A selective uranium extraction agent prepared by polymer imprinting†

Gregory D. Saunders,[a] Simon P. Foxon,[a] Paul H. Walton,*[a] Malcolm J. Joyce[b] and Simon N. Port[b]

[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: phw2@york.ac.uk*
[b] *BNFL Research and Technology, Salwick, Preston, Lancashire, UK PR4 0XJ*

Using a modified method in the preparation of an imprinted polymer, we report here the synthesis of a uranyl-imprinted copolymer of chloroacrylic acid and ethylene glycol dimethacrylate, which—after removal of the template—selectively extracts uranium from dilute aqueous solution over a range of +2, +3 and +4 competitor metal ions.

The technique of polymer imprinting has shown considerable promise as a method for preparing materials which are capable of molecular recognition.[1] Of late, the technique has seen some impressive successes in the selective absorption of both organic molecules and metal ions.[2] One important goal is the preparation of absorbents specific for uranium, because of uranium's large environmental impact and importance as an energy resource. Recent progress has been made by Murray *et al.* who showed that a uranyl-imprinted polydivinylbenzene/styrene-based polymer absorbs uranium over a range of +1 and +2 metal ions and also La^{3+} (at pH > 3).[3] We report here the preparation and characterisation of a new selective uranium-binding polymer. Importantly the polymer shows excellent selectivity against a range of 'strong' competitor metal ions, including Th^{4+} and Fe^{3+} (at pH < 3).

In our studies we have used the uranyl complex of chloroacrylic acid (caaH) as a template [Scheme 1(a)]. ^{13}C NMR in CD_2Cl_2 studies of $UO_2(caa)_2(OH_2)_2$ suggest that this complex contains a uranyl ion coordinated by two bidentate chloroacrylate ligands and two water molecules.‡ We have been unable to crystallise this complex, but we have studied the analogous $UO_2(caa)_2(O=PPh_3)_2$ complex by single crystal X-ray diffraction (Fig. 1).§ The structure of this complex shows both bidentate and monodentate chloroacrylate ligands along with two triphenylphosphine oxide ligands coordinating to the uranyl ion.

Co-polymers of 2-chloroacrylic acid (caaH) and the cross-linking agent ethylene glycol dimethacrylate (egdma) can be prepared by free-radical solution polymerisation, thermally initiated with azoisobutyronitrile (aibn) in refluxing dichloro-
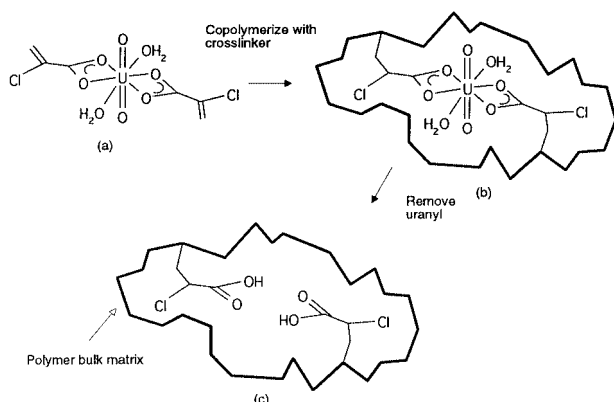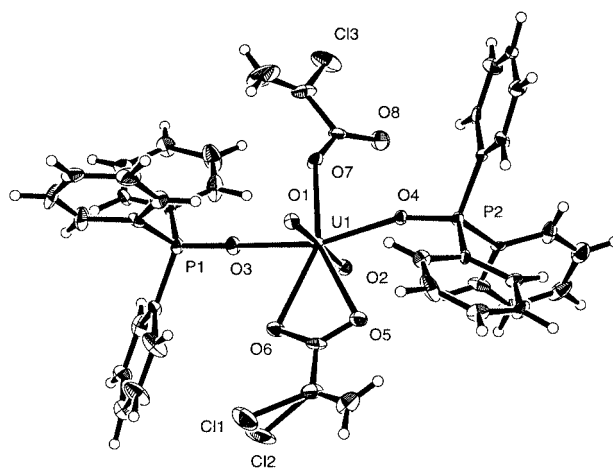
Fig. 1 ORTEP representation of the $[UO_2(caa)_2(O=PPh_3)_2]$ structure. Cl1 and Cl2 represent a single Cl atom disordered over two positions. Selected distances (Å): U1–O1 1.772(8), U1–O2 1.776(9), U1–O5 2.496(8), U1–O6 2.499(8), U1–O7 2.309(8), U1–O3 2.361(8), U1–O4 2.320(7).

