

Complexation of Uranyl Ions by Polypyrrole Doped by Sulfonated and Phosphonated Polyethyleneimine

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ABSTRACT: Branched polyethyleneimine (PEI) was sulfonated by reaction with chloropropanesulfonylchloride and phosphonated by reaction with phosphorous acid and formaldehyde. The accordingly formed polyanions were used as doping agents for polypyrrole (PPy). The amount of doping polyanions into thin films of PPy was measured by Rutherford back-scattering. These films were tested for their capacity to extract uranyl ions from liquid wastes of low level activity. The uranium content was determined by neutron

activation analysis, autoradiography, and gravimetry of uranium oxide after calcination. The resistance against static and dynamic leachings was also estimated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 352–359, 2003

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

INTRODUCTION

In a previous article,¹ some of us reported on a new method to extract UO_2^{2+} ions by complexation from low level activity liquid wastes (LLW). The extracting agent was polypyrrole (PPy) doped by two uranyl complexing polyanions—i.e., polyacrylamidomethylpropanesulfonic acid (PAMPS) and polyacrylamidoglycolic acid (PAGA), respectively. In this article, two new complexing polyanions derived from polyethyleneimine (PEI) have been synthesized and tested as dopants for PPy. PEI is well known for its capability to complex uranyl ions.² Moreover, various complexing functions can be easily attached to it.^{2–6} PEI was reacted with chloropropane sulfonyl chloride in order to attach propane sulfonic acid moieties randomly along the backbone³ (PEIPrSO₃H). PEI has also been modified by phosphonic acid according to a method proposed by Smith et al.^{6,7} (PEIPOH). These authors used water-soluble polyanions to extract uranyl ions by a concentration–ultrafiltration technique.⁷ The water-soluble polymer/metal ions complex was concen-

trated by ultrafiltration, through a molecular weight cutoff (MWCO) membrane. The metal ions were recovered either by electrolysis (only for ions reducible in water) or by elution of the membrane by diluted solutions of nitric acid. In this work, the water-soluble PEI derivatives have been incorporated as doping agents in PPy prepared by electropolymerization. In this new technique, the compartment of the ultrafiltration cell that contains the soluble PEI/uranyl complex is used as the anodic compartment for the pyrrole electropolymerization. For the technique to be successful, the PEI derivatives must be water-soluble polyelectrolytes with strong complexing properties toward uranyl cations. These cations are ultimately immobilized in the insoluble PPy.

EXPERIMENTAL

Sulfonation of PEI

Branched PEI was purchased from Acros (M_w : 50–60,000; molar ratio of primary, secondary, and tertiary amines = 1:1:1). One equivalent of chloropropanesulfonyl chloride (ClPrSO₂Cl; Aldrich) was reacted with one equivalent of ethylene imine unit in tetrahydrofuran (THF). After reaction, the SO₂Cl functions were hydrolyzed into sulfonic acids by addition of water to the medium. The modified PEI was recovered by evaporation of the solvent and purified by dialysis against water (membrane with a 10,000 molecular weight cutoff from Poly-LAB).

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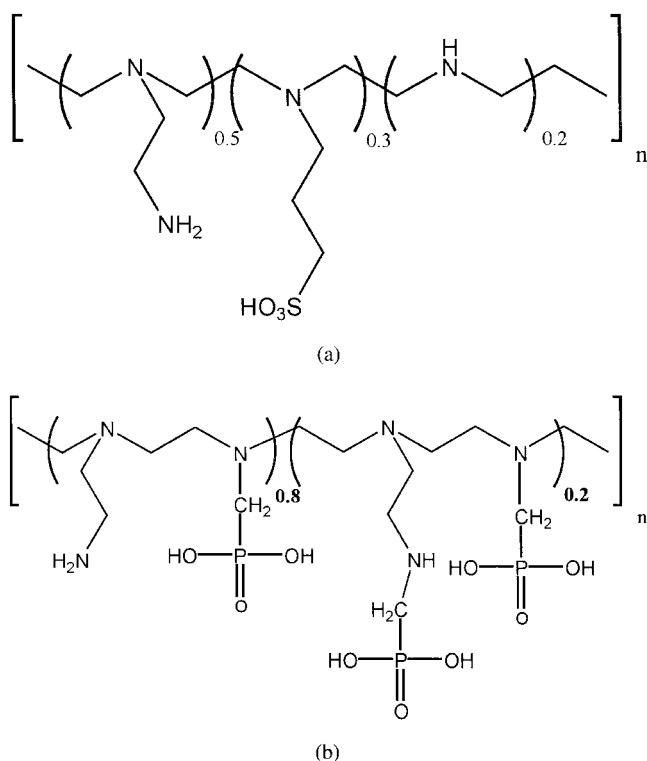


