Stability Constants of Polymer-Bound Iminodiacetate-Type Chelating Agents with Some Transition-Metal Ions

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ABSTRACT: A chelating vinyl monomer, glycidyl methacrylate (GMA)–iminodiacetic acid (IDA), was formed by the reaction between GMA and IDA. Three polymeric chelating agents, PGMA–IDA, PGMA–IDA-co-methyl acrylate (MA), and PGMA–IDA-co-acrylamide (AAm), were also synthesized. Acid dissociation constants and stability constants of these chelating agents with Ni(II), Zn(II), and Co(II) were determined by means of potentiometric titration and ultraviolet–visible spectrophotometry, respectively. The values of K_{a1} and K_{a2} of all the polymeric chelating agents were smaller than those of GMA–IDA. The stability constants of all the polymeric chelating agents were larger than those of GMA–IDA. Increasing the MA content within PGMA–IDA-co-MA affected the stability constant only slightly. A proper molar ratio of AAm in PGMA–IDA-co-AAm, stability constants was 30–60 times greater than that of GMA–IDA. However, as the molar content of AAm increased, the stability constant of PGMA–IDA-co-AAm decreased. The results obtained in the polymer system are explained in terms of the polymer's stereo and entanglement structure, the neighboring effect, and the hydrophobic/hydrophilic nature of MA or AAm. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1986–1994, 2002

Key words: copolymerization; radical polymerization; UV-vis spectroscopy; FT-IR

INTRODUCTION

Polymer–metal complexes have been extensively studied and successfully employed in nuclear chemistry, wastewater treatment,[1,2] gas–membrane separation,[3] organic synthesis catalysts,[4,5] and many other fields.[6] As in low-molecular-weight compounds, a polymer ligand must also donate unshared electrons to the metal ion to form metal–ligand bonds. Accordingly, numerous conventional polymers, including poly-(acrylic acid),[7–9] poly(methacrylic acid),[10] poly(vinyl pyridine),[11–13] and poly(vinyl imidazole),[14,15] have formed polymer–metal complexes. However, to increase coordinating ability, in most studies, researchers have either introduced low-molecular-weight ligands (e.g., thiol —SH) to the polymer chain (or side chain)[16–19] or grafted a chelating vinyl monomer (e.g., acrylic acid) to form a copolymer.[20,21] To improve the chelating ability, many researchers have attempted to synthesize a new vinyl monomer that possesses a coordinating site.[22,23] These chelating vinyl monomers are extremely beneficial in polymeric molecule design for homopolymerization and for copolymerization with other vinyl monomers.

Among the multidentate ligands, ethylenediaminetetraacetic acid (EDTA) forms strong 1:1 stable complexes with various metal ions in a single step. However, it is difficult to introduce EDTA into polymer chains or vinyl monomers. With regard to the chemical structure, two aminopolycarboxylates of EDTA can share six pairs of electrons with a single metal ion. Furthermore, iminodiacetic acid (IDA) possesses one aminopolycarboxylate and provides a reactive secondary amine hydrogen to react with alternate functional groups. Hence, IDA can be more easily introduced to the side chain of a polymer or vinyl monomer. Therefore, this article presents an attempt to prepare a chelating vinyl monomer via an epoxy group reaction of glycidyl methacrylate (GMA) with IDA. This reaction has two primary advantages. Firstly, GMA is a commercial industrial material, which is cheaper than any other vinyl monomers that possess an epoxy ring in the side chain. Secondly, it produces a vinyl monomer that can be polymerized by the addition of initiators or copolymerized with other vinyl monomers. Accordingly, the synthesis of poly(GMA–IDA) hydrogels or copolymerization with other monomers have been obtained in our laboratory and successfully used in metal ion recovery and organic catalyst synthesis.[1,2,5]

To our knowledge, only limited studies have concentrated on the introduction of an iminodiacetate chelating group into a polymer that contains GMA to remove metal ions from an aqueous solution.[24–26] Including our previous studies, all the studies have focused on the adsorption capacities and efficiencies of metal ions. The developments of chelating polymers
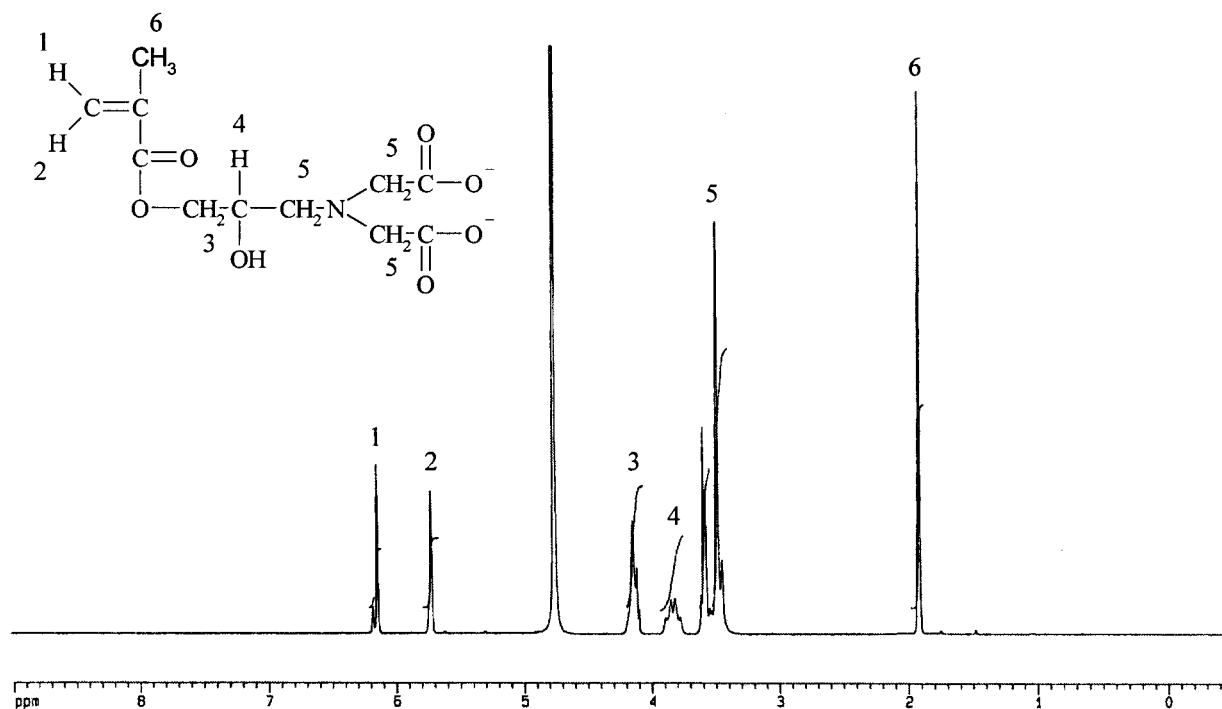
Figure 1 ^{1}H-NMR spectrum of GMA–IDA in D$_2$O.

