Template Synthesis of Iminodiacetic Acid Polysiloxane Immobilized Ligand Systems and their Metal Uptake Capacity

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Abstract Porous solid polysiloxane ligand systems bearing an iminodiacetic acid chelating ligand of the general formula P-IDA (where P- represents $[Si-O]_n$ polysiloxane network and IDA represent an organofunctional group) were achieved in a two-step reaction. The first step includes a template synthesis of 3-iodopropylpolysiloxane (P-I) or 3-aminopropyl-polysiloxane (P-MA) by hydrolytic polycondensation of TEOS and the corresponding silane agent in the presence of CTAB as a surfactant. The second step includes a modification of 3-iodopropylpolysiloxane with diethyliminodiacetate or 3-aminopropylpolysiloxane with ethylchloroacetate to produce IDA-functionalized polysiloxane ligand systems P-IDA-I & P-IDA-II respectively. It was found that the modified IDA-functionalized polysiloxane ligand systems exhibited higher capacities for uptake of the metal ions (Ni^{2+}, Cu^{2+} and Pb^{2+}) than those prepared without surfactants.

1 Introduction

Heavy metals are given special attention throughout the world due to their toxic effects even at very low concentrations [1, 2]. Many technological methods have been developed over the years for removing toxic/heavy metal contaminants from different media [3, 4]. Chemical precipitation, ion exchange, filtration, adsorption, electrodeposition and membrane systems are the most important methods [5, 6]. Some of these approaches suffer from limitations especially the low ability to remove quantities at trace levels. Recently, immobilization of chelating groups on the surface of inorganic solid supports, especially silica gel and polysiloxanes, are gaining high importance due to their excellent thermal, mechanical and chemical stability [7, 8]. Polysiloxanes functionalized by chelating ligands have been widely exploited for extraction and preconcentration of trace metal ions from different media by batch and dynamic methods [9–18]. There is consequently interest in developing functionalized polysiloxanes with suitable complexing agents which have high potential for uptake of metal ions [9–18]. These immobilized ligand systems could be synthesized either directly by the sol-gel method or by chemical modification of the pre-prepared polysiloxanes [9–18]. These functionalized systems have been used in many important applications including extraction and separation of metal cations from organic solvents and aqueous solutions, chromatographic stationary phases and heterogeneous

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catalysis [9–18]. In previous research, iminodiacetic acid (IDA) functionalized polysiloxane ligand systems were prepared by the sol-gel process in the absence of surfactants [15] or by modification of silica with an IDA-functionalized silane coupling agent [19, 20]. More recently IDA-functionalized mesoporous silica was prepared by treatment of iodopolysiloxane or iodofunctionalized mesoporous silica with diethyliminodiacetate [11, 21, 22].

In the present work, we used a template method for preparation of immobilized-polysiloxane iminodiacetic acid ligand systems at different molar ratios of TEOS/CTAB and investigated their metal uptake capacities and compared with those prepared in the absence of CTAB. CTAB surfactant was used to modify morphology and porosity of the polysiloxane adsorbents. The resulting iminodiacetic acid functionalized derivatives (P-IDA-I and P-IDA-II) were characterized using FTIR, CP/MAS ^{13}C NMR , TGA and XPS analyses.

2 Experimental

2.1 Reagents and Materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, iminodiacetic acid and ethylchloroacetate were purchased from MERCK and used as received. Acetone, diethyl ether, tetrahydrofuran (THF) and ethanol (spectroscopic grade) were used. Cetyltrimethylammoniumbromide (CTAB) surfactant was purchased from MERCK and used as received. Surfactant solutions of different concentrations were prepared in ethanol. Metal ion solutions of the appropriate concentration were prepared by dissolving the metal nitrate (AnalaR grade) in deionized water. Different pH values in the range of (3.5–6) were controlled using acetic acid/sodium acetate buffer solution.

2.2 General Techniques

^{13}C CP-MAS Solid State NMR experiments were carried out at room temperature on a Bruker MSL-400 MHz spectrometer at a frequency of 100.6 MHz (^{13}C) using a Bruker CP/MAS probe. Proton decoupling was always applied during acquisition. Solid samples were spun at 5 kHz using 7 mm ZrO2 rotors filled in a glove-box under dried argon atmosphere.

The X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250, spectrometer equipped with a monochromatic AlKα X-ray source (hn = 1486.6 eV, 650 μm spot size). An electron flood gun was used to obtain a perfectly uniform static charge over the sample area analyzed. The filament current was 3A and the emission current

0.2 mA. These conditions yield negative but uniform static charge over the powder surface. Binding energy positions were calibrated against the main C-C/C-H C1s component set at 285 eV. The surface elemental composition was determined by considering the peak areas and the corresponding Scofield sensitivity factors corrected for the electron analyzer transformation function.

Thermogravemetric analysis TGA was carried out using a Mettler Toledo SW 7.01 analyzer in the range of 25-600 °C under nitrogen.

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 a KBr disk in the range 4000 to 400 cm^{-1}. All pH measurements were obtained using a AD1020 pH Meter. All ligand samples were shaken with aqueous metal ion solutions using an ELEIA-Multi Shaker.

2.3 Preparations

2.3.1 Preparation of Iodopolysiloxane Ligand System (P-I) (A-D)

The 3-iodopropyltrimethoxysilane was first prepared as previously described [9] by treating the 3-chloropropyltrimethoxysilane with sodium iodide in acetone. The iodopropylpolysiloxane (P-I) was prepared as previously reported [9] by adding 3-iodopropyltrimethoxysilane (14.5 g, 0.050 mol) to a stirred solution of tetraethylorthosilicate (20.8 g, 0.10 mol) in 20 ml ethanol and 4.95 ml of 0.42 M HCl was added as a catalyst. Different molar ratios of CTAB/TEOS 0:1(A), 1:32(B), 1:16(C) and 1:8(D) were used separately to obtain samples of variable CTAB content (Table 1). Each mixture was stirred at room temperature for several hours. Gelation occurred after 24 hours. The xerogel material was left for 12 hours then dried at 100 °C overnight. The material was crushed, sieved, and washed with successive portions of 50 ml of water, ethanol and diethyl ether. CTAB was extracted from the material by refluxing with ethanol. The

Table 1 Immobilized polysiloxanes P-MA and P-I prepared at different CTAB/TEOS molar ratios

CTAB/ TEOS molar ratios	P-I	P-MA
0:1	A	A
1:32	B	B
1:16	C	C
1:8	D	D

material was then washed successively with 50 ml portions of 0.025 M NaOH, water, ethanol and diethyl ether. Finally the products were dried for 12 hours at 100 °C.