Figure 1 (a) PEIPrSO₃H structure (random functionalization of PEI). (b) PEIPOH structure.

The infrared (IR) absorptions characteristic of the S=O and S—O bonds at 1169, 1031, and 650 cm⁻¹ confirmed the PEI was at least partly sulfonated (Fig. 2 and Table I). We observed also a strong decrease of the N—H (II) stretching /C—H stretching (1460–1480 cm⁻¹) band ratio when compared to PEI. The extensive reaction of the secondary amines was confirmed by the substantial decrease of their absorption at 3290 cm⁻¹ compared to the CH absorption at 2980 cm⁻¹. The sulfur content was determined by neutron activa-

tion of ³²S (n, γ) ³⁵S followed by β liquid scintillation.⁸ The amount of 9.8 wt % of S was found in sulfonated PEI. Thus, 20% of the ethyleneimine units or 2/3 of the secondary amines were sulfonated, as schematized in Figure 1(a).

Phosphonation of PEI

According to Smith et al.,⁷ PEI was reacted with formaldehyde and phosphorous acid. The phosphorus content was determined by neutron activation of ³¹P (n, γ) ³²P followed by β liquid scintillation. The amount of 15.4 wt % of P was found in reasonable agreement with the value (16.8 wt %) reported by Smith et al.⁷ on the basis of elemental analyses. Forty percent of the ethylene imine units were phosphonated.

The IR absorption of the P=O, P—O, and P—OH bonds confirmed the phosphonation of PEI (Table I, Fig. 2) as schematized in Figure 1(b).

Rutherford back-scattering

Rutherford back-scattering (RBS) was detailed elsewhere as a technique of surface analysis.^{10,11} A beam of energetic ions (α particles in our case) was directed to the solid surface. Some of the incident ions elastically collided the lattice nuclei and were scattered back toward a detector that counted the number of scattered particles and measured their energy. The scattered particles gave information on the composition of the sample, the distribution of the constitutive components, and the sample thickness.

Electronic autoradiography

An Instant Imager (Packard) device was used to analyze quantitatively the radioactive distribution in flat

TABLE I
Tentative IR Band Assignments⁹ for PEI, PEIPrSO₃H, PEIPOH, and Corresponding Uranyl Complexes

Band type (cm ⁻¹)	PEI	PEI/UO ₂ ²⁺	PEIPOH	PEIPOH/UO ₂ ²⁺	PEIPrSO ₃ H	PEIPrSO ₃ H/UO ₂ ²⁺
N—H (I) asym st	3412		3422		3427	
N—H (II) asym st	3290					
C—H asym st	2950				2984	
C—H sym st	2842				2817	
N—H (I)*	1657		1657		1619	
N—H (II)*	1580		1517 (vw)		1580 (vw)	
C—H*	1487		1468		1467	
S—O asym (S=O) st					1169	
S—O sym (S=O) st					1031	
PO—H st			2719			
P—O asym st			1101			
P—O sym st			972			
P=O st			1309			
U—O as st		920		908		925
S—O st					650	

