

# New System for Complexation of Uranyl Ions from Liquid Wastes of Low-Level Activity: Polypyrrole Doped with Complexing Polyanions

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Received 26 May 1999; accepted 3 November 1999

**ABSTRACT:** Polymer composites consisting of polypyrrole doped by uranyl complexing polyanions [i.e., poly(2-acrylamidoglycolic acid) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid)] were electrochemically synthesized. Bulk material and thin layers strongly adhering to inert supporting electrodes were prepared. These composites were used to precipitate uranyl ions from simulated radioactive wastes. Among different experimental techniques used for the analysis of uranium immobilized in the composites, the Rutherford backscattering of  $\alpha$  particles proved efficient in thin layers. Leaching tests confirmed the persistence of the uranium complexation in the solid composites. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1230–1239, 2000

**Key words:** polypyrrole; polyanion doping agent; uranyl complexation; electropolymerization; low-level radioactivity liquid waste treatment

## INTRODUCTION

In the early 1980s the possible use of polymers for the treatment of nuclear wastes of low-level activity was outlined. In 1984 Westinghouse patented the electrochemical synthesis of poly(vinylimidazole) (PVI) with the purpose of complexing uranium compounds from low activity and secondary liquid wastes.<sup>1</sup> This technique was pro-

gressive compared to the usual processes using polymer resins (polyesters, epoxy resins), bitumen, and cement<sup>2</sup> as containment materials.

Indeed, in the Westinghouse patent, the chemical complexation of the  $\text{UO}_2^{2+}$  cations is very advantageously substituted for physical entrapment, and this substitution is expected to improve the persistence of the cations' fixation. Nevertheless, no leaching tests were reported in this patent. Recently, the complexing properties of PVI toward cations were widely discussed by Rivas et al.<sup>3</sup>

Complexation of uranyl ions by various water soluble polymers based on poly(ethylenimine) was also reported Rivas et al.,<sup>4</sup> and such a complexation strategy was patented by the Los

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Contract grant sponsors: IISN (to D.L. and L.M.); Fonds de la Recherche pour l'Industrie et l'Agriculture (to C.J.); Services Fédéraux des Affaires Scientifiques Techniques et Culturelles (to C.J. and R.J.).

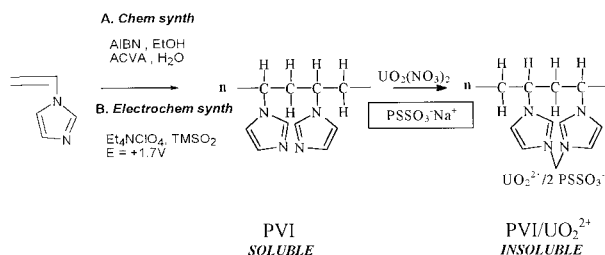
*Journal of Applied Polymer Science*, Vol. 77, 1230–1239 (2000)  
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Alamos Laboratories and the University of California.<sup>5</sup> Egawa et al.<sup>6</sup> reported on the complexation of uranyl ions from seawater by crosslinked chelating resins containing dihydroxyphosphono groups whereas Güler et al.<sup>7</sup> studied a new complexing interpenetrating polymer network prepared by  $\gamma$  irradiation of acrylonitrile in a solution of poly(ethylene glycol), followed by functionalization of the nitrile groups into uranyl complexing amidoxime functions.

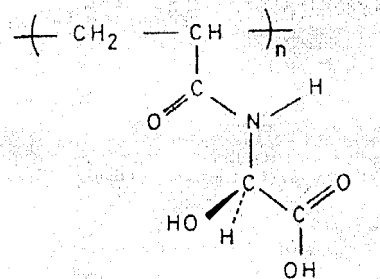
The aim of this study was the electrosynthesis of polymer composites able to complex uranyl ions with formation of insoluble compounds that are very suitable for the recovery of uranium as uranium oxides by calcination in air or for safe containment as a result of the high resistance of solids to leaching. This process is designed for being conducted in aqueous solution at room temperature, which are experimental conditions that are easily achievable in pilot plants.

We previously investigated the potential of PVI<sup>8</sup> but, in contrast to the Westinghouse process, we precipitated the water soluble PVI- $\text{UO}_2^{2+}$  complex by the addition of poly(sodium styrenesulfonate) or poly(sodium styrenecarboxylate) as shown in Scheme 1. We prepared PVI chemically (in water, ethanol, DMA, and DMF) and electrochemically [in sulfolane ( $\text{TMSO}_2$ ) and DMF]. The major drawback of this process based on the electrochemical synthesis of PVI in these organic solvents in the presence of  $\text{UO}_2^{2+}$  is the passivation of the electrode as soon as it is covered by an insulating PVI layer that stops the process.