2.3.2 Preparation of Polysiloxane Immobilized Iminodiacetic Acid Ligand System (P-IDA-I) (A-D) [11, 21, 22]

Diethyliminodiacetate polysiloxane material (P-DIDA-I) was prepared by adding diethyliminodiacetate (9.45 g 0.05 mol) to (10 g, 0.032 mol) of iodopolysiloxane (A-D) (Table 1) in (50 ml, 0.610 mol) of THF. The mixture was stirred and refluxed at 95 °C for 48 hours. The product was filtered off, washed successively with 50 ml portions of 0.025 M NaOH, water, ethanol and diethyl ether and then dried at 100 °C for 12 hours. The immobilized diethyliminodiacetate system (P-DIDA-I) (5.0 g) was then hydrolyzed by refluxing the immobilized ligand system with 150 ml of 2.0 M HCl for 12 hours with stirring. The solid material (P-IDA-I) was then filtered, washed with 0.025 M NaOH and dried at 100 °C for 12 hours.

2.3.3 Preparation of Monoamine Polysiloxane Ligand System (P-MA) (A-D)

The monoamine polysiloxane ligand system (P-MA) was prepared as previously reported [23] by adding 3-aminopropyltrimethoxysilane (8.96 g, 0.05 mol) to a stirred solution of tetraethylorthosilicate (20.83 g, 0.1 mol) in 15 ml methanol and 4.95 ml of 0.42 M HCl in the presence of CTAB. Different molar ratios of CTAB/TEOS 0:1(A), 1:32(B), 1:16(C) and 1:8(D) were used separately to obtain samples of variable CTAB content (Table 1). Each mixture was stirred at room temperature where a gel material occurred within a few minutes. The product was left to stand for 12 hours at room temperature, then dried in a vacuum oven at 90 °C. The solid material was crushed, seived and washed successively with 50 ml portions of 0.025 M NaOH, water, ethanol and diethyl ether, then dried at 100 °C for six hours. CTAB was extracted from the materials by refluxing with ethanol. The product was then dried in an oven at 100 °C for 12 hours.

2.3.4 Preparation of Polysiloxane Immobilized Iminodiacetic Acid Ligand System (P-IDA-II) (A-D)

Diethyliminodiacetate polysiloxane material (P-DIDA-II) was prepared by the reaction of P-MA (A-D) (5.0 g, 0.022 mol) (Table 1) with an excess of ethylchloroacetate (12.2 g, 0.1 mol) in (50 ml, 0.61 mol) of THF. The mixture was refluxed with stirring at 95 °C for 48 hours. The product was filtered off, washed successively with 50 ml portions of 0.025 M NaOH, water, ethanol and diethyl ether

and then dried at 100 °C for 12 hours. The immobilized diethyliminodiacetate polysiloxane, P-DIDA-II (5.0 g) was hydrolyzed by refluxing the ligand system with 150 ml of 2.0 M HCl for 12 hours with stirring. The solid material was then filtered, washed with 0.025 M NaOH aqueous solution, water, ethanol and diethyl ether. The material was dried at 100 °C for 12 hours.

2.4 Metal Uptake Experiments

One hundred milligram of the functionalized polysiloxane-immobilized ligand system (P-IDA-I or P-IDA-II) was shaken with 25 ml, of 0.02 M of aqueous solution of the appropriate metal ions (Ni^{2+}, Cu^{2+} and Pb^{2+}) using 100-ml 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 as mmole of M^{2+}/g ligand. Each study was performed at least in triplicate. Metal uptake was examined under various factors including the amount of surfactant, pH, shaking time, and shaking effect.
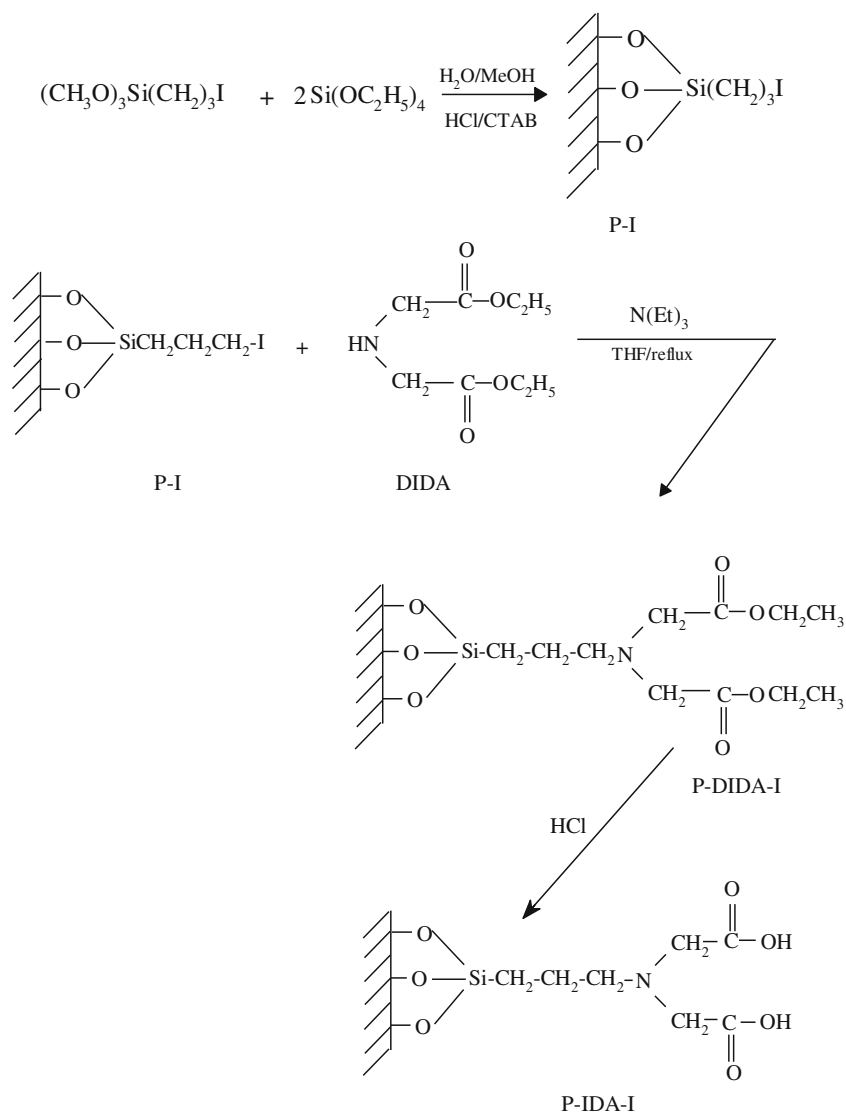
3 Results and Discussion

3.1 Synthesis

The functionalized polysiloxane immobilized iminodiacetic acid ligand system, P-IDA, was prepared using a template procedure in the presence of different amounts of CTAB by two different routes, the first route was achieved by the following steps:

i   Preparation of polysiloxane-immobilized diethyliminodiacetate (P-DIDA-I) (A-D) by the reaction of diethyliminodiacetate with iodopolysiloxane (P-I) in THF, Scheme 1 [11, 21, 22].
ii Hydrolysis of P-DIDA-I using hydrochloric acid to form polysiloxane-immobilized iminodiacetic acid (P-IDA-I) (A-D) as given in Scheme 1.