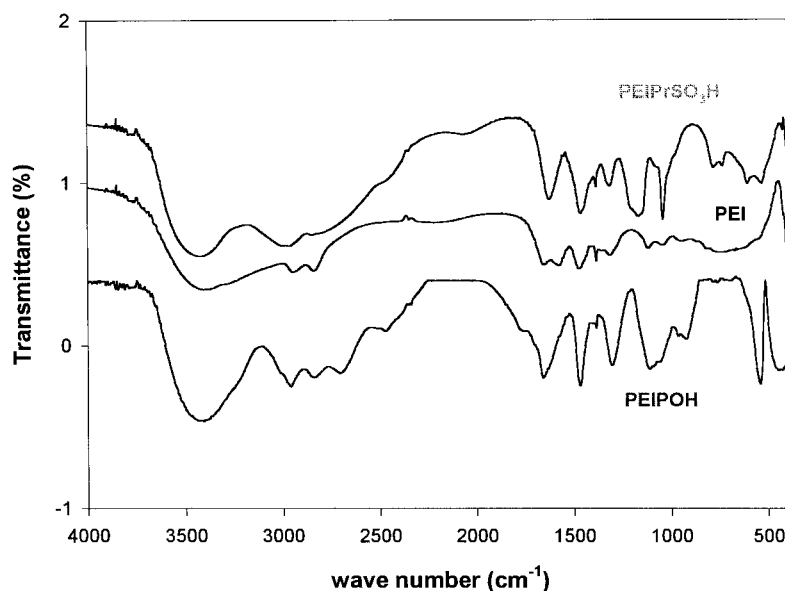


Figure 2 IR spectra of PEI, PEIPOH, and PEIPrSO₃H.

samples. It was equipped with a microchannel array detector.

Neutron activation analysis

Phosphorous-, sulfur-, and uranyl-containing polymers were irradiated by thermal neutrons in order to produce quantitatively ³²P, ³⁵S, and ²³⁹Np, respectively. Their content was determined by β liquid scintillation or γ spectrometry.

Leaching tests

In addition to static tests, dynamic leaching tests were carried out with a Soxhlet extractor.¹ The volume ratio of water (65°C) compared to the sample to be extracted was ca. 50,000 (24 h of extraction).

RESULTS AND DISCUSSION

Synthesis of PEI/Uranyl, PEIPrSO₃H/Uranyl, and PEIPOH/Uranyl complexes

These complexes were synthesized by mixing an aqueous solution of uranyl nitrate ([Uranyl] = 0.1M) with an aqueous solution of the polymer of interest ([CH₂CH₂N] = 0.05M). The uranyl cations were thus in a twofold molar excess with respect to the ethylene imine units. The water-soluble complexes were precipitated in acetone and analyzed by IR spectrometry (Table I). The shift of the U—O asymmetric stretching vibration from 950 cm⁻¹ to values as low as 908 cm⁻¹, in the case of PEIPOH/Uranyl complexes (Table I), is evidence for uranyl complexation. Similar observa-

tions, i.e., absorption in the range from 918 to 944 cm⁻¹, were reported for uranyl complexation by polyacrylamide, polyvinylimidazole, PAMPS, and PAGA.

The uranium content was measured by neutron activation analysis (NAA) of ²³⁸U. The complexes were also carbonized in air in order to recover uranium oxides that were characterized by X-ray diffraction. A mixture of UO₃ and U₃O₈ was systematically observed, and the uranium content was calculated from the weight of the collected uranium oxides (Table II). Although the amount of uranium complexed by PEI and derivatives is significant, it is less important compared to complexation by PVI, PAMPS, and PAGA.^{12,13} Complexation of uranium by PEI and PEIPrSO₃H is similar, which suggests that the sulfonate anions do not contribute extensively to the uranyl complexation. The same conclusion was drawn elsewhere.¹⁴ PEIPOH complexes uranium more extensively, which emphasizes the role of the phosphonic acid groups.¹⁴ The P/U molar ratio was found equal to 2 for the PEIPOH/Uranyl complex, compared to 6

