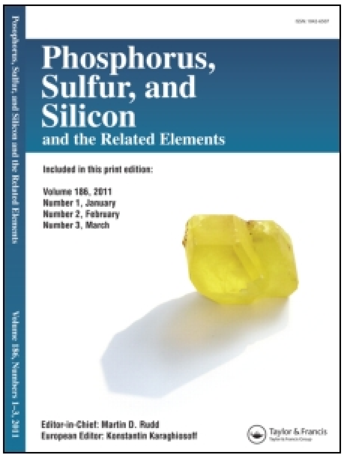

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Synthesis of New Polysiloxane-Immobilized Ligand System Di(amidomethyl)aminetetraacetic Acid

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Synthesis of New Polysiloxane-Immobilized Ligand System Di(amidomethyl)aminetetraacetic Acid

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A new chelating porous polysiloxane-immobilized tetraacetic acid ligand system has been prepared. This material was made by chemical modification of the iminodiacetic acid polysiloxane with thionyl chloride and diethyliminodiacetate, respectively. The polysiloxane functionalized with di(amidomethyl)aminetetraacetic acid of the general formula $P\text{-}(CH_2)_3N(CH_2C(O)N)_2(CH_2COOH)_4$ *[where* P *represents the polysiloxane backbones* $(Si{-}O{-}Si)_n$*] was characterized by Thermogravimetric Analysis (TGA) and FTIR spectra. The FTIR results proved that tetraacetic acid groups are successfully grafted onto the polysiloxane surface. This ligand system exhibits high potential for extraction of divalent metal ions (*Co^{+2}*,* Ni^{+2}*,* Cu^{+2}*, and* Zn^{+2}*) from aqueous solution.*

Keywords Diethyliminodiacetate ligand; iminodiacetic acid; metal uptake; polysiloxanes; polysiloxane-immobilized ligand systems

INTRODUCTION

Much attention has been dedicated to the chemical modification of a silica surface with silane coupling agents.[1–5] Recently, greater attention has been paid to the preparation of immobilized ligand systems using the sol-gel method.[6–8] The technological importance of this method is due to its simplicity in preparation.[8] These materials have been obtained through the hydrolysis and polycondensation of tetraethoxysilane $(EtO)_4Si$ and the appropriate silane coupling agent $(RO)_3SiX$ (where $R =$ Et or Me and $X =$ ligand containing group).[9–11] The halogen groups Cl and/or I atoms on the surface of polysiloxane

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were substituted by chemical modification using the appropriate ligand groups.[12–15] These polysiloxane immobilized ligand systems have several applications, including extraction of metal ions from aqueous solutions,[12–15] supports for a hydrogenation catalysts,[10] and chromatography, especially as stationary phases for the separation of metal ions.[13,16] These materials have good thermal and hydrolytic stability over the modified silica ligand systems and the more conventional organic resins.[17] The chelating resins containing iminodiacetic groups are widely used for the separation of heavy metal ions from complex matrices since they are able to chemisorb them steadily and selectively.[18–20] The iminodiacetic acid polysiloxane was made, characterized, and evaluated for its binding capacity for heavy metal ions.[13,21,22] In this work, a polysiloxane containing a diaminetertaacetic acid functionalized system was prepared and characterized by TGA and FTIR spectra. This material showed high potential for the uptake of metal ions from aqueous solutions.

EXPERIMENTAL

General Techniques

The carbon, hydrogen, chlorine, iodine, sulfur, and nitrogen analysis were carried out by the Microanalytical Service Laboratories in the Department of Chemistry (UMIST) UK.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) were carried out using a Mettler Toledo Star SW 7.01 analyzer in the range of 25–600°C under nitrogen. The tested polysiloxane material was 15 mg.

The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer AAnalyst-100 spectrometer.

The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR spectrometer using KBr disk in the range 4000 to 400 cm^{-1}.

All pH measurements were obtained using a HM-40 V pH meter.

All ligand samples were shaken in aqueous metal ion solutions using an ELEIA-Multi Shaker.

Reagents and Materials

The starting materials, which include tetraethylorthosilicate and 3-chloropropyltrimethoxysilane, were purchased from Aldrich chemical company and used without further purification. The iminodiacetic acid and triethylamine were also obtained from Aldrich Company and used without further purification. All solvents were dried before use. Diethylether was stored over sodium wire. Ethanol and methanol were dried and stored over molecular sieves. Toluene was dried over sodium wire and distilled before use. Metal(II) solutions of the appropriate concentration were prepared by dissolving the metal(II) chloride (analar grade) in deionized water. Different pH ranges were controlled using buffer solutions. pH (1–2) was obtained by using appropriate mixture of HCl (0.1 M)/KCl (0.1 M), while pH (3.5–6) by using appropriate mixture of acetic acid (0.1 M)/sodium acetate (0.1 M).

