

## Synthesis of Some New Polysiloxane Ligand Systems (Glycinate)-Part II†

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Polysiloxane-immobilized glycinate chelating ligand system of the general formula  $\text{P}-(\text{CH}_2)_3\text{NHCH}_2\text{CO}_2\text{H}$  (where  $\text{P}$  represents the polysiloxane network) have been prepared by two methods. The first method used is through the reaction between 3-aminopropyltriethoxysilane and chloroethylacetate,  $\text{ClCH}_2\text{COOEt}$ , followed by hydrolytic polycondensation with tetraethoxysilane (before polymerization). The second method, which was used, is through the reaction of 3-aminopropylpolysiloxane and haloethylacetate  $\text{XCH}_2\text{COOEt}$ ,  $\text{X} = \text{Cl}$  or  $\text{I}$  (after polymerization). The elemental analysis indicates that more glycinate ligand groups were obtained by functionalization before polymerization than after polymerization process. The glycinate polysiloxane ligands show high potential for copper ion uptake.

### INTRODUCTION

Porous polysiloxane immobilized organofunctional ligand systems are either anchored on silica surface<sup>1-5</sup> or incorporated into polysiloxane network<sup>6-10</sup> through hydrolytic condensation processes. These materials have advantages over the more conventional organic-polymer systems in having good hydrolytic stability over a wide range of conditions and resistance to swelling in organic solvents<sup>11, 12</sup>. A variety of ligand groups have been employed ranging from simple amines, phosphines and macrocycle<sup>6-9</sup>. These materials have several types of applications, such as extraction of metal ions from solutions<sup>6, 8</sup> and catalysis<sup>7</sup>. Recently, high resolution solid-state nuclear magnetic resonance (NMR) techniques have been used to determine the structural properties of these ligand systems<sup>13-19</sup>. In the previous paper, the preparation of iminodiacetate ligand system was reported<sup>20</sup>. This work involves the preparation of the glycinate ligand system and the comparison of these materials with those obtained by prior reaction of  $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$  with haloethylacetate. Different synthetic methods and conditions were used in order to establish the optimum conditions under which maximum density of glycinate ligand groups are introduced. The new glycinate ligands have been examined for copper ion uptake from aqueous solution.

†Part I: see *Asian J. Chem.*, **11**, 790 (1999).

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## EXPERIMENTAL

## Methods

The Microanalytical Service Laboratories in the Department of Chemistry (UMIST) England were used to carry out the elemental analysis of carbon, hydrogen, chlorine, iodine, nitrogen and copper. Results are given in Tables 1, 3 and 4.

TABLE-1  
ANALYTICAL DATA OF ETHYLGLYCINATEPROPYLTRIETHOXYSILANE AND  
ETHYLIODOACETATE

Compound	% Analysis, Found (Calcd.)						
	C	H	N	I	Cl	C/X	C/N
Ethylglycinate-A propyltriethoxysilane	43.7 (45.5)	8.5 (8.5)	4.3 (4.0)	—	44 (10.4)	—	12.0 (13.3)
Ethylidoacetate	22.6 (22.4)	3.4 (3.3)	—	51.2 (59.3)	2.0 (0.0)	4.1 (4.0)	—

TABLE-2  
<sup>1</sup>H-NMR DATA FOR ETHYLCHLOROACETATE AND ETHYLIODOACETATE

Structural type	CH <sub>2</sub> CH <sub>3</sub>	O—CH <sub>2</sub>	Cl—CH <sub>2</sub>	I—CH <sub>2</sub>	CDCl <sub>3</sub>
Ethylchloroacetate (ppm) ClCH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1.23 (t)	4.19 (q)	3.99 (s)	—	7.26
Ethylidoacetate (ppm) ICH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1.22 (t)	4.12 (q)	—	3.63 (s)	7.26

t = triplet, s = singlet, q = quartet.