TABLE II
Uranium Content of the Complexes as Determined by NAA and Carbonization—Gravimetry

Complexes	U content (U wt %) NAA	UO ₃ —U ₃ O ₈ content (U Oxides wt %) gravimetry
PEIPOH/Uranyl	13	15
PEIPrSO ₃ H/Uranyl	8	7
PEI/Uranyl	9	10
PPy/PEIPOH/Uranyl	1.5	3
PPy/PEIPrSO ₃ H/Uranyl	0.5	1

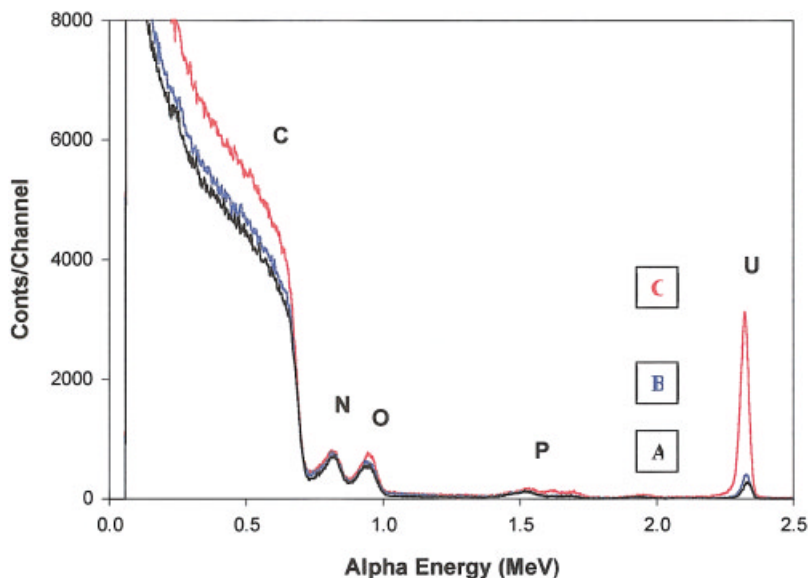


Figure 3 RBS spectra of PPy/PEIPOH/ UO_2^{2+} complexes (dipping time in UO_2^{2+} : A, 1 min; B, 5 min, C, 2 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for the S/U molar ratio in case of the PEIPrSO₃H/ UO_2^{2+} complexes.

The two anionic polyelectrolytes, PEISO₃H and PEIPOH, have been used as dopants for the pyrrole electropolymerization. The accordingly insolubilized PEI chains have then been tested for their capacity to extract uranyl from aqueous solution.

Doping of PPy by PEIPOH or PEISO₃H, and UO_2^{2+} immobilization

PPy thin layers doped by one complexing polyanion were prepared according to the procedure reported elsewhere.¹ Aqueous solutions of Py ([Py] = 0.1M) and PEIPrSO₃H or PEIPOH ([CH₂-CH₂N] = 0.1M) were anodically polymerized ($E = +0.8$ V, $t = 500$ – 1000 s, $Q = 50$ – 100 mC), the polyanions playing the role of conducting salt. The thicknesses of the films were estimated from the charge consumed through the electrolysis.¹⁵ It must be noted that the two PEI derived polyanions are less conducting than the PAMPS and PAGA polyanions, which requires longer time of electrolysis. This lower conductivity merely results from the partial modification of PEI by sulfonate and phosphonate groups, respectively, compared to PAMPS and PAGA, in which each monomer unit is ionic. The thin PPy films (thickness: 250–500 nm, $Q = 50$ – 100 mC, Pt or carbon electrode) were dipped in a nonstirred solution of uranyl nitrate. The films were then thoroughly washed with water to remove any adsorbed uranyl nitrate and dried. The thickness and the relative content of N, P, S, and U were measured by RBS.

