Detection of Lead Ion Binding on Bifunctional Chelating/Ion-Exchange Resins by Cross-Polarization/Magic-Angle Spinning Solid-State Nuclear Magnetic Resonance

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ABSTRACT: Solid-state nuclear magnetic resonance (S-NMR) can reveal much useful information, including conformations, stereoregularity, defect structures, and comonomer sequence. S-NMR is especially useful for revealing microstructural differences that can alter local polymer chains. A series of bifunctional chelating/ion-exchange resins, containing differing ratios of iminodiacetic acid to acetic acid, were synthesized. Cross-polarization magic-angle spinning (CP/MAS) ^{13}C-NMR was employed to measure conformation changes both before and after the bonding of ligands and lead ion adsorbed on bifunctional chelated/ion-exchange resins in this investigation. From the ^{13}C-NMR spectra, as the lead ion was adsorbed by the iminodiacetic acid chelating group, the motion of molecular chain would be inhibited and the resonance peaks of the carboxylate anion at 170 ppm would shift downfield. Compared to the FTIR results, the downfield shift of the resonance peaks indicated that the bonding of carboxylate anion and lead ion adsorbed displayed an ionic trend. Furthermore, the bonding of the carboxylic group and lead ion adsorbed changed from ionic to covalent as the chelating group in bifunctional/ion-exchange resins decreased. The linear relationship between the areas of those resonance peaks and the amount of lead ion adsorbed was obtained from the spectra fitting. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 919–928, 2002

Key words: heavy metal recovery; chelating polymer; solid-state NMR

INTRODUCTION

Over the past two decades researchers have gradually begun to characterize insoluble polymers, such as crosslinked polymer[1,2] and crystalline polyethylene,[3,4] by cross-polarization and magic-angle spinning (CP/MAS) ^{13}C-NMR, and these methods are now integral to polymer science. Compared to solution NMR, in which chemical shift anisotropy and the dipolar interactions averaged nearly zero, because of the rapid chain motion of the polymers, the spectra of solid-state NMR was more complex, because the chain motion is restricted by the polymer matrix and the high solution spectra can be observed only by rapid MAS to average the chemical shift anisotropy. Although the resolution of solid-state NMR is less than that for a solution, solid-state NMR

Table I Ratio of Chelating Group Contained in Bifunctional Ion-Exchange Resins

	—N(CH$_2$COO$^-$)$_2$ (mmol/g)	—RCH$_2$COO$^-$ (mmol/g)	—N(CH$_2$COO$^-$)$_2$—RCH$_2$COO$^-$
PIDA[a]	1.68	0	—
PIDA1	1.90	0.59	3.22
PIDA2	1.68	1.40	1.20
PIDA3	1.36	2.55	0.52
PIDA4	0.87	4.35	0.20
PAA[b]	0	7.55	0

[a] Copoly(glycidyl methacrylate-iminodiacetic acid sodium salt).
[b] Polymethacrylic acid.

reveals much useful information, including conformations, stereoregularity, defect structures, comonomer sequence, and so on. These microstructural differences produce changes in the average local polymer chain conformation, which are in turn manifested as different ^{13}C chemical shifts for the carbon atoms surrounding each unique microstructure.[5,6] For example, the amorphous carbons in semicrystalline polyethylene (PE) resonate 2–3 ppm upfield from the crystalline carbons, as reported by Earl et al.[4] Previous research by Natansohn[7] revealed that the carbonyl carbon will be shifted upfield following complexation.

Previous studies have synthesized the bifunctional chelating/ion-exchange resins, which contained various iminodiacetic acid and diacetic acid ligand ratios.[8] The bonding of the heavy metal ions and carboxylic acid group changed from covalent to ionic covalent in the infrared spectra when the quantity of iminodiacetic acid was increased in bifunctional chelating/ion-exchange resins. However, the resolution of the infrared spectra is inadequate for analyzing the conformation change of the polymer chain and the amount of lead ions adsorbed. Furthermore, all the bifunctional chelating/ion-exchange resins were crosslinked polymer,[9–11] and thus insoluble in organic solvent. Consequently, CP/MAS ^{13}C solid-state NMR was used herein to study the conformation and bonding of lead ions adsorbed by bifunctional chelating/ion-exchange resins series.

EXPERIMENTAL

Materials

The bifunctional chelating/ion-exchange resins were prepared by methacrylic acid and glycidyl methacrylate (Ferck Co. Ltd.) with iminodiacetic acid (Sigma Co. Ltd.). β,β'-Methylenebisacrylamide (Ferck Co. Ltd.) was used as crosslinking agent. The polymerization process was described in a previous study.[8] Table I shows the composition and abbreviated name of bifunctional chelating/ion-exchange resins.
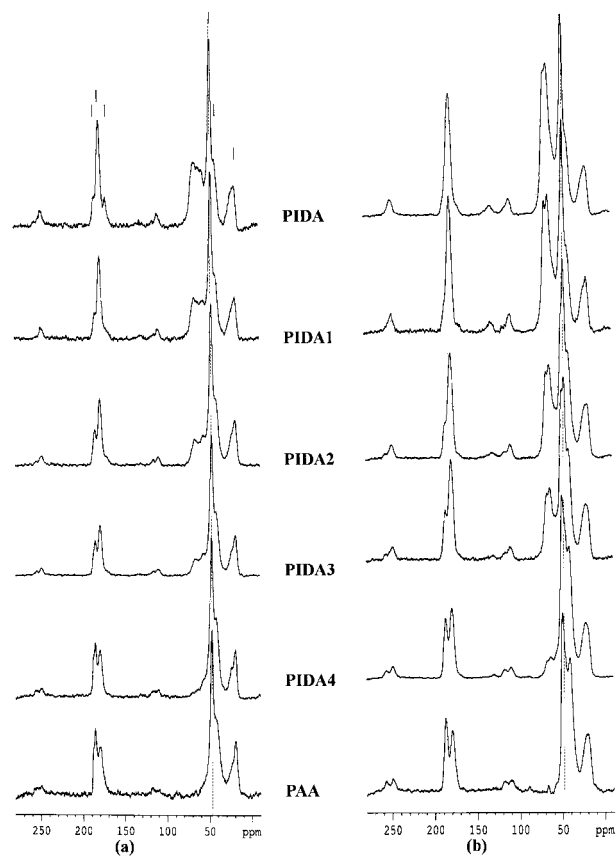

