JOURNAL OF
Materials
CHEMISTRY
Communication

Selective sorption of gold(III) by polystyrene-supported α-pyridylamino oligomers

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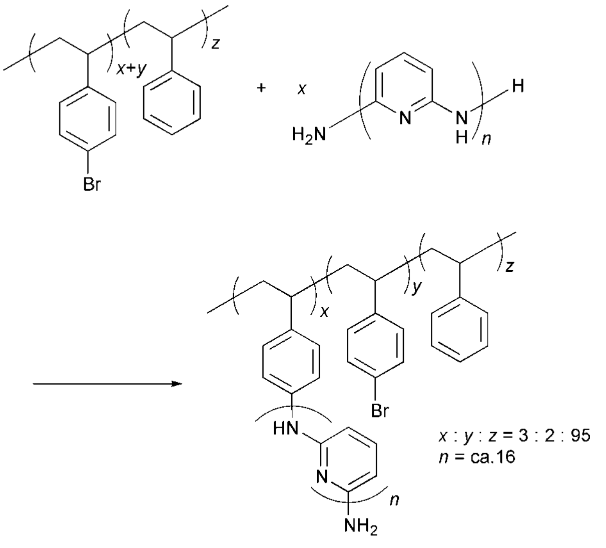
Received 7th August 2000, Accepted 22nd August 2000
First published as an Advance Article on the web 19th September 2000

α-Pyridylamino oligomer was immobilised on a polystyrene support, and the sorption of some metal ions by the polymer was investigated. This polymer was able to preferentially sorb gold(III) from aqueous solutions also containing palladium(II), platinum(IV), ruthenium(III) or copper(II) at pH 1.

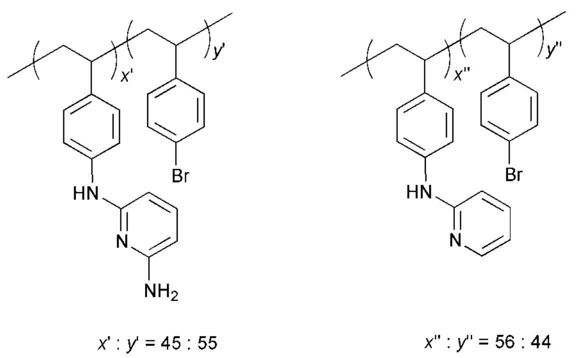
On the separation of desired metal ion by chelate resin from a solution containing various metal ions, the selectivity is one of the most significant functions. Since the choice of ligand introduced into the resin plays an important role in achieving the selectivity, a variety of functional groups which can selectively chelate with desired metals have been utilised.[1] 2,2′-Dipyridylamine is one of the well-known chelating ligands for metal ions, and polymers containing this compound have been prepared as sorbents of iron(III), chromium(III), cobalt(II), copper(II) and nickel(II).[2,3] Recently, the new oligo-α-pyridylamino ligand has been of great interest because this ligand is able to bind some metal ions, including copper, in a string.[4–7] On the other hand, we have examined the utility of the palladium-catalysed amination of aryl bromides in polycondensation as well as polymer reactions to afford new functional polymers.[8–11] In the course of our investigation, we have found that the polycondensation of 2,6-dibromopyridine with 2,6-diaminopyridine gives poly(2,6-pyridinediylimine) in good yield.[11] This information prompted us to introduce the α-pyridylamino oligomer into the side chain of polystyrene in a one-pot palladium-catalysed polycondensation and polymer reaction according to Scheme 1. Using the new polystyrene bearing α-pyridylamino oligomer (**1**), we investigated the sorption behaviour of some metal ions, and found that **1** was a selective sorbent for gold(III); **1** was able to preferentially sorb gold(III) from an aqueous solution which also contained palladium(II), platinum(IV), ruthenium(III) or copper(II) at pH about 1. In this communication, we report the preparation of **1** and preliminary investigations to evaluate the sorption ability of **1** for some metal ions.

Preparation of **1** was carried out under N_2 in a manner analogous to the previous reports.[10,11] A mixture of 2,6-dibromopyridine (746.2 mg, 3.15 mmol) and 2,6-diaminopyridine (382.0 mg, 3.5 mmol) was dissolved in toluene (20 ml). Sodium *tert*-butoxide (1009.4 mg, 10.5 mmol), tris(dibenzylideneacetone)dipalladium (80.1 mg, 0.0875 mmol), and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (163.7 mg, 0.2625 mmol) were added to the solution. The reaction mixture was stirred at 100 °C for 2 h to afford α-pyridylamino oligomer with a primary amino end group. After cooling to room temperature, poly(*p*-bromostyrene-*co*-styrene) (P(*p*-BrSt-*co*-St), $(x+y)/z=1/19$)[12] was added to the reaction mixture solution and stirred at 100 °C for 16 h. After reaction, the mixture was poured into a mixture of aqueous ammonia and methanol, and the precipitate was washed thoroughly with aqueous ammonia and methanol. The obtained pale brownish powder of **1** was insoluble in common organic solvents, indicating that **1** has a partly cross-linked structure.[13] From the results of elemental analysis, the degree of substitution of the polymer and the degree of polymerisation of α-pyridylamino oligomer were estimated at about 0.6 and 16, respectively.[14] The other polystyrene-immobilised pyridylamino groups were also prepared by using poly(*p*-bromostyrene) and 2,6-diaminopyridine (**2**) or 2-aminopyridine (**3**) to compare the sorption ability for metal ions with **1** (Scheme 2). The amounts of pyridylamino



