chlorides to aqueous solutions of poly(maleic anhydride-*alt*-acrylic acid) [poly(MA-*alt*-AA)] in different pH media. The thermal properties of poly(MA-*alt*-AA) and its metal complexes were investigated with thermogravimetry and differential scanning calorimetry (DSC) measurements. The polychelates showed higher thermal stability than poly(MA-*alt*-AA). The thermogravimetry of the polymer–metal complexes revealed variations of the thermal stability by complexation with metal ions. The relative thermal stabilities of the systems under investigation were as follows: poly(MA-*alt*-AA)–Cd(II) > poly(MA-*alt*-AA)–Cu(II) > poly(MA-*alt*-AA)–Ni(II) > poly(MA-*alt*-AA). The effects of pH on the complexation and gravimetric analysis of the polychelates were also studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3926–3930, 2006

Key words: poly(maleic anhydride-*alt*-acrylic acid); polymer-metal complex; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC)

INTRODUCTION

Polymer–metal complexes are composed of polymeric ligand and metal ions. Complexation reactions and their resultant coordination structures are studied mostly by spectroscopy, such as ultraviolet–visible (UV–vis), infrared (IR), nuclear magnetic resonance, electron spin resonance, circular dichroism, and optical rotary dispersion. These spectra often show characteristics specific to the polymeric ligand structure. The stability of a polymeric complex usually differs from that of a monomeric complex.[1]

During the past few years, the alteration of existing polymeric materials by means of chelation reactions with various metal ions has attracted a good deal of attention, and studies of the metal complexation of crosslinked and water-soluble poly(acrylic acid) have been conducted with potentiometric titration, coupling ultrafiltration, UV–vis spectroscopy, IR spectroscopy, electron spin resonance spectroscopy, X-ray fluorescence spectroscopy, mechanical measurements, and so forth.[2–11]

Regularly structured water-soluble polymers should be useful in biomedical applications, and in common with carboxylic acid polymers, maleic anhydride (MA) copolymers have been found to exhibit biological activity.[12] Poly(acrylic acid maleic acid) is of technical importance as a component of commercial dental cements. The interaction of poly(acrylic acid maleic acid) with various metal salts was investigated by IR spectroscopy.[13] The synthesis, characterization, and structure of poly(acrylic acid-*co*-maleic acid)–metal complexes with copper(II), cobalt(II), and nickel(II) ions have been assigned to the chelates by elemental analysis, IR spectroscopy, thermal analysis, magnetic susceptibility, and electrical conductivity measurements.[14]

In a previous work,[15] we studied the complexation of Cu(II), Ni(II), and Cd(II) ions with poly(maleic anhydride-*alt*-acrylic acid) [poly(MA-*alt*-AA)] in aqueous solutions; the stability constants of the obtained polychelates were determined by UV–vis spectroscopy, and the polyelectrolyte behavior of poly(MA-*alt*-AA) was investigated in the presence of metal salts. The crystallinity degrees and temperature-dependent electrical conductivities of poly(MA-*alt*-AA)–Cu(II), poly(MA-*alt*-AA)–Ni(II), and poly(MA-*alt*-AA)–Cd(II) complexes were investigated by the X-ray powder diffraction method[16] and electrical conductivity measurements.[17]

The aim of this work was to investigate the metal complexation and thermal stability of poly(MA-*alt*-AA) in the presence of copper(II), nickel(II), and cadmium(II) chlorides. At a distinct pH, the influence of these metal ions on the formation of the complexation was studied with gravimetric analysis and thermal analysis measurements.

EXPERIMENTAL

Materials

Acrylic acid (AA; Fluka Chemie, Buchs, Switzerland) was distilled before use. It had the following characteristics: boiling point = 141.6°C, melting point = 13.5°C, d_4^{20} = 1.0510, and n_d^{20} = 1.4215. MA (Fluka) was purified before use by recrystallization from anhydrous benzene and by sublimation in vacuo (melting point = 52.8). Benzoyl peroxide (Fluka) was purified by recrystallization twice from a chloroform solution by methanol when it was dried in vacuo (melting point = 106°C). Other reagents, including organic solvents, were purified by ordinary methods. Metal salts were used without further purification, and metal-ion stock solutions were prepared from the corresponding metal salts (CuCl₂ · 2H₂O, CdCl₂ · 2H₂O, and NiCl₂ · 6H₂O; BDH, Poole, UK). Buffer stock solutions were prepared from KH₂PO₄ and NaHPO₄ (BDH). The water used for the solutions was deionized and twice distilled.