The second route was achieved by the following steps:

i   Preparation of polysiloxane-immobilized diethyliminodiacetate (P-DIDA-II) (A-D) by the reaction of ethylchloroacetate with monoamine polysiloxane (P-MA) in THF, Scheme 2 [23].
ii Hydrolysis of P-DIDA-II using HCl to form polysiloxane-immobilized iminodiacetic acid (P-IDA-II) (A-D) as given in Scheme 2.

Scheme 1 Synthesis of
P-IDA-I

$$(CH_3O)_3Si(CH_2)_3I \quad + \quad 2\,Si(OC_2H_5)_4 \xrightarrow[\text{HCl/CTAB}]{\text{H}_2\text{O/MeOH}}$$

P-I

P-I   +   DIDA $\xrightarrow[\text{THF/reflux}]{\text{N(Et)}_3}$

P-DIDA-I

HCl

P-IDA-I

3.2 ^{13}CNMR Spectra

The CP/MAS ^{13}C NMR spectrum for the immobilized P-IDA-I (D) derivative is given in Fig. 1. The spectrum shows three peaks or shoulders at 11.6 , 22.4 41.2(sh) ppm corresponding to three methylene carbons -CH$_2$-, -CH$_2$- and CH$_2$-N respectively. The small signal at 164.8 ppm is due to the carbonyl C=O. The strong peak around 50 ppm is assigned to the methylene carbon of the NCH$_2$-COOH group. These assignments are based on spectral data reported for simillar systems [11, 15, 19, 22].

The CP/MAS NMR ^{13}C spectra for PMA, P-DIDA-II; ester form and P-IDA-II; acid form (D samples) are given in Appendix 1.

3.3 FTIR Spectra

FTIR spectra for P-I/CTAB, P-I , P-DIDA-I and P-IDA-I (D samples) are given in Figs. 2a-d. The spectra show three regions of absorption at 3500–3000 cm^{-1} due to v(OH) or v(N-H), 1750–1500 cm^{-1} due to δ(OH) or δ(NH), v(C=O) or v(CO-N) and 1200–900 cm^{-1} due to v(Si-O) vibration. Figures 2a and b show the spectra of P-I/CTAB and P-I, where the two absorptions at 2290 and 1474 cm^{-1} disappear upon removal of CTAB. The introduction of diethyliminodiacetate groups was evident from the strong absorption at 1740 cm^{-1} due to the v(C=O) (Fig. 2c). The disappearance of the peak at 1738 cm^{-1} after hydrolysis of the diethyliminodiacetate polysiloxane system (P-DIDA-I)

**Scheme 2** Synthesis of
P-IDA-II
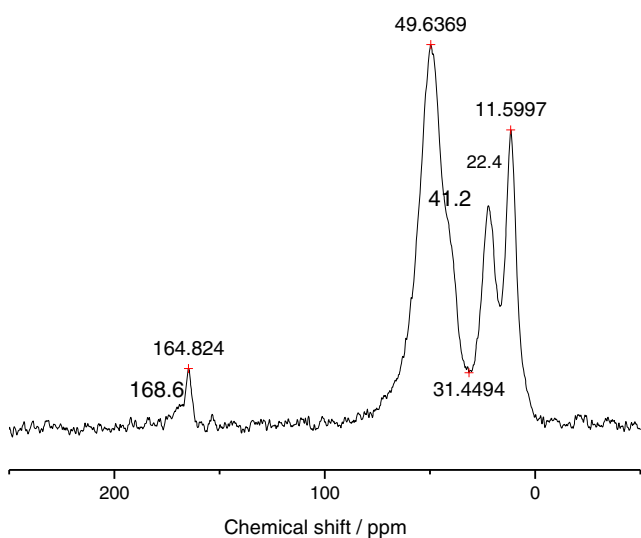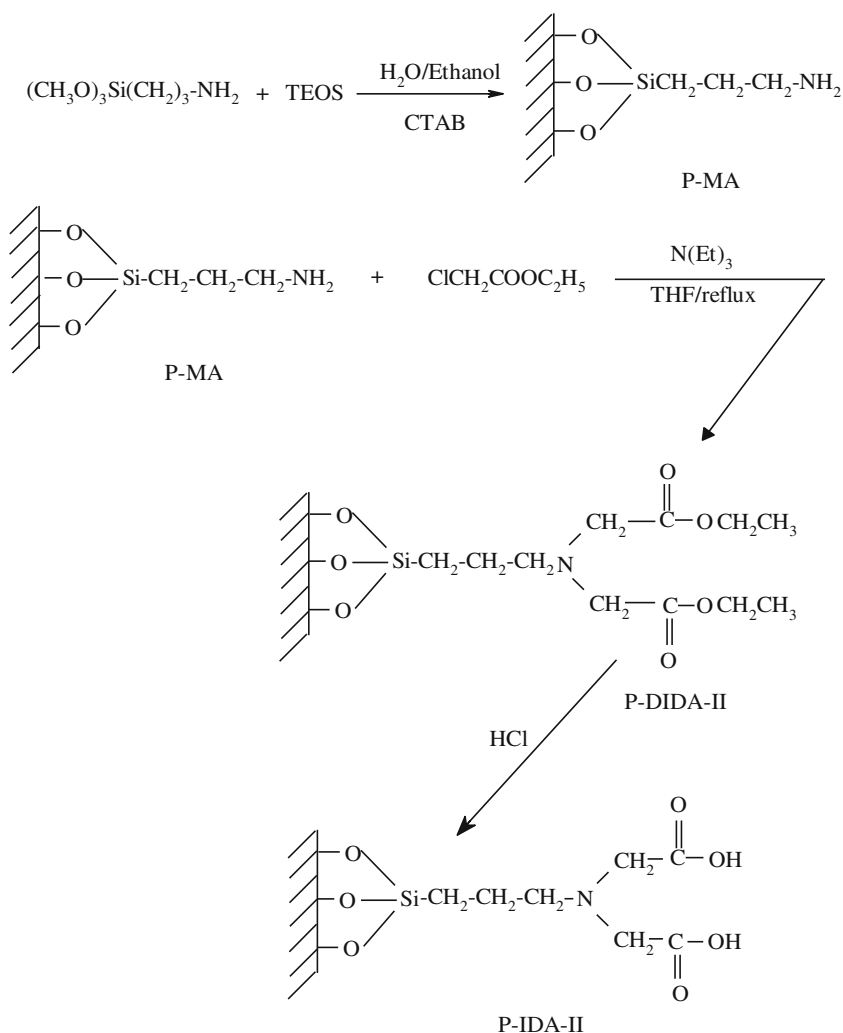
Fig. 1 CP/MAS ^{13}C NMR spectrum for the immobilized P-IDA-I

with HCl indicates that all ester groups (-CH$_2$COOEt) were converted into the acid form (-CH$_2$COOH) (Fig. 2d). These FTIR assignments were based on reported spectral data of similar materials [11, 13, 15, 19, 22]. Further confirmation for this change was obtained from XPS results discussed below. FTIR spectral results for P-MA/CTAB, P-MA, P-DIDA-II and P-IDA-II (D samples) are given in Appendix 2.