contribute greatly to industrial wastewater treatments. However, investigations into complex stability constants and coordination numbers between metal ions with chelating agents have generally been disregarded. These factors indicate strong and stable complexes between chelating agents and various metal ions.[23] They are also essential for determining potential reuses of polymer–metal complexes and for judging the selectively of a specific metal ion within a mixture to, in turn, isolate vital metal ions from wastewater.[11]

In this study, the stability constants and coordination numbers of GMA–IDA and its homopolymer complexes with Ni(II), Zn(II), and Co(II) were examined. The effect of polymer chains modified through copolymerization with methyl acrylate (MA) and acrylamide (AAm) on their complex formation was also investigated.

EXPERIMENTAL

Materials

GMA and MA were purified by distillation under reduced pressure. Potassium persulfate (KPS) and AAm were recrystallized by standard procedures before use. The concentrations of Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$, and Zn(NO$_3$)$_2$ solutions were determined by titration with EDTA solution. EDTA was standardized against a standard solution of calcium(II) ion by standard procedures. IDA (Fluka, Geneva, Switzerland), potassium hydroxide, and potassium chloride (Showa,

Tokyo, Japan) were used as received. All the reagents were certified as ACS reagent grade.

Synthesis of GMA–IDA

Before the reaction of IDA with GMA, we neutralized IDA with KOH solution to keep carboxylic acid from reacting with epoxy ring of GMA. Dipotassium salt of IDA solution (1M, 300 mL) was added slowly to GMA at a 1:1 molar ratio. The mixture was kept at 65°C for 1 h under powerful stirring. When the reaction finished, the oil–water mixture changed to a transparent water phase. We purified the yellow liquid of the monomer by pouring into acetone and dissolving in distilled water repeatedly. The product obtained was confirmed as the monomer by an elemental analyzer (HERAEUS CHN-O rapid analyzer, Germany), by a gas chromatography-mass spectrometry (GC-MASS) (VG-70-2505, England), and in addition, by ^{1}H-NMR (Bruker AC-400; D$_2$O solvent, Billerica, MA), as shown in Figure 1.

Polymerization and copolymerization

PGMA–IDA, PGMA–IDA-co-MA, and PGMA–IDA-co-AAm were prepared by solution polymerization with KPS (0.3%) as an initiator by standard procedures. Chemical compositions of copolymers were determined by elemental analysis of C, H, and N and, in addition, by the acid–base titration of aminopolycar-
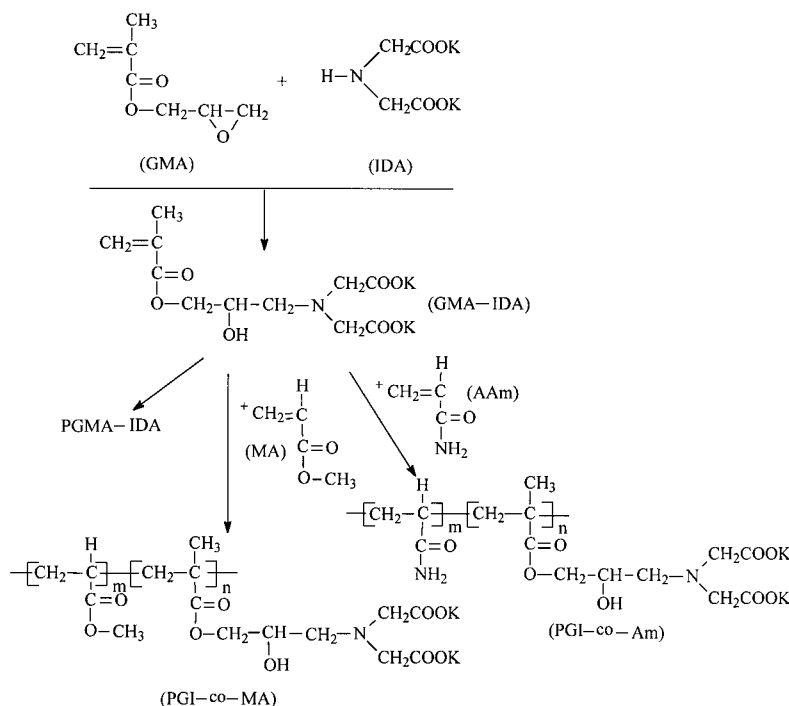
Scheme 1 Polymerization process of the polymeric chelating agents.

boxylic acid of the copolymers. The basic polymerization process is shown in Scheme 1.