1

Scheme 1



2 **3**

Scheme 2

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DOI: 10.1039/b006425o

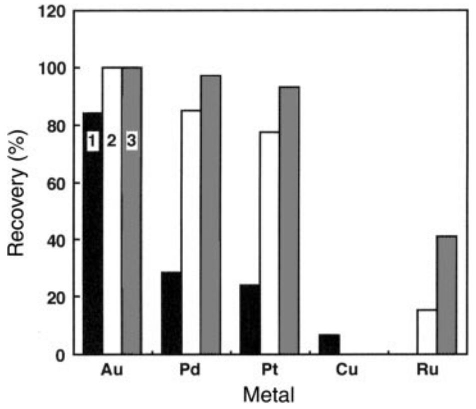

Fig. 1 Recovery of some metal ions by **1**, **2** and **3**. Each metal, 1 mmol l^{-1}; sample volume, 10 ml; each polymer, 10 mg; pH, *ca.* 1.

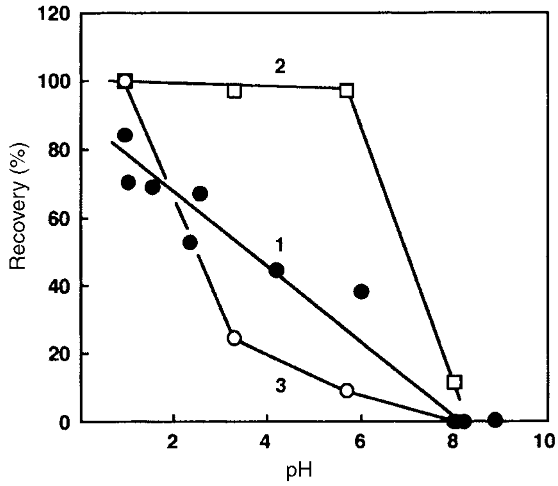

Fig. 2 Effect of pH on the sorption of gold(III) by **1**, **2** and **3**. Au(III), 1 mmol l^{-1}; sample volume, 10 ml; each polymer, 10 mg.

unit in 1 g of the polymers were approximately 4.3 mmol (**1**), 2.6 mmol (**2**) and 3.1 mmol (**3**).[14]

The sorption of some metal ions by **1**, **2** and **3** was investigated using 10 ml of 1 mmol l^{-1} metal solutions at pH about 1 and 10 mg of each polymer. The aqueous solutions containing metal ions were prepared by diluting the commercially available metal stock solutions (Kanto Chemical Co.) or dissolving the metal chloride in dilute hydrochloric acid and, if necessary, adjusting the pH using dilute hydrochloric acid or sodium hydroxide solution. The solution was then added to the polymer and stirred vigorously for about 16 h at room temperature (about 25 °C). The concentration of metal ions in the solution was then measured using inductively coupled plasma atomic emission spectrometry after filtration using a membrane filter (pore size 0.2 μm). The obtained results are shown in Fig. 1. The concentration of gold(III) in the solution was significantly decreased by the addition of **1**, although the concentration varied little ($<5\%$) upon addition of P(*p*-BrSt-*co*-St) in the absence of α-pyridylamino oligomer. These results indicate that **1** is able to sorb gold(III). Palladium(II) and platinum(IV) were also sorbed by **1**, however, the recoveries of these metal ions were much lower than that of gold(III). In contrast, **2** and **3** were able to sorb not only gold(III) but also palladium(II) and platinum(IV) at high recoveries, as shown in Fig. 1. The recoveries of ruthenium(III) by **2** and **3** were also much higher than that by **1**. Copper(II) was little sorbed by **2** and **3** as well as **1** at pH about 1, though the other polymers containing the pyridylamino unit[2,3] could sorb copper(II).