RBS analyses of thin PPy films

PPy/PEIPOH/ UO_2^{2+}

Figure 3 shows the RBS spectra for PPy doped by PEIPOH and electrodeposited onto a glassy carbon electrode (film thickness: 250 nm) after dipping in an uranyl nitrate solution (0.1M). The $N_{\text{PPy}}/N_{\text{PEI}}$ molar ratio was calculated from the $P_{\text{PEIPOH}}/(N_{\text{PPy}} + N_{\text{PEIPOH}})$ ratio determined by RBS for PPy/PEIPOH, from the $P_{\text{PEIPOH}}/N_{\text{PEIPOH}}$ ratio determined by liquid scintillation for PEIPOH, and from the PEI phosphonation degree ($P_{\text{PEIPOH}}/N_{\text{PEIPOH}}$). The P/U, N/P, and N/U atomic ratios are listed in Table III. In the best case, $N_{\text{PPy}}/N_{\text{PEI}}$ was found to be 25 for a sample containing 20 wt % of PEIPOH. This means that the doping level of PPy by phosphonate functions remains quite low. The P/U ratio decreases with increasing dipping time in the uranyl nitrate solution, from 15 (1 min) to 2 (2 h), and then it levels off. Because the P/U ratio is also

TABLE III
Atomic Ratios for PPy/PEIPOH and PPy/PEIPrSO₃H Calculated by RBS

	P/U	N/P	N/U	S/U	N/S
PPy/PEIPOH/ UO_2^{2+}					
A Figures 3 and 4	15	30	450		
PPy/PEIPOH/ UO_2^{2+}					
B Figures 3 and 4	11	31	350		
PPy/PEIPOH/ UO_2^{2+}					
C Figures 3 and 4	2	23	50		
PPy/PEIPrSO ₃ H/ UO_2^{2+}					
A Figure 5			325	7	43
PPy/PEIPrSO ₃ H/ UO_2^{2+}					
B Figure 5			188	7	24

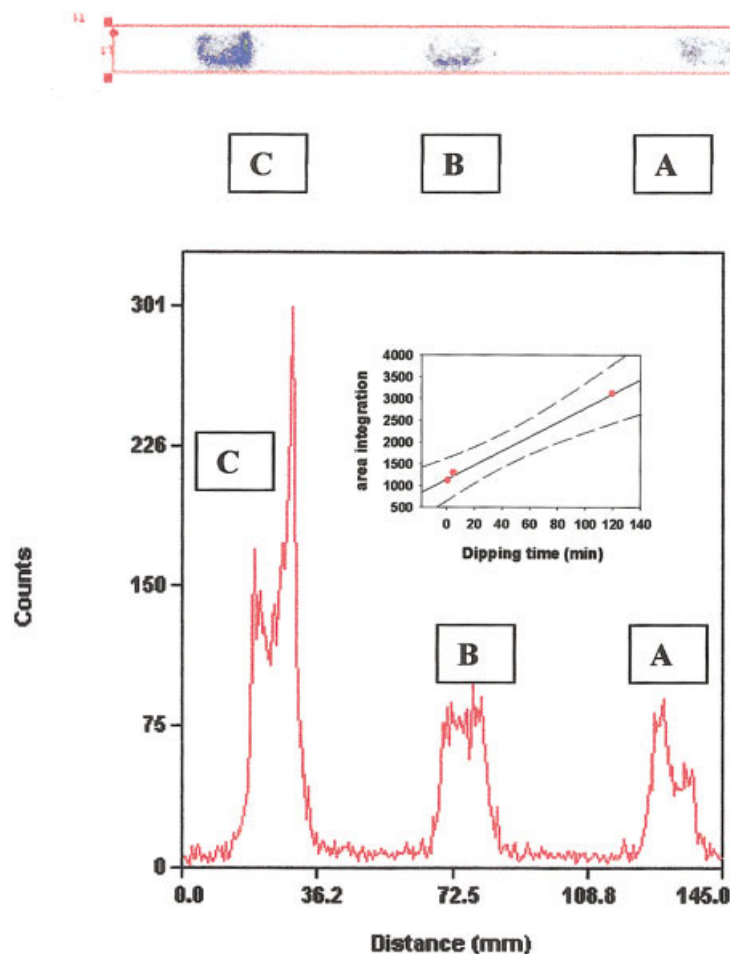


Figure 4 Imager and density profiles for the three PPY/PEIPOH-coated glassy carbon electrodes after dipping in uranyl nitrate solutions. (A: 1 min; B: 5 min; C: 2 h). Inset: peak area integration vs dipping time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