Measurements

Viscosity measurements were carried out in an Ubbelohde viscometer (Schoot, Mainz, Germany) in 0.1M LiBr/H_2O solution at 25°C. The interactions between the aqueous solution of metal ions and chelating agents were measured with an ultraviolet–visible (UV–vis) spectrophotometer (Jasco 7850, Tokyo, Japan). The cells had an optical path length of 10 mm. The characteristic functional groups of chelating agents and their complexes were analyzed with a Fourier transform infrared (FTIR) spectrophotometer (Bio-Rad FIS-40A). We prepared the sample by mixing it with KBr and pressing to form pellets.

Determination of acid dissociation constants and stability constants

We carried out all titrations under a high-purity nitrogen atmosphere to remove carbon dioxide. A TOA HM-30S pH meter (Tokyo, Japan) was used to measure pH values and titration end points. All the measurements were carried out at ionic strength (I) = 0.1M (KCl) and 25±0.2°C. We calculated the coordination numbers of the polymer–metal complexes by applying a continuous variation method[27] with a UV–vis spectrophotometer. Acid dissociation constants of polymers were calculated by the modified Henderson–Hasselbach equation:[28]

$$pH = pK_{a1} - S_1\log[(1 - \alpha)/\alpha] \tag{1}$$

$$pH = pK_{a2} - S_2\log[(2 - \alpha)/(\alpha - 1)] \tag{2}$$

TABLE I
Chemical Compositions of Polymeric Chelating Agents Calculated from Elemental Analysis

Polymer	Elemental analysis			Molar fractions in copolymer		Brief symbol of polymer
	N(wt %)	C(wt %)	H(wt %)	GMA–IDA	MA (or AAm)	
PGMA–IDA				1	0	PGMA-IDA
PGMA–IDA-co-MA	3.81	38.41	4.39	0.838	0.162	PGI-co-MA15
	3.62	39.26	4.52	0.707	0.293	PGI-co-MA30
	3.22	41.07	4.79	0.508	0.492	PGI-co-MA50
	2.77	43.13	5.09	0.358	0.642	PGI-co-MA65
PGMA–IDA-co-AAm	4.55	38.06	4.37	0.844	0.156	PGI-co-Am15
	5.26	38.64	4.49	0.697	0.303	PGI-co-Am30
	8.31	41.21	5.03	0.348	0.652	PGI-co-Am65

where α is the degree of neutralization, S_1 and S_2 are constants, and K_{a1} and K_{a2} are the first and second acid dissociation constants, respectively. Determination of the stability constants by use of potentiometric titration was done according to the Bjerrum method.[29]

RESULTS AND DISCUSSION

Polymerization

In this study, a GMA–IDA monomer and three polymeric chelating agents, PGMA–IDA, PGMA–IDA-co-MA, and PGMA–IDA-co-AAm, were synthesized. Table I presents the chemical compositions of these polymers. The intrinsic viscosities of the polymers are illustrated in Table II. We carried out all of the measurements in $0.1M$ LiBr/H$_2$O solutions to eliminate hydrogen bonding of carboxylic acids or hydroxyl groups. Larger values of intrinsic viscosities in Table II indicate that all the polymeric chelating agents possessed higher molecular weights. Water-soluble chelating polymer concentrations are expressed as monomeric units of GMA–IDA in moles per liter. Furthermore, Table I also lists the symbols for polymers (last column).

Spectrophotometric measurements

Figure 2 displays the UV–vis spectra of Ni^{2+} and a PGI-co-Am15–Ni^{2+} complex solution. Absorption spectra of PGI-co-Am15 and chelating polymers were also measured; however, there was no absorbance band in the region (450–850 nm). A maximum Ni^{2+} absorption value was obtained at 720 nm. As PGI-co-Am15 was added to the Ni^{2+} solution, the maximum value shifted to shorter wavelengths (625 nm), and the absorbance at 625 nm enlarged to approximately sevenfold larger than that of the Ni^{2+} solution. This empirical result indicates that PGI-co-Am15 possessed chelating ability with Ni^{2+}. Several theories (e.g., crystal field theory)[29] have been advanced to account for these properties. The absorption spectra of both GMI–IDA and other chelating polymers with metal ions were similar to those in Figure 2. However, when a polyacrylamide solution was mixed with metal ions,
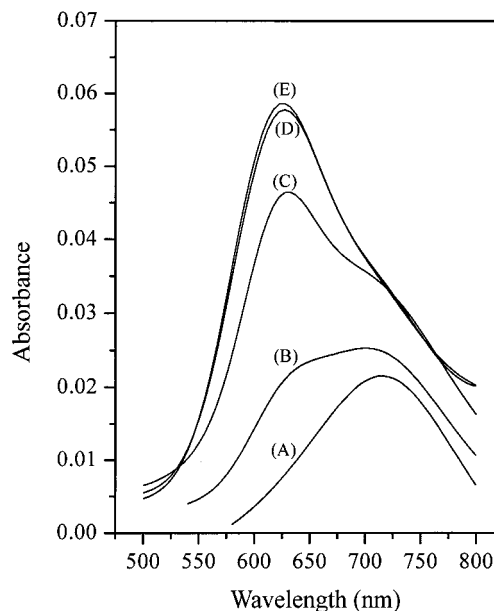