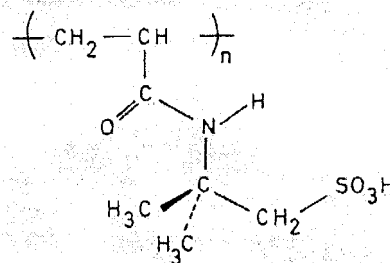
In another study<sup>9</sup> we also demonstrated that the  $\text{UO}_2^{2+}$  ions could be complexed by polyacrylamide derivatives [poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) and poly(2-acrylamidoglycolic acid) (PAAG), Scheme 2) electrochemically prepared in water.<sup>9</sup> The water soluble complex of uranium/polyacrylamide was precipitated in water by either crosslinking of the water soluble polyacrylamide-type polymers by  $N,N'$ -



**Scheme 1** PVI/ $\text{UO}_2^{2+}$  precipitation by  $\text{PSSO}_3^- \text{Na}^+$ .



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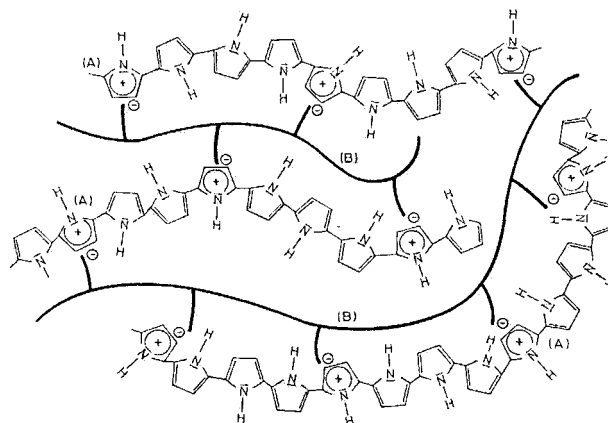
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**Scheme 2** Poly(2-acrylamidoglycolic acid) (1) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (2).

methylene-bis-acrylamide or the addition of polyanions (polystyrenesulfonate or polystyrenecarboxylate). Nevertheless, the large amount of polyanions required to precipitate the complex and the ill-defined long-term insolubility of these compounds are unacceptable drawbacks.

To overcome these difficulties, we report on a new process for the electrochemical synthesis of polymer composites containing polypyrrole (PPy) combined with polyanions (PAAG and PAMPS). The last two polymers have already been used as polyanion doping agents.<sup>10</sup>

The use of a conducting polymer (PPy) allows for the easy control of the electrochemical synthesis. PPy also has the advantages of being stable in acidic media (i.e., nitric acid), which is always present in liquid wastes of low activity, and insoluble in most common solvents, including water, which is favorable to the insolubility of the final composite. The dual role of polyanions as doping agents for PPy and complexing agents for  $\text{UO}_2^{2+}$  can make insoluble composites available for the treatment of radioactive liquid wastes of low activity. To illustrate this opportunity, two polyanions



**Scheme 3** The tentative structure of PPy/polyanion composites; B, the polyanion.

PAMPS and PAAG were used for their capability to complex uranyl cations.<sup>9</sup> Scheme 3 shows a tentative structure for the PPy/polyanion composite.

Although these composites can be prepared either chemically or by electrolysis, the electrochemical approach was thought to be more convenient for the preparation of thin layers on an inert support (platinum or graphite anode). The high specific surface associated with thin layers (10–500 nm) is desirable for efficient waste treatment. It is worth noting that the adhesion of PPy/polyanion<sup>11</sup> composites on various solid substrates is stronger compared to the more usual PPy/ $\text{ClO}_4^-$ , PPy/ $\text{NO}_3^-$  counterparts, possibly because the mobility of the PPy chains is improved by the polymeric doping agent. This feature should allow different types of supports (grids, filters, tubes, etc.) to be coated by the complexing material, which is closely related to the flexibility of the electrochemical technique (which is also suited to the synthesis of bulky material). Compared to the electrochemical approach, the usual chemical synthesis of PPy involves the use of oxidizing cationic agents, such as  $\text{Fe}^{3+}$ , that are competitors with the actinide cations for the complexation by the composite.

After synthesis, the envisioned composites were tested for their ability to complex  $\text{UO}_2^{2+}$  and to impart resistance to the final composite for severe leaching tests.

## EXPERIMENTAL

The  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  was purchased from Fluka (catalog no. 94270). The three monomers

supplied by Aldrich were 2-acrylamidoglycolic acid monohydrate (AAG; 26,049-5), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS; 28,273-1), and pyrrole (Py). They were used as received except for Py, which was freshly distilled before use. The two doping polyanions (PAMPS and PAAG) were synthesized by free radical polymerization as detailed elsewhere.<sup>9</sup> They were characterized by IR and  $^1\text{H-NMR}$  spectroscopy. The viscosity-average molecular weight ( $M_v$ ) was measured by viscosimetry:<sup>12,13</sup> PAMPS  $M_v = 800,000$  and PAAG  $M_v = 10^6$ .

Ammonium persulfate (21,558-9) and tetramethylethylenediamine (TMEDA; T2,250-0) from Aldrich were used as initiators of the free radical polymerization.

The electrochemical cell was fitted with three electrodes. The working electrode (anode) was a platinum plate ( $S = 2 \text{ cm}^2$ ), a vitreous carbon plate, or a plate of a polyethylene/carbon black composite containing 15 wt % of carbon black (to exceed the conductivity threshold of the composite). The cathode and the pseudo reference electrode were platinum foils of about  $4 \text{ cm}^2$  and a platinum wire, respectively. The experiments were carried out at room temperature under ambient conditions.