TABLE-3  
ELEMENTAL ANALYSIS OF MONOAMINE, ETHYLGLYCINATE AND  
GLYCINATEPOLYSILOXANE

Ligand	% Analysis, Found (Calcd.)					
	C	H	N	I	Cl	C/N
APS	13.6 (15.7)	3.9 (3.5)	5.5 (6.8)	—	—	2.9 (3.0)
GPS1	18.1 (17.1)	3.8 (2.9)	4.1 (2.9)	—	4.6 (0.0)	5.2 (7.0)
GPS2	14.5 (19.5)	2.5 (3.3)	3.0 (3.3)	6.8 (0.0)	—	5.6 (7.0)
GPS2h	13.5 (17.1)	3.5 (3.1)	3.9 (4.0)	—	10.2 (10.1)	4.1 (5.0)
GPS3	23.0 (26.6)	4.4 (4.4)	5.0 (4.4)	1.1 (0.0)	4.7 (0.0)	5.4 (7.1)
GPS3h	15.4 (23.8)	3.9 (4.0)	4.1 (5.5)	—	6.2 (0.0)	4.4 (5.0)

APS =  $\text{P}-(\text{CH}_2)_3\text{NH}_2$ , GPS =  $\text{P}-(\text{CH}_2)_3\text{NHCH}_2\text{CO}_2\text{Et}$ , GPS<sub>h</sub> =  $\text{P}-(\text{CH}_2)_3\text{NHCH}_2\text{CO}_2\text{H}$

TABLE-4  
ANALYTICAL DATA FOR COPPER(II) COMPLEXES OF MONOAMINE AND  
GLYCINATEPOLYSILOXANE

Ligand	% Analysis				
	% C	% H	% N	% Cu	N/Cu
Cu(II) complex of APS	6.8	2.2	2.9	12.4	1.0
Cu(II) complex of GPS2	12.7	3.5	3.5	2.4	6.6
Cu(II) complex of GPS3	14.1	3.4	3.9	3.5	5.1

Infrared spectra in the range of 4000–200  $\text{cm}^{-1}$  were obtained on a Perkin-Elmer 598 infrared spectrophotometer using KBr disks.

NMR spectra was measured on Bruker 300 MHz NMR spectrometer.

Reagents of  $\text{R}_4\text{Si}$  and  $\text{R}_3\text{SiR}'$  ( $\text{R} = \text{OEt}$ ;  $\text{R}' = (\text{CH}_2)_3\text{NH}_2$ ) were purchased from Aldrich Chemical and used without further purification. The ethylchloroacetate was 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. Acetone was dried by standing for three days over anhydrous potassium carbonate and filtered. The filtered solvent was then dried over 4A molecular sieves, and then the solvent was distilled before use.

*Preparation of ethyliodoacetate:* To a solution of sodium iodide (57.0 g, 0.38 mol) in dry acetone 270  $\text{cm}^3$ , ethylchloroacetate (46.3 g, 0.38 mol) was added dropwise at room temperature. The reaction mixture was heated for 2 h at 70°C. The colour of the solution changed to yellow and a white solid was formed. The mixture was filtered and the solvent was removed under reduced pressure to give yellow oil. (Table-2 for  $^1\text{H-NMR}$  results and Table-1 for elemental analysis).

*Preparation of 3-aminopropylpolysiloxane (APS):* This polysiloxane ligand was prepared as previously described<sup>6,8</sup> as follows: Tetraethoxysilane (40.0 g, 1.92 mol) and distilled water (9.5 g, 0.52 mol) were stirred together in an ice-bath for 5 min, after which the 3-aminopropyltriethoxysilane (22 g, 0.96 mol) was added. After a few minutes of further stirring, the mixture was solidified. It was allowed to stand at room temperature for 5 h and then dried overnight at 100°C. The solid was washed with distilled water, ethanol, and petroleum ether, then dried *in vacuo* (0.1 torr) at 80°C for 2 h. The analytical data are given in Table-3.

*Preparation of ethylglycinatepropyltriethoxysilane:* Ethylchloroacetate (3.7 g, 0.03 mol) was stirred with 3-aminopropyltriethoxysilane (5.1 g, 0.021 mol). The reaction was proceeding in presence of 0.019 mol triethylamine, a white solid was filtered off and ethylglycinatepropyltriethoxy silane was obtained. This material was used without further purification. The analysis are presented in Table-1.

*Preparation of ethylglycinatepolysiloxane (GPS):* These polysiloxane ligand systems were prepared by two methods. First, by the reaction between the polysiloxane monoamine (APS) and ethylchloroacetate or ethyliodoacetate to produce the glycinatepolysiloxanes GPS1 and GPS2 respectively as follows: The

3-aminopropylpolysiloxane (2.0 g, 0.007 mol N) was refluxed at 110°C with excess of ethylchloroacetate or ethyliodoacetate (0.09 mol) for different reaction times ranging from 24–72 h in presence of triethylamine (1.0 g, 0.009 mol). The mixture was cooled to room temperature, filtered and washed with portions (100 cm<sup>3</sup>) of distilled water, methanol, and diethylether. The products GPS1 and GPS2 were dried *in vacuo* (0.1 torr) for at least 2 h at 80°C.