3.4 XPS Results

Figure 3 displays the survey regions of P-I/CTAB (D) (Fig. 3a) and after removal of CTAB for P-I (Fig. 3b). The main peaks Si2p, C1s, N1s, O1s and I3d are centered at ∼ 102, 285, 400, 532 and 619–630 eV, respectively [11]. Efficient removal of CTAB from P-I/CTAB is readily visible by the massive attenuation of I3d relative intensity and absence of the N1s region in the P-I survey spectrum (Fig. 3b). The surface compositions are given in Table 2.

Fig. 2 FTIR spectra for (**a**) P-I/CTAB (**b**) P-I after CTAB removed (**c**) P-DIDA-I and (**d**) P-IDA-I
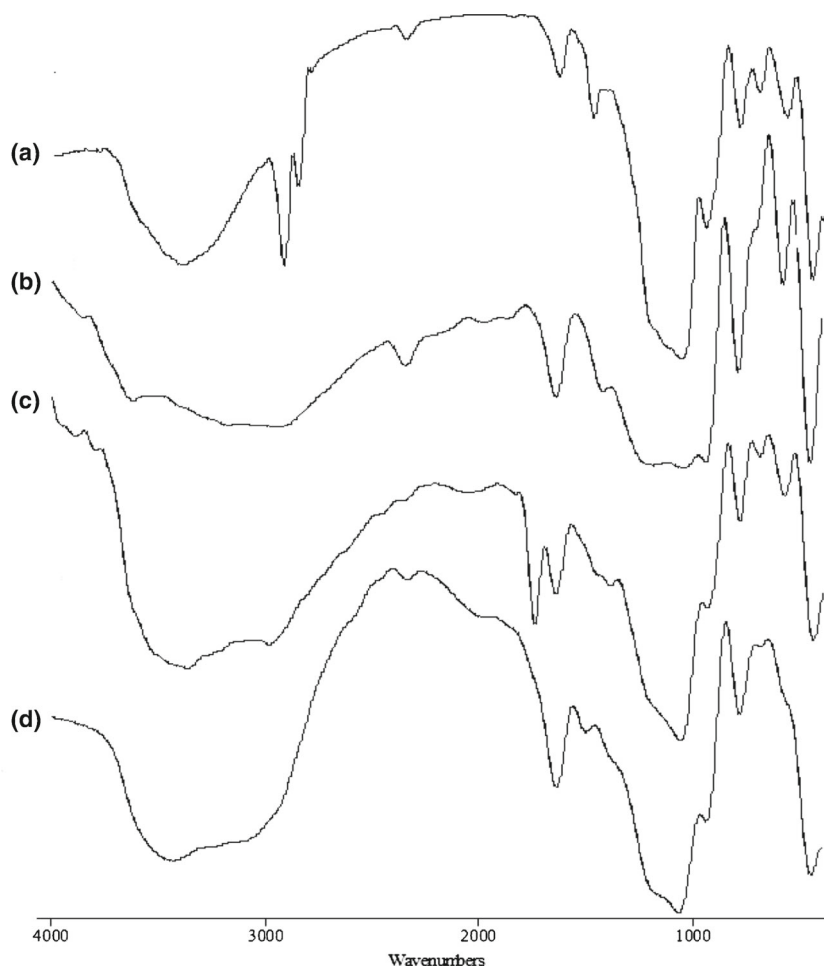
Synthesis of P-I in the presence of CTAB produces a material that showed the highest content of carbon (57.4 %). Removal of CTAB yields a quantitative decrease of carbon from 57.4 to 32 %. Modification of P-I by diethyliminodiacetate (DIDA) which yields P-DIDA-I gives an increase of the C/Si ratio from 1.2 to 1.9. Although hydrolysis is expected to remove ethyl groups from the ligand and therefore decrease the C/Si ratio, a slight increase of this ratio to 2.2 is observed, nevertheless still higher than 1.2 determined for P-I.

Fig. 3 XPS survey regions of immobilized monoamine polysiloxane (**a**) P-I/CTAB (**b**) P-I after CTAB removed
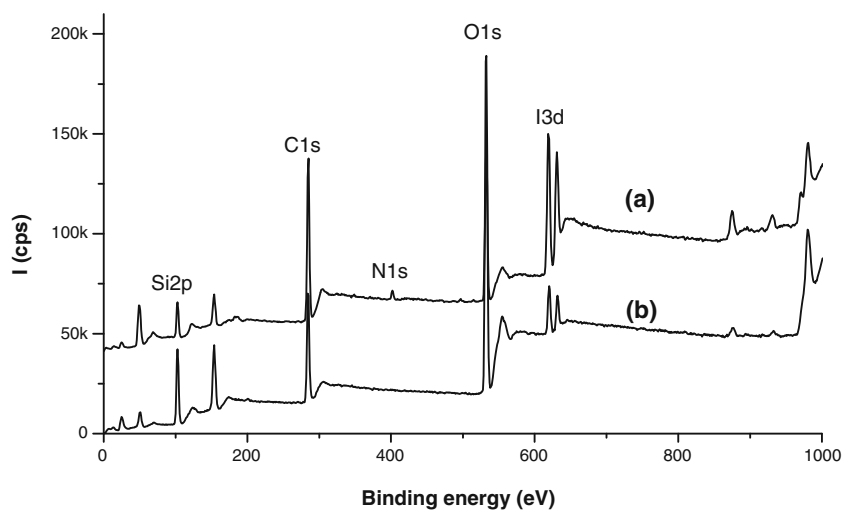
Table 2 XPS data and % surface composition of P-I and its derivatives

System	Element	Si	C	O	N	I	Cl
	Core-line	Si2p	C1s	O1s	N1s	I3d	Cl2p
	BE (eV)	102	285	532	399.5	619	200
P-I/CTAB	% Composition	15.1	57.4	22.4	2.0	3.0	–
P-I	% Composition	25.9	32.0	40.0	–	1.5	0.6
P-DIDA-I	% Composition	20.9	40.6	34.4	2.5	1.2	0.4
P-IDA-I	% Composition	20.3	44.5	32.2	2.2	–	0.8

The high resolution C1s regions from P-I, P-DIDA-I and P-IDA-I (D samples) are displayed in Fig. 4. P-I has a simple structure (Fig. 4a) that is very well distinguished from that of P-DIDA-I (Fig. 4b) as a result of reaction of P-I with diethyliminodiacetate. The C1s region for P-DIDA-I exhibits three components centered at 285, 286.5 and 289.1 eV (in the 1:0.52:0.07 ratio) assigned to C-C/C-H, C-O and O-C=O, respectively (Fig. 4b). Upon hydrolysis of P-DIDA-I, the sol-gel material P-IDA-I was obtained. Effective hydrolysis gave three similar components centered at 285, 286.4 and 288.8 eV (in the 1:0.35:0.05 ratio), however with significantly lower relative intensity for the C-O bond component centered at 286.4 eV (Fig. 4c) [11, 13]. Indeed the transformation of $-N(COO-CH_2CH_3)_2$ into $-N(COOH)_2$ induces the loss of the alkoxy $O-CH_2CH_3$ and thus the attenuation of the C1s component due to the $O-CH_2$ band.