Electrochemical polymerization of Py was conducted with an EG&G Princeton Applied Research model 263 A potentiostat/galvanostat. Coulometric measurements were recorded with a current integrator (type IG6-N, Tacussel).

A VEMI (PM/6305/type 6099B) counter working at 1,240 V was used for the  $\alpha$  counting of either electrode surfaces or crushed composites.

The Rutherford backscattering spectrometry (RBS) analysis technique was used to analyze the uranium-containing thin layers. Samples were deposited by electrolysis onto polyethylene/carbon black and vitreous carbon electrodes and not onto Pt ones because the  $\alpha$  particles are able to reach the electrode through the thin layers, giving a broad peak that would cover the N and S peaks entirely because the energy of the  $\alpha$  particles backscattered by Pt is higher than those of carbon. The 3-MeV incident  $\alpha$  particles were produced by a Van de Graaff accelerator. The backscattered particles were detected by an annular PIPS detector with an active detection area of  $100 \text{ mm}^2$  and a resolution of 19 keV. The detection of  $\alpha$ -backscattered particles occurs on a solid angle of  $0.007 \text{ sr}$ .

### Synthesis of PPy/PAMPS and PPy/PAAG Composites

A typical recipe for the preparation of these composites was as follows. An aqueous solution of polyanion (0.1M) and Py (concentration range of 0.5–1M) was used as the electrochemical bath of an appropriate conductivity.

The potentiostatic polymerization of Py required the anodic polarization of the working electrode at +0.8 V with respect to the pseudo reference. In the synthesis of bulk composites the pH increased all along the synthesis from 3 to 5 for the PPy/PAMPS composite and from 6 to about 8 for the PPy/PAAG one. This pH effect was previously pointed out by Pei and Qian.<sup>14</sup>

The current quantity ( $C$ ) was integrated for the whole synthesis, the composite being precipitated on the anode during electrolysis.

Thin layers (100–500 nm) were prepared with current quantities not exceeding 500 mC. Under these conditions the polymer films strongly adhered to the electrode, which agrees with previous observations.<sup>11</sup> The electrodes were carefully rinsed with water to remove any possibly adsorbed polyanion and finally rinsed with acetone. The electrodes were dried under a dynamic vacuum at room temperature.

In larger current quantities the composite fell into the cell and it was recovered by filtration, washed, and dried.

Under these experimental conditions, thin layers were formed after 5–30 s whereas bulk material was collected after several hours. For instance, electrolysis of 50 mL of 1M Py and 0.1M PAMPS solution produced 1.9 g of composite after 12 h, and the integrated quantity of current was 1500 C.

### Characterization of PPy/PAMPS and PPy/PAAG Composites

The IR spectra of these composites were ill defined as commonly observed for PPy derivatives. TGA analysis of each polyanion and the two types of composites were differently shaped and gave essentially qualitative information.

Incorporation of polyanion in the final composite was estimated according to a procedure reported in a previous article.<sup>15</sup> Yield of the electrochemical synthesis was first determined by accurately weighing the platinum electrode of an average mass of 0.75 g ( $S = 1 \text{ cm}^2$ ) with a Micro

Cahn electrical balance (ultimate sensitivity = 0.1  $\mu\text{g}$ ).

PPy doped with perchlorate was then electrodeposited on this electrode under the conditions described for the composites, except for the polyanion that was replaced by  $\text{LiClO}_4$  (0.1M).

A charge quantity of 4.0053 C was measured with a Coulometric integrator, such that a theoretical mass of 2.0528 mg would be deposited in case of a 100% yield. This theoretical mass was calculated by using Faraday's law and assuming the incorporation of 0.35 perchlorate ions by the Py unit as reported by Naoi et al.<sup>16</sup> After rinsing and drying, the electrode was weighed and subtraction of the weight of the original electrode gave the mass of the PPy layer ( $1.89 \pm 0.025 \text{ mg}$ ).

The electrochemical yield ( $92 \pm 3\%$ ) was calculated by comparison with the theoretical mass.

The same synthesis was then repeated with the doping polyanion instead of  $\text{LiClO}_4$ . For example, for PAMPS and a total charge quantity of 4.36345 C, the mass of the Py/PAMPS layer was  $1.81 \pm 0.025 \text{ mg}$ . From the electrochemical yield of 92% and the integrated Coulometric value, the PPy mass in the layer was calculated as  $1.45 \pm 0.09 \text{ mg}$ , thus leading to the PAMPS mass in the layer (0.36 mg).

The polyanion/composite mass ratio was  $0.25 \pm 0.05$  in the PAMPS/PPy composite and  $0.29 \pm 0.03$  for the PAAG/PPy composite (the error was averaged over three independent measurements), leading to the following molar ratios of PPy/PAMPS = 10 and PPy/PAAG = 5.

### Uranyl Complexation Procedures

#### One-Batch Process

In the one-batch procedure, aqueous solutions of uranyl nitrate (0.01 and 0.001M), polyanions PAMPS or PAAG (0.1M), and Py (1M) were prepared and poured into an electrolysis cell consisting of anodic and cathodic compartments separated by a fritted glass plug, so that the expected insoluble complex formed at the anode was not contaminated by solid  $\text{UO}_2$  that could be formed at the cathode. The solution was electrolyzed under an anodic potential of +0.8 V and the electrolysis times ranged from a few seconds (thin electrode layers) to several hours (bulk material formed in the anodic compartment). After careful washing with water and acetone and drying *in vacuo*, the uranium incorporation was estimated by  $\alpha$  counting.