Figure 1 (a) CP/MAS ^{13}C-NMR spectra of bifunctional chelating/ion-exchange resins at various ratios of polymethacrylic acid contained. (b) CP/MAS ^{13}C-NMR spectra of bifunctional chelating/ion-exchange resins after lead ion adsorbed.
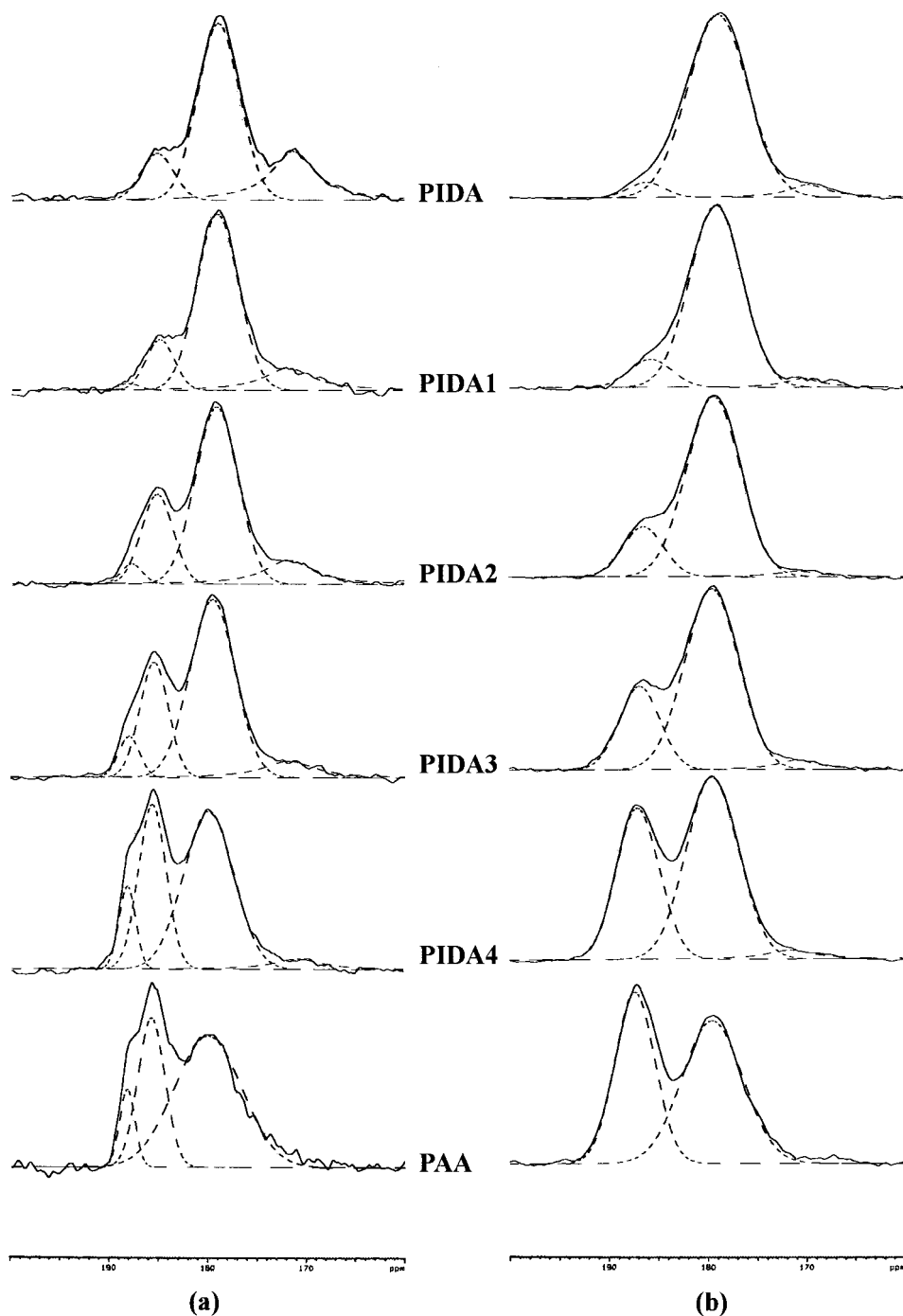
Figure 2 (a) Spectra fitting of carbonyl group in Figure 1(a). (b) Spectra fitting of carbonyl group in Figure 1(b).