Copolymerization

Poly(MA-*alt*-AA) was prepared by the free-radical copolymerization of MA with AA in *p*-dioxane.[17,18]

Preparation of polychelates

Polychelates were prepared by the dissolution of the copolymer (0.002 g/10 mL) in buffer solutions to pHs 4.62, 5.63, 6.36, and 7.26. The pHs of poly(MA-*alt*-AA) solutions were adjusted with a phosphate buffer, and these buffer solutions were prepared by the ordinary method. The pH value for each of the solutions was measured with a digital pH meter. Aqueous solutions of metal salts (MCl₂ · *n*H₂O; 0.05*M*) were added dropwise to solutions of the respective poly(MA-*alt*-AA) sample at room temperature while the mixture was stirred vigorously, and polymeric complexes were precipitated instantaneously and filtered and were then dried in vacuo at 50°C.

The obtained polychelates were completely insoluble in water and had different colors: Cu(II) polychelates were dark green, Cd(II) polychelates were white, and Ni(II) polychelates were light green.

Measurements

Fourier transform infrared (FTIR) spectra of copolymer films were recorded with a Nicolet 510 spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–400-cm⁻¹ range; 30 scans were taken at a 4-cm⁻¹ resolution. The acid number (AN) of the anhydride-containing copolymer was determined by a known nonaqueous titration method. The intrinsic viscosity of the synthesized copolymer was deter-

mined in *p*-dioxane at 25 ± 0.1°C in the concentration range of 0.1–1.0 dL/g with an Ubbelohde-type capillary viscometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses of the copolymer and polychelates were carried out with a Setaram instrument (France) in a nitrogen atmosphere, and the temperature was raised from 25 to 500°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Copolymerization of poly(MA-*alt*-AA)

The copolymer, synthesized with a 1:1 molar ratio of the initial monomers, had the following characteristics:[17,18] glass-transition temperature = 125.1°C and melting temperature = 153°C (by DSC analysis), intrinsic viscosity in *p*-dioxane at 25°C = 1.25 dL/g, AN = 878 mg of KOH/g, and monomer unit ratio in the copolymer = 1:1.12.

The structure of poly(MA-*alt*-AA) is
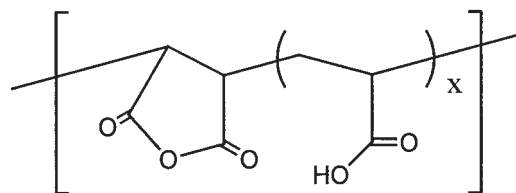
where *x* is 1.12 (AA unit = 52.83)

FTIR spectra (film, cm⁻¹): νOH 3060 (broad, in —COOH), νCH₃ 2950 (as) and 2880 (s), νCH₂ 2930 (as) and 2870 (s), νCOOH 2545 (broad), νC=O 1836 (as) and 1766 (s; C=O in anhydride unit), νC=O 1585 (as; in COO⁻), νC—O—C 1035 (in anhydride units), δOH 943 (out-of-plane OH bending).