Synthesis

Synthesis of 3-Iodopropylpolysiloxane (P-I)

This was prepared using the sol-gel method as described previously[12] by adding 3-iodopropyltrimethoxysilane (14.5 g, 0.05 mol) to a stirred solution of tetraethylorthosilicate (20.8 g, 0.1 mol) in 20 cm^3 methanol, followed by 4.95 cm^3 of 0.42 M HCl as a catalyst. The mixture was stirred at room temperature for several hours. Gelation occurred after 24 h, the gel was left for 12 h and then dried at 100°C overnight. The material was crushed, sieved, and washed with successive portions of 50 cm^3 of water, methanol, and diethyl ether. Finally the product was dried for 12 h at 100°C. The elemental analysis are given in Table I.

TABLE I Elemental Analysis of Polysiloxane-Immobilized Ligand Systems

Sample	% C	% H	% N	% Cl	% I	% S	C/N
P-I							
Expected*	10.5	1.8			37.2		
Found	9.3	2.5			30		
P-DEIDA							
Expected**	22.6	3.4	2.4		0.0		11.0
Found	24.8	5.0	2.7		1.5		10.7
P-IDAA							
Expected**	18.2	2.6	3.0	0.0			7.2
Found	18.1	3.8	2.9	6.3			7.4
P-IDACl							
Expected**	15.2	1.5	2.5	12.8		0.0	7.1
Found	15.4	2.1	2.9	12.0		2.5	6.1
P-DATA							
Expected**	39.7	4.8	5.4	0.0		0.0	8.5
Found	32.9	6.3	6.1	6.6		2.0	6.4
P-DATAA							
Expected**	27.2	3.8	6.3	0.0		0.0	5.0
Found	19.3	3.3	4.1	3.9		1.5	5.5

*The expected values are based on assuming 100% reaction silane agents.

**The expected values are based on the found values of the previous step.

Synthesis of Iminodiacetic Acid Polysiloxane (P-IDAA)

This ligand system was prepared as previously described[13,21] using three steps reactions as follows:

1. Preparation of Diethyliminodiacetate (DIDA). The diethyliminodiacetate (DIDA) was prepared as described previously[7] by treatment the iminodiacetic acid with ethanol in the presence of thionyl chloride.
2. Immobilization Step. Diethyliminodiacetate polysiloxane was prepared by adding diethyliminodiacetate (9.45 g, 0.05 mol) to 10 g of iodopolysiloxane in 50 cm^3 of toluene. The mixture was stirred and refluxed at 95°C. The product was filtered off and washed with 0.025 M NaOH, water, methanol, and diethyl ether, then dried *in vacuum* oven (0.1 torr) at 90°C for 12 h. The elemental analysis for the diethyliminodiacetate polysiloxane is given in Table I.
3. Hydrolysis Step. Polysiloxane immobilized diethyliminodiacetate (5.0 g) was hydrolyzed by refluxing the ligand system with 150 cm^3 of 5.0 M HCl for 6 h with stirring. The solid material was then filtered and washed with 0.025 M NaOH aqueous solution, water, methanol, and diethyl ether. The material was dried in vacuum oven (0.1 torr) at 90°C for 12 h. The elemental analysis for the iminodiacetic acid polysiloxane is given in Table I.

Synthesis of Iminodiacylchloride Polysiloxane (P-IDACl)

Iminodiacetic acid polysiloxane (4.0 g, 0.03 mol) was refluxed with an excess of thionyl chloride (0.552 mol) for 32 h at 80°C. The mixture was dried *in vacuum* to remove SO_2. The solid product was filtered, washed with 50 cm^3 petroleum ether, and then dried *in vacuum* (0.1 torr) for 3 h. The elemental analysis are shown in Table I.

Synthesis of Di(ethylamidomethyl)aminetetraacetate Polysiloxane (P-DATA)

Diethyliminodiacetate (10.58 g, 0.028 mol) was added to stirred mixture of iminodiacylchloride polysiloxane (1.0 g) in 30 cm^3 toluene and triethylamine (2.0 g, 0.015 mol)). The mixture was stirred and refluxed at 90°C for 60 h. The mixture was filtered and washed, with successive portions of 30 cm^3 of methanol and diethylether. The solid product was dried *in vacuum* (0.1 torr) at room temperature for 2 h. The analytical data for the resulting product are presented in Table I.

Synthesis of Di(amidomethyl)aminetetraacetic Acid Polysiloxane (P-DATAA)

A known amount of the functionalized di(ethylamidomethyl)-aminetetraacetate polysiloxane (5.0 g) was refluxed with 25 cm^3

hydrochloric acid (5 M) at 100°C for 24 h. The mixture was cooled to room temperature and filtered. The product was washed with successive portions of 30 cm^3 of water, methanol, and diethylether. The material was then dried *in vacuum* (0.1 torr) at room temperature for 3 h. The elemental analysis are given in Table I.

Metal Uptake Experiments

A 100 mg of functionalized polysiloxane-immobilized ligand system was shaken with 25 cm^3, 0.02 M of aqueous solution of the appropriate metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) using 100 cm^3 polyethylene bottles. Determination of the metal ion concentration was carried out by allowing the insoluble complex to settle and an appropriate volume of the supernatant was withdrawn using a micropipette then diluted to the linear range of the calibration curve for each metal. The metal ion uptake was calculated in mmole of M^{2+}/g ligand. Each study was performed at least in triplicate. Metal uptake was examined at different time and pHs.

