Supporting Information

Bifunctional Polymeric Microspheres for Efficient Uranium Sorption from Aqueous Solution: Synergistic Interaction of Positive Charge and Amidoxime Group

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Synthesis of poly(*N*-vinylimidazole)-*block*-polystyrene (PVim-*b*-PSt)

PVim-*b*-PSt was synthesized according to the related reference [1]. PVim was first synthesized by RAFT polymerization, and the typical recipe was as follows: 4 mL solution comprising Vim (2.0 g, 21.3 mmol), DDATC (0.1458 g, 0.4 mmol), AIBN (0.0328 g, 0.2 mmol) in DMF (2.0 mL) was prepared and placed in an ampoule. The contents were purged with argon for 30 min to eliminate the oxygen. Then, the ampoules were flame-sealed and placed in oil bath thermostated at 70 °C. After a preset reaction time, each ampoule was cold with ice water and opened, and the mixture was diluted with DMF and then precipitated in diethyl ether for three times. The obtained polymer was dried in vacuum at 40 °C until a constant weight was obtained gravimetrically. PVim with different molecular weight was obtained as macro-RAFT agent, and the same procedure was used for the extension reaction of St. Finally, the block copolymer PVim-*b*-PSt was obtained.

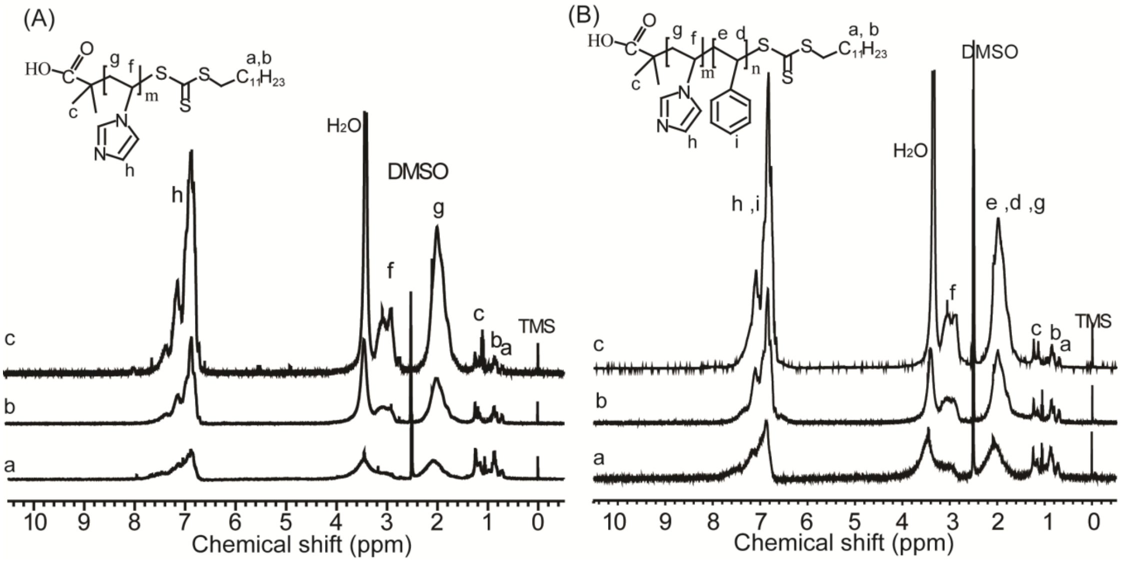

Figure S1. ^{1}H NMR spectrum (400MHz, DMSO-d_6) of A) PVim (a) PVim$_{40}$ (b) PVim$_{58}$ (c) PVim$_{82}$; B) PVim-*b*-PSt (a) PVim$_{40}$-*b*-PSt$_9$; (b) PVim$_{58}$-*b*-PSt$_{11}$; (c) PVim$_{82}$-*b*-PSt$_{10}$. (The unit numbers can be calculated as below: m = $(I_g/2)/(I_a/3)$; n = $[(I_{h,i}-3m(I_a/3))]/5$, where I_g , and I_a are the integration values of the peaks at δ = 1.60–2.45 ppm and δ = 0.90–0.92 ppm in Figure A, $I_{h,i}$, and I_a are the integration values of the peaks at δ = 6.60–8.00 ppm and δ = 0.90–0.92 ppm in Figure B, respectively.)