methane. Imprinting with uranyl is achieved by replacing caaH with the soluble template complex $UO_2(caa)_2(OH_2)_2$ [prepared *in situ* by reaction of caaH with NEt_3 and $UO_2(NO_3)_2 \cdot 6H_2O$ prior to polymerisation]. In the solution polymerisation reaction the ratio of reactants was 91/9 mol/mol% egdma/UO_2-$(caa)_2(OH_2)_2$—typically a total of 3.5 g reactants in 100 cm³ of CH_2Cl_2. The imprinted polymer was obtained as a pale yellow precipitate after 5 h [Scheme 1(a) and (b)]. The material was washed with CH_2Cl_2 and then dried *in vacuo* prior to grinding to a fine powder (particle diameter *ca.* 50 μm). As a comparison, a 'random polymer' was prepared in an analogous manner without the addition of NEt_3 and $UO_2(NO_3)_2 \cdot 6H_2O$. We denote this as a 'random polymer' since the orientations and relative positions of the α-chloropropionic acid (cpaH) groups in the polymer are presumed to be random.

Extraction of the uranyl from the imprinted polymer was achieved by treatment of the polymer with conc. HNO_3 under ultrasonication (30 kHz) for 15 min [Scheme 1(c)]. Following extraction, thorough washing of the polymer with deionised water and then drying *in vacuo* gave the imprinted polymer as a white powder. Elemental analysis of the polymer for uranium confirmed > 95% extraction of the uranium from the polymer. Treatment of the random polymer with conc. HNO_3 in a 30 kHz sonic bath for 15 min did not change the percentage content of cpaH (determined by elemental analysis for chlorine), showing that the cpaH is tightly bound—probably *via* a covalent bond—to the polymer.

To investigate the effectiveness of the imprinting technique, rebinding of uranyl by the imprinted polymer was determined in the pH range 1–3. Approximately 2.60 g of polymer was stirred with a dilute aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (50 cm³, 0.5 mmol dm⁻³) such that there was a fifty-fold mole excess of polymer-bound cpaH compared to uranyl. The pH was recorded after 4 min, after which the uranyl binding had equilibrated,¶ and the concentration of the uranyl ion in a small sample of the supernatant was determined by visible spectrophotometry using

Scheme 1 Schematic reaction scheme for the preparation of uranyl-imprinted polymer.

† S. N. Port, M. J. Joyce, P. H. Walton and G. D. Saunders, *UK Pat. Appl.*, 979946.7, 1997; *Int. Pat.*, WO 99/15707, 1998.

the Arsenazo I method.[4] The pH was changed by the addition of small quantities of dilute HNO_3 or NaOH solutions and the extraction analysis procedure repeated.

