Effect of Ni(II), Cd(II), and Cu(II) Metal Ions on the Crystallinity of Poly(maleic anhydride-*alt*-acrylic acid)

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ABSTRACT: The chelation of poly(maleic anhydride-*alt*-acrylic acid) [poly(MA-*alt*-AA)] with nickel (II), cadmium (II), and copper (II) ions was carried out under various pH conditions. Polychelates were prepared by precipitation from the aqueous solutions of metal salts at different pH values. The effects of metal salts (NiCl$_2$·6H$_2$O, CdCl$_2$·2H$_2$O, CuCl$_2$·2H$_2$O) on the degree of crystallinity of poly(MA-*alt*-AA) were investigated by X-ray diffraction spectroscopy at different pH values. The degree of crystallinity was found to be in the following order: Cd(II)–polychelate > Cu(II)–polychelate > Ni(II)–polychelate at pH 6.36; this result was also supported by gravimetric studies. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1708–1715, 2003

Key words: poly(maleic anhydride-*alt*-acrylic acid); metal–polymer complexes; crystallization; X-ray diffraction; polychelatogens

INTRODUCTION

Regularly structured water-soluble polymers should be useful in biomedical applications and, in common with carboxylic acid polymers, maleic anhydride copolymers have been found to exhibit biological activity.[1] Polymers containing ligand moieties can perform several functions in contact with metal ion solutions, including separation, removal, concentration, and fractionation. All of these processes, resulting from metal ion complexation by polymer ligands, are influenced by ligand selectivity and matrix structure among others. Several functional hydrophilic polymers with chelating ligands used for complexation have been investigated for complexation in the homogeneous phase. These hydrophilic, noncrosslinked, functional polymers that are able to complex metal ions have been termed polychelatogens. These polychelatogens are characterized by two components: the polymer backbone, which usually provides solubility and stability; and the functional groups, which are necessary for metal complexation. Different approaches, introduction of metal-complexing groups into the polymer backbone, and varying the type of polymeric chain were previously investigated.[2]

The synthesis and investigation of metal-containing polymers are important because these systems offer advantages over nonpolymeric metal complexes and metal salts in a variety of chemical reactions. Polymeric metal chelates, moreover, are of great significance in different fields of chemistry, such as catalytic reactions, mining separations, biochemistry, medicine, and environmental chemistry.[3]

Complexes of linear and crosslinked poly(acrylic acid)s (PAAs) were also revisited, with investigations focusing on the interaction with copper, nickel, lead, and cadmium. PAA is often chosen as a model for the complexation of natural humic acids and is used both as a flocculant in water treatment and as a sludge thickener.[4] Potentiometric study of Cd(II), Pb(II), Cu(II), and Ni(II) complexations with PAA were investigated in dilute solution and the stability constants of the complexes were determined.[5] The polychelates obtained by addition of the copolymer poly(acrylic acid-*co*-maleic acid) to aqueous solutions of Cu(II), Co(II), and Ni(II) were characterized by elemental analysis; magnetic, spectral, and thermal properties; and electrical conductivities.[3] The interaction of metal salts with acrylic acid–maleic acid copolymer was also studied by infrared spectroscopy.[6]