Adsorption Experiment

A fixed amount of dry bifunctional chelating/ion-exchange resin (2 g) and 250 mL of metal ion [Pb(NO$_3$)$_2$; Ferck Co. Ltd.] solution was placed in a thermostated oscillation bath for 48 h for the isothermal adsorption experiment. The initiation concentration of Pb^{2+} in solution was in the range of 200 to 500 ppm, to prepare the different Pb^{2+} concentrations of bifunctional chelating/ion-exchange resins. After filtration, the concentration of lead ions was measured by an atomic adsorption spectrophotometer (AA model 932; GBC Co.
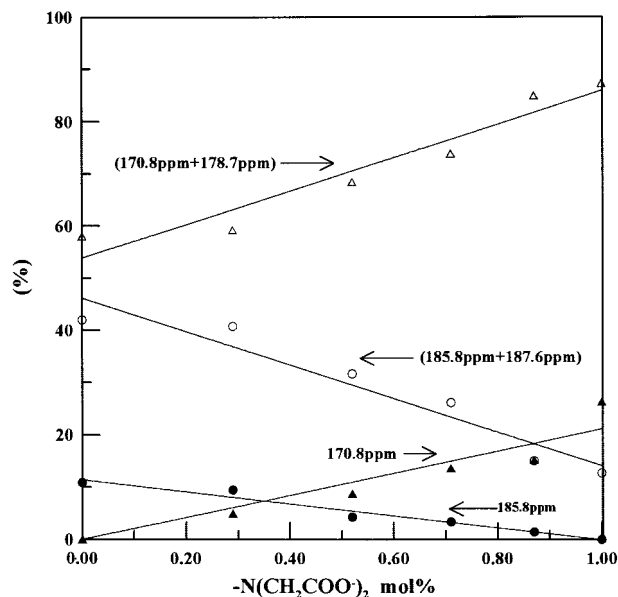
Figure 3 Relation of carbonyl resonance peak area to quantity of iminodiacetic acid contained in bifunctional chelating/ion-exchange resins from spectra fitting.

Ltd.). The amount of metal ions adsorbed q_e (mmol/g) was obtained by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{g}$$

where C_0 and C_e are the initial and equilibrium solution concentrations (mmol/L), respectively; V is the volume of solution (liter); and g is the weight of the bifunctional chelating/ion-exchange resin (g).
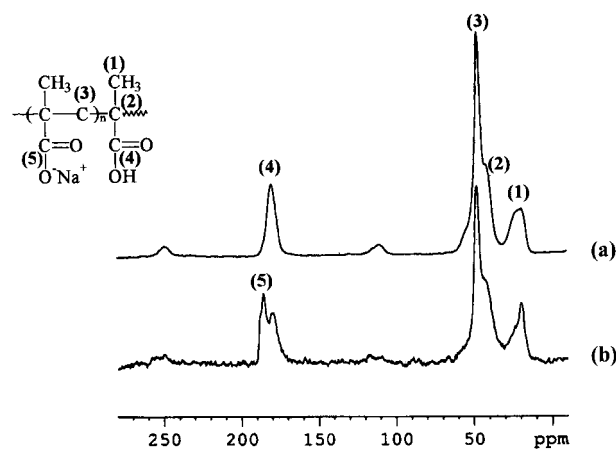

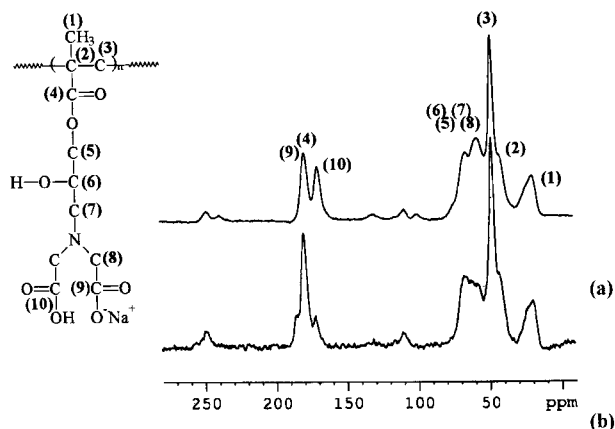**Figure 4** CP/MAS ^{13}C-NMR spectra of PAA in (a) acid type and (b) sodium salt type.

Figure 5 CP/MAS ^{13}C-NMR spectra of PIDA in (a) acid type and (b) sodium salt type.

IR Measurement

The characteristic functional groups of the products were analyzed by using an FTIR spectrophotometer (Bio-Rad Co. Ltd.). The samples were prepared by mixing with approximately 100 mg of dry, powdered KBr and pressed to form pellets.