2 for the soluble PEIPOH/ UO_2^{2+} complex, it may be concluded that the doped PPY film is saturated and that the complexing functions trapped into this film remain accessible to the uranyl ions. Figure 4 shows the images and density activity profiles for the three electrodes, whose the RBS spectrum is shown in Figure 3. The uranyl content is maximum after 2 h, which is twice as long compared to the PPY/PAMPS and the PPY/PAGA combinations under the same conditions.¹ This difference may be explained by the higher hydrophobicity of the PPY/PEIPOH films as assessed by the contact angle measured (Table IV) by the sessile drop

method.¹⁶ The doping level of PPY can be also expressed by the N_{PPY}/P ratio equal to 6, which must be compared to the doping of four in case of traditional doping of PPY by perchlorate and nitrate anions.¹⁷

PPY/PEIPrSO₃H/ UO_2^{2+}

The S/U, N/S, and N/U atomic ratios were similarly collected for the PPY/PEIPrSO₃H/ UO_2^{2+} system (Table III). Figure 5 shows the imager profiles, which illustrate the uranium fixation by two thin PPY films of a different composition (A: N/S = 43; B: N/S = 24) and for the same dipping time (5 min). The S/U ratio is the same for the two films and close to the value noted for the soluble PEIPrSO₃H/ UO_2^{2+} complex. Therefore, although immobilized within the PPY matrix, the complexing groups remain available to the uranyl cations. Figure 5 expectedly shows that the higher uranium content of the electrode B is related to the higher content of the complexing polymer in this film. It also appears that the saturation of thin films by the uranyl ions is faster in case of PPY/PEIPrSO₃H (5

TABLE IV
Contact Angle of a 5:1 Drop of Water
onto Thin PPY Films

Sample	Contact angle (θ°) ^a
PPy/PSSO ₃	(40) ± 5
PPy/PAMPS/ UO_2^{2+}	(55) ± 5
PPy/PEIPOH/ UO_2^{2+}	(92) ± 5
PPy/PEIPrSO ₃ H/ UO_2^{2+}	(66) ± 5

^a The higher the θ value, the more hydrophobic the film.