Metal-complexation studies

The metal-ion complexations were carried out with Cu(II), Ni(II), and Cd(II) ions at four different pH values (4.62, 5.63, 6.36, and 7.26). The chelation of a metal ion by a polymeric ligand is highly dependent on the equilibrium pH of the medium. The chelating process of a metal ion by a polymer may be preceded by long-range attractive electrostatic interactions, and once the metal ion is condensed on the polymer surface, it is site-fixed by the polymer ligands. The most accepted mechanism for carboxylic-type complexes can be shown as follows:
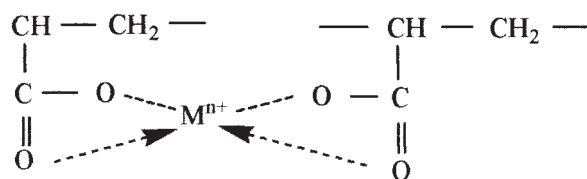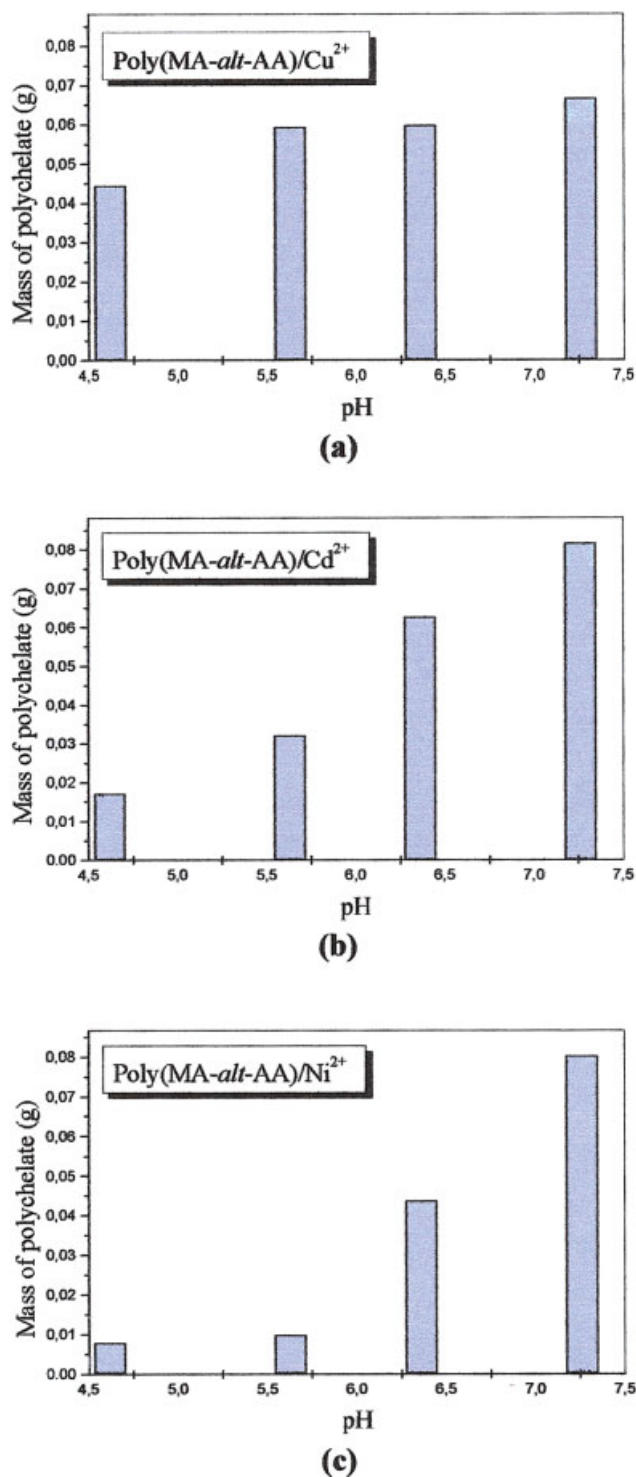
Figure 1 Dependence of the mass of (a) poly(MA-*alt*-AA)/Cu^{2+}, (b) poly(MA-*alt*-AA)/Cd^{2+}, and (c) poly(MA-*alt*-AA)/Ni^{2+} on the pH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The carboxylic groups can act as monodentate and bidentate ligands, depending on the pH values.[19]

Gravimetric results depending on the pH can be seen in Figure 1. Although the mass of the Cu(II)

polychelate was large at low pH values, the Cd(II) polychelate was dominant at high pH values [Fig. 1(a,b)], and at low pH values, proper amounts of the Ni(II) and Cd(II) polychelates were not obtained for the analysis. Thus, the structures of the polychelates at pH 6.36 were examined. One other reason is that there is a possibility of the metal ion turning into a hydroxide form when a sufficiently high pH is reached. This reaction competes, of course, with the formation of the polymer–metal complex [the metal hydroxide precipitates at a high pH (~6.5)]. In addition, the optimum pHs for various metal ions have been reported to be 6.2 for Ni(II) and 5.4 for Cu(II).[20]