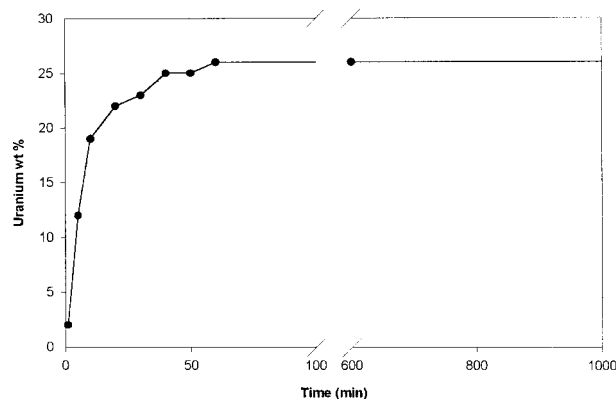
### Two-Batch Process

This process differs from the one batch by the fact that no uranyl nitrate is present in the electrolysis cell. The contact between the complexing composites and the uranyl occurs in a separate aqueous uranyl nitrate solution ( $\text{UO}_2^{2+} = 0.1$  and  $0.001M$ ). In this case, the uranyl is incorporated by diffusion into the insoluble composite. The dipping time of the composites into the uranyl solution has an influence on the level of uranium incorporation into the solid composites. As can be seen in Figure 1, an equilibrium is achieved after a mean dipping time of 1 h.

The behavior of the solid PPy/PAAG and PPy/PAMPS composites in the presence of uranyl ions, which were used either in excess or in defect with respect to the complexing group, was studied. Indeed, the monomeric unit/ $\text{UO}_2^{2+}$  molar ratio was 0.12 ( $\text{UO}_2^{2+} = 0.1M$ ) and 12 ( $\text{UO}_2^{2+} = 0.001M$ ) for the PPy/PAMPS composite and 0.17 and 17 for the PPy/PAAG composites. After stirring for 1 h the complexes were filtered and washed with hot water ( $T = 80^\circ\text{C}$ ) and acetone (a very good solvent for uranyl nitrate) to completely remove uranyl ions that would be merely adsorbed. The uranium content of these composites was estimated by  $\alpha$  counting.

In this respect, the weight percentage of uranium is more likely underestimated as a result of the absorption of part of the  $\alpha$  particles by the composite itself.

In a second series of experiments, the behavior of thin layers of composites deposited on inert supports was analyzed:  $2\text{ cm}^2$  plates were dipped



**Figure 1** Evolution of the uranium content in the PPy/PAAG powder composite with dipping time for  $[\text{UO}_2^{2+}] = 0.1M$ .

**Table I** Composition of Granitic and Clay Water

	Granitic Water (pH 7) (ppm)	Clay Water (pH 8.5) (ppm)
MgCl <sub>2</sub>	5	
KF	5	
KCl		10
CaSO <sub>4</sub>	20	10
NaHCO <sub>3</sub>	100	900
FeCl <sub>2</sub>	1	0.5
HCl		30
CaCl <sub>2</sub>		5

The compositions of the waters are from Merli.<sup>19</sup>

into the  $\text{UO}_2^{2+}$  solutions for 1 h under stirring. In this case, the monomeric unit/ $\text{UO}_2^{2+}$  molar ratio was always far below unity, whatever the uranyl concentration of the starting solution. After purification and drying, the  $\alpha$  activity was measured.

### Leaching Tests

We investigated dynamic and static leaching tests; these tests are derived from the MCC-5 Soxhlet test<sup>17</sup> and the MCC-1 static leaching test.<sup>18</sup> The Soxhlet extraction dynamic leaching test<sup>17</sup> consists of a continuous flow of condensed water ( $T = 65^\circ\text{C}$ ) with a water/composite volume ratio of 50,000, which is typical of a continuous 24-h extraction. The static test consists of dipping the composite in granitic or clay type water ( $T = 50^\circ\text{C}$ ) for 28 days. All the extraction solutions are collected and the uranium content is measured by inductively coupled plasma (ICP) analysis.

The composition of the granitic and the clay-type waters<sup>19</sup> used in the static leaching tests is reported in Table I. Granitic water is representative of the leaching conditions when the radioactive wastes are deeply stored in soil whereas clay water is a good model for leaching by surface water.

It must be pointed out that less severe tests were commonly used in comparable studies.<sup>20,21</sup>

## RESULTS AND DISCUSSION

### One-Batch Procedure

The experimental data listed in Table II show that the uranium fixation by the PPy/polyanion

**Table II Uranium Content of PPy/Polyanions and PPy/Anions Resins ( $\alpha$  Counting) with One-Batch Process**

	Powder U (wt %)		Thin Layer U (wt %)	
	0.001M UO <sub>2</sub> <sup>2+</sup>	0.1M UO <sub>2</sub> <sup>2+</sup>	0.001M UO <sub>2</sub> <sup>2+</sup>	0.1M UO <sub>2</sub> <sup>2+</sup>
PPy/PAMPS	0.1	0.2	0.3	0.4
PPy/PAAG	0.2	0.3	0.4	0.9

composites prepared according to the one-batch procedure is very low. This observation suggests that the nitrate anions of the uranyl salt act as an efficient PPy doping agent that is able to compete with the polyanions. This assumption was first checked by X-ray fluorescence analysis to get a qualitative measurement of the sulfur content in thin layers of composites. For quantitative analysis, we used the RBS analyses.