Solid-State NMR Measurement

Solid-state NMR experiments were carried out on a Bruker AVANCE 400 spectrometer (Bruker Instruments, Billerica, MA) with an operating frequency of 100.61 MHz for the ^{13}C nucleus and
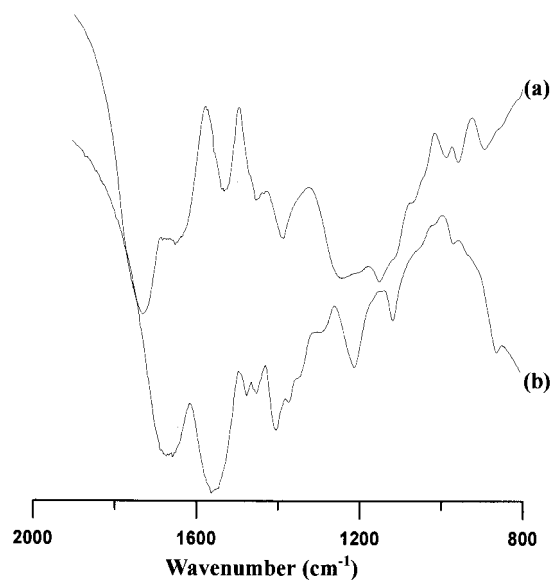

Figure 6 FTIR spectra of PAA in (a) acid type and (b) sodium salt type.
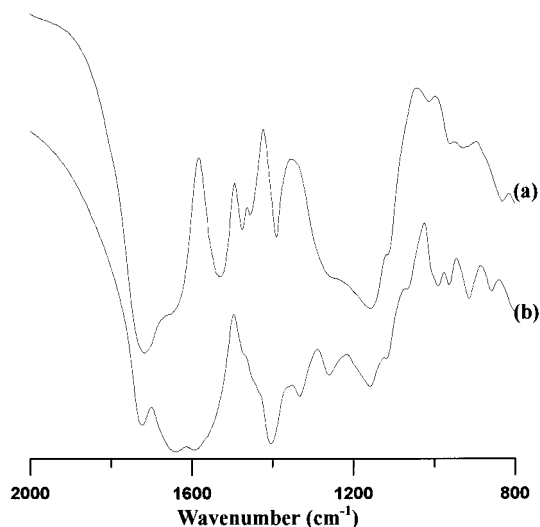
Figure 7 FTIR spectra of PIDA in (a) acid type and (b) sodium salt type.

Scheme 1 Type of bonding for lead ion absorbed by (a) PAA and (b) PIDA.

400.13 MHz for the ^{1}H nucleus at a constant temperature of 300 K throughout for all experiments. ^{13}C spectra were derived by performing the CP/MAS experiments, which use the Hartmann–Hahn transfer technique and proton decoupling during acquisition to enhance sensitivity of the spectra. Measurement parameters were as follows: recycle delay time, 5 s; 90° pulse width for ^{1}H excitation, 4 μm (which corresponds to a $B_{1,\text{H}}$

field strength of 62.5 kHz); contact time, 2 ms; acquisition time, 0.0336 s; spectral width, 303 ppm; number of scans, 560; spin rate, 7 kHz. The magic-angle spinning frequency of tetramethylsilane (TMS) was consistently used as the reference frequency for both the carbon and proton spectra.