Recently, the complexation behavior between metal cations and poly(maleic anhydride-*alt*-acrylic acid) [poly(MA-*alt*-AA)], in the electrostatic manner of polyelectrolytes, was investigated in aqueous solutions[7] and in solid states[8] by our group. Crystallinity degrees and common structural properties of semicrystalline poly(MA-*alt*-AA) and poly(MA-*co*-AA-*co*-vinyl acetate) were investigated by the X-ray powder diffraction method and energy minimization studies. The semiempirical PM3 method was undertaken to optimize the unit link for each polymer; thus the stabilization and predicted unit structures of the samples were determined.[9]
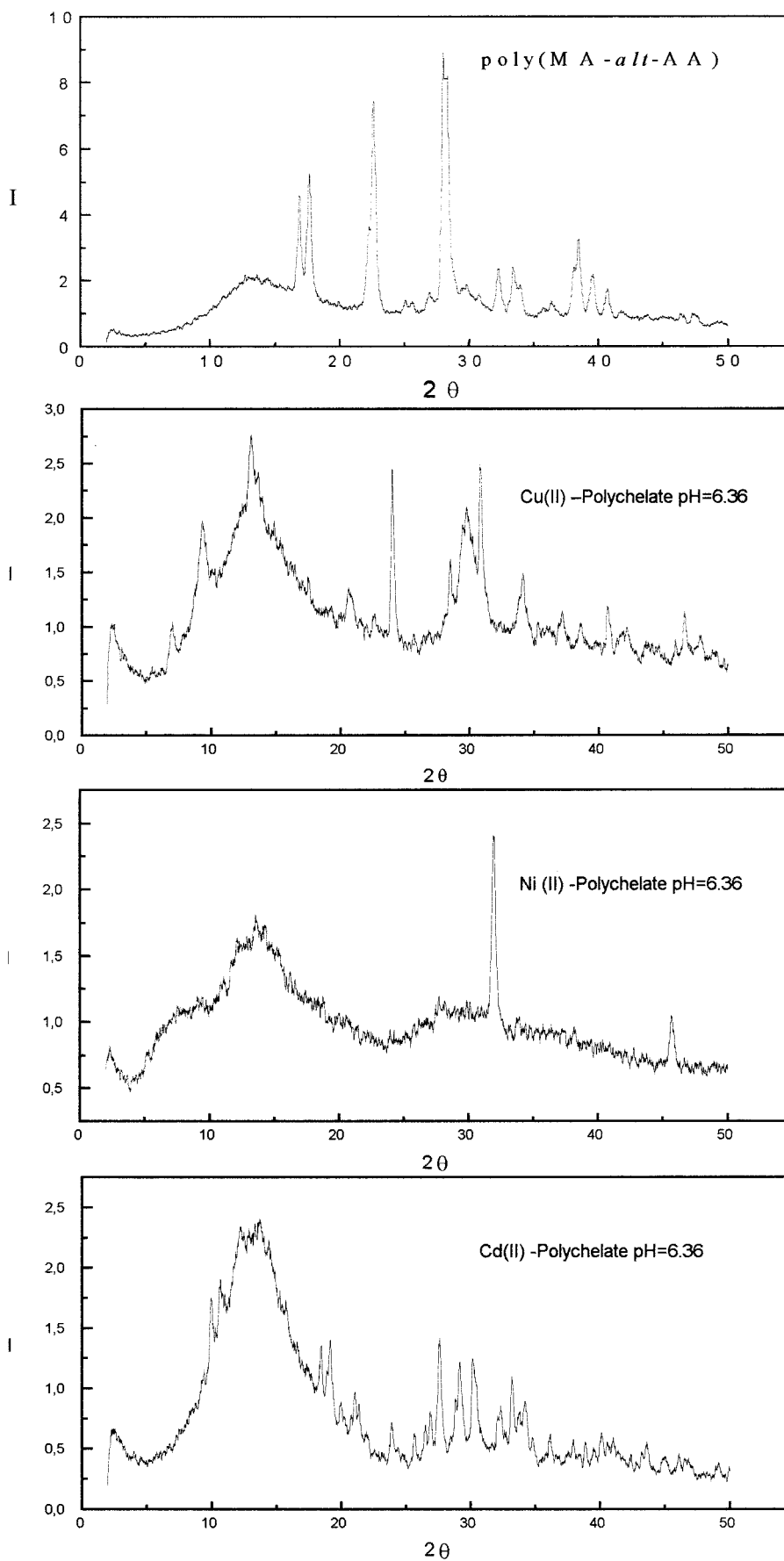
Figure 1 X-ray diffraction patterns of poly(MA-*alt*-AA), poly(MA-*alt*-AA)/Cu^{2+}, poly(MA-*alt*-AA)/Ni^{2+}, and poly(MA-*alt*-AA)/Cd^{2+} at pH 6.36.

TABLE I
X-ray Diffraction Analysis: Bragg Angles (2θ),
Interplanar Spacing (d), and Relative Intensities (I/I_0)

Type of polychelate	2θ	d (Å)	I/I_0
Poly(MA-*alt*-AA)	17.4	5.1	57.3
	22.3	4.0	45.3
	27.8	3.2	100.0
	38.0	2.4	29.3
Poly(MA-*alt*-AA)/Cu^{2+}	9.0	9.8	100.0
	15.0	3.0	90.0
	24.8	3.6	52.5
	34.5	2.6	32.5
Poly(MA-*alt*-AA)/Ni^{2+}	28.0	3.2	100.0
	32.5	2.8	72.7
	41.0	2.2	63.6
	46.0	2.0	31.8
Poly(MA-*alt*-AA)/Cd^{2+}	9.0	9.8	100.0
	10.0	8.9	91.1
	15.0	5.9	48.2
	19.0	4.7	83.9
	27.5	3.2	98.2
	31.0	2.9	91.1
	33.0	2.7	67.9
	41.0	4.4	33.9
	46.9	2.0	30.4

The main objective of our study was to establish the degree of crystallinity and the structure of poly(MA-*alt*-AA)/Me^{2+} networks as well as of the chemical nature of the synthesized polymer. The influence of Cu(II), Ni(II), and Cd(II) ions on the crystalline structure of the polychelates at different pH values considered in the present study was determined by X-ray diffraction spectroscopy.