For this purpose, three thin layers of composites were prepared electrochemically from a twice-distilled water bath containing Py and PAMPS ([Py] = 0.5M, [PAMPS]<sub>mon</sub> = 0.1M) and various amounts of LiNO<sub>3</sub> A, without LiNO<sub>3</sub>; B, [PAMPS]<sub>mon</sub>/[NO<sub>3</sub><sup>-</sup>] = 10; C, [PAMPS]<sub>mon</sub>/[NO<sub>3</sub><sup>-</sup>] = 1/10 [Fig. 2(A–C)]. These thin layers were prepared by chronoamperometry on a vitreous carbon electrode (Potential = +0.8 V against a platinum wire pseudo reference) by running out a defined quantity of electricity (1.875 C) on a known surface (2 cm<sup>2</sup>). One can so far estimate the average thickness of the layer at about 4 μm while knowing that for a PPy layer of 4 μm/cm<sup>2</sup>, 1 coulomb is needed.<sup>22</sup>

These three layers (samples A–C) were quantitatively analyzed by RBS after the standardization of the counting time and the quantity of the  $\alpha$  particles detected to compare the sulfur content of the different samples (Fig. 2). The N/S molar ratio was determined. This ratio rises from 10 for sample A (PPy/PAMPS) to 15 for sample C (PPy/NO<sub>3</sub><sup>-</sup>/PAMPS).

Concerning sample A, one has to compare the result found by RBS with the one found by accurate weighing with the microbalance. We observed that the two ratios of N/S matched at 10, proving the pertinence of the RBS technique applied to these thin layers.

These three RBS spectra clearly evidence the two following facts: a decrease in sulfur (PAMPS)

incorporation in the layers when the nitrate concentration rises in the bath and a change of the shape of the sulfur peaks that shows an evolution from a homogeneous sulfur incorporation occurring in all the thickness of the layer for sample A [Fig. 2(A)] to an incorporation of PAMPS only near the surface of the external layer [Fig. 2(B,C)] as demonstrated by the restricted sulfur peak toward higher  $\alpha$  energies.

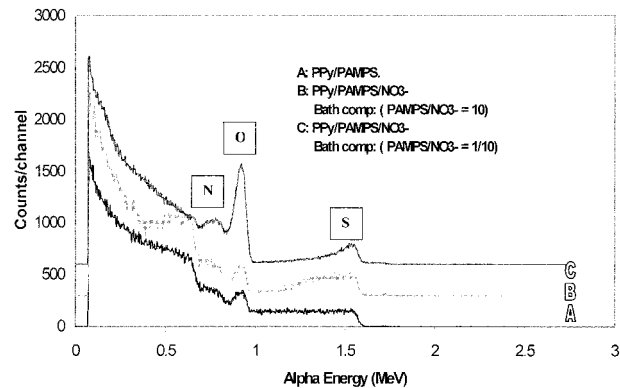
So the PAMPS dopant incorporates itself in smaller quantities in the bulk material layer and in larger quantities in superficial layers as the nitrate concentration rises in the bath. This phenomenon may be explained by the higher mobility of small nitrate anions as compared with the long chains of PAMPS and also by the changes in the concentration ratios between these two components.

Finally, our tentative hypothesis that the one-batch process would be a limiting process when PAMPS and the uranyl incorporation is involved was totally verified by these RBS experiments.

Because the incorporation of uranium is almost neglectable in the one-batch procedure, we investigated a two-batch procedure.

### Two-Batch Procedure

When PPy doped with PAMPS or PAAG is used to fix UO<sub>2</sub><sup>2+</sup> by the two-step method, high UO<sub>2</sub><sup>2+</sup> activity is measured in the sample (Table III). In this case the absence of any odd anions [NO<sub>3</sub><sup>-</sup> from UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> during the PPy/polyanion synthesis] avoids the competition for the insertion into PPy and thus significantly increases the amount of fixed UO<sub>2</sub><sup>2+</sup> compared to the one-batch process.


**Figure 2** RBS spectra of the PPy/PAMPS and PPy/NO<sub>3</sub><sup>-</sup>/PAMPS composites.

**Table III Uranium Content of PPy/Polyanions and PPy/Anions Resins after Equilibration with 0.001 and 0.1M Uranyl Solutions ( $\alpha$ -Counting) with Two-Batch Process**

	Powder U (wt %)		Thin Layer U (wt %)	
	0.001M UO <sub>2</sub> <sup>2+</sup>	0.1M UO <sub>2</sub> <sup>2+</sup>	0.001M UO <sub>2</sub> <sup>2+</sup>	0.1M UO <sub>2</sub> <sup>2+</sup>
PPy/PAMPS	10	15	15	25
PPy/PAAG	10	25	30	60
PPy/PSCOO <sup>-</sup>	0.1	0.2	0.1	0.1
PPy/PSSO <sub>3</sub> <sup>-</sup>	0.2	0.3	0.3	0.5
PPy/Cl <sup>-</sup>	0	0.1	0	0
PPy/NO <sub>3</sub> <sup>-</sup>	0.2	0.3	0.4	0.6

In order to clearly perceive the fixation mechanism of UO<sub>2</sub><sup>2+</sup> by the composites PPy/PAMPS and PPy/PAAG, two kinds of reference samples were synthesized.