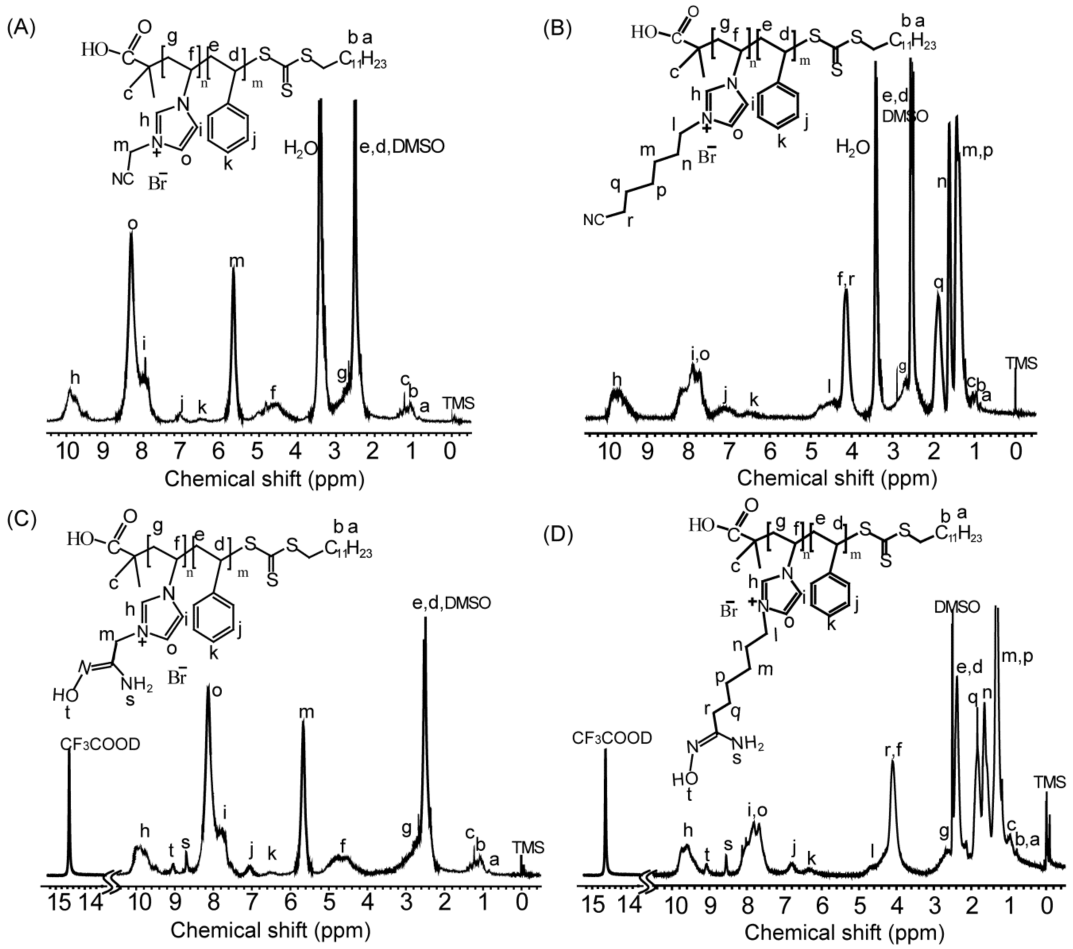

Figure S2. ^{1}H NMR spectra (400MHz) of A) poly(1-vinyl-3-(1-cyanomethyl)-imidazolium bromide)$_{40}$-*block*-poly(styrene)$_9$ (PANEI$_{40}$-*b*-PSt$_9$) in DMSO-*d*$_6$; B) poly(1-vinyl-3-(6-cyanohexyl)-imidazolium bromide)$_{40}$ -*block*-poly(styrene)$_9$ (PANHI$_{40}$-*b*-PSt$_9$) in DMSO-*d*$_6$. C) PAOEI$_{40}$-*b*-PSt$_9$ in DMSO-*d*$_6$ /trifluoroacetic acid-*d* (1:1, v/v); and D) PAOHI$_{40}$-*b*-PSt$_9$ in DMSO-*d*$_6$ /trifluoroacetic