On the basis of the results mentioned above, we further examined the sorption behaviour of gold(III) by **1**, **2** and **3** under various conditions. When gold(III) was sorbed by **1** from the solution containing various amounts of gold(III) at pH 1, the relation between the amount of sorbed gold(III) and its remaining amount in the solution followed the Langmuir adsorption isotherm. Similar tendencies were obtained for **2** and **3**. These results suggest that gold(III) is captured by the sorption site in **1**, **2** and **3**. The sorption capacities of **2** and **3** for gold(III) were much larger than that of **1**; the amounts of gold(III) sorbable by 1 mmol of pyridylamino unit in the polymers were about 0.2 mmol (**1**), 0.9 mmol (**2**) and 0.7 mmol (**3**). Fig. 2 shows the effect of pH on the sorption of gold(III) by the polymers. The recoveries of gold(III) by **1** and **3** decreased with increasing pH in the solution, and gold(III) was hardly sorbed at pH values higher than 8. **2** sorbed gold(III) quantitatively over the pH range from 1 to 6, however, the amount of sorbed gold(III) decreased considerably at pH 8. The pH dependence of the gold(III) sorption by **1**, **2** and **3** is of interest compared with those by the other sorbents for gold(III), which have immobilised nitrogen-atom-containing functional groups such as poly(vinyl aminoacetone),[15] 1-(2-aminoethyl)-piperazine,[16] thiourea,[17] imidazoline[18] and dithizone and pyridine.[19] Since the pK_a values of 2,2′-dipyridylamine and 2-aminopyridine are 6.69 ± 0.01[20] and 7.2,[20,21] respectively, α-pyridylamino oligomer in the polymers seems to be protonated under acidic conditions. Gold(III) would be present forming a chloro complex such as tetrachloroaurate(III) ion in the solution because the stock solution of gold used for the investigation was prepared by dissolving gold metal in aqua regia.[22] Cotton *et al.* have succeeded in isolating a crystal in which the protonated 2,2′-dipyridylamine cation and tetrachlorocobaltate(II) anion pack forming hydrogen bonds between the NH groups and a chloride ion of the tetrachlorocobaltate(II) anion.[23] The sorption of gold(III) by **1**, **2** and **3** may also be attributed to electrostatic forces and the release of gold(III) sorbed on the polymers could be expected by using alkaline solution as eluent, however, no details have yet been investigated. We will soon examine these points in detail.

Using **1**, **2** and **3**, the competitive sorptions of gold(III) and other metal ions from solutions containing 1 mmol l^{-1} of both metal ions were then examined at pH 1. The results are summarised in Table 1. The sorption of gold(III) by **1** was affected only slightly by the presence of the other metal ion, however, the recoveries of palladium(II) and platinum(IV) were

Table 1 Results of competitive sorption of gold(III) and each of the other metal ions[a]

Metal		Recovery [%]					
		1		**2**		**3**	
A	B	A	B	A	B	A	B
Au	Pd	57.6	5.7	92.0	66.9	96.9	58.8
Au	Pt	74.2	0.0	90.5	37.3	95.5	50.7
Au	Cu	69.2	6.2	96.8	4.1	98.9	3.0
Au	Ru	76.4	0.0	98.3	3.8	99.7	31.6

[a] Solutions containing 1 mmol l^{-1} of both gold(III) and the other metal ion were used. Sample volume, 10 ml; each polymer, 10 mg; pH, 1.

significantly decreased by the presence of gold(III), and copper(II) and ruthenium(III) were also little sorbed. For **2** and **3**, the sorption of gold(III) was scarcely influenced by the presence of the other metal ions. Although the recoveries of palladium(II) and platinum(IV) by **2** and **3** somewhat decreased in the presence of gold(III), the recoveries were still higher than those by **1** from each metal solution. From these results, it can be seen that **1** is inferior to **2** and **3** for the sorption capacity of gold(III), however, **1** is able to preferentially sorb gold(III) from solutions containing palladium(II) and platinum(IV). The difference in ability for the sorption of metal ions seems to be attributable to the chain length of the pyridylamino unit attached to the polystyrene.

In conclusion, the polystyrene bearing α-pyridylamino oligomer has the ability to selectively sorb gold(III). By optimisation of the chain length and the degree of substitution of the α-pyridylamino oligomer, this polymer may be useful for the selective separation of gold(III) from solutions containing other noble metal ions such as palladium(II), platinum(IV) and ruthenium(III), and heavy metal ions such as copper(II). It may also be suggested that the chain length of the ligand unit introduced to the resin may allow control over the selectivity for the sorption of metal ions. To make this point clear, further studies are in progress.

Acknowledgements

The authors are grateful for financial support from the Steel Industry Foundation for the Advancement of Environmental Protection Technology.

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13 Since the palladium-catalysed aryl amination of aryl bromide with a primary amine using a catalyst system generated from tris(dibenzylideneacetone)dipalladium and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl was much faster than that with a secondary amine,[11] the potential cross-linked reaction would occur between the primary amino end group of α-pyridylamino oligomer and the *p*-bromostyrene unit of P(*p*-BrSt-*co*-St).

14 The degree of substitution of the polymers and the degree of polymerisation of α-pyridylamino oligomer were calculated from C/Br and C/N ratios.

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