Figure 2 UV–vis spectra of Ni^{2+} and PGI-co-Am15–Ni^{2+} complex: (A) $0.012M$ Ni^{2+} solution, (B) $0.24M$ Ni^{2+} solution (5 mL) + $0.006M$ PGI-co-Am15 (5 mL), (C) $0.24M$ Ni^{2+} solution (5 mL) + $0.015M$ PGI-co-Am15 (5 mL), (D) $0.24M$ Ni^{2+} solution (5 mL) + $0.021M$ PGI-co-Am15 (5 mL), and (E) $0.24M$ Ni^{2+} solution (5 mL) + $0.024M$ PGI-co-Am15 (5 mL).

there was no shift or enlargement in the UV–vis spectrum. That is, there was no chelating ability between polyacrylamide and the metal ions.

Figures 3 and 4, for example, illustrate the FTIR spectra of PGI-co-MA15, PGI-co-Am15 and their polychelates, respectively. Guide lines have been placed to aid in comparison of the spectra and the major absorption bands. The shift in C=O stretching frequency of the ligand on chelation gives the most important information regarding the structure change.[30] The absorption band at 1723 cm^{-1} was caused by the stretching vibrations of the ester carbonyl groups. A strong band existed at 1635 cm^{-1}, which was ascribed to both the C=O of carboxylate salts (—COO$^-$) and amide groups. In the spectra of polychelates, the band at 1635 cm^{-1} shifted to lower frequencies with increasing the amounts of metal ions. This phenomenon indicated a strong correlation between metal ions and carboxyl group oxygens or amide carbonyl groups.[22,25,31–33] In sum, the UV–vis and FTIR spectra confirmed that the reactions between metal ions and GMA–IDA, PGMA–IDA, or copolymers were complex ones and were not due to physical adsorption.

Determination of the average coordination number

In the continuous variable method, the maximum absorption values of the complex solution are employed to investigate coordination numbers between chelating agents with metal ions. The average coordination number (n) is defined as

TABLE II
Intrinsic Viscosities of PGMA–IDA, PGI-co-MA, and PGI-co-Am at 25°C

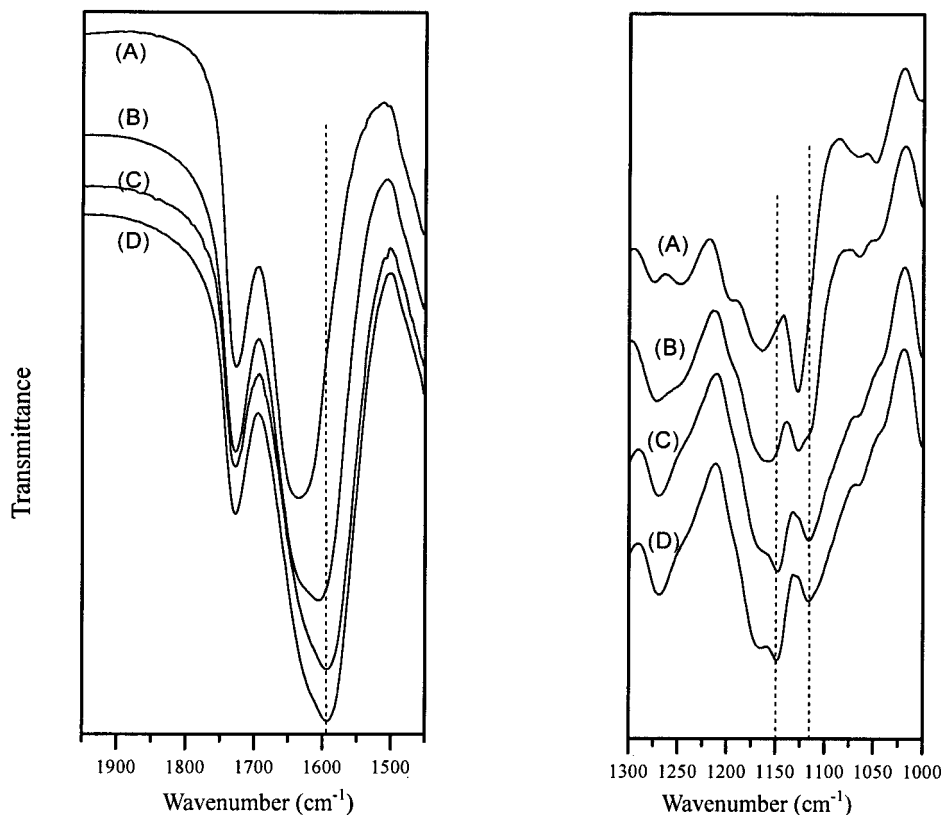| Chelating agent	Intrinsic viscosity (dL/g)
PGMA-IDA	0.688
PGI-co-MA15	0.500
PGI-co-MA30	0.498
PGI-co-MA50	0.497
PGI-co-MA65	0.495
PGI-co-Am15	0.615
PGI-co-Am30	0.620
PGI-co-Am65	0.622

Figure 3 FTIR spectra of PGI-co-MA15 and its polychelates: (A) spectrum of PGI-co-MA15 and spectra developed by the mixture of PGI-co-MA15 and Ni^{2+} at ratios of (B) 2:1, (C) 1:1, and (D) 1:1.25.

$$n = C_{AL}/C_{ML} \qquad (3)$$

where C_{AL} is the GMA–IDA concentration unit of the chelating agents that complexed with metal ions and C_{ML} is the metal ion concentration that complexed with GMA–IDA units of the chelating agents.