EXPERIMENTAL

Materials

AA (average characteristics: bp 141.6°C; mp 13.5°C; d_4^{20} 1.0510; n_D^{20} 1.4215; Fluka Chemie, Buchs, Switzerland) was distilled before use. MA (Fluka) was purified before use by recrystallization from anhydrous benzene and by sublimation *in vacuo* (mp 52.8°C). Benzoyl peroxide (BP, Fluka) was purified by recrystallizing twice from chloroform solution by methanol when dried under vacuum (mp 106°C). Other reagents including organic solvents were purified by ordinary methods.

Metal salts were used without any further purification and metal ion stock solutions were prepared from the corresponding metal salt (NiCl$_2$·6H$_2$O, CdCl$_2$·2H$_2$O, CuCl$_2$·2H$_2$O; BDH, Toronto, Canada). Buffer stock solutions were prepared from KH$_2$PO$_4$ and NaHPO$_4$ (BDH) by standard procedure.

Copolymerization

Copolymerization of MA with AA was carried out in *p*-dioxane in the presence of BPO (0.1%) as an initiator at

70°C under a nitrogen atmosphere. The copolymers were isolated from the reaction mixture by reprecipitation with anhydrous methanol and *n*-hexane, respectively. Copolymers were purified by twice reprecipitating from *p*-dioxane solution with *n*-hexane and by washing with several portions of hexane, benzene, and diethyl ether, and were dried *in vacuo* at 50°C to a constant weight with almost quantitative yields (∼ 75%).

Preparation of polychelates

Polychelates were prepared by dissolving the copolymer (0.016 g/dL) in different buffer solutions to pH values of 4.62, 5.63, 6.36, and 7.26. Aqueous solutions of metal salts (0.05*M*), MCl$_2$·*n*H$_2$O were added dropwise to solutions of the respective poly(MA-*alt*-AA) sample at room temperature while the mixture was stirred vigorously; polymeric complexes were precipitated instantaneously, filtered, and then dried in vacuum at 50°C.

The obtained polychelates showed different colors: Cu(II)–polychelates were dark green; Cd(II)–polychelates, white; Ni(II)–polychelates, light green.

Measurements

FTIR spectra of copolymer films or thin coatings on KBr pellets were recorded with an FTIR Nicolet 510 spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–400 cm^{-1} range, where 30 scans were taken at 4 cm^{-1} resolution. The acid numbers (AN) of the anhydride-containing copolymers were determined by a known nonaqueous titration method. Intrinsic viscosity values of the synthesized copolymers were determined in *p*-dioxane at 25 ± 0.1°C in the concentration range of 0.1–1.0 dL g^{-1} using an Ubbelohde viscometer. Differential scanning calorimetric (DSC) and thermogravimetric (TGA) analyses of copolymers were carried out with a DuPont V4.1C 2000 (DuPont, Boston, MA) and DuPont TA 2000 under a nitrogen atmosphere at a heating rate of 5°C/min.

X-ray studies

The powder diffraction patterns of synthesized samples were recorded using a Philips (The Netherlands) manual spectrogoniometer using Cu–K$_\alpha$ ($\lambda = 1.54184$ Å) radiation over the range $5° \leq 2\theta \leq 50°$. Table I

TABLE II
Specific Characteristics of Metal Ions
(Cd^{2+}, Cu^{2+}, and Ni^{2+})