Thermal analysis

To determine the impact of typical metal chlorides on the stability of poly(MA-*alt*-AA), TG was used. The nature of the polymer backbone, the degree of crosslinking, the coordination geometry of the metal centers, and the ligand structure are decisive in affecting the thermal stabilities of polymer–metal complexes. The thermal degradation of poly(MA-*alt*-AA) and its metal complexes is presented in Figures 2–5, and thermoanalytical results are also presented in Tables I and II. The TG and differential thermogravimetry (DTG) curves of poly(MA-*alt*-AA) (Fig. 2) showed a four-stage decomposition, with the temperature intervals at 60–85, 135–270, 270–367, and 367–450°C, respectively. The first stage corresponds to the loss of the solvent or water. The second decomposition stage is the decomposition of carboxylic groups, and the third and the fourth stages of decomposition are due to the rupture of the polymer chain. The Cu(II) polychelate showed three decomposition stages, the Cd(II) polychelate showed one decomposition stage, and the Ni(II) polychelate showed two-step decomposition
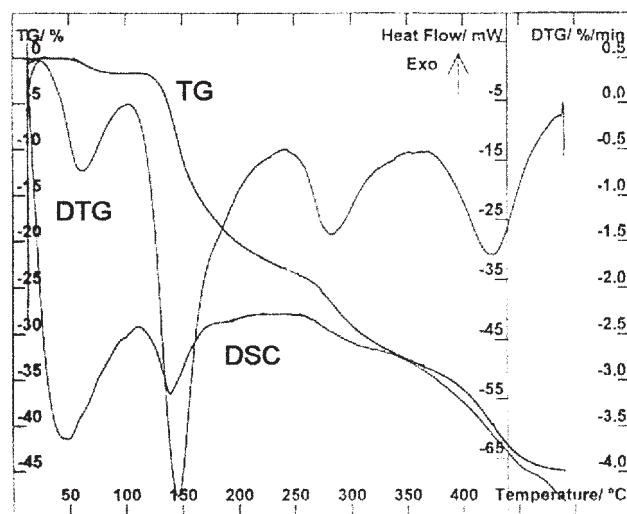
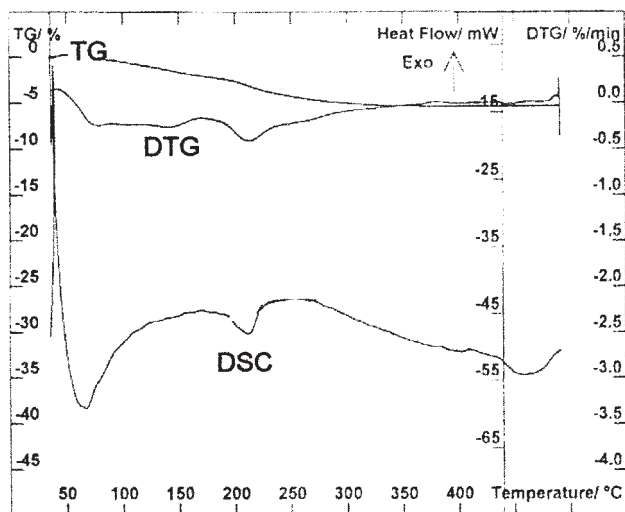**Figure 2** TG, DTG, and DSC curves of poly(MA-*alt*-AA).

Figure 3 TG, DTG, and DSC curves of the poly(MA-*alt*-AA)–Cu(II) complex (pH 6.36).

Figure 5 TG, DTG, and DSC curves of the poly(MA-*alt*-AA)–Ni(II) complex (pH 6.36).

(see Figs. 3–5 and Tables I and II). In all cases, the first steps correspond to a loss of the solvent or water (lattice of hydride). The loss of water molecules below 200°C can be due to free water, whereas that eliminated above 200°C may be due to water coordinated to the metal ion present in chelates.[14] The second and third stages of decomposition are due to the decomposition of the organic moiety, such as carboxylate groups and uncomplexed ligands, and the formation of metal oxides.

Polychelates show higher thermal stability than poly(MA-*alt*-AA). This may be due to the insertion of the metal ion into the polymer chain as a result of chelation. Another factor that may be responsible for the enrichment of the thermal stability of polymer–
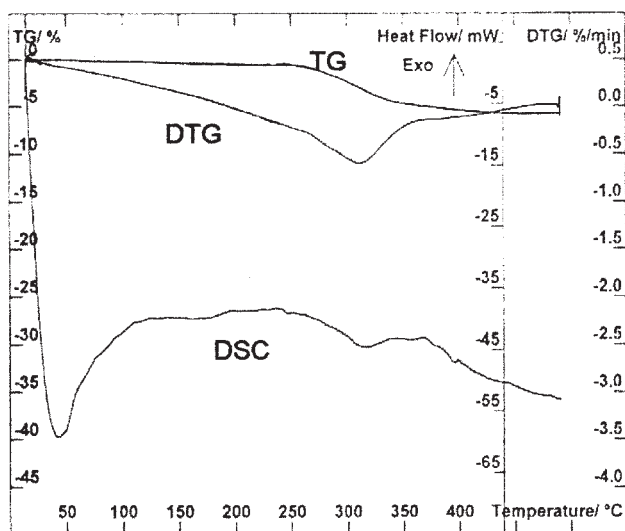
metal complexes is the increase in the molecular weight due to the joining of two different polymer chains.[21]