The high resolution N1s region is displayed for P-I after CTAB is removed, P-DIDA-I and P-IDA-I (D samples) (Fig. 5). There is no nitrogen signal in the case of P-I as CTAB has been removed (Fig. 5a). Instead, a N1s peak is readily detected for P-DIDA-I due to the reaction of P-I with DIDA which gave the functional group $-N(COO-CH_2CH_3)_2$ (Fig. 5b) [11, 13]. However the N1s region
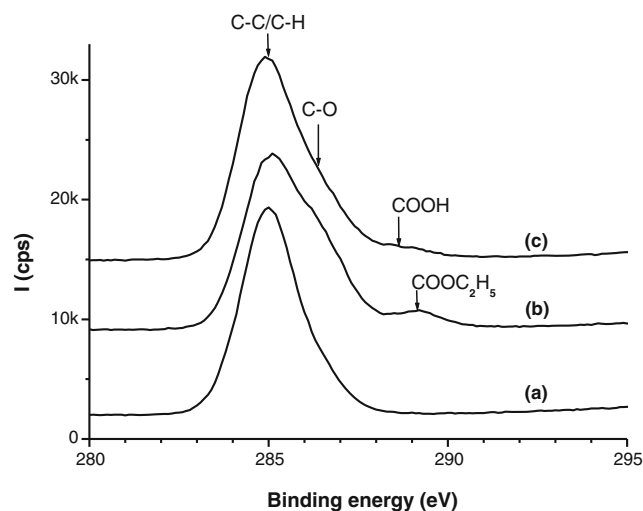
has two distinct components at 399.6 and 402.4 eV (in the 1:0.9 ratio) assigned to free and protonated amine, respectively. The amine cation is probably caused by the generated HI during the course of the reaction. Upon hydrolysis, the ratio becomes 1:0.88 indicating a slight increase in the protonated amine form (Fig. 5c). XPS survey regions of immobilized monoamine polysiloxane (P-MA) in the presence of CTAB and after removal of CTAB and the fitting curves (D samples) are given in Appendix 3.

3.5 Thermal Analysis

Thermogravimetric analysis (TGA) plots were examined for P-I/CTAB, P-I after CTAB was removed and P-IDA-I and its copper complex (D samples) under nitrogen atmosphere at 20–600 °C at a rate 10 °C/minute. Figures 6 and 7 show the thermograms of P-I after CTAB was removed and in the presence of CTAB respectively. Three peaks were observed in the case of P-I without CTAB (Fig. 6). The first peak occurs at ∼ 75 °C where the P-I system lost 2 - 3.5 % of its initial weight. This is attributed to loss of physisorbed water and alcohol from the system pores [11, 24–26]. The second peak at ∼ 350°C, where the P-I system lost 34.5 %, is probably due to degradation of organofunctional groups bound to silicon atoms as well as dehydroxylation of suface OH groups and loss of internal water and alcohol from silica. The third broad peak at temperature 400–600 °C is due to further loss of 6 % of the initial weight due to condensation and loss of hydroxyl groups forming siloxane bonds (dehydroxylation) [24–26]. The total loss of weight of the P-I system was about 41.5 %. The thermogram for the P-I/CTAB shows four main peaks at ∼ 75 °C, 230 °C, 300 °C and 500 °C (Fig. 7). The two peaks at 230 °C and 300 °C are probably due to further loss of internal alcohol, degradation of surface OH silica groups, and degradation of CTAB [24–26]. The total loss of weight for P-I/CTAB was 53.5 %. The high loss of weight for the P-I/CTAB compared with that of P-I prepared without CTAB is due to the amount of CTAB used.

The thermograms of P-IDA-I and P-IDA-I copper(II) complex (D samples) showed three characteristic peaks at
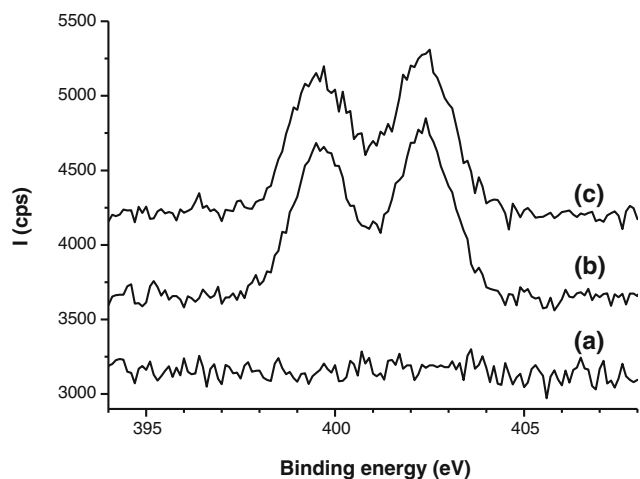

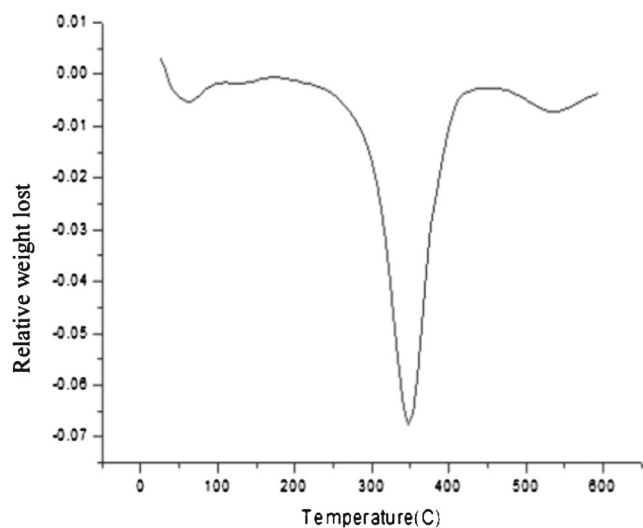**Fig. 4** High resolution C1s region for (**a**) P-I (**b**) P-DIDA-I (**c**) P-IDA-I
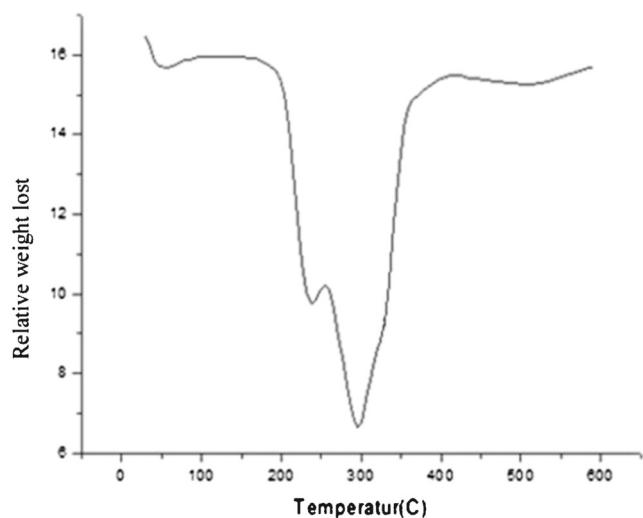
Fig. 5 High resolution N1s region for (**a**) P-I (**b**) P-DIDA-I (**c**) P-IDA-I