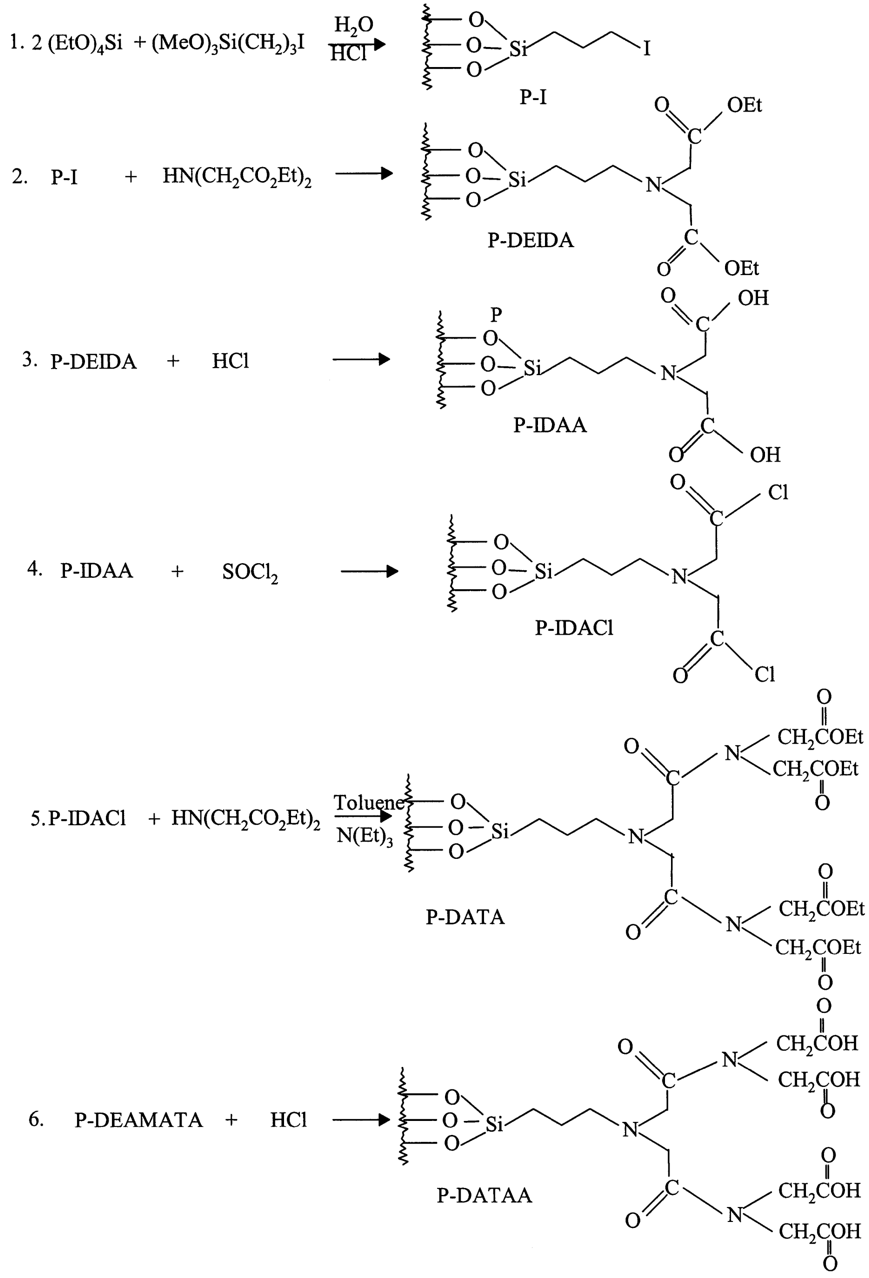
RESULTS

Synthesis

The immobilized-polysiloxane di(amidomethyl)aminetetraacetic acid ligand system was made by chemical modification of iodopolysiloxane through a multistep synthetic reaction as given in Scheme 1.

The iodopolysiloxane (P-I) was prepared as described previously[12] by the hydrolytic polycondensation of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3I$ (Scheme 1, step 1).

The immobilized diethyliminodiacetate was prepared by replacement the iodine atoms by diethyliminodiacetate molecules (Scheme 1, step 2) as described previously.[21] The results of elemental analysis show that most of the iodine atoms were replaced by the diethyliminodiacetate functional groups (Table I). The analytical data of the polysiloxane immobilized diethyliminodiacetate (P-DEIDA) showed an increase of carbon, nitrogen, and hydrogen percentages upon treatment of the iodopolysiloxane with diethyliminodiacetate. The slightly higher carbon, hydrogen, and nitrogen percentages than the expected (Table I) is probably due to some unreacted diethyliminodiacetate trapped into the silica pores The resulting solid diethyliminodiacetate polysiloxane was then hydrolyzed efficiently with hydrochloric acid (Scheme 1, step 3). The elemental analysis of the iminodiacetic acid polysiloxane (P-IDAA) showed a decrease of the carbon and hydrogen percentages after the



SCHEME 1 Synthetic steps for the preparation of di(amidoimethyl)-aminetetraacetic acid.

hydrolysis process (Table I). This was evident from the FTIR spectra discussed later.