The uranyl-binding behaviour of the imprinted and random polymers shows a reversible (*i.e.* the polymer can be reused) and smooth transition between low (*ca.* 10%) and high (>98%) uranyl binding between pH 1.0 and 3.0. A plot of $\log_{10}[D_{ex}]$ *vs.* pH for the two polymers is shown in Fig. 2.‖ The near linearity of the data in the plots shows that the 'pH swing' binding model[5] is an accurate representation of this system. The gradient of the plots can be equated to *n*, the average stoichiometry of the $[UO_2(cpa)_n]$ complexes formed within the polymer, which, in turn, can be related to the fraction of imprinted binding sites (those containing two cpaH ligands) compared to non-imprinted binding sites (those with a single cpaH). In the random polymer *n* is approximately 1.1, showing that *ca.* 10% of the binding sites contain two cpaH ligands able to interact with a single uranyl ion. In contrast, for the imprinted polymer *n* increases to nearly 1.8 showing that *ca.* 80% of the uranyl binding sites contain two cpaH ligands. This increase can be attributed to the imprinting effect of the uranyl in the polymerisation process. The pH dependence of Th^{4+} binding to the polymer was also investigated, giving $n = 0.5$; a strong indication that most binding of Th^{4+} is associated with non-imprinted sites.
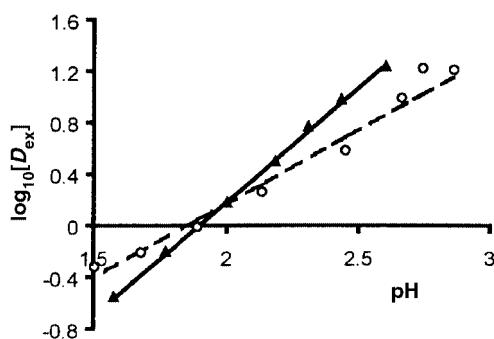

Fig. 2 $\log_{10}[D_{ex}]$ plots for the binding of uranyl by polymers as a function of pH. Black triangles, full line: imprinted polymer [gradient *n* - 1.77(3), R^2 = 1.00]. Circles, dashed line: random polymer [gradient $n = 1.14(7)$, R^2 = 0.97].

The selectivity of the imprinted polymer for uranyl was investigated by rebinding uranyl in the presence of various competitor metal ions. In a typical experiment 25 mg of polymer was mixed with a dilute aqueous solution of $UO_2(NO_3)_2$ (0.42 mmol dm^{-3}, 10 cm^3, 2.5 mmol dm^{-3} NO$_3^-$ made up with KNO_3, constant pH 2.5) containing an equal concentration of one other competitor metal salt: hydrated salts of $Cu(NO_3)_2$, $VO(SO_4)$, $Al(NO_3)_3$, $Fe(NO_3)_3$ or $Th(NO_3)_4$. These competitor ions were chosen as the potentially strongest competitor ions for the uranyl binding sites. The resulting suspensions were shaken periodically over a period of 12 h before filtration. UO_2^{2+} and competitor metal concentrations in the supernatant were then determined by ICP-AES.

Table 1 lists the selectivity ratios ($S_{U/M}$) of uranyl *vs.* competitor metal binding to both random and imprinted polymers. It is clear that the random polymer exhibits no selectivity for the binding of the uranyl ion ($S < 1$), binding less uranyl than competitor ion in every case except Cu^{2+}. In contrast, the imprinted polymer displays a remarkable increase and even *reversal* of selectivity over the random polymer, increasing the relative polymer selectivity for uranium by over ten times in one case. The imprinted polymer exhibits a consistently higher binding of uranyl compared to each of the competitor ions, even against competitor ions such as Fe^{3+} and Th^{4+}, which would be expected to compete very strongly with UO_2^{2+} for the carboxylate binding sites. The results of the binding experiments show that the difference in metal binding between the random and imprinted polymers is due to the imprinting effect.

Table 1 Selectivity ratios for uranyl binding *vs.* competitor ion binding for random and imprinted polymers (23 °C, pH 2.5). U = uranyl, M = competitor ion. $S_{U/M} = S_U/S_M$. $S_M = V(C_i - C_f)/(C_f m)$ where C_i = concentration of solution before extraction, C_f = concentration of solution after extraction, $S' = (S_{U/M}$ imprinted$)/(S_{U/M}$ random$)$, V = volume of solution, m = mass of polymer

| | Selectivity ratios for U binding *vs.* competitor binding | | |
Competitor metal	Random polymer $S_{U/M}$ (random)	Imprinted polymer $S_{U/M}$ (imprinted)	Selectivity ratio increase S'
Cu^{2+}	6.5	8.1	1.2
V^{4+} (as VO^{2+})	0.32	3.8	11
Al^{3+}	0.29	2.5	8.6
Fe^{3+}	0.17	1.4	8.1
Th^{4+}	0.76	2.0	2.7

Notes and references

‡ $[UO_2(caa)_2(OH_2)_2]$ $^{13}C\{H\}$ NMR (270 MHz, CD$_2$Cl$_2$); δ 125.7 (s, CH$_2$), 136 [s, C(Cl)=CH$_2$], 176.4 (s, COO).