Fig. 8 TGA for P-IDA-I

Fig. 6 TGA for P-I/CTAB

Fig. 9 TGA for P-IDA-I copper (II) complex

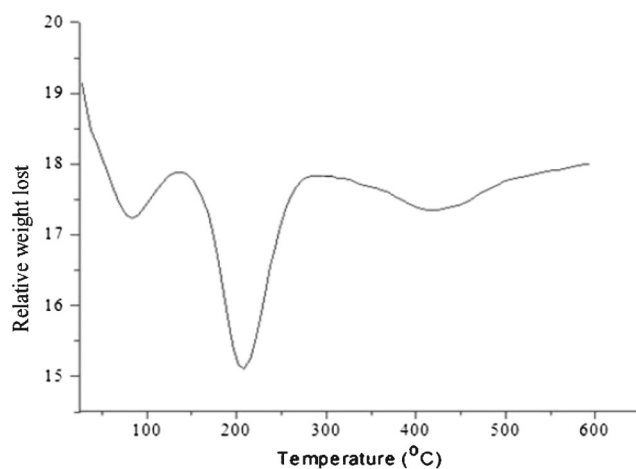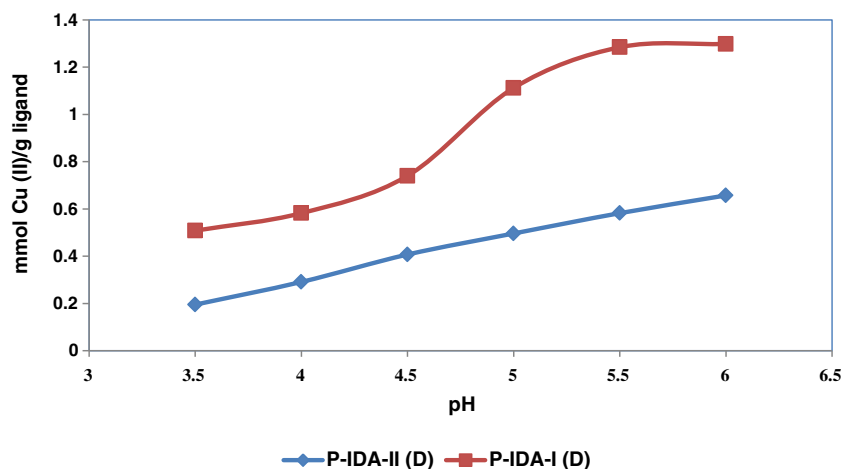**Fig. 7** TGA for P-I after CTAB removed

Table 3 Cu^{2+} uptake by P-IDA-I and P-IDA-II at different CTAB/TEOS ratios (pH = 6, T = 25 °C and t = 72 h)

CTAB/ TEOS *	Type	mmol Cu^{2+}/g ligand	
		PIDA-I	P-IDA-II
0:1	A	0.63	0.23
1:32	B	1.03	0.38
1:16	C	1.17	0.61
1:8	D	1.30	0.66

*molar ratio

Fig. 10 Uptake of Cu(II) by P-IDA-I and P-IDA-II versus pH values, (T = 25 °C and t = 72 hr)

70 °C, 220 °C and 430 °C (Figs. 8 & 9) respectively. The second peak at 220 °C is probably due to evaporation of internal alcohol and water, dehydroxylation of surface OH silica groups and degradation of the ligand functional groups. The third peak at 430 °C is probably due to futher condensation and loss of water forming siloxane bonds at the end. The total loss of copper complex (Fig. 9) is 22.5 % which is smaller than that of its parent functionalized ligand precursur P-IDA (Fig. 8) (43.4 %). This provides evidence that this material becomes more stable upon complexation with metal ions.

3.6 Metal Uptake Capacity

3.6.1 Effect of Surfactant Concentration

Table 3 shows the Cu^{2+} uptake capacity at different concentrations of surfactants with respect to TEOS (A-D). P-IDA-I showed higher Cu^{2+} uptake capcaity than P-IDA-II in all CTAB/TEOS ratios. Cu^{2+} uptake capacity of both ligand systems (P-IDA-I and P-IDA-II) increases with increasing the concentration of CTAB. Highest Cu^{2+} uptake capacity

by both immobilized ligand systems is observed at 1:8 surfactant to TEOS molar ratio (D samples). This is obviously attibuted to the formation of highly porous material [18]. In this case a different structure morphology material is probably obtained.

3.6.2 Effect of pH

The effect of the pH on the uptake of Cu^{2+} metal ion by both P-IDA-I (D) and P-IDA-II (D) is shown in Fig. 10. The results show an increase of Cu^{2+} uptake with increasing pH reaching its maximum at pH 6. Low uptake capacity occurs at lower pH values (pH = 3.5) due to protonation of amine groups [27].

3.6.3 Effect of Shaking Time

Measurements of metal uptake capacity of both P-IDA-I (D) and P-IDA-II (D) for different metal ions (Ni^{2+}, Cu^{2+} and Pb^{2+}) were carried out at different time intervals at pH = 6 for shaken samples. It is shown that the uptake of metal ions Ni^{2+}, Cu^{2+} and Pb^{2+} is increased as a function of shaking

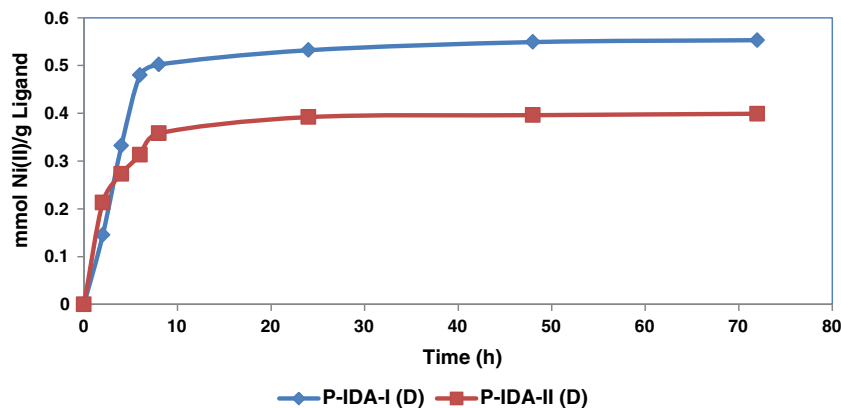**Fig. 11** Ni(II) uptake by P-IDA-I and P-IDA-II versus time (pH = 6, T = 25 °C and using shaking samples)

Table 4 Copper uptake by P-IDA-I with and without shaking (pH = 6, T= 25 °C and t = 72 h)

CTAB/ TEOS *	Type	mmol Cu²⁺/g ligand	
		Unshaken samples	Shaken samples
0:1	A	1.30	0.63
1:32	B	1.41	1.03
1:16	C	1.58	1.17
1:8	D	1.66	1.30

*molar ratio

time and reached equilibrium after nearly 24 hours when maximum uptake is obtained. The study of Ni^{2+} uptake as an example is given in Fig. 11.