RESULTS AND DISCUSSION

The CP/MAS ^{13}C-NMR Spectra of Bifunctional Chelating/Ion-Exchange Resins

Figure 1 presents the CP/MAS ^{13}C-NMR spectra of a series of bifunctional chelating/ion-exchange resins both before and after lead ion absorption. The resonance peaks at 19.3, 41.6, and 45.9 ppm were assigned to the methyl (–CH$_3$), quaternary carbon (–CR$_2$–), and methylene (–CH$_2$–) on the polymer chain for all bifunctional chelating/ion-exchange resins, respectively. The carbonyl (C=O) resonance peak in PIDA split into three, centered at 170.8, 178.7, and 185.2 ppm. This pattern was the result of the iminodiacetic acid in PIDA transforming into iminodiacetic acid sodium salt. The carbonyl resonance peaks in the polymethacrylic acid (PAA) sodium salt also split into three, but the peaks shifted downfield, to 180.3, 185.8, and 187.6 ppm. Chemical shifts for ^{13}C are influenced by substitutions as
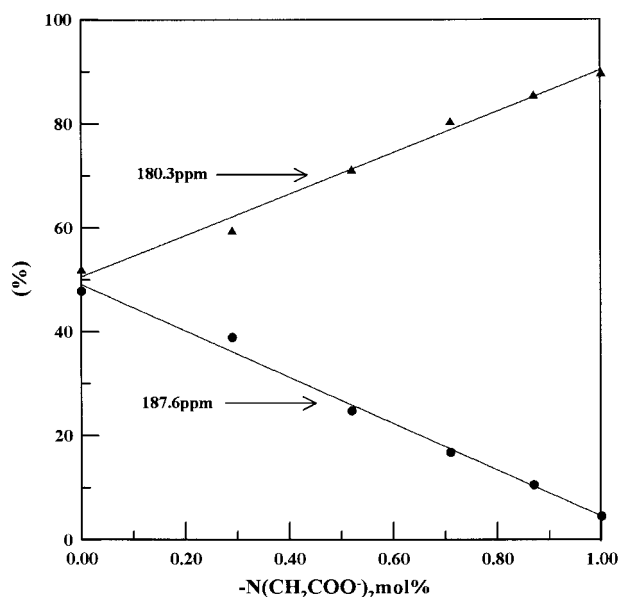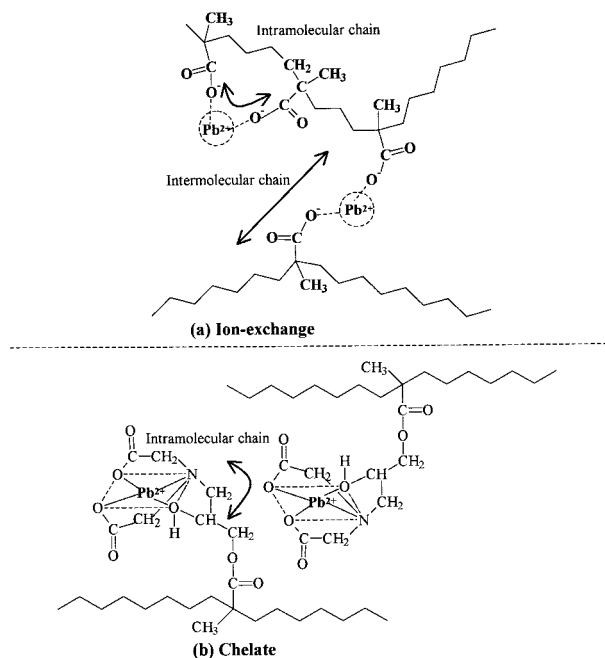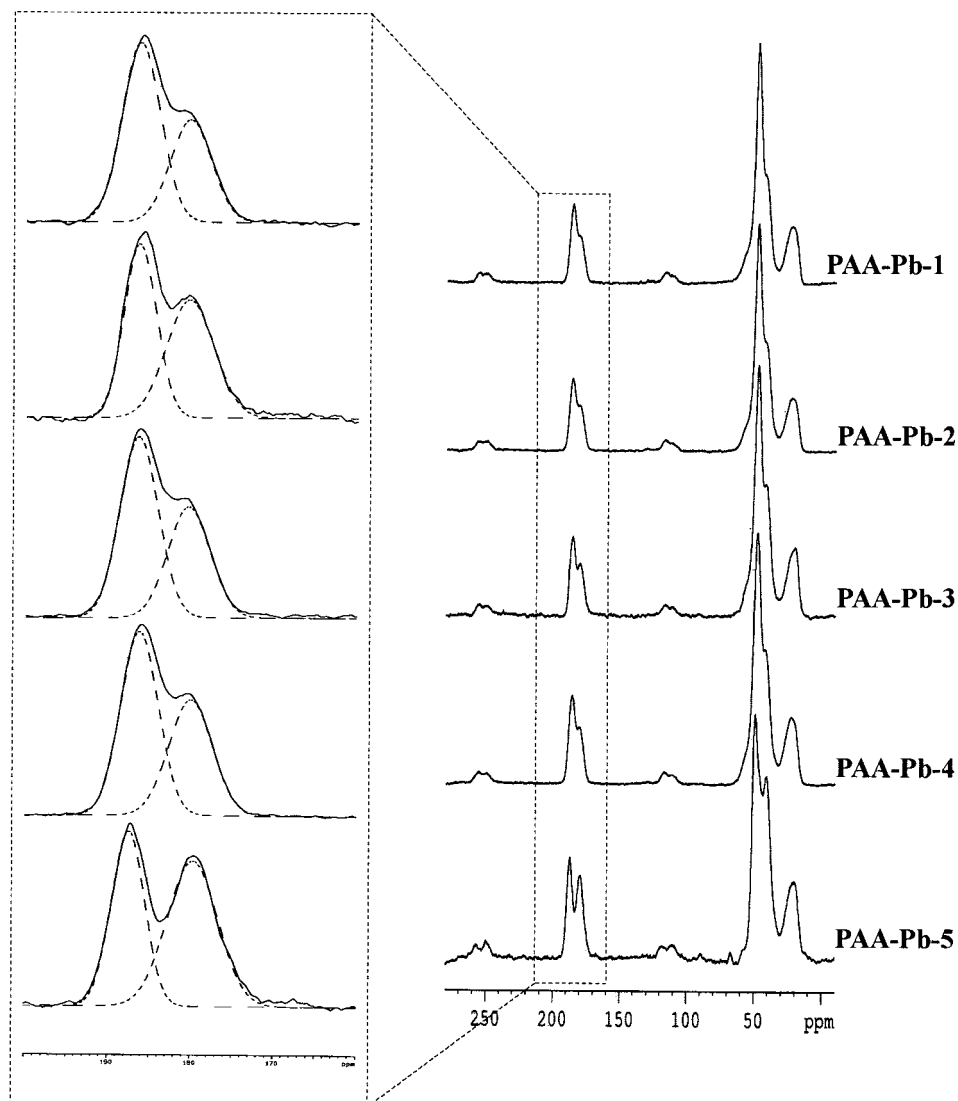

Figure 8 Relation of quantity of iminodiacetic acid within bifunctional chelating/ion-exchange resins to carbonyl resonance peak area after lead ion adsorbed.

Figure 9 CP/MAS ^{13}C S-NMR spectra of PAA in different amounts of lead ion adsorbed.

distant as the δ position. N-alkyation increases the upfield effect of the –NH group for carbonyl carbon of iminodiacetic acid in PIDA.[12] Consequently, the carbonyl resonance peaks shift downfield with decreasing quantity of iminodiacetic acid in bifunctional ion exchange resins, as illustrated in Figure 1(a). The correlation between the four resonance peaks of the carbonyl group in the range of 170.8–187.6 ppm corresponded to the ratio of PIDA/PAA in bifunctional chelating/ion-exchange resins. The area of the resonance peak at 170.8 ppm decreased, whereas that of the peak at 185.8 ppm increased with increased amount of PAA in the bifunctional chelating/ion-exchange resins. Following spectra fitting, the areas of the carbonyl resonance peaks at

170.8, 185.8, (170.8 + 178.7), and (185.8 + 187.6) ppm were linearly related to the quantity of iminodiacetic acid in the bifunctional chelating/ion-exchange resins, as illustrated in Figures 2(a) and 3. In fact, the CP/MAS methods are generally not used quantitatively because of differences in the efficiency of CP for carbon nuclei in different phases.[13] However, the quantity of the samples was controlled to install a rotor for NMR measurement. Consequently, an almost linear relation was obtained herein between the spectra peak and the size of the chelated group was obtained.