acid-*d* (1:1, v/v). (The unit numbers can be calculated as below: $m = (I_j/4)/(I_a/3)$; $n = I_h/(I_a/3)$, where I_j, I_h, and I_a are the integration values of the corresponding peaks, respectively.)

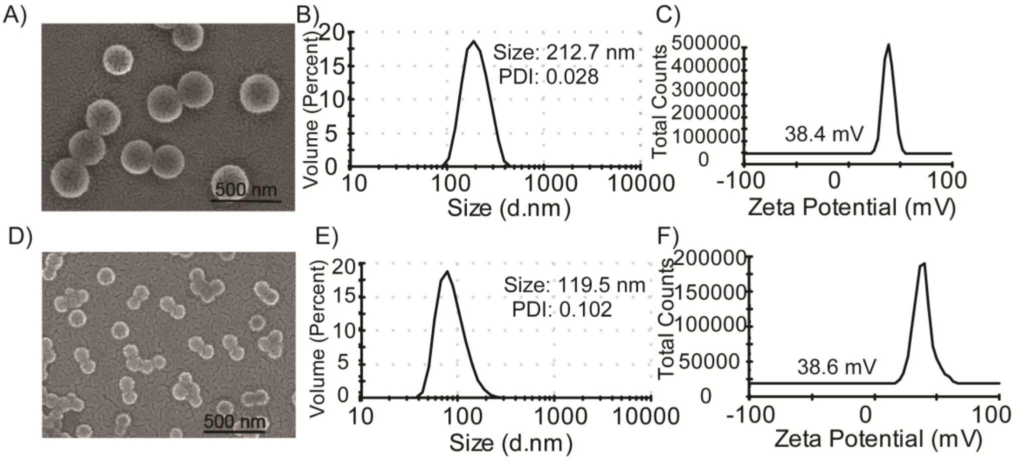

Figure S3. The A) SEM image, B) particle size distribution, C) zeta potential of polystyrene microspheres from emulsion polymerization using (A, B, C) PAOEI$_{40}$-*b*-PSt$_9$; (D, E, F) PAOHI$_{40}$-*b*-PSt$_9$ as surfactants with the concentration of 10^{-4} mol/L.