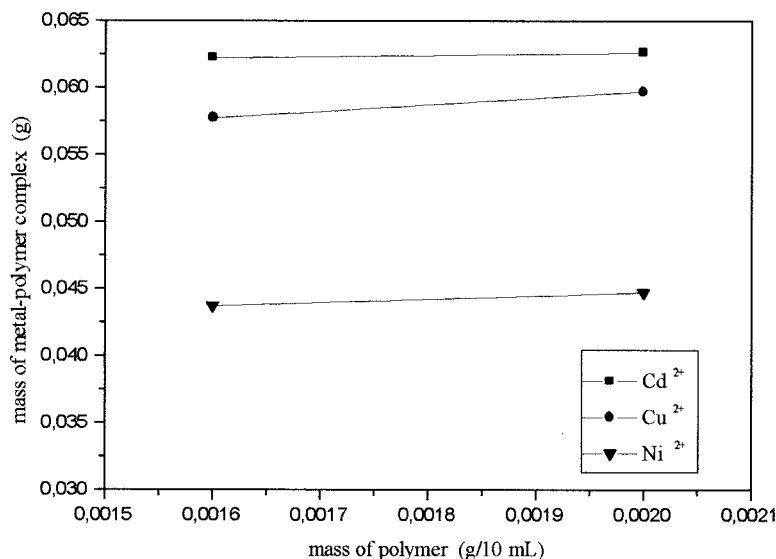| Ion	q/r	Ionic radius (pm)	Atomic radius (pm)
Cd^{2+}	1.82	109.0	149.0
Cu^{2+}	2.20	87.0	128.0
Ni^{2+}	2.40	83.7	125.0

Figure 2 Dependency of mass of metal–polymer complex (g) on mass of polymer (g/10 mL).

shows the Bragg angles (2θ), interplanar spacing (d), and relative intensities (I/I_0) of the samples.

In the second step of our X-ray studies, poly(MA-*alt*-AA) and polymer–metal complexes were studied. The degree of crystallinity (X_c) of new products was determined by the area ratio method, expressed as

$$X_c = \frac{\int_0^\infty s^2 I_c(s)\ ds}{\int_0^\infty s^2 I(s)\ ds}$$

where s is the magnitude of the reciprocal-lattice vector and is given by $s = (2\sin\theta)/\lambda$, where θ is one-half the angle of deviation of the diffracted rays from the incident X-rays and λ is the wavelength; $I(s)$ is the intensity of coherent X-ray scatter from a specimen (both crystalline and amorphous); and $I_c(s)$ is the intensity of coherent X-ray scatter from the crystalline region. In this method, the areas of amorphous and crystalline parts of the patterns were calculated.[13]

RESULTS AND DISCUSSION

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. This interest can be understood when one considers the ease with which the chelation reactions of polymers in general take place and the useful properties of some chelated polymers. Depending on their structure, metal chelates of polymers can be used, for instance, as catalysts, high-temperature and flame-resistant fibers, semiconductors, and ion-exchange resins. There may also be some applications for medical

and agricultural purposes and as model compounds in biochemical processes.[10]

One of the important intra- and intermolecular structural characteristics of polyfunctional polymers is structural regularity and bond flexibility of their macromolecules. When the polar polymers process H-bonding capability, the most energetically favored crystal structure will tend to capitalize on these features. The synthesized copolymer by the use of $1:1M$ ratios of initial monomers, respectively, had the following characteristics.[11]

MA—AA alternating copolymer
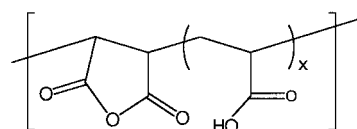
where $x = 1.12$ (AA unit = 52.83).