This order has been confirmed by X-ray diffraction studies.[16] Depending on the crystal structures of the metals [Cd, hexagonal close-packed (hcp), and Cu and Ni, cubic close-packed (ccp)],[22] a metal-polymer arrangement can exist in the crystal structure. Semicrystalline polymer chains were placed properly at the Cd ion in an hcp arrangement. As a result of this arrangement, the degree of crystallinity in the Cd(II) polychelate was higher than that in the Cu(II) and Ni(II) polychelates because the crystal structures of Cu and Ni were in the ccp form. In addition, there is a possibility of the metal turning into a hydroxide at pH 6.36, and this reaction competes, of course, with the formation of the polymer–metal complex (the metal hydroxide precipitates at pH ~ 6.5). The formation of the metal hydroxide and intermolecular and intramolecular hydrogen bonding affected the crystallinity of the copolymer and polychelates. The high acidity character of the Cd(II) ion increased the complexation against the polymeric ligand in a basic medium in comparison with Ni(II) and Cu(II).

Figure 4 TG, DTG, and DSC curves of the poly(MA-*alt*-AA)–Cd(II) complex (pH 6.36).

TABLE I
Thermoanalytical Results of Poly(MA-*alt*-AA) and Its Polychelates (pH 6.36)

Polymer sample	Weight loss (%) at different temperatures (°C)				
	100	200	300	400	450
Poly(MA-*alt*-AA)	1.5	20.5	30.0	36.0	43.0
Poly(MA-*alt*-AA)–Cu(II)	0.5	2.5	5.0	5.5	5.5
Poly(MA-*alt*-AA)–Ni(II)	5.0	12.6	16.5	18.0	18.0
Poly(MA-*alt*-AA)–Cd(II)	0.0	0.0	2.4	5.5	5.5

TABLE II
Glass-Transition Temperature (T_g) and Thermal Degradation Temperatures (T_{d1}, T_{d2}, T_{d3}, and T_{d4}) of Poly(MA-*alt*-AA) and Its Polychelates (pH 6.36)

Polymer sample	T_g	T_{d1} (°C)	T_{d2} (°C)	T_{d3} (°C)	T_{d4} (°C)
Poly(MA-*alt*-AA)	125.1	60.1	145.4	229.5	420.8
Poly(MA-*alt*-AA)–Cu(II)	127.0	80.1	144.8	214.5	—
Poly(MA-*alt*-AA)–Ni(II)	79.8	99.2	380.5	—	—
Poly(MA-*alt*-AA)–Cd(II)	151.0	315.2	—	—	—

TG of the polymer–metal complexes revealed variations of the thermal stability by complexation with metal ions. The relative thermal stabilities of the system under investigation were as follows: poly(MA-*alt*-AA) < poly(MA-*alt*-AA)–Ni(II) < poly(MA-*alt*-AA)–Cu(II) < poly(MA-*alt*-AA)–Cd(II).

CONCLUSIONS

Poly(MA-*alt*-AA) and its Cd(II), Cu(II), and Ni(II) polychelates were prepared. The resulting copolymer and polychelates were analyzed by gravimetric and thermal analysis. The stabilities of these polymer–metal complexes were highly dependent on the pH of the medium. At high pH values, the Cd(II) polychelate was dominant. Thermal studies indicated that the metal chelates exhibited higher stability than the free polymer chelate. The thermal stability of poly(MA-*alt*-AA) and its metal chelates increased in the following order: poly(MA-*alt*-AA) < poly(MA-*alt*-AA)–Ni(II) < poly(MA-*alt*-AA)–Cu(II) < poly(MA-*alt*-AA)–Cd(II).

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