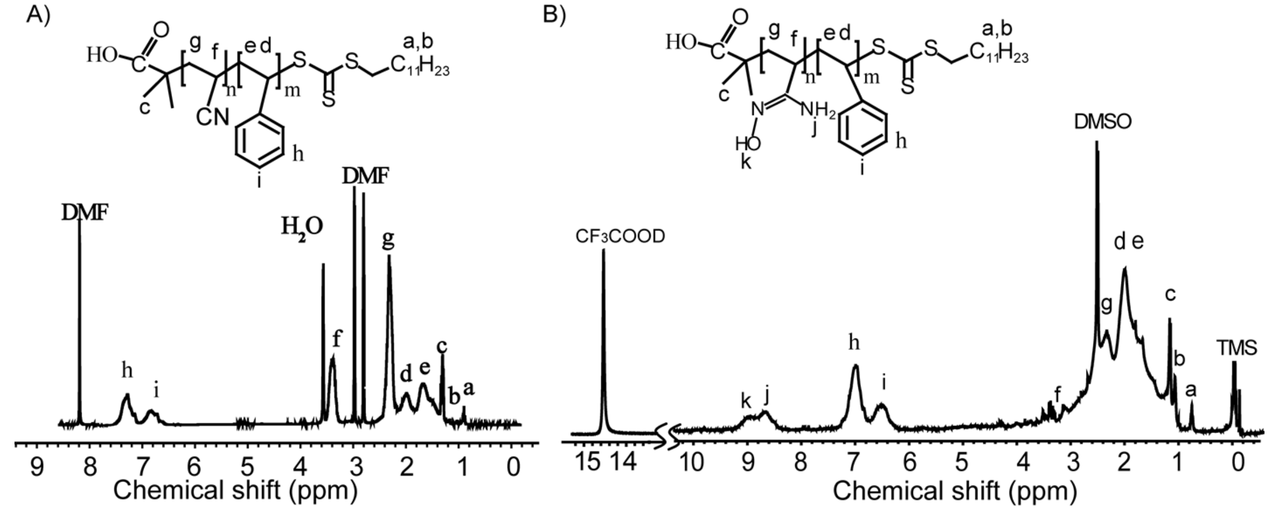

Figure S4. ^{1}H NMR spectra of: A) poly(acrylonitrile)$_{42}$-*block*-poly(styrene)$_8$ (PAN$_{42}$-*b*-PSt$_8$) in DMF-d_7; B) Poly(*N*-hydroxyacrylamidine)$_{42}$-*block*-poly(styrene)$_8$ (PAO$_{42}$-*b*-PSt$_8$) in DMSO-d_6 /trifluoroacetic acid-*d* (1:1, v/v). (The unit numbers can be calculated as below: $m = (I_h/4)/(I_a/3)$; $n = I_f/(I_a/3)$, where I_h , I_f and I_a are the integration values of the peaks at δ = 7.15–7.65 ppm, δ = 3.22–3.65 ppm and δ = 0.90–0.92 ppm in Figure A, respectively.)

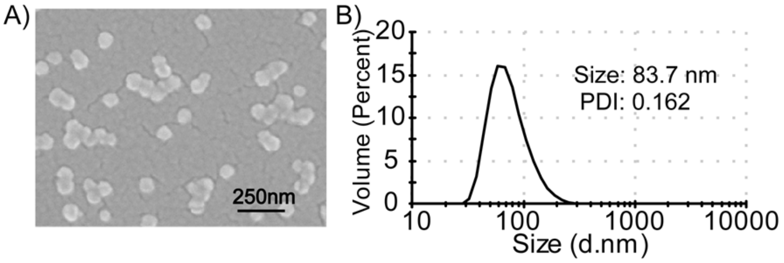

Figure S5. A) SEM image, B) particle size distribution of polystyrene microspheres from emulsion polymerization using PAO_{42}-*b*-PSt_8 as surfactants with the concentration of 10^{-4} mol/L.