Yield 75%; glass-transition temperature (T_g) 111°C and melting temperature (T_m) 153°C (by DSC analysis); intrinsic viscosity $[\eta]_{in}$ in p-dioxane at 25°C 1.25 dL g^{-1}; AN = 878 mg KOH/g; monomer unit ratio in copolymer ($m_1 : m_2$) = $1:1.12$.
FTIR spectra (film), cm^{-1}: νOH 3060 (broad, in –COOH), νCH$_3$ 2950 (as) and 2880 (s), νCH$_2$ 2930 (as) and 2870 (s), νCOOH 2545 (broad), νC=O 1836 (as) and 1766 (s) (C=O in anhydride unit), νC=O 1730 (C=O in ester group), νC=O 1585 (as) (in COO$^-$), δCH$_2$ 1478 and 1443 (doublet), δCH$_3$ 1385 and 1357 (doublet), δC—O 1240–1170 (ester and carboxyl), νC—O—C 1035 (in anhydride unit), δOH 943 (out-of-plane OH bending), δCH 886 and 871 (doublet), δCH$_3$ 842 (rock), δCH$_2$ 720 (rock), δCH 645 (in main chain from anhydride unit), and δO—C=O 560 (s) (bend of COOH); 645 (in main chain from anhydride unit), and δO—C=O 578 (s) (bend of ester group). In the FTIR spectra of hydrolyzed copolymers, some characteristic bands for anhydride units
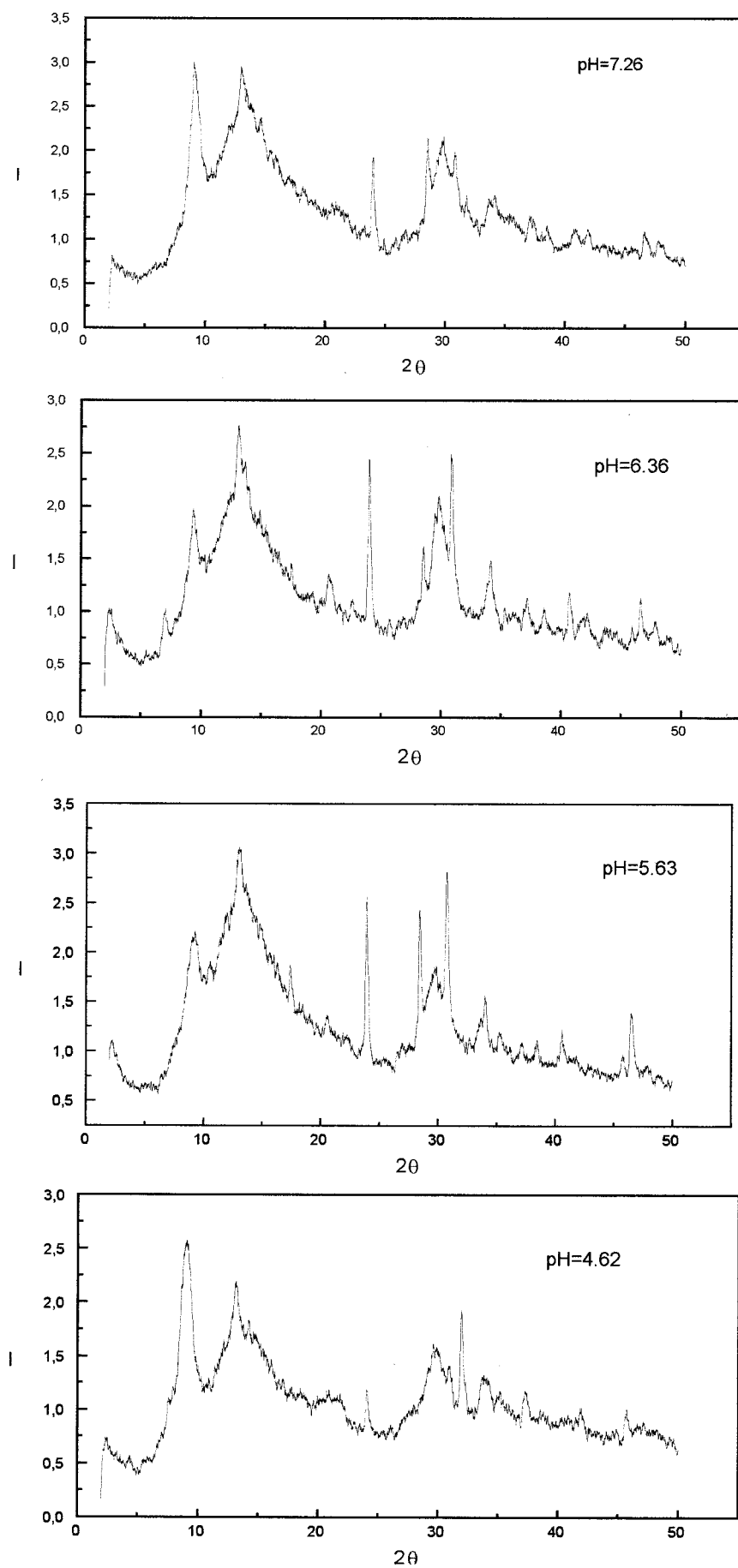
Figure 3   X-ray diffraction patterns of poly(MA-*alt*-AA)/Cu²⁺ at pH 7.26, 6.36, 5.63, and 4.62.
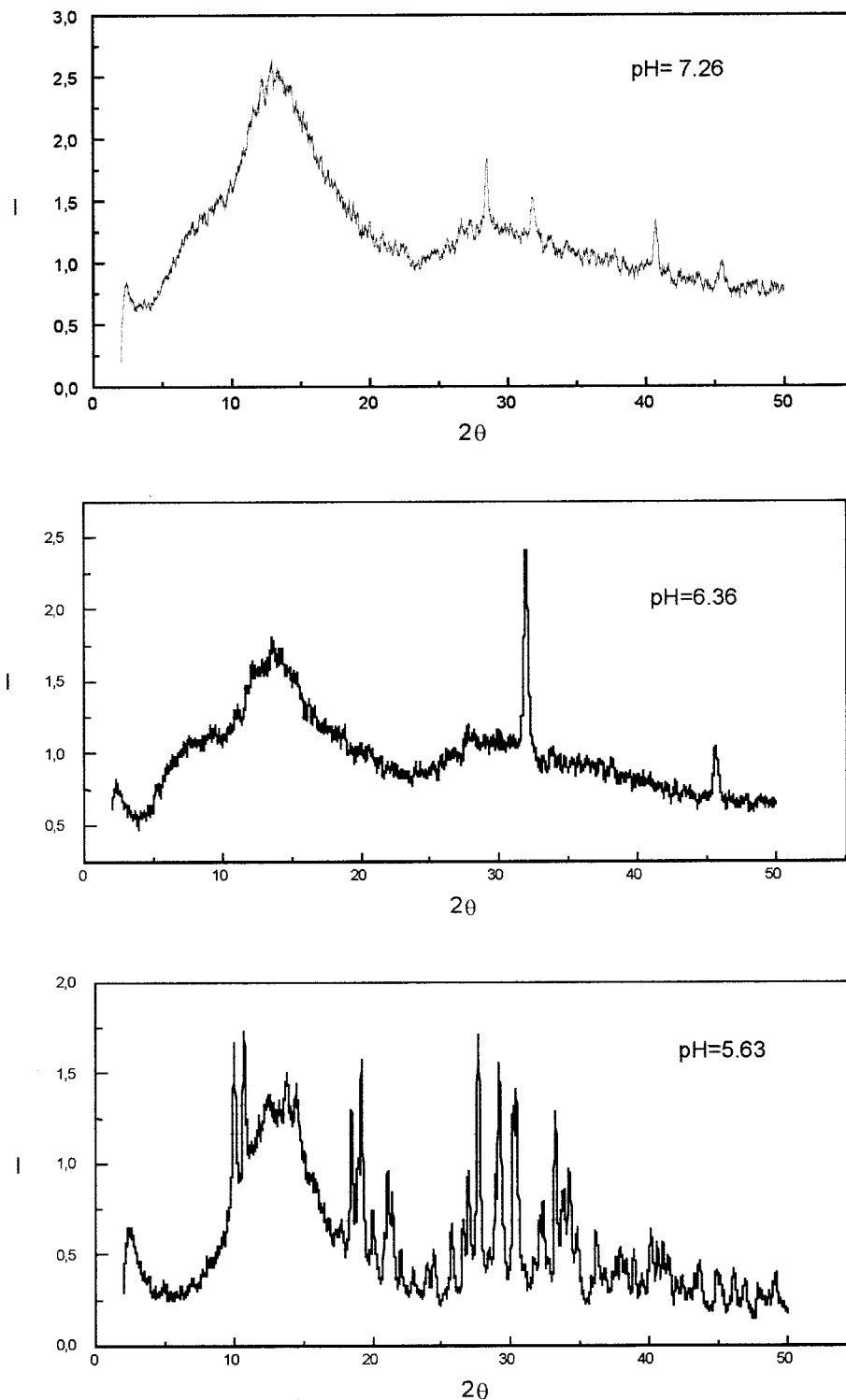
Figure 4   X-ray diffraction patterns of poly(MA-*alt*-AA)/Ni^{2+} at pH 7.26, 6.36, and 5.63.