The iminodiacylchloride polysiloxane (P-IDACl) was obtained by the reaction of the iminodiacetic acid polysiloxane with excess of thionyl chloride (Scheme 1, step 4). The immobilized-polysiloxane di(ethylamidomethyl)aminetetraacetate (P-DATA) was made by the reaction of iminodiacylchloride polysiloxane with diethyliminodiacetate (Scheme 1, step 5). The elemental analysis (Table I) for the di(ethylamidomethyl)aminetetraacetate polysiloxane showed an increase of carbon and nitrogen percentages and a decrease of chloride percentage, compared with that of the P-IDACl immobilized system, upon treatment the iminodiacylchloride polysiloxane with diethyliminodiacetate groups. This was also evident form the FTIR spectra discussed later. The immobilized di(ethylamidomethyl)aminetetraacetate was then hydrolyzed with HCl to produce the immobilized di(amidomethyl)aminetetraacetic acid ligand system (P-DATAA) (Scheme 1, step 6).

FTIR Spectra

The FTIR spectra for the polysiloxane-immobilized ligand systems P-I, P-DEIDA, P-IDAA, P-IDACl, P-DATA, and P-DATAA, are shown in Figure 1. The IR spectra show three characteristic regions at 3100–3500 cm^{-1}, 1600–1750 cm^{-1}, and 950–1200 cm^{-1} due to υ(OH), υ(C═O), and υ(Si─O) stretching vibrations, respectively. These assignments agreed well with previous IR investigations of similar systems.[23–25] The spectrum of iodopolysiloxane (Figure 1(a)) was used as background and to examine the effect of replacement of iodine by the functional groups.

The IR spectrum for diethyliminodiacetate polysiloxane ligand (P-DEIDA) (Figure 1(b)) showed a strong absorption band at 1747 cm^{-1}, due to the ester υ(C═O) stretching vibration. In the hydrolyzed product, two absorption bands at 1740 cm^{-1} and 1629 cm^{-1} are observed (Figure 1(c)) due to υ(C═O) and δ(OH) vibrations, respectively.

The IR spectrum for the iminodiacylchloride polysiloxane (P-IDACl) (Figure 1(d)) showed a strong absorption band at 1731 cm^{-1}, due to the acylchloride υ(COCl) stretching vibration. The absorption peak at 1629 cm^{-1} of δ(OH) vibration of the acid form had disappeared.

The IR spectrum for the di(ethylamidomethy)aminetetraacetate polysiloxane ligand system P-P-DATA, (Figure 1(e)) showed the same pattern in the range 1500–1750 cm^{-1} as that of P-DEIDA. The spectrum of the ester form (Figure 1(e)) showed two characteristic peaks at 1640 cm^{-1} and 1749 cm^{-1} that were assigned to the δ(OH) and the