3.6.4 Effect of Shaking

A comparison between the metal ions uptake using shaking and non-shaking for samples at 25 °C was performed for P-IDA-I (A-D). The results are given in Table 4. In general shaken samples exhibit higher metal ion uptake than unshaken samples. This could be due to better diffusion of the metal ion in the case of shaken samples, as the ligand groups become more accessible for the metal ions. Similar trends were reported for previously prepared ligand systems [10].

3.6.5 Comparison between the Uptake of Different Metal Ions

The metal ion uptake capacity of Ni^{2+}, Cu^{2+} and Pb^{2+} by the functionalized P-IDA-I and P-IDA-II immobilized ligand systems as mmol M^{2+}/g ligand at the optimum conditions (T = 25 °C, pH = 6, t=72 h and using sample shaking) are collected in Table 5. Higher metal uptake capacities for all studied metal ions are found in the case of

P-IDA-I than that of P-IDA-II, where the uptake capacity of metal ions increases in the following order:

$$Cu^{2+} > Ni^{2+} > Pb^{2+}$$
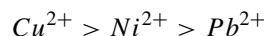
In the case of P-IDA-I, the functionalized iodopolysiloxane (P-I), which bears larger iodine atoms can be easily replaced by iminodiethylacetate groups and more space within the matrix is generated compared with that of P-IDA-II, where the amino functionalized precursor ligand system (P-MA) was used. This reflects better diffusion of metal ions into P-IDA-I material than for P-IDA-II.

4 Conclusion

Iminodiacetic acid functionalized polysiloxane materials P-IDA-I and P-IDA-II were prepared by modification of 3-iodopropylpolysiloxane (P-I) with diethyliminodiactate and 3-aminopropylpolysiloxane (P-MA) with chloroethylacetate respectively after removal of CTAB. The immobilized ligands P-IDA-I and P-IDA-II were well characterized using the CP/MAS ¹³C NMR, FTIR, TGA and XPS analyses. Template synthesis of P-I and P-MA using CTAB surfactant before the modification process leads to increase in the metal uptake capacities for the immobilized polysiloxane ligand systems compared with their corresponding polysiloxane ligands prepared without CTAB. The thermogravimetric analysis provided evidence that these materials are thermally stable at elevated temperatures. This work conclusively showed that CTAB–polysiloxane containing samples provide high capacity for removal of metal ions.

Table 5 Comparison between the uptake of different metal ions by P-IDA-I and P-IDA-II (T = 25 °C, pH = 6, t = 72 h and using sample shaking)

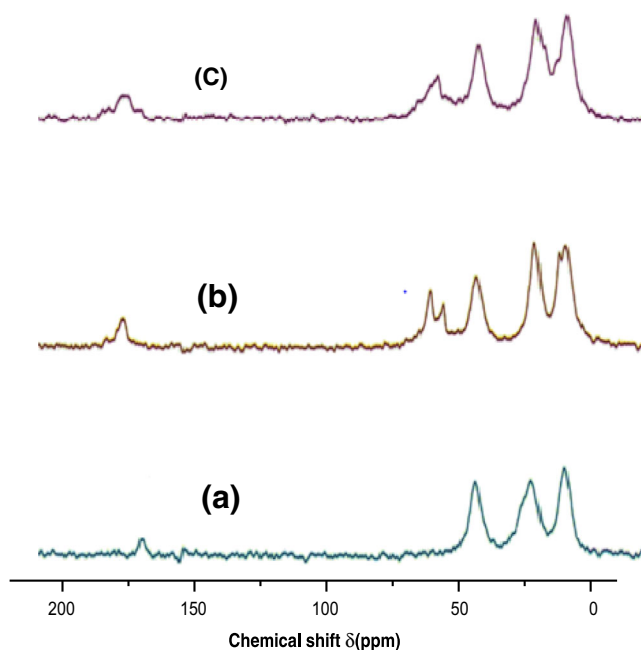| CTAB/ TEOS *	Type	mmol M (II)/g ligand					
		P-IDA-I			P-IDA-II		
		Pb (II)	Ni (II)	Cu (II)	Pb (II)	Ni (II)	Cu (II)
0:1	A	0.072	0.36	1.30	0.027	0.13	1.26
1:32	B	0.14	0.37	1.41	0.074	0.23	1.30
1: 16	C	0.19	0.40	1.58	0.11	0.35	1.40
1:8	D	0.34	0.55	1.66	0.24	0.40	1.51

*molar ratio

Appendix 1

Fig. 12 CP/MAS ^{13}C NMR spectrum for the immobilized (**a**) PMA, (**b**) P-DIDA-II; ester form and (**c**) P-IDA-II; acid form
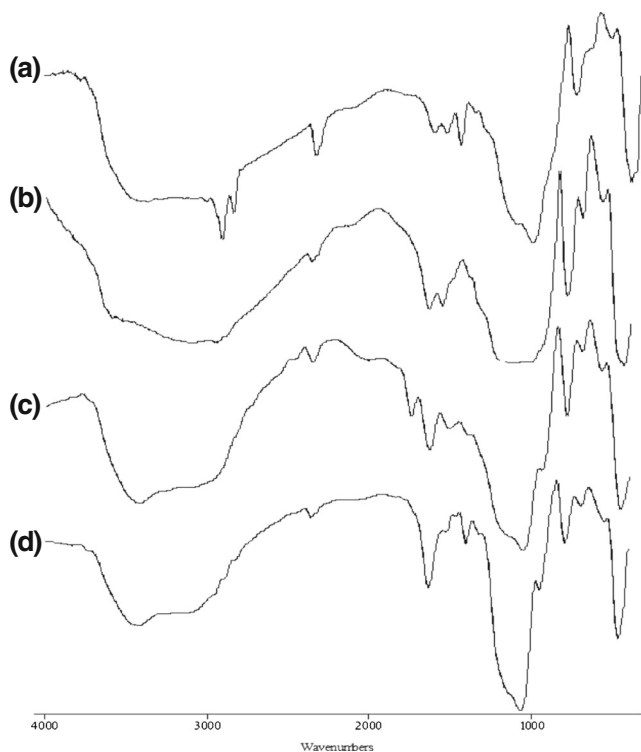
Appendix 2