Meanwhile, the shoulder resonance peak of the carbonyl group downfield resembled the character resonance peak of sodium salt for all bifunc-
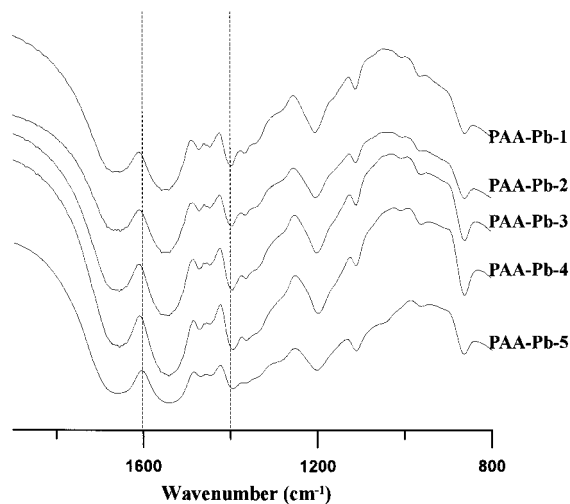
Figure 10 FTIR spectra of PAA in different amounts of lead ion adsorbed.

Figure 11 Areas of carbonyl resonance peak versus the amount of lead ion adsorbed curves for PAA.

tional chelating/ion-exchange resins because it did not appear in the acid type (Figs. 4 and 5) or the lead ions adsorbed type [Fig. 1(b)]. Furthermore, although the resonance peak at 170.8 ppm almost disappeared in PIDA, the intensity of the peak at 180.3 ppm was increased in PAA when the lead ion was adsorbed, as displayed in Figure 2(b). This pattern demonstrated that the bonding of the lead ion and the carboxylate group clearly differed for both PIDA and PAA. In fact, this finding was consistent with the FTIR spectra, as shown in Figures 6 and 7. Figures 6(a) and 7(a) show that the adsorption bands of carboxylate at around 1680 cm^{-1} shift to high frequency after both PIDA and PAA were immersed into 0.1M HCl aqueous, respectively. This shift of the FTIR

Table II   Quantity of Lead Ions Absorbed (mmol/g) in PIDA and PAA

	q_e (mmol/g)	pH[a]
PIDA–Pb-1	0.24	5.1
PIDA–Pb-2	0.42	4.6
PIDA–Pb-3	0.60	4.5
PIDA–Pb-4	0.90	4.2
PIDA–Pb-5	1.37	3.8
PAA–Pb-1	0.10	5.3
PAA–Pb-2	0.17	5.2
PAA–Pb-3	0.24	5.3
PAA–Pb-4	0.36	5.0
PAA–Pb-5	0.76	4.6

[a] The pH value at metal ion adsorption equilibrium.

adsorption bands could indicate that the bonding of carboxylate tends toward either an ionic or a covalent trend.[14] The higher the frequency of the adsorption band of the carboxylate group shift, the greater the covalent. Consequently, the resonance peaks in the ^{13}C-NMR spectra shifted upfield when the carboxylate group was anionic, but shifted downfield when the bonding was more covalent. Restated, the bonding of the lead ion and carboxylate group of iminodiacetic acid in PIDA was more ionic than the bonding of the lead ion and carboxylic group in PAA, based on FTIR and ^{13}C-NMR spectra as presented above. Using the same method of spectra fitting, after the lead ion was adsorbed, the quantity of iminodiacetic acid contained in bifunctional chelating/ion-exchange resins displayed a linear relation to the areas of the carbonyl's resonance peaks, at 180.3 and 187.6 ppm, as shown in Figures 2(b) and 8.