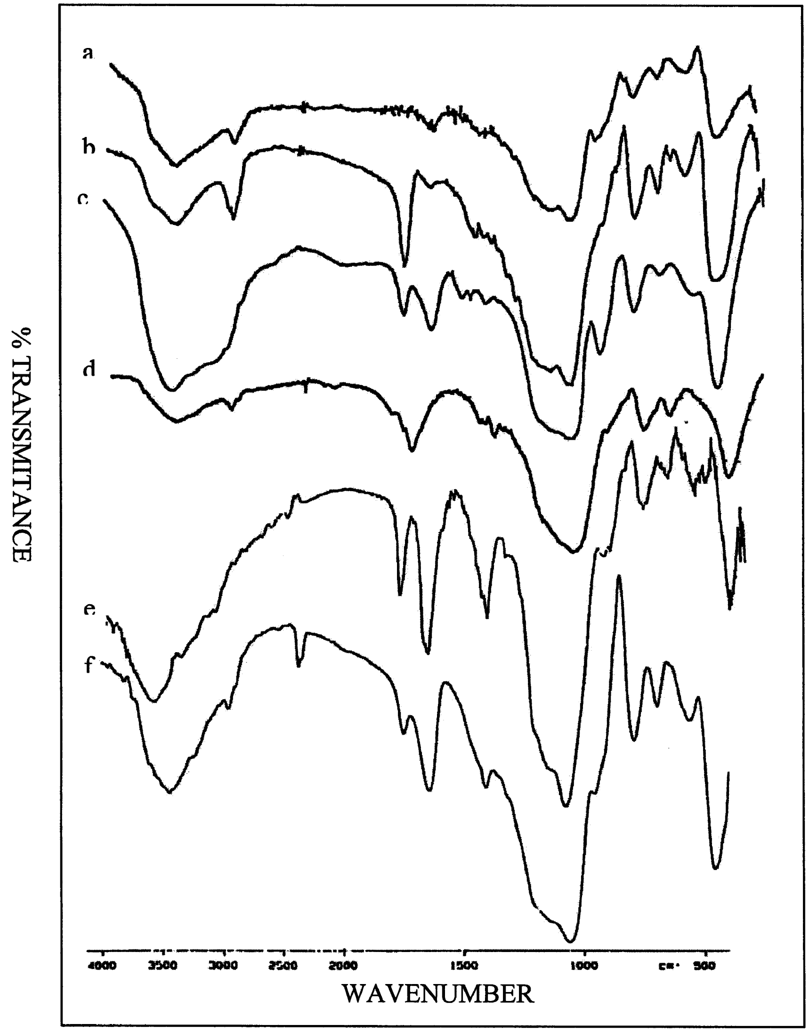


FIGURE 1 FT-IR spectra of (a) 3-iodopropylpolysiloxane P-I, (b) diethyliminodiacetate polysiloxane P-DEIDA, (c) iminodiacetic acid polysiloane P-IDAA, (d) iminodiacylchloride polysiloxane P-IDACl, (e) di(ethylamidomethyl)aminetetraacetate polysiloxane P-DATA, and (f) di(amidomethyl)aminetetraacetic acid polysiloxane P-DATAA.

ester υ(CO) vibrations, respectively. Figure 1(f) showed an increase in the intensity of the υ(OH) peak and a decrease of υ(Si—O) region upon treatment with HCl. The strong peak at 1500 cm^{-1} is probably due to a υ(C—N) vibration.

Thermal Analysis

TGA and DTG were examined for the free polysiloxane immobilized ligand system (P-DATAA) and its copper(II) complex (15 mg was used). The results are shown in Figures 2 and 3, respectively.

The thermograms show four DTG peaks, which are explained by a four-stage degradation process. In case of P-DATAA (Figure 2) the first peak at 65°C where the ligand system lost 9.5% of its initial weight, was attributed to loss of physisorbed water and alcohol from the pore system.[26–28] The second peak was observed at 180°C, the immobilized ligand system lost 3.8% of its weight. This was attributed to further loss of water and alcohol trapped in the bulk. The third broad peak in the range of 250–450°C was due to further loss of 11.2% weight of the polymer which was probably due to cleavage and degradation of the organofunctional group bound to the silicon atoms.[26–28] The DTG curve also exhibited a fourth broad peak at 520°C, corresponding to a 9.6% weight lost due to condensation of the hydroxyl groups that remain in the polymer, forming siloxane bonds (dehydroxylation).[26–28] The thermal analysis showed that the total weight lost from the P-DATAA was 34.8%.

The thermogram of the Cu(II) complexed of P-DATAA (Figure 3) is very similar to the free form in which four peaks were observed at 65°C (9.7% weight lost), 180°C (5.4% weight lost), 340°C (8.5% weight lost), and 450–600°C (6.5% weight lost). The total weight lost from the

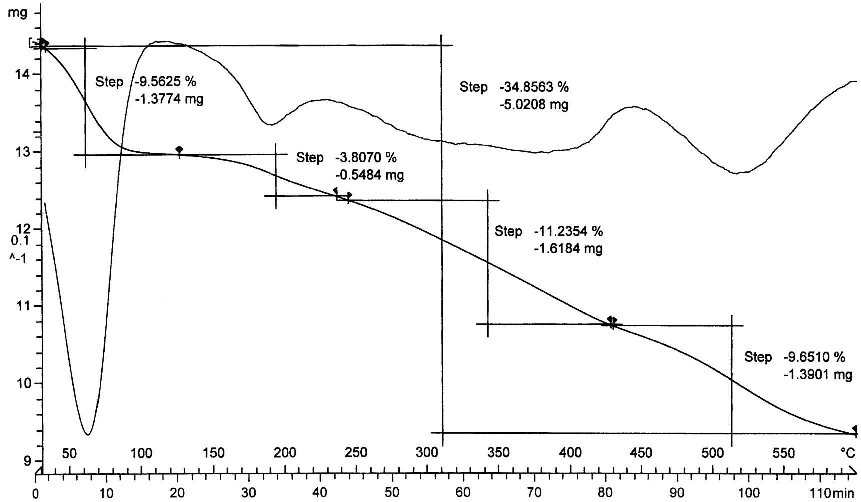


FIGURE 2 Thermogravimetric analysis of P-DATAA.

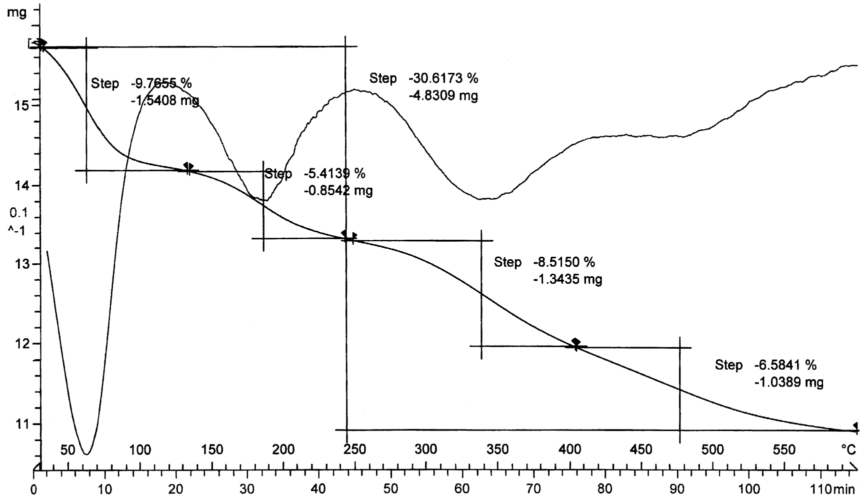


FIGURE 3 Thermogravimetric analysis of Cu(II)-P-DATAA complex.

complex form is 30.6%, which was lower than that lost from the free ligand system.