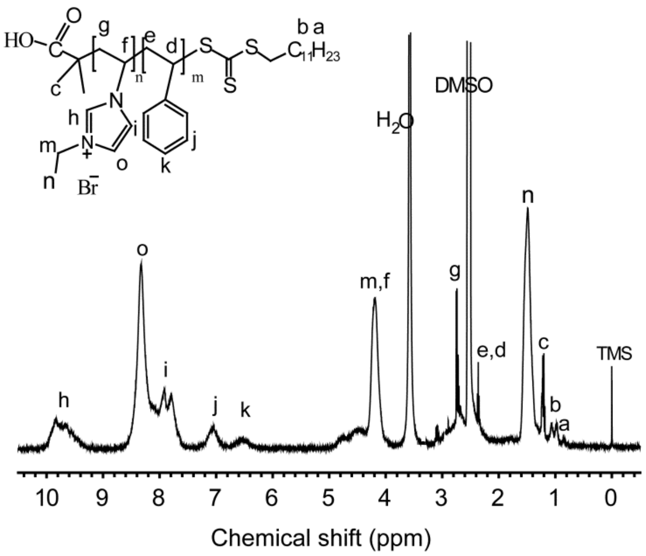

Figure S6. ^{1}H NMR spectrum (400MHz, DMSO-d_6) of poly(1-vinyl-3-ethylimidazolium bromide)$_{40}$-*block*-poly(styrene)$_9$ (PEI_{40}-*b*-PSt_9). (The unit number can be calculated as below: $m = (I_j/4)/(I_a/3)$; $n = I_h/(I_a/3)$, where I_j, I_h, and I_a are the integration values of the corresponding peaks, respectively.)

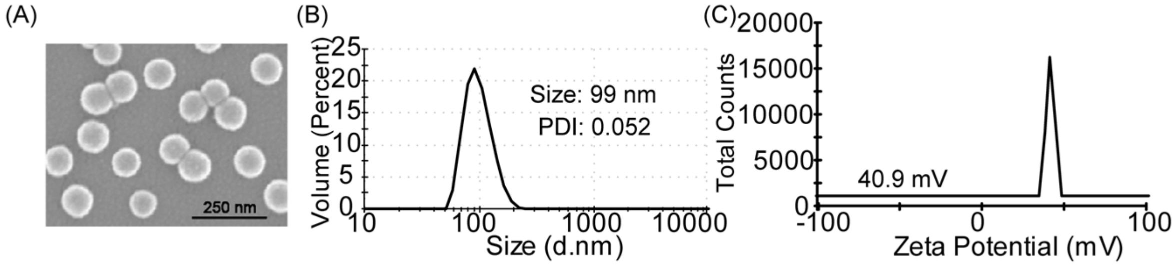

Figure S7. The A) SEM image, B) particle size distribution, C) Zeta potential of polystyrene microspheres from emulsion polymerization using PEI_{40}-*b*-PSt_9 as surfactants with the concentration of 10^{-4} mol/L.

Sorption thermodynamics

The effect of temperature was studied over the temperature range of 298.15-328.15 K. The enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) of were calculated according to the equilibrium constant (K_c), which depends on temperature [2] :

$$K_c = \frac{q_e}{C_e} \qquad (1)$$

$$\Delta G = - RT lnK_c \qquad (2)$$

$$lnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (3)$$

ΔH and ΔS can be obtained from the slope and intercept of the plot of ln K_c versus 1/ T (Figure S8), and the results are shown in Table S1.

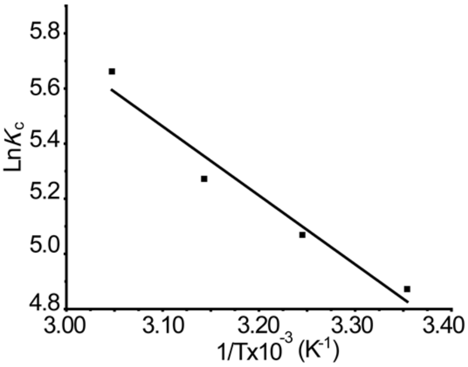

Figure S8. Effect of temperature on the sorption of uranium (VI) by the microspheres from emulsion polymerization using PAOBI$_{40}$-b-PSt$_9$ as surfactants. (Experimental conditions: 200 mL solution, 5×10^{-5} mol/L uranyl ions, 88 mg/L adsorbent, pH 7.00).

Table S1. Thermodynamic data for uranium sorption on the microspheres from emulsion polymerization with PAOBI$_{40}$.

ΔH	ΔS	ΔG (kJ/mol)			
(kJ/mol)	(J/mol K)	298.15K	308.15K	318.15K	328.15K
20.81	109.92	-12.08	-12.99	-13.94	-15.45

(The data shows an increase in the randomness during the endothermic sorption, and an expected spontaneity of the sorption within the temperature range.)