The second method used is through polycondensation of tetraethoxysilane and ethylglycinatepropyltriethoxysilane as follows: Ethylglycinatepropyltriethoxysilane (6.14 g, 0.02 mol) was added to stirred solution of tetraethoxysilane (8.7 g, 0.039 mol) in 3.0 cm<sup>3</sup> of 0.42M HCl. The mixture was stirred for 7 h and left overnight for gelation. The solid product (GPS3) was crushed and kept in an oven at 100°C overnight. The polymer was washed with water, methanol and diethylether and dried *in vacuo* (0.1 torr) for 2 h at 80°C. The analyses of these ligand systems are given in Table-3.

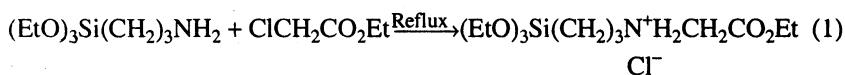
*Hydrolysis of ethylglycinate functionalised polysiloxanes (GPS2h and GPS3h):* A known amount of the appropriate functionalised polysiloxane (5.0 g) was stirred and refluxed with 50 cm<sup>3</sup> hydrochloric acid (5 M) at 100°C for 24 h. The mixture was cooled to room temperature, filtered and the product was washed with water, methanol and diethylether. The material was dried *in vacuo* (0.1 torr) at room temperature for 3 h. The elemental analyses of the hydrolyzed polysiloxane materials are given in Table-3.

*Metal uptake:* The appropriate polysiloxane monoamine and glycinate ligand system (0.1 g) was shaken with twice the required amount of an aqueous solution of copper(II) ion (0.1 M). After 24 h contact time at room temperature the polysiloxane metal complex was separated by filtration, washed with water, methanol and diethylether. The resultant blue solid products were dried *in vacuo* (0.1 torr) for at least 2 h at 100°C and kept in vacuum desiccator at room temperature. The elemental analyses for the copper(II) complexes are given in Table-4.

## RESULTS AND DISCUSSION

*Synthesis:* Polysiloxane-immobilized glycinate ligand systems were prepared by two methods: firstly by hydrolytic condensation of Si(OEt)<sub>4</sub> and the silane coupling agent (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NHRCH<sub>2</sub>CO<sub>2</sub>Et; the gelation occurs after a few hours yielding a porous material. The second method used is the reaction between the prepared 3-aminopropylpolysiloxane and ethylchloroacetate or ethyliodoacetate.

*Preparation of the silane coupling agent (ethylglycinatepropyltriethoxysilane):* In this work the ethylglycinatepropyltriethoxysilane was prepared by the reactions of 3-aminopropyltriethoxysilane and chloroethylacetate. The microanalyses data are given in Table-1. The expected values are calculated based upon complete reaction. The molar ratio of C/N values of the expected and found values suggest a 1 : 1 molar ratio reaction and not 1 : 2 reaction as shown in Eq. (1).



The lower C and N percentages than the expected ones are consistent with the higher Cl percentage due to generated HCl and, therefore, decrease the found C and N percentages and increase the Cl percentage.

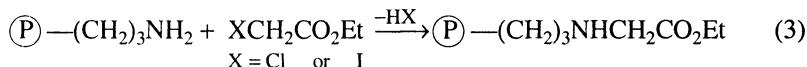
*Preparation of ethyliodoacetate:* The ethyliodoacetate was prepared by reaction of ethylchloroacetate with sodium iodide as shown in Eq. (2).



The  $^1\text{H-NMR}$  and chemical shift assignments of ethylchloro- and ethyliodoacetate are given in Table-2. The elemental analysis of the resulting material is given in Table-1.

*Preparation of monoamine ligand system:* The immobilized monoamine ligand system was made as previously described<sup>6,8</sup> by hydrolytic polycondensation of  $(\text{OEt})_4\text{Si}$  and  $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ , where the amine group act as self-catalyzed. The elemental analyses results (Table-3) indicate that the found and the expected values are very similar, but the carbon and nitrogen percentages lower than those expected can be explained due to leaching of small oligomers of ligand containing groups; this was confirmed by several studies<sup>15</sup>.

*Preparation of glycinate polysiloxane ligand systems:* The glycinate ligand system was prepared by the reaction of the polysiloxane immobilized monoamine ligand with haloethylacetate as given in Eq. (3).