First, PPy doped with small anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) was tested for the UO<sub>2</sub><sup>2+</sup> fixation (Table III). The very low content of uranyl ions in these films shows that the heteroaromatic structure of PPy has no tendency to complex UO<sub>2</sub><sup>2+</sup>, meaning that PPy chains have no active role in the uranium incorporation into the composite. The polyanions are thus essential to the uranyl incorporation.

Second, when polyanions are used to dope PPy, the anionic sulfonate or carboxylate site and the complexing amide sites could both be responsible for the UO<sub>2</sub><sup>2+</sup> insertion.

Thus, PPy was doped by PSSO<sub>3</sub><sup>-</sup> and PCOO<sup>-</sup> to simulate PAMPS and PAAG, respectively, but without the complexing amide sites. Low activities were also observed in these cases (Table III). Moreover, the doping level calculated for PAMPS and PAAG (one doping sulfonate function for ca. 10 Py units and one doping carboxylate function for ca. 5 Py units) means that the majority of the sulfonate and carboxylate groups in the composite will act as a counterion of the polycationic PPy.

All these observations led us to conclude that UO<sub>2</sub><sup>2+</sup> is incorporated in a major way by complexation with the amide function of PAMPS and PAAG rather than as a counterion of the sulfonate or carboxylate functions as tentatively sketched in Scheme 4.

Two concentrations (0.1 and 0.001M) of the uranyl nitrate solutions were analyzed in order to check the complexation process in waste solutions

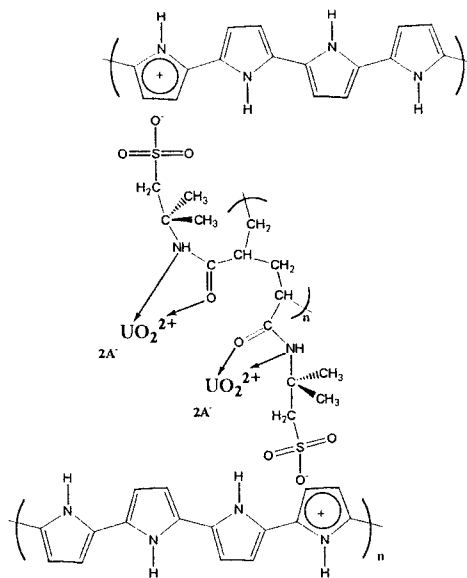
(0.1M) and in dilute solutions (0.001M) as used in the last step before the classical release in water. The results are gathered in Table III.

The PPy/PAAG based composite in the thin layer seems to offer the maximum uranium loading (as high as 60 wt %), which is a huge value compared with uranium loading into usual complexing polymers.<sup>23,24</sup>

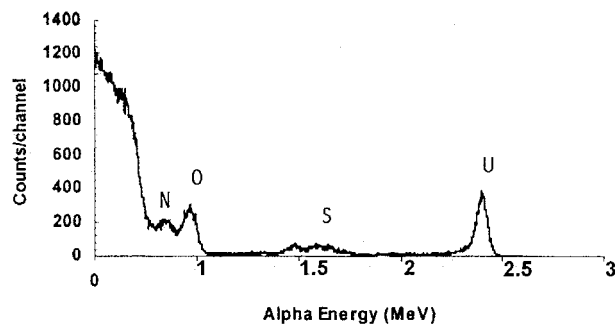
The weight percentage of uranium is almost twice as high in thin layers as in the powdery material for the two composites. This conclusion can be partly explained by more reliable measurements of the  $\alpha$  activity and a larger specific surface area of the bulk composite. The PPy/PAAG composite seems to be more effective than the PPy/PAMPS one. This same tendency was previously reported<sup>9</sup> for the binary PAMPS/UO<sub>2</sub><sup>2+</sup> and PAAG/UO<sub>2</sub><sup>2+</sup> complexes. The lower PPy/PAAG molar ratio compared to the PPy/PAMPS ratio (5 and 11, respectively) might contribute to this difference.

Fixation of uranium by the composites (thin layers or powders) increases with the concentration of the uranyl solutions. Although the dipping time in the uranyl solution might also have an effect, an increase from 1 to 24 h proved to have no beneficial effect on the uranium content. The average equilibration time of the composites in the uranyl solutions was lower than 1 h (Fig. 1).