Fig. 13 FTIR spectra for (**a**) P-MA/CTAB, (**b**) P-MA/without CTAB, (**c**) P-DIDA-II and (**d**) P-IDA-II
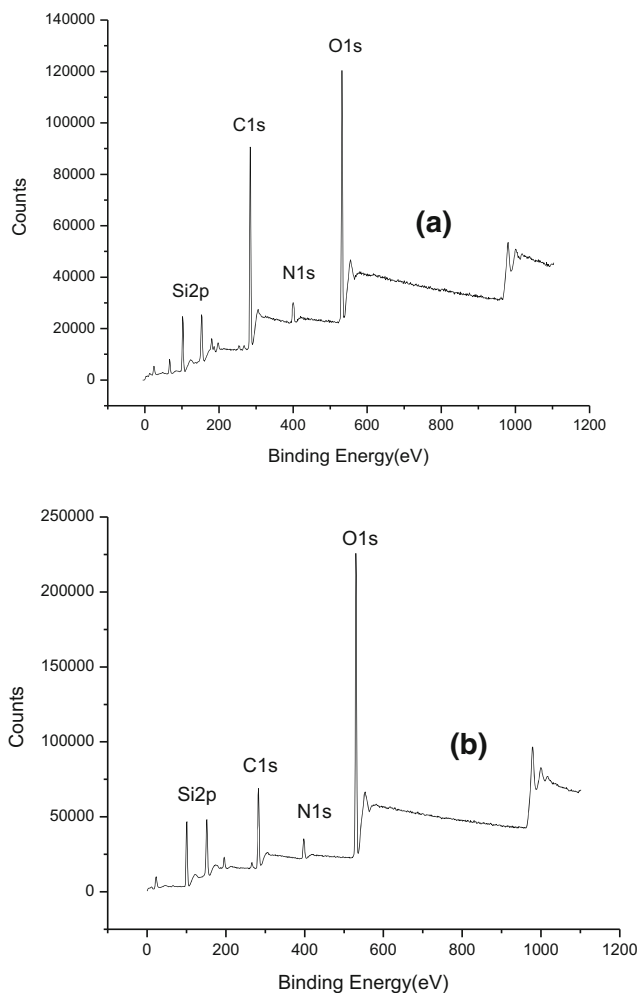
Appendix 3

Fig. 14 XPS survey regions of immobilized monoamine polysiloxane (**a**) P-MA/CTAB and (**b**) P-MA/CTAB removed (D-samples)

It is notable that after CTAB was removed from P-MA/CTAB sample, there was a significant reduction of the C1s peak (Fig. 14b).

The C1s region for P-DIDA-II exhibits three components centered at 285, 286.5 and 289.1 eV assigned to C-C/C-H, C-O and O-C=O, respectively (Fig. 15a). Upon hydrolysis of P-DIDA-I, the sol-gel material P-IDA-II was obtained. Effective hydrolysis gave three similar components centered at 285, 286.4 and 288.8 eV (Fig. 15b). The transformation of –N(COO-CH$_2$CH$_3$)$_2$ into –N(COOH)$_2$ induces the loss of the alkoxy O-CH$_2$CH$_3$ and thus the attenuation of the C1s component due to the O-CH$_2$ band.

The N1s peak is readily detected for P-MA and P-IDA-II (Fig. 16 a & b). However the N1s region for P-MA has two distinct components at 399.6 and 402.4 eV of equal intensity assigned to free and protonated amine, respectively. The amine cation is probably caused by the protons generated from the acidic silanols. After hydrolysis, the decrease
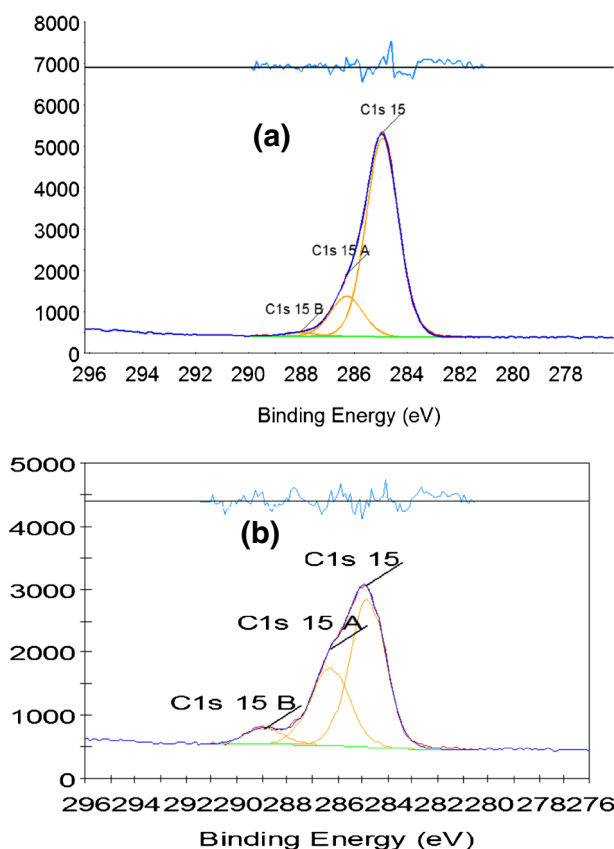
Fig. 15 High resolution C1s region for (**a**) P-DIDA-II, (**b**) P-IDA-II (D-samples)
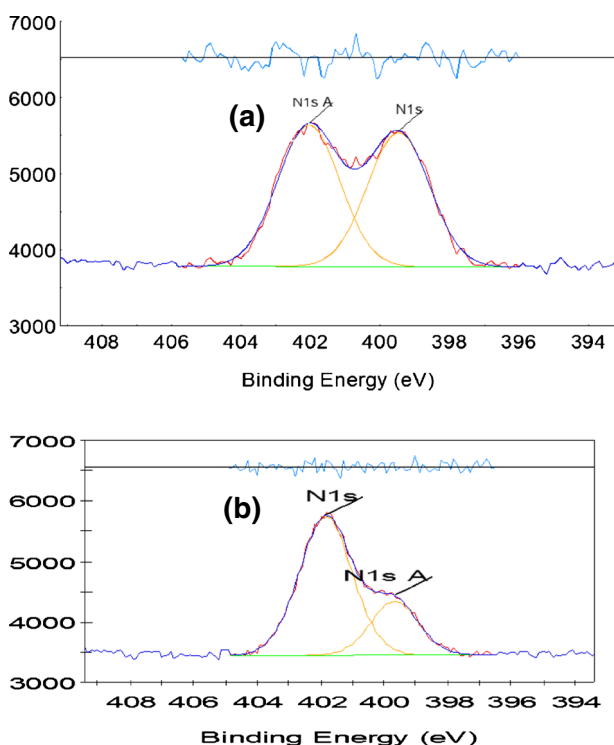

Fig. 16 High resolution N1s region for (**a**) P-MA, (**b**) P-IDA-II (D-samples)

Table 6 XPS data and % surface composition of P-MA and its derivatives

System	Element	Si	C	O	(N + N$^+$)	Cl
	Core-line	Si2p	C1s	O1s	N1s	Cl2p
	BE (eV)	102	285	532	399.5	200
P-MA/CTAB	% Composition	16.2	53.9	23.9	5.1	0.95
P-MA	% Composition	25.0	27.2	39.2	5.85	1.7
P-DIDA-II	% Composition	20.7	35.1	35.5	5.0	3.1
P-IDA-II	% Composition	21.7	39.5	32.6	3.7	2.9

of the protonated amine component for P-IDA-II sample is probably due to treating the sample with dilute NaOH solution to remove the excess of HCl.

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