Metal Uptake

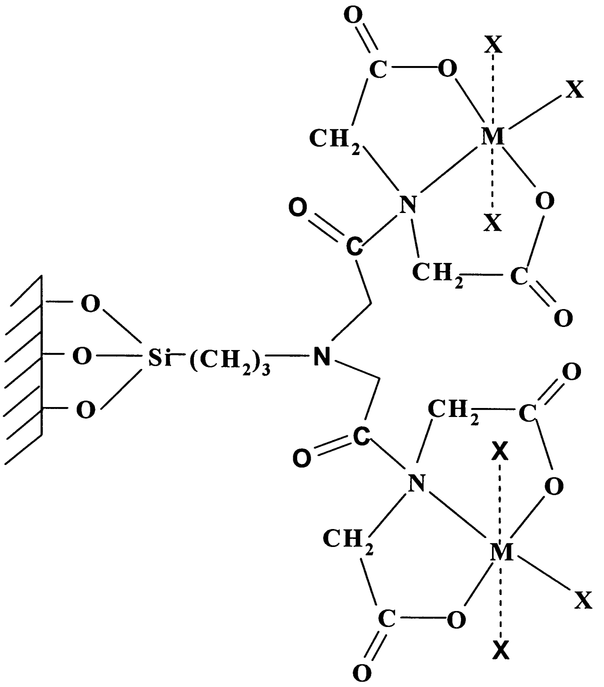
The metal-ion uptake capacity (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) was determined by shaking the functionalized ligand system (P-DATAA) with buffered solutions. The maximum metal uptake capacities by the immobilized ligand system as mmol M^{2+}/g ligand are in Table II.

The maximum metal uptake was calculated by subtracting the remaining mmole of metal ions in the used solution from the original mmole added to 1 g sample of (P-DATAA) at equilibrium. Maximum capacity was occurred after 48 h of shaking time.

The elemental analysis of N of the immobilized tetraacetic acid ligand system (P-DATAA) was found to be (4.1%, 2.9 mmol N/g ligand). There are three N atoms per 1 ligand, so, there is nearly 1.00 mmol ligand per 1.0 g polymer. It is possible to suggest that 2:1 metal-to-ligand complexes are expected for all metal ions as given in Scheme 2.

TABLE II Maximum Metal Uptake Capaceties (mmol m^{2+}/g Ligand)

Metal ion	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Maximum uptake (mmol M^{2+}/g ligand)	2.15	2.30	2.46	2.00



Where, $X=Cl^-$ or H_2O, $M = Co^{2+}$, Ni^{2+}, Cu^{2+} or Zn^{2+}

SCHEME 2 M(II) complexes of P-DATAA.

Effect of Shaking Time

Measurements of metal uptake capacities of P-DATAA were carried out at different time intervals. Figure 4 shows the uptake of copper ions as a function of time; similar results were observed for the other metal ions. It is shown that the metal ion uptake increased as a function of shaking time and reached equilibrium nearly 24 h after the maximum uptake was obtained.

Effect of pH

The effect of the pH on the uptake of divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) by P-DATAA is shown in Figure 5. The results showed an increase of metal ion uptake with increasing pH values and reached a maximum at a pH 5.5.

DISCUSSION

Several studies have focused on the preparation and characterization of polysiloxane-immobilized ligand systems.[9–17] In this work, the

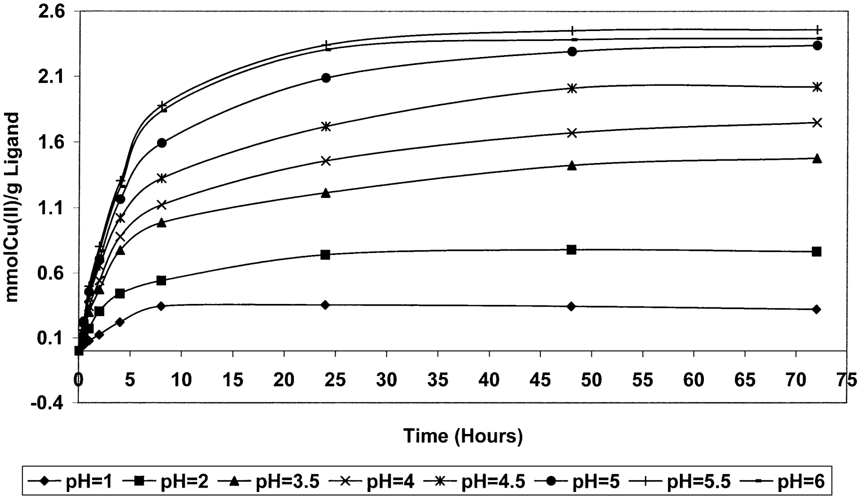


FIGURE 4 Uptake of Cu(II) ions by P-DATAA versus time.

immobilized tetraacetic acid ligand system was prepared by treatment of the iminodiacylchloride and excess of diethyiminodiacetate. Elemental analysis, FTIR spectra, and atomic absorption methods were used to examine and characterized the di(amidomethy)aminetetraacetic acid polysiloxane and its complexes.