§ *Crystal data* for $C_{42}H_{34}O_8Cl_2P_2U_1$; monoclinic, space group $P2_1$ (no. 4), yellow block, $a = 14.927(3)$, $b = 8.8708(12)$, $c = 15.795(3)$ Å, $\beta = 97.735(15)°$, $V = 2072.4(6)$ Å^3, 150 K, $Z = 2$, $R1 = 0.034$, $wR2 = 0.087$, GOF = 1.007. CCDC 182/1518. See http://www.rsc.org/suppdata/cc/a9/a909691d/ for crystallographic files in .cif format.

¶ In separate experiments the maximum capacity of the polymer for uranyl was determined by measuring the extent of uranyl uptake by the imprinted polymer as a function of [uranyl]. (Contact time between polymer and solution was *ca.* 12 h.) The data were then fitted to a Langmuir isotherm, with excellent agreement. Further experiments showed that uranyl binding by the imprinted polymer was >95% of maximum binding after 4 min, with no subsequent significant increase.

‖ D_{ex}, the distribution coefficient of extraction, defined for a given volume of solution, given nitrate concentration and given mass of polymer as: (mol of uranyl ion bound to the polymer)/(mol of uranyl ion left in solution) for eqn. (1).

$$m\text{NO}_3^- + \text{UO}_2^{2+} + \text{polymer}\cdot n\text{H}^+ = \text{polymer}\cdot\text{UO}_2^{2+}\cdot m\text{NO}_3^- + n\text{H}^+ \quad (1)$$
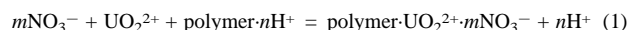
Separate experiments showed that 100% egdma polymers do not bind uranium to any significant extent; demonstrating that the amount of uranyl binding to non-carboxylic acid sites (*i.e.* $n = 0$) is low. It is also assumed that the number of sites where three carboxylic acids can interact with a single uranyl is statistically very low. Hence the average value of *n* obtained from our experiments is approximately the number weighted average of the $n = 1$ and $n = 2$ binding sites within the polymer. For non-integral values of *n* a slight curve is expected in the $\log[D_{ex}]$ *vs.* pH plots. However, this curve is very shallow over the pH range studied and the relationship can be considered as linear. For a treatment of D_{ex} and the calculation of complex stoichiometries and applications to solid phase absorbents, see ref. 5.

1 G. Wulff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1812; M. Kempe and K. Mosbach, *J. Chromatogr. A*, 1995, **694**, 3; J. Steinke, D. C. Sherrington and I. R. Dunkin, *Adv. Polym. Sci.*, 1995, **123**, 81.

2 H. Chen, M. M. Olmstead, R. L. Albright, J. Devenyi and R. H. Fish, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 642; Y. Kiode, H. Senba, H. Shosenji, M. Meada and M. Takagi, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 125; K. Inoue, Y. Baba and K. Yoshizuka, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2915; M. Chanda and G. L. Rempel, *React. Polym.*, 1992, **16**, 149; W. Kuchen and J. Schram, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1695; R. Garcia, C. Pinel, C. Madic and M. Lemaire, *Tetrahedron Lett.*, 1998, **39**, 8651.

3 G. M. Murray and O. M. Uy, *Report to Environmental Management Science Program, Project ID Number 59977*, June 1998; Z. Xiangfei, A. Bzhelyansky, S. Y. Bae, A. L. Jenkins and G. M. Murray, *ACS Symp. Ser. 703*, Washington DC, p. 218.

4 J. S. Fritz and M. Johnson-Richard, *Anal. Chim. Acta*, 1959, **20**, 164.

5 H. Bernhard and F. Grass, *Monatsh. Chem.*, 1967, **98**, 1464; Y. Fujii, H. Maie, S. Kumagai and T. Sugai, *Chem. Lett.*, 1992, 995.

Communication a909691d