Sorption isotherm

In order to study the capacity of adsorbent, the equilibrium data were evaluated according to Langmuir and Freundlich models. The sorption experiments were conducted at 298.15 K with uranyl ions concentration over the range of 10^{-3}-5×10^{-5} mol/L. The experimental data were applied to Langmuir and Freundlich models, and the isotherm parameters and the correlation coefficients were calculated accordingly.

Langmuir isotherm describes monolayer sorption. The linear form of Langmuir isotherm is given as Equation (4):

$$\frac{1}{q_e} = \frac{1}{q_{max} b c_e} + \frac{1}{q_{max}} \qquad (4)$$

Error!Where $q_{\max}$ (mg/g) is the maximum sorption amount which signifies the sorption capacity, and b (L/mg) is the Langmuir constant. $q_{\max}$ and b can be calculated from the linear plot of C_e/q_e against C_e.

The Freundlich isotherm can be applied for the sorption on heterogeneous surfaces and multilayer sorption. The linear form of Freundlich isotherm can be expressed as Equation (5):

$$log q_e = log K_F + \frac{1}{n} log C_e \qquad (5)$$

Where K_F (L/g) and n are Freundlich constants related to sorption capacity and sorption intensity, respectively. K_F and n constants can be calculated from the slope and intercept of the linear plot of log q_e versus log C_e, respectively.

Sorption kinetics

The sorption kinetics experiments were performed at pH 7.00, and the sorption rate was analyzed by using two common semi-empirical kinetic models: the pseduo-first-order and pseudo-second-order equations, proposed by Lagergren[3] and Ho[4] and Mckay [5], respectively.

Pseduo-first-order kinetic equation relates the sorption rate to uranyl ion adsorbed amount at time *t*, which is depicted as equation (6):

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right) \times t \qquad (6)$$

Where q_t (mg/g) is the amount of ion adsorbed at time t, k_1 (h^{-1}) is the sorption rate constant. The plot of $\log(q_e - q_t)$ versus t gives a straight line, and k_1 and q_e can be calculated from the slope and the intercept, respectively.

Pseudo-second-order model is expressed as the following Equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where k_2 (g/mg/h) is the second order rate constant. The plot of t/q_t versus t shows linearity, and k_2 and q_e can be determined from the slope and intercept.

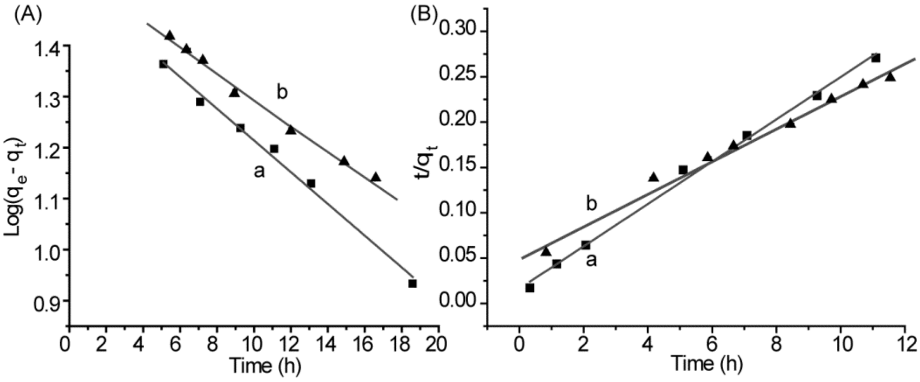

Figure S9. (A) Pseudo first order kinetics and (B) pseudo-second order kinetics of U(VI) sorption onto microspheres using surfactants with the concentration of 10^{-4} mol/L: (a) $PAOBI_{40}$, (b) PAO_{42}. (Experiment condition: 200 mL solution, 5×10^{-5} mol/L uranyl ion, 88 mg/L adsorbent, pH 7.00, 298.15 K.)

References

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5. Y. S. Ho, *Chem. Eng. J.*, 1998, **70**, 115.