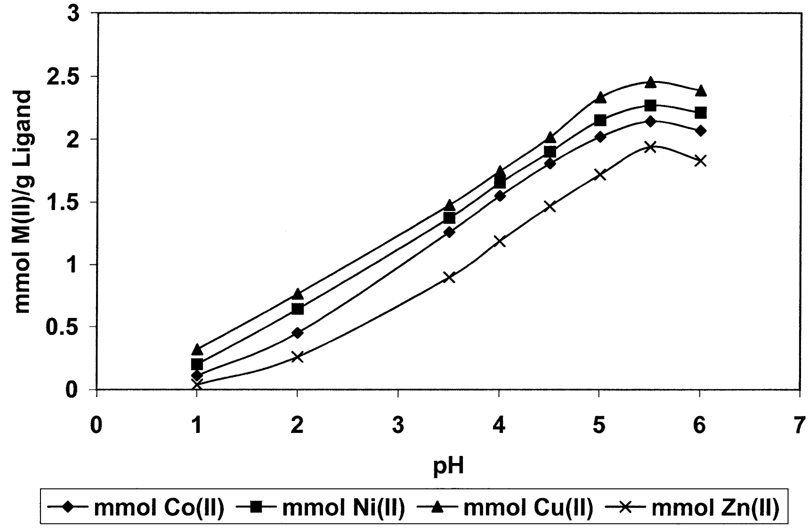


FIGURE 5 Uptake of metal ions by P-DATAA versus pH values (72 h shaking time).

The introduction of diethyliminodiacetate groups, $N(CH_2CO_2Et)_2$, was evident from the decrease of iodine and an increase of carbon and nitrogen percentages. Additional evidence was obtained from the IR spectrum of the P-DEIDA ligand system (Figure 1b), which showed a strong absorption peak at 1747 cm^{-1} due to the ester carbonyl υ(CO) vibration. The formation of iminodiacetic acid polysiloxane (P-IDAA) was evident from a decrease of the carbon percentage. Further evidence was also supported by the FTIR spectrum of the P-IDAA (Figure 1(c)), which showed two vibration modes at 1740 cm^{-1} and 1629 cm^{-1} attributed to the free carboxylic acid carbonyl υ(CO) and δ(OH) vibrations, respectively.[21] The presence of chlorine in the hydrolyzed product is probably due to hydrolysis of Si—O—Si linkages where the chlorine became part of the material.[15,21]

The formation of the iminodiacylchloride polysiloxane (P-IDACl), was evident from the increase of chlorine percentage and a shift of the υ(CO) vibration from 1747 cm^{-1} to 1731 cm^{-1} (Figure 1(d)).

The formation of di(ethylamidomethyl)aminetetraacetate polysiloxane (P-DATA) was evident from the increase of carbon and nitrogen and decrease of chlorine percentages. This also was evident from the presence of two absorption peaks at 1749 cm^{-1} and 1640 cm^{-1} due to the ester υ(CO) and δ(OH) vibrations, respectively. The lower carbon and nitrogen percentages than the expected values is probably due to the fact that not all the chlorides have been replaced by diethyliminodiacetate groups (Table I).

This may suggest that most of the chlorine atoms are available for nucleophilic substitution reaction and the ligand groups were incorporated into the siloxane framework. The presence of chlorine in the final product is probably due to the presence of some unreacted acylchloride groups.

The immobilized tetraacetic acid polysiloxane (P-DATAA) was obtained by hydrolysis of di(ethylamidomethyl)aminetetraacetate polysiloxane with an aqueous solution of HCl. The elemental analysis indicated that there was a considerable decrease in the percentage of carbon. This can be explained by the hydrolysis of the ester form (COOEt) into the acid form (COOH).

From thermogravimeric analysis of the P-DATAA and its complexed form (Figures 2 and 3, respectively), it was obvious that the ligand was thermally stable at ambient temperature and about only 15% weight was lost in the temperature range 25–250°C. The weight loss was attributed to evaporation of volatile physisorbed species such as water, alcohols, and solvent in the polysiloxane pores without changing the polysiloxane matrix. A further 15–20% of the initial weight was lost in the range of 250–600°C with some modification in the surface and bulk of the immobilized ligand system leading to formation of silica like network at the end.