Thin layers of PPy/PAMPS composites were characterized by further RBS analyses that allow



**Scheme 4** A sketch of the PPy/PAMPS/UO<sub>2</sub><sup>2+</sup> structure.



**Figure 3** The RBS spectrum of the PPy/PAMPS/ $\text{UO}_2^{2+}$  complex.

the U/S ratio to be determined. Figure 3 shows well-defined RBS peaks for S and U. In the PPy/PAMPS/ $\text{UO}_2^{2+}$  complex the U/S molar ratio is 1/7, which is close to the ratio of 1/6 measured for the binary PAMPS/ $\text{UO}_2^{2+}$  complex (ICP analysis of the mineralized complexes). This comparison confirms that the access of the uranyl ions to the complexing groups of PAMPS is only slightly restricted in the PPy based composites.

### Recovery of Uranium

Uranium can be easily recovered as an oxide by burning the powdery composites in air. Actually, the composites were calcinated in an air stream at  $950^\circ\text{C}$  for 10 h. X-Ray diffraction analysis of the calcinated material showed that a mixture of  $\alpha\text{-UO}_3$  and  $\text{U}_3\text{O}_8$  was formed in all the cases. At  $950^\circ\text{C}$  the more stable uranium oxide in contact with the atmosphere is  $\text{U}_3\text{O}_8$ . Formation of  $\alpha\text{-UO}_3$  would result from the reaction of gaseous degradation products with  $\text{U}_3\text{O}_8$ . No quantitative information is available on the relative amount of these two oxides. However, the uranium content

**Table IV** Uranium Oxide Content of PPy/PAMPS and PPy/PAAG Composites after Equilibration with 0.001 and 0.1M Uranyl Solutions and Calcination

	U (wt %)		Uranium Oxides <sup>a</sup>
	0.001M $\text{UO}_2^{2+}$	0.1M $\text{UO}_2^{2+}$	
PPy/PAMPS	12	17	$\alpha\text{UO}_3\text{-U}_3\text{O}_8$
PPy/PAAG	14	35	$\alpha\text{UO}_3\text{-U}_3\text{O}_8$

<sup>a</sup> Determined by X-ray diffractograms.

**Table V** Dynamic Leaching Tests in Soxhlet Extrator

Uranyl Complexes	$\text{UO}_2^{2+}$ Released in Leaching Solution (wt %) <sup>a</sup>
PPy/PAMPS/ $\text{UO}_2^{2+}$	6
PPy/PAAG/ $\text{UO}_2^{2+}$	2
PAMPS/ $\text{UO}_2^{2+}$	100 (hot water soluble)
PAAG/ $\text{UO}_2^{2+}$	100 (hot water soluble)
PAMPS/ $\text{PSSO}_3^-$ / $\text{UO}_2^{2+}$	100
PAAG/ $\text{PSSO}_3^-$ / $\text{UO}_2^{2+}$	4
PAMPS/ $\text{PSCOO}^-$ / $\text{UO}_2^{2+}$	31.2
PAAG/ $\text{PSCOO}^-$ / $\text{UO}_2^{2+}$	7

<sup>a</sup> Calculated with respect to the initial amount in the composite.

of each composite can be approximated and compared to the values estimated by  $\alpha$  counting. In these calculations all the uranium is supposed to exist as  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$  in a 1/1 (w/w) ratio, the approximation being reasonable because of the small difference in the stoichiometry of the oxides. These data are listed in Table IV, and they are consistent with the data in Table II in relation to the doping polyanion and the concentration of the uranyl solution (0.1 and 0.001M).

### Leaching Tests

It is a usual procedure in the immobilization of nuclear wastes to check the suitability of the final material by leaching tests in water. The results of the dynamic and static leaching tests are listed in Tables V and VI, respectively, for the two composites obtained by the two batch process with  $[\text{UO}_2^{2+}] = 0.1\text{M}$ . For comparison, the results for the simple PAMPS/ $\text{UO}_2^{2+}$  and PAAG/ $\text{UO}_2^{2+}$  complexes and for the four neutral complexes based on PAMPS, PAAG, and two polyanions<sup>9</sup> (polystyrenesulfonate,  $\text{PSSO}_3^-$ , or polystyrenecarboxylate,  $\text{PSCOO}^-$ ) are reported in the same tables.

It appears that the insoluble PPy component significantly enhances the stability of complexes toward leaching compared to the basic PAMPS/ $\text{UO}_2^{2+}$  and PAAG/ $\text{UO}_2^{2+}$  complexes that are completely soluble in hot water.

The relative quantities of uranyl leached out from the two PPy based composites are comparable.

The results of the two series of static tests are shown in Table VI for the same complexes listed



**Table VI Static Leaching Tests in Granitic and Clay Water**

Uranyl Complexes	UO <sub>2</sub> <sup>2+</sup> Released in (%) <sup>a</sup>	
	Granitic Water	Clay Water
PPy/PAMPS/UO <sub>2</sub> <sup>2+</sup>	3	9
PPy/PAAG/UO <sub>2</sub> <sup>2+</sup>	5	5
PAMPS/UO <sub>2</sub> <sup>2+</sup>	56	17
PAAG/UO <sub>2</sub> <sup>2+</sup>	21	100
PAMPS/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	41	13
PAAG/PSSO <sub>3</sub> <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	19	100
PAMPS/PSCOO <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	36	17
PAAG/PSCOO <sup>-</sup> /UO <sub>2</sub> <sup>2+</sup>	23	100

<sup>a</sup> Calculated with respect to the initial amount in the composite.

in Table V. Again, the resistance of the PPy based composites toward static leaching tests is much better than all the other composites.