Figures 5 and 6 demonstrate the average coordination numbers between Ni^{2+} with PGI-co-MA15 or PGI-co-Am15, respectively, following the application of the continuous variable method. Various metal ions complexes with GMA–IDA, PGMA–IDA, and various PGI-co-MA compositions were similar to those presented in Figure 5. The average coordination number between these chelating agents with metal ions was 1:1. When various constitutions of PGI-co-Am were complexed with metal ions, they presented curves identical to that in Figure 6. Alternately, PGI-co-Am and metal ions had an average coordination of 1:1.13. As stated previously, polyacrylamide could not complex with metal ions, however, from these data, it seems that AAm units could improve the chelating capacity of copolymers. Analysis of FTIR spectra also provided the same information.

Consider Figures 3 and 4 again; Figure 3 shows the FTIR spectra of PGI-co-MA15 and its polychelates. Spectra of FTIR for the other PGI-co-MA copolymers were similar to this one. The absorption band at 1635 cm^{-1} shifted to 1604 cm^{-1} when 0.59 mmol of PGI-co-

MA15 was mixed with 0.3 mmol of Ni^{2+}. When the mixing ratio was 1:1, the band shifted to 1594 cm^{-1}. That is, the absorption band at 1635 cm^{-1} shifted to lower frequencies with increasing quantities of metal ions. The fact that frequencies of C=O absorption decreased indicated that metal ions formed complexes with carbonyl groups and the bonding of metal ions to carbonyl groups changed from covalent to ionic.[31–33] However, when excess metal ions were mixed with PGI-co-MA15, the absorption band still shifted to 1594 cm^{-1}. In other words, average coordination number between GMA–IDA units of the chelating agents with metal ions was 1:1. The other absorptions observed are presented in Table III, which were taken as further evidence for the chelate formation. Figure 4 depicts the FTIR spectra of PGI-co-Am15 and its chelates, and the data of absorption bands obtained are also presented in Table III. For the other PGI-co-Am chelating agents, FTIR spectra were similar to this one. As Ni^{2+} was added to PGI-co-Am15 by molar ratios of 1:2 and 1:1, the band at 1635 cm^{-1} shifted to 1604 and 1594 cm^{-1}, respectively. Apparently, when the quantities of Ni^{2+} were less than those of chelating agents, the shifts in absorption frequencies were similar to those observed for PGI-co-MA15, which could mean that both copolymers showed the same chelating behaviors. As excess Ni^{2+} was added to PGI-co-Am15, further shifts of absorption frequencies occurred. This
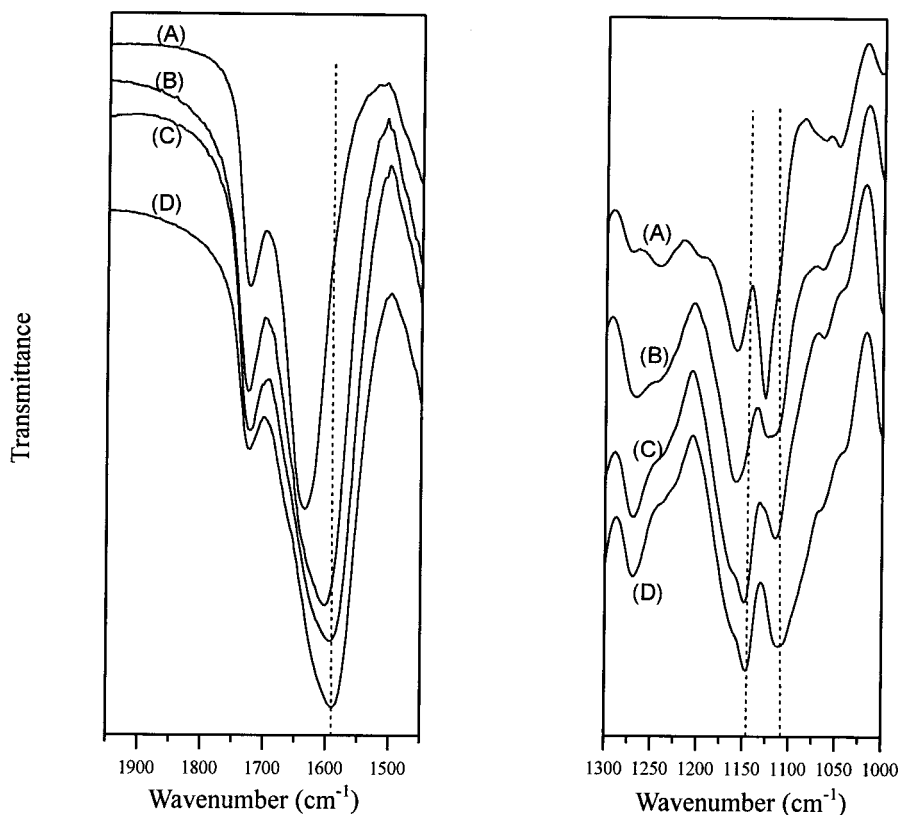
Figure 4 FTIR spectra of PGI-co-Am15 and its polychelates: (A) spectrum of PGI-co-Am15 and spectra developed by the mixture of PGI-co-Am15 and Ni^{2+} at ratios of (B) 2:1, (C) 1:1, and (D) 1:1.25.

result indicated that chelating capacity of PGI-co-Am15 was greater than that of PGI-co-MA15. That is, the average coordination number between PGI-co-Am copolymers with metal ions was greater than 1.