Change of Polymer Chain Conformation with Lead Ion Adsorption

Notably, the conformation of the –C–C– main chain in a series of bifunctional chelating/ion-exchange resins changed with lead ion absorption, as illustrated in Figure 1(b). The single resonance peak of methylene carbon peak at 45.9 ppm did not change in PIDA, but split into two when the proportion of PIDA to PAA fell to below 1.20
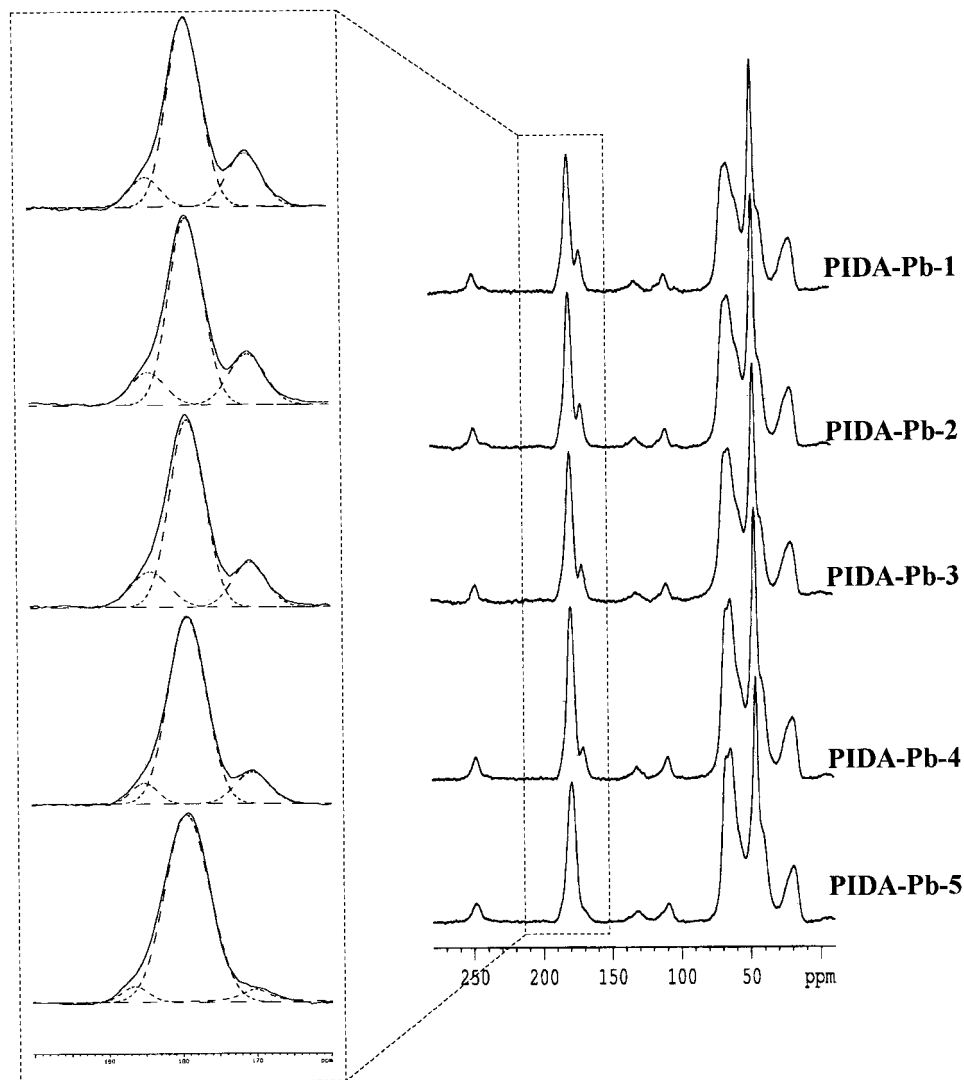
Figure 12 CP/MAS ^{13}C-NMR spectra of PIDA in different amounts of lead ion adsorbed.

(PIDA2) after the lead ion was adsorbed. Furthermore, the shift of the resonance peak clearly corresponded to the quantity of PAA in the bifunctional chelating/ion-exchange resins from the ^{13}C-NMR spectra [Fig. 1(b)]. Additionally, not only did the methylene carbon resonance peak at 45.9 ppm shift to 49.3 ppm in PAA but the intensity of the tertiary carbon peaks at 41.6 ppm also increased. However, the intensity of the tertiary carbon resonance peak at 41.6 ppm was correlated to the C—H dipolar coupling. Moreover, the carboxylic acid group was directly connected to the main chain of PAA, and both the diameter and the valence of the lead ion exceeded those of the sodium ion. Consequently, the intermolecular bonding was formed and the motion of the main

chains slowed as the lead ion was adsorbed in PAA. Meanwhile, the lead ion adsorbed in PIDA did not influence the conformation of the polymer's main chain because the side chain of iminodiacetic acid was sufficiently long, as illustrated in Scheme 1. Consequently, the effect of intermolecular bonding and C—H dipolar coupling on the main chain of the bifunctional chelating/ion-exchange resins would increase with PAA quantity.

Quantity Analysis for the Lead Ion Adsorbed in PAA and PIDA

Figures 9 and 10, respectively, display the ^{13}C-NMR and FTIR spectra for various amounts of
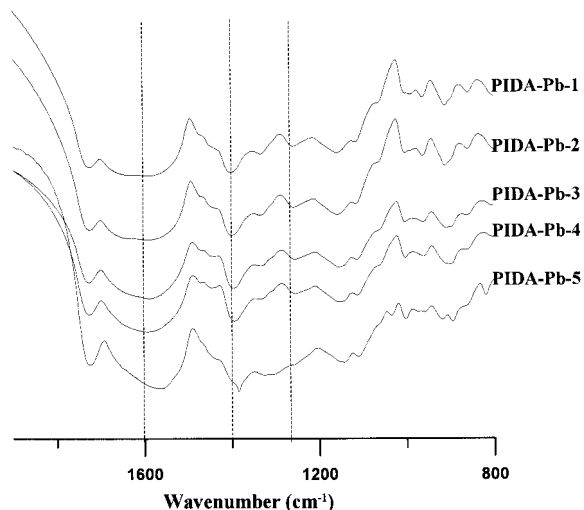
Figure 13 FTIR spectra of PIDA in different amounts of lead ion adsorbed.