The uranium release from the composites can proceed by two mechanisms: exchange of uranyl cations with cations dissolved in the granitic and clay waters and dissolution of the uranium-containing complexes. In contrast to the six other composites, the two PPy based composites do not lose weight during the leaching tests (average weight accuracy of 0.001 g on 1-g samples), showing the good insolubility of the complexes so that the origin of the uranium release is basically an ion exchange process.

## CONCLUSIONS

Electrochemical synthesis of PPy in the presence of polyanions selected for their capability of doping the conducting polymer and efficiently complexing uranyl cations is a valuable approach to produce resins suited for the extraction of radioactive uranyl cations from liquid wastes.

Resins containing PAAG and PAMPS polyanions have quite comparable capacity to fix uranium, and a small dominance for PAAG is possibly due to a more efficient doping of PPy by this polyanion.

The uranyl adsorption capacity of the composite is greatly enhanced by using a two-step process. In the one-step process the nitrate anions compete with polyanions for the PPy doping, lead-

ing to an important decrease of polyanion insertion and consequently a decrease in the capacity of fixation of the composite. This competition effect was fully demonstrated in the PPy/PAMPS composite by using the RBS technique.

As far as dynamic leaching tests are concerned, the PAAG-containing composite has better resistance. The same conclusion holds for a static test with granitic water whereas the situation is reversed when clay water is used. These observations suggest that the resin composition has to be optimized according to the storage conditions of the uranium-containing solid materials.

As a rule, the two major properties of the PPy resins are the complexing properties of the entrapped polyanion for UO<sub>2</sub><sup>2+</sup> and the insolubilization of the otherwise water soluble polyanion/UO<sub>2</sub><sup>2+</sup> complexes.

The authors are grateful to D. R. Machiroux (University of Liège) for the ICP analysis.

## REFERENCES

1. Castle, P. M.; Hills, P.; Smith, J. D. B.; Phillips, D. C. (to Westinghouse Electric Corp.). U.S. Pat. 4,474,688, 1984.
2. Dozol, M.; Krisher, W.; Pottier, P.; Simon, R. In Leaching of Low and Medium Level Waste Packages under Disposal Conditions, International Workshop, Commission of the European Communities (DG XII.D1) and CEA (CEA-IRDI-DERDCA); CEA-Cadarache: France, November 13–15, 1984.
3. Rivas, B. L.; Maturana, H. A.; Molina, M. J.; Gomez-Anton, M. R.; Piérola, I. F. *J Appl Polym Sci* 1998, 67, 1109.
4. Rivas, B. L.; Maturana, H. A.; Catalan, R. E.; Perich, I. M. *J Appl Polym Sci* 1989, 38, 801.
5. Smith, B.; Robison, T. (to Los Alamos). PCT WO 96/38220, 1996.
6. Egawa, H.; Nonaka, T.; Ikari, M. *J Appl Polym Sci* 1984, 29, 2045.
7. Güler, H.; Sahiner, N.; Aycik, G. A.; Güven, O. *J Appl Polym Sci* 1997, 66, 2475.
8. Martinot, L.; Leroy, D.; Jérôme, C.; Leruth, O. *J Radioanal Nucl Chem* 1997, 224, 1–2, 71.
9. Leroy, D.; Martinot, L.; Jérôme, C.; Jérôme, R. *J Radioanal Nucl Chem* 1999, 240, 3, 867.
10. Bates, N.; Cross, M.; Lines, R.; Walton, D. *J Chem Soc Chem Commun* 1985, 871.
11. Janssen, W.; Beck, F. *Polymer* 1989, 30, 353.
12. Muqbill, R.; Muller, G.; Ferryo, J. C. *J Polym Sci Polym Lett Ed* 1979, 17, 369.
13. Fisher, L. W.; Sochor, A. R.; Tan, J. S. *Macromolecules* 1977, 10, 5, 949.
14. Pei, Q.; Qian, R. *Synth Met* 1991, 45, 35.

15. Jérôme, C.; Mertens, M.; Martinot, L.; Jérôme, R.; Strivay, D.; Weber, G. *Radiochim Acta* 1998, 80, 193.
16. Naoi, K.; Lien, M.; Swyrl, N. *J Electrochem Soc* 1991, 138, 440.
17. Material Characterization Center. MCC-5S Soxhlet Leach Test Method; 1981.
18. Material Characterization Center. MCC-1P Static Leach Test Method; 1983.
19. Merli, L. Ph.D. Dissertation, University of Liège, 1997.
20. Dacheux, N.; Le Dû, J. F.; Brandel, V.; Genet, M. *New J Chem* 1996, 20, 507.
21. Venkobachar, C.; Iyengar, L. *Cement Concrete Res* 1995, 25, 8, 1639.
22. Diaz, A. F.; Castillo, J. *J Chem Soc Chem Commun* 1980, 397.
23. Rivas, B. L.; Maturana, H. A.; Pereira, E. *Angew Makromol Chem* 1994, 220, 61.
24. Rivas, B. L.; Maturana, H. A.; Perich, I. M.; Pereira, E. *Polym Bull* 1996, 37, 191.