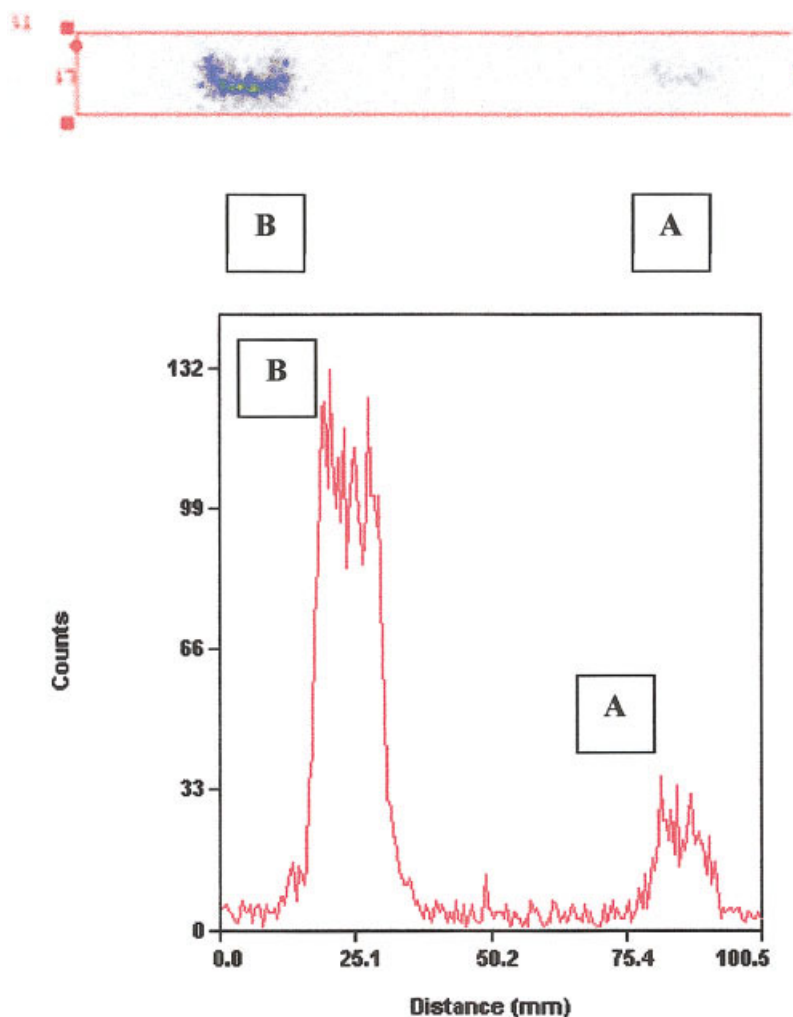


Figure 5 Imager and density profiles for the two PPy/PEIPrSO₃H-coated glassy carbon electrodes after dipping in uranyl nitrate solutions. (A: 5 min, S/U = 7, N/S = 43; B: 5 min, S/U = 7, N/S = 24). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

min) compared to PPy/PEIPOH (2 h). This observation is consistent with the fast saturation of PPy/PAMPS films (10 min), which are also doped by highly hydrophilic sulfonated polyanions. The contact angles of water on the PPy layer (θ) (Table IV) confirm that sulfonated doping agents make the PPy film more hydrophilic than the phosphonated one. In the best case, $N_{\text{PPy}}/N_{\text{PEIPrSO}_3\text{H}} = 43$, which corresponds to a doping of PPy by 12 wt % of PEIPrSO₃H. Accordingly, the N_{PPy}/S ratio is equal to 19, which is a low doping, consistent with the low conductivity and the long electrolysis time required. The branched structure of PEI might be a restriction to its diffusion into the PPy matrix compared to the linear PAMPS and PAGA chains.

The uranium content of PPy/PEIPOH/UrO₂²⁺ and PPy/PEIPrSO₃H/UrO₂²⁺ complexes was also estimated by NAA (Table II) and by gravimetry of the residual uranium oxides after carbonization. These oxides were also identified by X-ray diffraction analysis (Table II). The measurements show that the wt % of

uranium incorporated ranges from 0.5 to 13 wt % (by NNA). The higher content is noted for the PEIPOH/UrO₂²⁺ complexes. Accordingly, the uranium capacity (mol %) of the PPy/PEIPOH films is higher than that one of the PPy/PEIPrSO₃H films. The weight capacities shown in Table II are low when compared to PPy/PAMPS or PPy/PAGA¹ (15–60 wt % of uranium in the composite). The higher hydrophobicity of the PEI-based polyanions tested in this study is thought to be at the origin of the lower uranium content. Because the uranyl is not complexed by sulfonates,¹⁴ it may be suggested that the amines in PPy/PEIPrSO₃H are less effective ligands for uranyl than the amide functions in PPy/PAMPS composites.

The experimental P/U ratio of 2 in PPy/PEIPOH indicates the quasi-saturation of the phosphonic acid functions. As reported elsewhere,¹⁴ the uranyl complexation in PEIPOH proceeds mainly through the phosphonates ligands.