lead ion adsorbed in PAA, whereas Table II lists the quantity of lead ion adsorbed. Once a small quantity of lead ions was adsorbed by PAA, the resonance peak at 187.7 ppm disappeared. Additionally, the area of the resonance peak at 180.3 ppm increased with the amount of lead ion adsorbed. However, no adsorption bands were found to shift on the FTIR spectra (Fig. 10) because FTIR had a lower resolution than that of NMR. On the other hand, the resonance peaks at 180.3 and (185.8 + 187.6) ppm were assigned to the C=O of carboxylic acid and carboxylate anion, respectively (Fig. 4). Additionally, a rapid rate of ion exchange was generally taken to indicate ionic bonds, whereas slow exchange rates were presumed to be the rule for essentially covalent linkages. Thus, the carboxylate anion preferred adsorbing lead ion to carboxylic acid in PAA, and the shoulder resonance peaks downfield should be the first to disappear when the lead ions were adsorbed. Furthermore, the bonding of lead ion–PAA was more covalent with the preceding result, causing the area of peak at 180.3 ppm to increase with the amount of lead ion adsorbed. Consequently, the peak area at 180.3 ppm was found to be linearly related to the amount of lead ion adsorbed from the spectra fitting, as illustrated in Figure 11.

Figures 12 and 13 present the ^{13}C-NMR and FTIR spectra of PIDA, respectively, for various levels of lead ion absorption. The resonance peak at 170.8 ppm would decrease with the amount of lead ion adsorbed from the ^{13}C-NMR spectra. Meanwhile, the resonance peak area at 170.8

ppm also expressed a linear relation to the amount of lead ion adsorbed from the spectra fitting, as illustrated in Figure 14. However, the upfield shift of the resonance peak corresponded to the ionic group described earlier. This result was more clearly evident from the FTIR spectra (Fig. 13). The absorption banding at 1400, 1550, and 1650 cm^{-1} shifted to lower frequency with increasing lead ion absorption, as illustrated in Figure 13. Unexpectedly, the area of the resonance peak at 185.2 ppm first increased and then decreased after the spectra fitting. However, the total areas of the resonance peaks at 178.7 and 185.2 ppm still followed a linear relationship to the amount of lead ion adsorbed, as presented in Figure 14. The special structure of chelate was perhaps the result of low lead ion absorption. On the other hand, the resonance peaks in the range of 60 to 70 ppm were marked for the iminodiacetic acid side chain of PIDA, and narrowed with the level of lead ion absorption, as illustrated in Figure 12. This result could be explained by the motion of the iminodiacetic acid chain, which was restrained by the lead ion–chelate formation. Restated, regardless of what kind of bonding occurred for the lead ion and carboxylate group, the lead ions would influence the motion of the adjacent carbon molecule.

To sum up, ^{13}C-NMR was found suitable herein for studying the bonding of adsorbed lead ion and the conformation of the polymer chain.
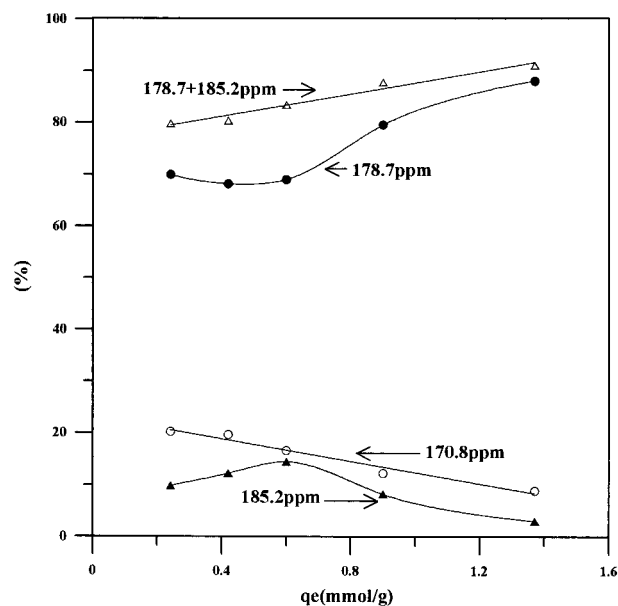

Figure 14 Areas of carbonyl resonance peak versus the amount of lead ion adsorbed curves for PIDA.

The bonding of the lead ion and carboxylate group tended toward a covalent bond in PAA (weak-acid ion-exchange resins). Additionally, the bonding of the lead ion and carboxylate group transformed from covalent to ionic with the increasing quantity of the chelating group in bifunctional chelating/ion-exchange resins from the ^{13}C-NMR and FTIR spectra. Another significant phenomenon was that the conformation of molecular chain changed when the bifunctional chelating/ion-exchange resins adsorbed the lead ion. In the present study, the areas of the resonance peaks of the carboxylate group in the bifunctional chelating/ion-exchange resins were linearly related to the amount of lead ions adsorbed.

CONCLUSIONS

CP/MAS ^{13}C-NMR is a highly effective means of investigating conformation and the bonding of lead ion and carboxylic groups in bifunctional chelating/ion-exchange resins. The ^{13}C-NMR spectra reveal that the motion of the molecular chain is inhibited and the resonance peak shifts when the lead ion is adsorbed by the carboxylate anion. The upfield shift of the resonance peak indicated that the bonding of the lead ion and carboxylate anion displayed an ionic trend. Moreover, the bonding of lead ion and carboxylate group changed from covalent to ionic with increased size of the chelating group in bifunctional chelating/ion-exchange resins. Finally, a linear relationship between the areas of those resonance peaks and the amount of lead ion adsorbed was shown to exist from the spectra fitting.

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