Regarding the chemical structure of amide, a resonance effect can be observed when the unpaired electrons on a nitrogen atom conjugate with carbonyl group (Scheme 2) because an amide group can more
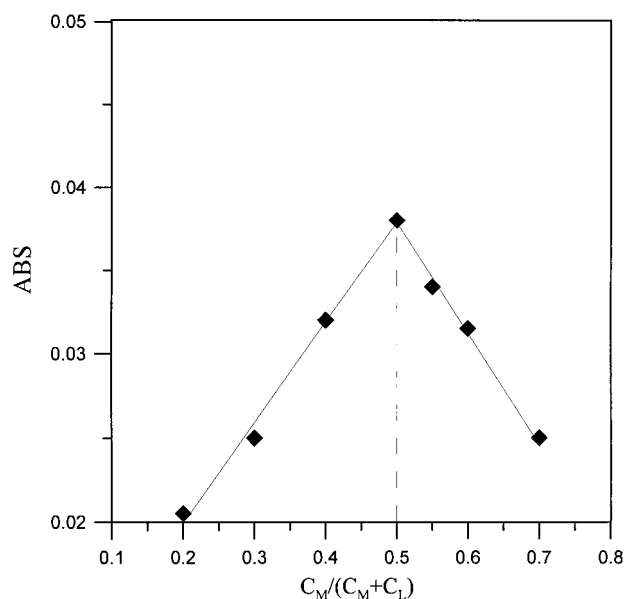

Figure 5 UV–vis absorption values (λ_{max} = 625 mm) of PGI-co-MA15–Ni^{2+} complex solution at different $C_M/(C_M + C_L)$ ratios. C_M and C_L represent the initial concentrations of Ni^{2+} and chelating polymer, respectively.

Figure 6 UV–vis absorption values (λ_{max} = 625 mm) of PGI-co-Am15–Ni^{2+} complex solution at different $C_M/(C_M + C_L)$ ratios. C_M and C_L represent the initial concentrations of Ni^{2+} and chelating polymer, respectively.
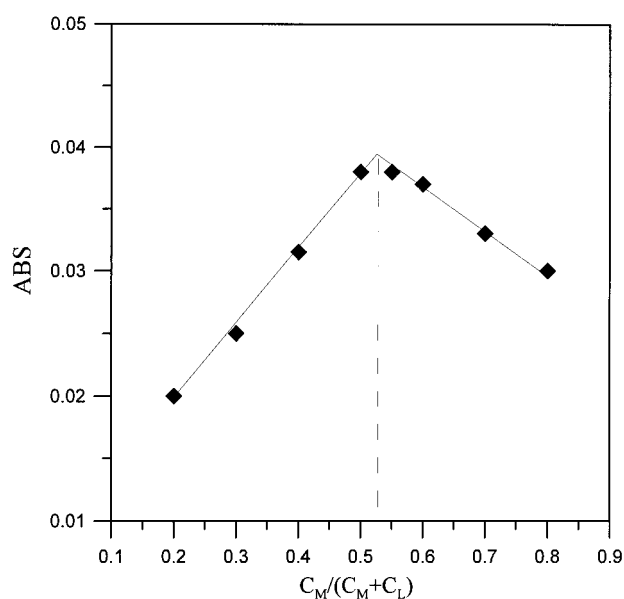
TABLE III
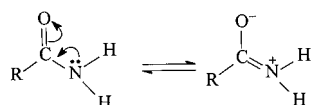**FTIR Spectra Data of PGI-co-MA15 and PGI-co-Am15 and Their Metal Chelates**

| | C=O | | | |
Chelating agent	Ester	Carboxylate salts or amide	C—OH	C—N
PGI-co-MA15	1723	1635	1163	1127
PGI-co-MA15–Ni(II) (2:1)	1723	1604	1155	1124
PGI-co-MA15–Ni(II) (1:1)	1723	1594	1148	1116
PGI-co-MA15–Ni(II) (1:1.25)	1723	1594	1148	1116
PGI-co-Am15	1723	1635	1163	1127
PGI-co-Am15–Ni(II) (2:1)	1723	1604	1154	1123
PGI-co-Am15–Ni(II) (1:1)	1723	1594	1148	1115
PGI-co-Am15–Ni(II) (1:1.25)	1723	1591	1146	1112

easily accommodate a positive charge than an ester group does. However, a metal ion may in fact react with many ligands to form a complex. For polyacrylamide, it was more difficult to provide many partial negative oxygen atoms to metal ions at the same time. That is, there was no complexation reaction between polyacrylamide and metal ions. For PGI-co-Am, the GMA–IDA unit possessed one iminodiacetate chelating group and provided three electron pairs to a metal ion to form a complex. A hydroxyl group of a secondary alcohol in GMA–IDA could also share one electron pair with a metal ion. In other words, a metal ion could easily form a coordination complex with an iminodiacetate chelating group, and the shifts of the FTIR absorption bands of PGI-co-MA were similar to those of PGI-co-Am. However, for PGI-co-Am, C—O$^-$ of amide and —OH of GMA–IDA may have reacted with excess metal ions to form complexes. This reaction decreased the quantities of C=O groups (1635 cm^{-1}), C—OH groups (1163 cm^{-1}), and C—N groups (1127 cm^{-1}) and produced further shifts in FTIR spectrum.