TABLE V
Dynamic and Static Leaching Tests

Uranyl complexes	% of UO_2^{2+} released in granitic water ^a (static leaching test)	% of UO_2^{2+} released in clay water ^a (static leaching test)	% of UO_2^{2+} released in Soxhlet extraction ^a (dynamic leaching test)
PEI/PSSO ₃ ^{-b} /UO ₂ ²⁺	25	20	55
PEIPrSO ₃ H/PSSO ₃ ^{-b} /UO ₂ ²⁺	22	17	54
PEIPOH/PSSO ₃ ^{-b} /UO ₂ ²⁺	38	45	42
PPy/PEIPOH/UO ₂ ²⁺	12	21	10
PPy/PEIPrSO ₃ H/UO ₂ ²⁺	7	11	26

^a The wt % of UO_2^{2+} calculated with respect to the initial amount in the film.

^b PEI/ UO_2^{2+} soluble complexes made insoluble by reaction with polystyrenesulfonate (PSSO₃).¹

Leaching tests

Leaching of the complexed uranyl ions was tested to estimate their stability. Results are listed in Table V. For the sake of comparison, soluble preformed PEIPOH/ UO_2^{2+} complexes were precipitated by addition of polystyrenesulfonate ($\text{SSO}_3/\text{CH}_2\text{CH}_2\text{N} = 5$) as discussed elsewhere,^{1,14} and the stability of the insoluble PEIPOH/ UO_2^{2+} /PSSO₃ complexes was also tested by the same method. It appears that the PPy/PEIPOH/ UO_2^{2+} complexes are more resistant to dynamic and static leaching than the PPy/PEIPrSO₃H/ UO_2^{2+} complexes, in agreement with the theoretical stability scale (K , stability constant) established for the water-soluble PEIPOH/ UO_2^{2+} and PEIPrSO₃H/ UO_2^{2+} complexes.¹⁴ The higher hydrophilicity of the PPy/PEIPrSO₃H/ UO_2^{2+} films can explain their lower resistance to leaching compared to the PPy/PEIPOH/ UO_2^{2+} counterparts.

The complexes immobilized in PPy are more stable than the ones precipitated by PSSO₃. The same observation was reported in case of the PAMPS and PAGA polyions.¹

CONCLUSIONS

PEI, a water-soluble polymer known for uranyl complexing ability,² has been modified by acid groups, such as phosphonic and sulfonic acid. After neutralization, the polyions have been used as doping agents for the pyrrole polymerization. This is an original method to make the complexing agent insoluble and ultimately to trigger the insolubility of the uranyl-containing complexes. It must be kept in mind that the unmodified PEI cannot promote the doping reaction of PPy.

Although immobilized in the PPy matrix, the PEI chains retain their complexing properties, which is even improved by phosphonation.

Moreover, PEIPOH is a better doping agent for PPy and a stronger complexing agent of the uranyl ions than PEIPrSO₃H, which makes the PPy/PEIPOH pair superior to the PPy/PEIPrSO₃H one for the extraction of uranyl ions from liquid wastes of low level activity.

That more PEIPOH than PEIPrSO₃H is incorporated into PPy mainly results from the higher content of the phosphonate ions compared to the sulfonate ones in modified PEI.

The entanglement of the PEIPOH and PEIPrSO₃H chains within the insoluble PPy matrix is the origin of the higher stability of the PEIPOH/ UO_2^{2+} and PEIPrSO₃H/ UO_2^{2+} complexes against leaching when compared to the same complexes merely precipitated by PSSO₃. The PPy/PEIPOH/ UO_2^{2+} is more stable than the PEIPrSO₃H-containing complex because of a higher hydrophobicity. Conversely, the PPy/PEIPOH film is saturated by uranyl more slowly than the PPy/PEIPrSO₃H equivalent.

The uranyl capacity of the PPy/PEIPrSO₃H pair can be improved by increasing the sulfonation degree of PEI. In parallel, the hydrophilicity will increase and the resistance to leaching test will decrease. An optimum has thus to be found in the sulfonation degree, which is also the case for phosphonation. Partial modification of PEI by ionic groups (for the doping reaction) and by nonionic complexing groups (for better balance of uranyl capacity and hydrophilicity) is a possible way to improve further the performance of the new system under consideration.

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