The elemental analyses for these products (GPS1 and GPS2) are given in Table-3. Figure 1 shows the analytical data of N% and C/N versus the time of the

Time(h) vs C/N and N

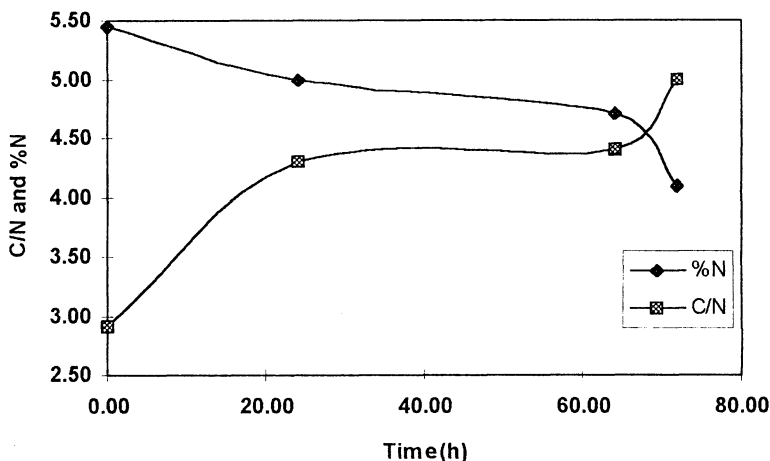


Fig. 1. Analytical data of N % and C/N versus time for the reaction between ethylchloroacetate and polysiloxane monoamine ligand

reaction. In the reaction between chloroethylacetate and the polysiloxane monoamine, the results summarized in Table-3 show higher carbon percentage than that of monoamine ligand which suggests that the ethylacetate groups become incorporated into the polymer surface GPS1. This was also obvious from the increase of C/N molar ratio from 2.9 for the monoamine to 5.2 for the glycinate ligand system. From figure 1 it can be noted that on the one hand, as the time of the reaction proceeds (72 h) the percentage of N decreases and more ethylglycinate becomes incorporated into the surface of the polymer. On the other hand, the found elemental analysis values are a little far from the calculated values due to incomplete reaction. This could be due to some of the amine groups which are buried inside the polymer and do not react with ethylchloroacetate, and only the amine on the surface of the polymer reacts and may block access to deeper sites.

In the case when the iodoethylacetate was used instead of chloroethylacetate the analyses show higher carbon and lower nitrogen percentages than those found for the monoamine polysiloxane GPS2 (Table-3). This also provides strong evidence for introduction of acetate group into polymer surface, which was confirmed by IR spectra (Fig. 2b).

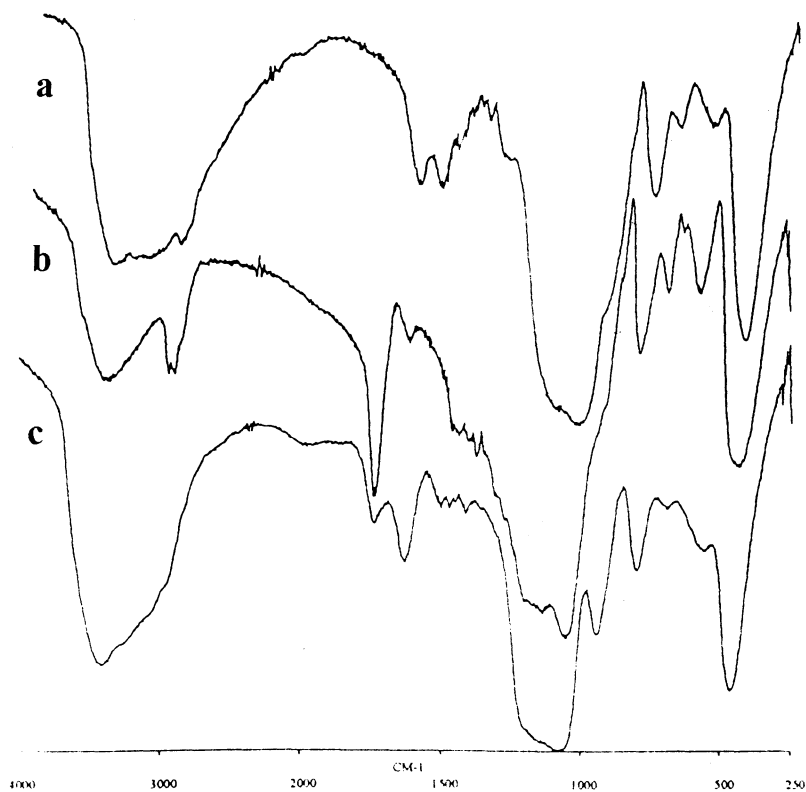


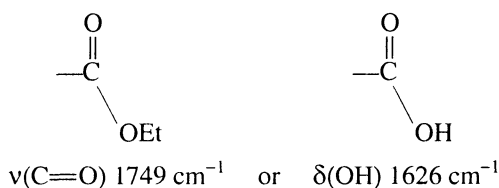
Fig. 2. FTIR Spectra of (a) polysiloxane monoamine (APS)  
(b) Ethylglycinate polysiloxane (GPS)  
(b) Glycinate polysiloxane (GPSH)