Determination of acid dissociation constants

Figure 7 illustrates typical titration curves for GMA–IDA. Notably, titration curves for the other remaining polymeric chelating agents were similar to this one. First-derivative plot analysis and the same plot were employed to determine the first and second end points, respectively. In addition, we used conductivity analysis to confirm our experimental results. Notably, all titration curves had two inflection points, which corresponded to a dibasic acid.

Figures 8 and 9 depict modified Henderson–Hasselbach plots, that is, pH versus $\log[(1 - \alpha)/\alpha]$ for the first acid dissociation constant and pH versus $\log[(2$

$- \alpha)/(\alpha - 1)]$ for the second acid dissociation constant for GMA–IDA, PGMA–IDA, and PGI-co-Am15, respectively. Similar plots were also obtained for various PGI-co-MA and PGI-co-Am constitutions. Table IV lists the estimated pK_{a1}, pK_{a2}, S_1, and S_2 values. It was evident that these polymeric chelating agents values were greater than those of GMA–IDA (monomer). This result has been supported by many authors for carboxylic acid monomers (e.g., methacrylic acid) that were converted to polyacids.[10,28,34] This is due to the stereo structure of the polymer, which induces the carboxyls to be close in proximity. Furthermore, the electrostatic attraction of the neighboring carboxylate group impedes proton removal.[35] Moreover, there was no noticeable difference in the pK_{a1} of all polymeric chelating agents; however, as the content of MA (or AAm) copolymers increased, S_1 increased. As the molar ratios of MA (or AAm) copolymers increased, the pK_{a2} and S_2 values decreased slightly and stably. This may have been due to the incorporation of MA (or AAm) with GMA–IDA, forcing GMA–IDA mono-
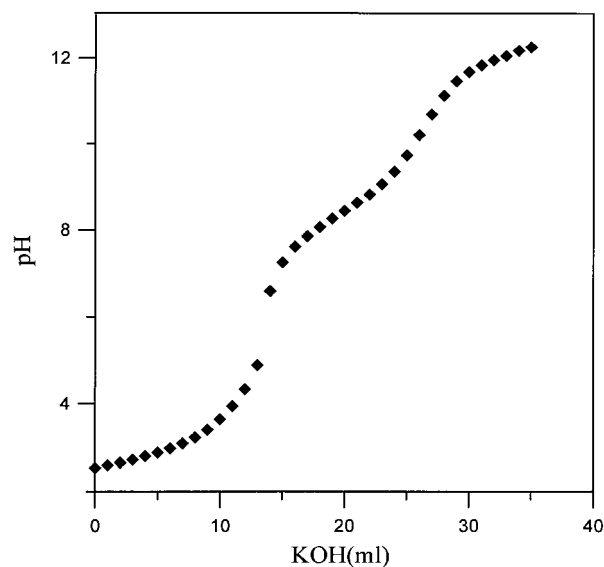

Figure 7 Titration of 0.0290M GMA–IDA with 0.0428M KOH at $I = 0.1M$ and 25°C.

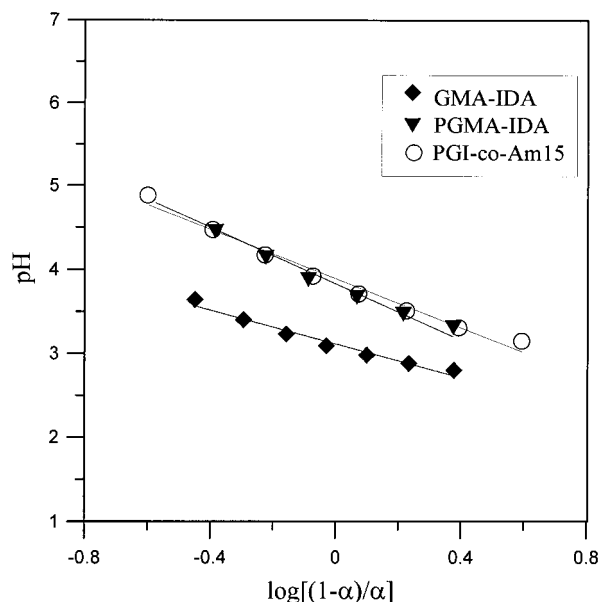**Scheme 2** Resonance of an amide group.

Figure 8 Modified Henderson–Hasselbach plots of pH versus $\log[(1 - \alpha)/\alpha]$.

meric units far apart. The electrostatic attraction of the neighboring carboxylate groups between GMA–IDA monomeric units decreased, and the ionization behavior emulated that of the GMA–IDA monomer.

Determination of stability constants

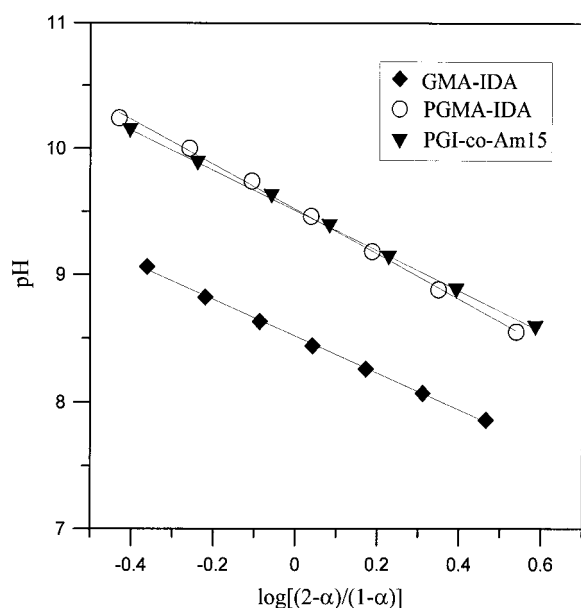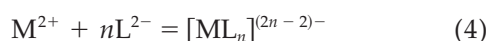For a typical complex that formed a reaction herein

$$M^{2+} + nL^{2-} = [ML_n]^{(2n-2)-} \qquad (4)$$

Figure 9 Modified Henderson–Hasselbach plots of pH versus $\log[(2 - \alpha)/(1 - \alpha)]$.