disappeared, and new bands appeared in the field of 1970, 1585, and 1630 cm^{-1} relating to –COOH groups, as well as increased intensity of 3060 and 2545 cm^{-1} broad bands.

As can be seen from diffraction patterns of poly(MA-*alt*-AA), the polymer has noticeable crystallinity (degree of crystallinity 36%). This result was obtained from partially hydrolyzed anhydride groups from the maleic anhydride units and this group can easily undergo hydrogen bonding with acrylic acid monomer units. This seems to be related to the crystalline phase, which is formed through intermolecular H-bonding between the –COOH groups containing functional macromolecules.

Figure 1 shows the X-ray patterns of poly(MA-*alt*-AA), Cd(II)–polychelates, Cu(II)-polychelates, and Ni(II)-polychelates at pH 6.36. According to Figure 1,
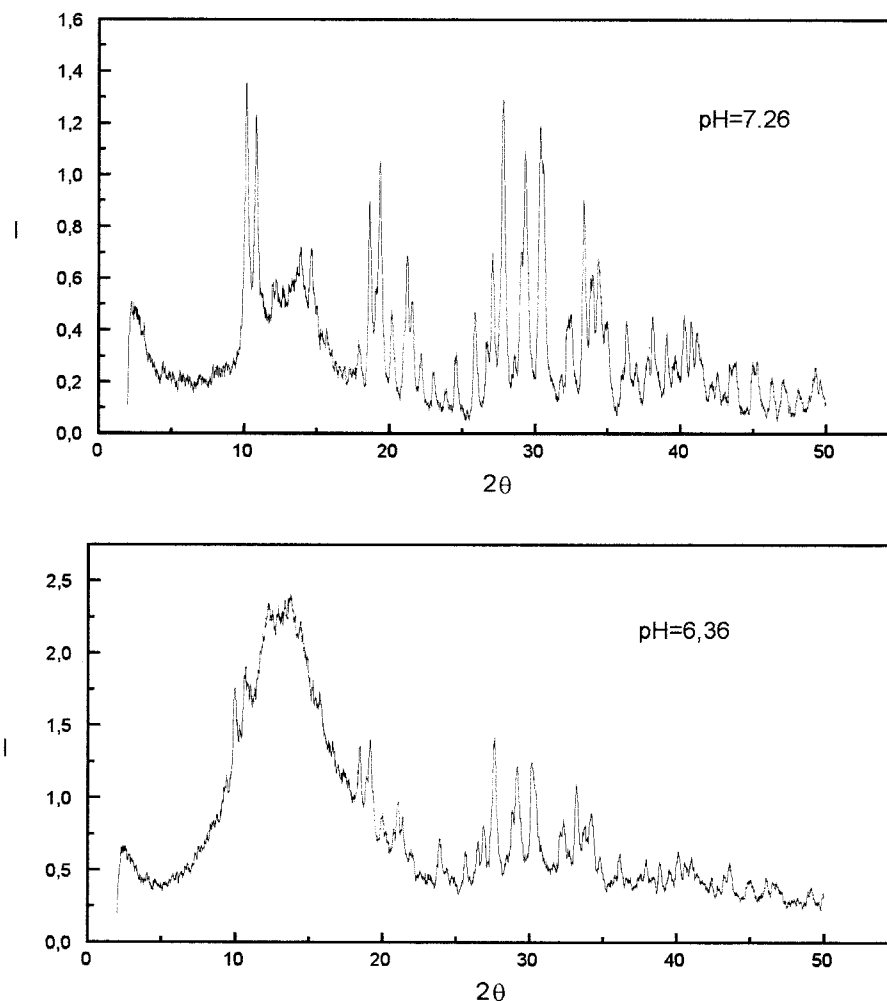
Figure 5 X-ray diffraction patterns of poly(MA-*alt*-AA)/Cd^{2+} at pH 7.26 and 6.36.

the maximum crystallinity was observed in the Cd(II)–polychelates. Degrees of crystallinity of the poly(MA-*alt*-AA), Cd(II)–polychelates, Cu(II)–polychelates, and Ni(II)–polychelates were 36.0, 22.8, 17.6, and 9.9%, respectively. These results can be explained by the order of ionic radius of metal ions, and the crystal structures of metal ions. The crystal structures of metals (Cd: hcp, hexagonal close-packed; Cu and Ni: ccp, cubic close-packed)[12] occur by chance metal–polymer arrangements in the crystal structure. In the hcp arrangement at Cd ion semicrystalline polymer chains place properly. As a result of this arrangement, the degree of crystallinity of Cd(II)–polychelates was higher than that of the semicrystalline polymer and also that of Cu(II)–and Ni(II)–polychelates, given that the crystal structures of Cu(II) and Ni(II) were of the ccp form. The highly symmetrical ccp structure has slip planes of close-packed layers along four directions (corresponding to the threefold axes, the body diagonals of the cube) compared with only one direction for the hcp structure.