The alternative route for preparing the polysiloxane glycinate ligand system is a two-step reaction: first producing an ethylglycinate silane coupling agent was produced by the reaction of chloro or iodoethylacetate with 3-aminopropyltriethoxysilane and then the resulting product was reacted with tetraethoxysilane to give the required ethylglycinatepolysiloxane. The analysis results (Table-3) show higher nitrogen and less carbon percentages than the expected values. This can be explained due to formation of small soluble oligomers formed from self-condensation of the tetraethoxysilane agent.

The acid hydrolysis of polysiloxane-immobilized glycinate ligand systems GPS2 and GPS3 indicates that ethoxy groups were mostly hydrolyzed (Table-3) with only little residual of ethoxy groups still unhydrolyzed upon treatment of acid. This was supported by IR spectra Figure 2c.

### Infrared spectra

The FTIR spectra for these polysiloxane-immobilized ligands show three characteristic regions at 3300, 1740 and 1100  $\text{cm}^{-1}$  corresponding to  $\nu(\text{OH})$  or  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{O})$  and  $\nu(\text{Si}-\text{O})$  vibration respectively. These assignments are based on IR data obtained from literature<sup>21</sup>. The IR spectra for the polysiloxane monoamine ligand system, the polysiloxane ethylglycinate and its hydrolysis form by hydrochloric acid (5 M) are shown in Figure 2. The IR spectrum for the immobilized monoamine (Figure 2a) shows two bands at 3340 and 1610  $\text{cm}^{-1}$  respectively which are probably assigned for the  $\nu(\text{NH})$  and  $\delta(\text{OH})$  vibrations respectively. Upon the reaction with chloroethylacetate, the IR spectrum (Figure 2b) shows strong absorption band at 1741  $\text{cm}^{-1}$  due to the ester  $\nu(\text{CO})$  stretching vibrations. This provides an evidence for the introduction of the ethylacetate group. The IR spectrum of acid form (Figure 2c) shows two absorption bands at 1626 and 1749  $\text{cm}^{-1}$  due to the  $\delta(\text{OH})$  and  $\nu(\text{CO})$  vibrations for the acid form respectively as follows:



The presence of low intensity absorption band at 1749  $\text{cm}^{-1}$  may confirm that not all ester ethoxy groups ( $-\text{OEt}$ ) have transformed to the acid form ( $-\text{OH}$ ).

*Metal uptake:* The microanalytical data for the interaction of polysiloxane monoamine and glycinate ligands with un-buffered (pH = 4.5) solutions of copper(II) chloride, are listed in Table-4. These ligands undergo some further loss of carbon and nitrogen, presumably by leaching of small oligomeric species. This was confirmed by other workers<sup>6-9, 14-16</sup>. The polysiloxane-immobilized monoamine ligand systems show reactivity toward aqueous Cu(II) ions solution. The white 3-aminopropylpolysiloxane changed into a blue solid. It has been reported<sup>6,8</sup> that these immobilized monoamine ligands form 1 : 1 and 1 : 2 Cu(II) complexes. Recently El-Nahhal found that Cu(II) complexes form 1 : 1 and 1 : 2 metal to ligand complexes<sup>15</sup> per monoamine group.

For glycinate it might be expected that the maximum metal-loading achievable would correspond to one metal ion per two glycinate ligand groups, but it is evident that this stoichiometry is not achieved. The low metal uptake by glycinate compared to the amount of ligand substituted on the polymer may be due to irregularity of distribution of glycinate groups on the polymer matrix, so that sufficient ligand groups are not available at all sites and the initial binding of copper ion may block access to deeper sites.

In addition the hydrolysis of ethylglycinatepolysiloxane may be not complete which was confirmed by elemental analysis and FTIR spectra which decreases the metal-binding ability of the ligand. In this case, the starting polymer probably contained a mixture of glycinate, unhydrolysed ethylglycinate and unfunctionalised propylamine groups. It is therefore difficult to observe any stoichiometry.

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