TABLE IV
First and Second Dissociation Constants (pK_{a1} and pK_{a2}) and S_1 and S_2 for GMA–IDA, PGMA–IDA, PGI-co-MA, and PGI-co-Am at $I = 0.1$ M and 25°C

Chelating agent	pK_{a1}	S_1	pK_{a2}	S_2
GMA–IDA	3.06	1	8.5	1.44
PGMA–IDA	3.81	1.46	9.54	1.76
PGI-co-MA15	3.87	1.47	9.47	1.58
PGI-co-MA30	3.88	1.55	9.41	1.50
PGI-co-MA50	3.81	1.64	9.31	1.48
PGI-co-MA65	3.86	1.76	9.20	1.43
PGI-co-Am15	3.77	1.67	9.53	1.57
PGI-co-Am30	3.77	1.74	9.31	1.53
PGI-co-Am65	3.86	1.76	9.10	1.43

where M^{2+} is the metal ion (Ni^{2+}, Co^{2+}, or Zn^{2+}), L^{2-} is the deprotonated form of the GMA–IDA moiety of the chelating polymer, and n is the average coordination number.

The stability constant (formation constant) can be expressed as

$$K_s = \frac{C_{ML}}{C_M C_L^n} \qquad (5)$$

where C_{ML}, C_M, and C_L represent the concentrations of the metal chelate, the metal ion, and the deprotonated form of the GMA–IDA moiety, respectively. Thus, according to the Bjerrum method, Table V presents K_S values for all chelating agents with metal ions. As with the dissociation constant, stability constants of all the polymeric chelating agents exceeded that of GMA–IDA (monomer). Restated, the polymer–metal complex was more stable than the small-molecule complex was. As stated previously, the polymers had a stereo and entanglement structure, which could, in turn, cage the metal ions and stabilize the intrachain and interchain coordination bonds.

The stability constant of PGMA–IDA was compared to that of PGI-co-MA. It was evident that increasing

TABLE V
Stability Constants of Ni^{2+}, Zn^{2+}, and Co^{2+} with GMA–IDA or Polymeric Chelating Agents at $I = 0.1$ M and 25°C

	Log K_s		
Chelating agent	Ni^{2+}	Zn^{2+}	Co^{2+}
IDA[a]	8.13	7.24	6.94
GMA–IDA	8.29	7.83	7.63
PGMA–IDA	9.18	8.99	8.83
PGI-co-MA15	9.16	8.87	8.83
PGI-co-MA30	9.15	8.88	8.80
PGI-co-MA50	9.15	8.83	8.73
PGI-co-MA65	8.92	8.64	8.55
PGI-co-Am15	9.83	9.57	9.39
PGI-co-Am30	9.29	9.05	8.94
PGI-co-Am65	8.83	8.52	8.24

[a] Ref. 36.

the MA content within the PGI-co-MA only slightly affected the stability constant. For PGI-co-MA, the incorporation of MA with GMA–IDA forced the GMA–IDA chelating groups apart and decreased the stability constant. Notably, within the copolymer, the hydrophobic nature of PGI-co-MA increased with increasing MA content. That is, the water-soluble copolymers retained their stereo and entanglement structure with which to cage the metal ions. Hence, MA units did not cause remarkable changes in the stability constant. As the AAm molar content within PGI-co-Am increased, the stability constant decreased. This could be explained by three factors that affected the stability of polymer–metal complex:

1. AAm units improved the chelating capacity of copolymers, which stabilized the polymer–metal complex and increased the K_S value.
2. The presence of AAm in PGI-co-Am also forced the GMA–IDA chelating groups far apart and reduced the K_S value.
3. The hydrophilic nature of AAm enhanced PGI-co-Am solubility within water. Hence, water was a good solvent for PGI-co-Am, and the polymer chain extended fully. Thus, the stereo structure domain disappeared, and the K_S value decreased.

Table V reveals that PGI-co-Am15 chelates had the largest stability constants, and the K_S values were larger than those of GMA–IDA chelates by 30–60 times. This may be explained by the fact that factor 1 had a greater effect than factors 2 or 3 did. However, as the AAm increased, effects of factors 2 and 3 were more prevalent than that of factor 1. Thus, the stability constant decreased as PGI-co-Am15 > PGI-co-Am30 > PGI-co-Am65.

CONCLUSIONS

A vinyl monomer, GMA–IDA, was formed easily via a reaction between GMA and IDA. The UV–vis and FTIR spectra confirmed that GMA–IDA, PGMA–IDA, and their copolymers were all chelating agents. Due to the polymer's stereo and entanglement structure, which could cage metal ions, the stability constants of all the polymeric chelating agents were greater than those of GMA–IDA. Increasing the MA content within PGI-co-MA affected the stability constant only slightly. However, AAm units could improve the chelating capacity. Furthermore, a proper molar ratio of AAm in PGI-co-Am increased the stability constant. However, as the molar content of AAm increased, the stability constant decreased.

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