It was observed from thermal analysis also that the total weight lost from Cu(II) complex of P-DATAA (30.6%) was lower than that of the free ligand (34.8%) in the temperature range 25–600°C. This suggested that the immobilized ligand system became more thermally stable on complexation with metal ions.

The immobilized tetraacetic ligand system (P-DATAA) showed high potential for extraction and binding to divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}). From the elemental analysis of nitrogen of the immobilized ligand system and that of the maximum metal ion uptake, it was possible to suggest that 2:1 metal-to-ligand complexes are obtained. The metal ion uptake increases with increasing pH value and reached its maximum at pH 5.5. Only minor uptake capacity occurred at lower pH values (pH 1–3) due to protonation of the amine group.[20,21]

CONCLUSION

The polysiloxane-immobilized ligand system di(amidomethyl)amine-tetraacetic acid has been prepared by a multistep modification reaction of iodopolysiloxane. The elemental analysis and FTIR results indicate that this ligand was chemically immobilized into the polysiloxane network through the chemical modifications of the preformed polymer. TGA result showed that only 30–34% of the initial weight lost in the range of 25–600°C. This ligand system showed high potential for extraction of divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) and formed 2:1 metal-to-ligand complexes.

REFERENCES

[1] D. E. Leyden, G. H. Luttrel, and T. A. Patterson, *Anal. Letters*, **8,** 51 (1975).

[2] D. E. Leyden and G. H. Luttrel, *Anal. Chem.*, **47,** 1612 (1976).

[3] D. E. Leyden, In D. E. Leyden and W. T. Collins (eds.), *Silylated Surfaces*, Gordon and Breach, New York (1980), and reference therein.

[4] O. Leal, D. L. Anderson, R. G. Bowman, F. Basolo, and R. L. Burwell, *J. Am. Chem. Soc.*, **97,** 5125 (1975).

[5] D. C. Bailly and S. H. Lange, *Chem. Rev.*, **81,** 109 (1981).

[6] U. Schubert, *J. Chem. Soc. Dalton Trans.*, **14,** 3343 (1996).

[7] J. K. West and L. Hench, *Chem. Rev.*, **90,** 33 (1990).

[8] P. R. Rao, *Solid State Commun.*, **99,** 439 (1996).

[9] I. S. Khatib and R. V. Parish, *J. Organomet. Chem.*, **369,** 9 (1989).

[10] R. V. Parish, D. Habibi, and V. Mohammadi, *J. Organomet. Chem.*, **369,** 17 (1989).

[11] I. M. El-Nahhal and R. V. Parish, *J. Organomet. Chem.*, **452,** 19 (1993).

[12] I. Ahmad and R. V. Parish, *J. Organomet. Chem.*, **452,** 23 (1993).

[13] A. A. El-Nasser and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, **19,** 3463 (1999).

[14] I. M. El-Nahhal, F. R. Zaggout, and N. M. El-Ashgar, *Anal. Letters*, **33,** 2031 (2000).

[15] I. M. El-Nahhal, F. R. Zaggout, and N. M. El-Ashgar, *Anal. Letters*, **34,** 3373 (2000).

[16] K. K. Unger, N. Becker, P. Roumeliotis, *J. Chromatog.*, **125,** 115 (1976).

[17] Yu. L. Zub and R. V. Parish, *Studies In Surface Science and Catalysis*, **99,** 285 (1996).

[18] J. P. Riley and D. Taylor, *Anal. Chim. Acta.*, **40,** 490 (1968).

[19] M. Pesavento, R. Biesuz, F. Baffi, and C. Gnecco, *Anal. Chim. Acta*, **401,** 265 (1999).

[20] E. M. Moyers and J. S. Frits, *Anal. Chem.*, **49,** 418 (1977).

[21] H. M. El-Kurd, I. M. El-Nahhal, R. M. Baraka, and R. V. Parish, *Asian J. Chem.*, **11,** 790 (1999).

[22] I. M. El-Nahhal, F. R. Zaggout, M. A. Nassar, N. M. El-Ashgar, J. Maquet, F. Babonneau, and M. M. Chehimi, *J. Sol-Gel Sci. Tech.*, **28,** 255 (2003).

[23] T. Lopes, L. Herrera, J. Mendez, P. Bosch, R. Gomes, and R. Gonzakz,*J. Non-Cryst. Solids*, **107,** 773 (1992).

[24] T. Lopes, P. Bosch, M. Moranz, R. Gomes, and R. Gonzakz, *J. Phys. Chem.*, **97,** 1671 (1993).

[25] I. M. El-Nahhal, M. M. Chehimi, C. Cordier, and G. Dodin, *J. Non-Cryst. Solids*, **275,** 142 (2000).

[26] A. M. Klonkowski, K. Koehler, and C. W. Schlaepfer, *J. Mater. Chem.*, **3,** 105 (1993).

[27] A. M. Klonkowski, T. Widernik, and B. Grobelna, *J. Sol-Gel Sci. Tech.*, **20,** 161 (2001).

[28] J. D. Jovanovic, M. N. Govedarica, P. R. Dvornic, and I. G. Popovic, *Polym. Degrad. and Stab.*, **61,** 87 (1998).