The main differences in X-ray patterns were observed in the position of 2θ values. The peaks occurred at 17.0, 22.0, 28.0, and 38.0° for copolymer and 9.0, 15.0, 30.0, 32.0, and 41.0° are the common peaks for poly(MA-*alt*-AA)/Cu^{2+}, poly(MA-*alt*-AA)/Cd^{2+}, and poly(MA-*alt*-AA)/Ni^{2+} (Table I). Small deviations at low and high theta values show slightly smaller and larger unit cells of these semicrystals. If the intensive peak location deviates to low theta range, it will cause formation of a large unit cell. According to Table I, the intensive peak locations of both Cu(II)–polychelate and Cd(II)–polychelate are at low theta range. However, the intensive peak of Ni(II)–polychelate location is at high theta range. These results can be explained by use of ionic radius, atomic radius, and q/r ratios of the cations. The charge density (q/r) of a cation is useful in comparing the complex ability of ions of different charges in the electrostatic model, given that the energy of interaction varies with the charge (q) and inversely with the radius (r) of an ion, and the stability of complexes increases as the charge density increases. As shown in Table II,

ionic radius (pm): Cd^{2+} > Cu^{2+} > Ni^{2+}
charge density: Ni^{2+} > Cu^{2+} > Cd^{2+}

TABLE III
Degree of Crystallinity (%) of Metal(II)–Polychelate at Different pH Values

pH	Cu(II)–Polychelate	Ni(II)–Polychelate	Cd(II)–Polychelate
7.26	17.6	9.9	49.5
6.36	18.6	10.3	22.8
5.63	16.2	31.8	—
4.62	17.8	—	—

Because of the high ionic and atomic radius of Cd(II), the location of intensive peaks of Cd(II) was at the low theta region. These results can be also explained by the high degree of crystallinity of Cd(II)–polychelates.

All polychelates were prepared at four different pH values (4.62, 5.63, 6.36, 7.26), but at low pH values we could not obtain the proper amount of Ni(II)– and Cd(II)–polychelates for X-ray diffraction studies (Figures 3–5). Gravimetric results depending on the pH can be seen in Figure 2. According to Figure 2 and X-ray diffraction patterns, the structures of the polychelates at pH 6.36 were discussed because there is a possibility for the metal to turn into hydroxide when a sufficiently high pH is reached. This reaction competes of course with the formation of the polymer–metal complex [metal hydroxide, Me(OH)$_2$ precipitates at pH $\sim$ 6.5]. According to Table III, the degree of crystallinity ($\sim$ 18%) of Cu(II)–polychelates does not change depending on the pH. The maximum degree of crystallinity was observed in Cd(II)–polychelate at pH 7.26 (49.5%). This result can be explained in one of four ways. The first explanation is the precipitation form of the metal hydroxide and the second is the crystal structure of Cd(II) ion (hcp). As the precipitated metal hydroxide formed inter- and intramolecular H-bonding, crystallinity of the polychelate was increased. In addition, the Cd(II)–polychelate, which has hcp crystal structure including water molecules, undergoes increasing crystallinity by the addition of H-bonding. The third explanation is the high acidity character of Cd(II) ion compared with that of Ni(II) and Cu(II) against the polymeric ligand in basic medium. At low pH, the crystallinity of the Ni(II)–polychelates is also high. These unexpected results confirmed the small radius of the Ni(II) ion. The fourth and final explanation is that Ni(II) and Cu(II) ions are borderline acids, although Cd(II) has a soft acidic character; the polymeric ligand (COO$^-$) places it in the soft base region. The interaction of a soft base with a soft acid shows covalent character, so Cd(II)–polymeric ligand interactions are more predominant than either Ni(II)– or Cu(II)–polymeric ligand interaction (which has ionic character).

CONCLUSIONS

By the results presented in this study we brought new evidence to light on the crystallinity of poly(MA-*alt*-AA) and its metal chelates. Cd(II), Cu(II), and Ni(II) ions affected the crystallinity of the copolymer, and pH is also important for the degree of crystallinity for the polychelates. Maximum crystallinity was observed in the Cd(II)–polychelate, a result that was also supported by gravimetric studies. At pH 6.36 mass values of obtained polychelates demonstrated the following order: poly(MA-*alt*-AA)/Cd^{2+} > poly(MA-*alt*-AA)/Cu^{2+} > poly(MA-*alt*-AA)/Ni^{2+} and degree of crystallinity values demonstrate the same order.

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