Polymer Materials

DOI: 10.1002/anie.201307825

Seawater Uranium Sorbents: Preparation from a Mesoporous Copolymer Initiator by Atom-Transfer Radical Polymerization**

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The world's oceans, where uranium is found quite uniformly at a concentration of 3.3 $\mu g L^{-1}$, present an alternative source of uranium to terrestrial mining for nuclear fuel. Environmental concerns associated with mining will undoubtedly increase as reserves are depleted, thus increasing the utility of more environmentally friendly feedstocks.[1–4] Hence, before terrestrial resources become scarce, the development of sorbents designed for seawater extraction is of strategic importance to guarantee future uranium resources. From the first inorganic adsorbents, which showed poor selectivity and mechanical resistance, to the most recent polyethylene-fiber-based sorbents containing amidoxime–carboxylic acid copolymers, and more recently layered metal sulfides and metal–organic frameworks, interest in uranium seawater extractions has continuously increased among governments worldwide.[5–10]

Because the concentration of uranium in the oceans is relatively low, maximization of the adsorption properties of sorbents, for example, through changes in their surface area and pore structure, can greatly improve the kinetics of uranium extraction and the adsorption capacity simultaneously.[11] To facilitate the uptake of uranyl ions with fast kinetics, various sorbents containing the amidoxime group, such as hydrogels,[12] particles and beads,[13] membranes,[14] macroporous fibers,[15] and composites,[16] have been prepared by suspension polymerization, radiation-induced grafting, and even sonochemical functionalization. However, silica beads and most carbon materials have a relatively small accessible surface area for the growth of large polymers or a low number of surface sites available for the grafting of functional groups. Thus, the design of substrates with large numbers of accessible reactive sites for the grafting of polymeric surface groups is necessary for the development of materials with improved uranium-adsorption capacity.

Recently, porous polymers based on divinylbenzene (DVB) have been developed for applications in separations and catalysis.[17] For example, the copolymerization of *p*-styrene sulfonate with divinylbenzene led to a catalytically active porous polymer. This method has the additional advantage that polymers can be obtained with controlled porosity and high surface areas without porogens. It is thus time- and cost-effective, as well as more environmentally friendly than the templated synthesis of carbonaceous materials.[18] Motivated by these findings, we report herein nanoporous polymers based on the vinylbenzyl chloride (VBC) monomer and the DVB cross-linking agent. As well as a well-developed nanoporous structure of micro- and mesopores, the obtained polymers contain large numbers of accessible chlorine species, which can be used as initiators for atom-transfer radical polymerization (ATRP). These materials are the first examples of ATRP initiators in which the initiator species is located within the framework of the mesoporous support. The accessible framework and surface chlorine species were used to grow polyacrylonitrile chains, which were then converted into polyamidoxime for uranium adsorption from seawater with tailorable adsorption and surface properties.

Three copolymer monoliths were synthesized by free-radical polymerization; that is, the monomer 4-vinylbenzyl chloride was cross-linked by divinylbenzene with 2,2′-azobisisobutyronitrile (AIBN, 98%) as the initiator to give copolymers hereafter referred to as p(xDVB-VBC) (in which x stands for the molar ratio of DVB to VBC).[10] By varying the ratio of the monomer and the cross-linking reactant, it was possible to adjust the pore structure, that is, the surface area and pore volume (Figure 1). Since these adjustments arose from changes in the DVB to VBC ratio, the initiator concentration (i.e. the amount of chloride substituents present) was also varied. The nitrogen isotherms measured at −196 °C for the samples show that nonporous materials as well as materials with tailorable mesopore volumes can be

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[**] This research was sponsored by the US Department of Energy, Office of Nuclear Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, Office of Basic Energy Sciences, US Department of Energy. The JAEA adsorbent was kindly donated for testing by the Japan Atomic Energy Agency. We acknowledge Dr. Tomonori Saito for constructive discussions and advice on ATRP reactions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307825.

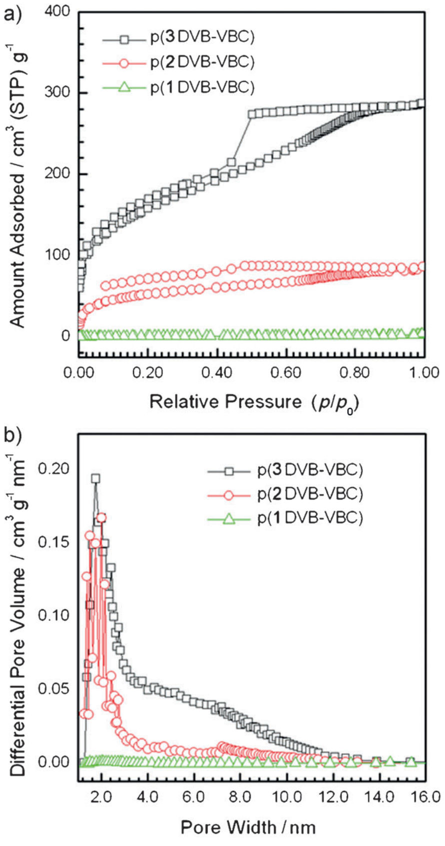

Figure 1. a) N_2 isotherms at −196 °C and b) corresponding pore-size distributions of the p(xDVB-VBC) copolymers. STP = standard temperature and pressure.

prepared in this way. Samples p(3DVB-VBC) and p(2DVB-VBC) had large well-developed mesopores, with hysteresis loops characteristic of materials with constricted mesopores, that is, ink-bottle pores (Figure 1; see also Table S2 in the Supporting Information).[19] The wide capillary-condensation steps for these samples resulted from the broad distribution of mesopores, as confirmed by the calculated pore-size distributions (PSDs). Furthermore, both porous samples contained significant amounts of micropores: a micropore volume of more than 15 %. Transmission electron microscopy (TEM) of the mesoporous copolymers provided additional evidence for the presence of nonuniform mesopores distributed within the copolymer particles (see Figure S1 in the Supporting Information).

In the porous structure, the chloride substituents present can initiate polymerization reactions, including ATRP, a common method for the control of polymer growth.[20] This technique can be used to prepare well-defined polymers with defined molecular weights determined by the ratio of consumed monomer to introduced initiator. The initiator used determines the end group of the polymer, whereas the monomers can be tailored to meet the desired application; thus, acrylonitrile (AN) can be used for polyamidoxime-based uranium adsorbents. We screened the copolymers with varying molar ratios of acrylonitrile and the ligand tris[2-(dimethylamino)ethyl]amine (Me$_6$tren) to gain an understanding of the effect of varying the initiator density within the pore structure (Figure 2; see also Figure S2 and Table S1).[21,22] The effect of adding copper(II) bromide as a catalyst to influence the redox equilibrium was also investigated. Chain extension of the p(xDVB-VBC) polymers with AN in dimethyl sulfoxide (DMSO) at 60 °C led to graft copolymers with a degree of grafting (DOG) of 280, 509, and 310 % for p(1DVB-VBC), p(2DVB-VBC), and p(3DVB-VBC), respectively. The results indicate a synergistic effect of the porosity and the density of initiator active sites on the DOG under these conditions; that is, the DOG increases as the density of the active sites in the copolymer increases, but as a result of grafting, the mesopores may become filled or blocked, and the theoretically available surface area may become inaccessible to the monomer, AN.

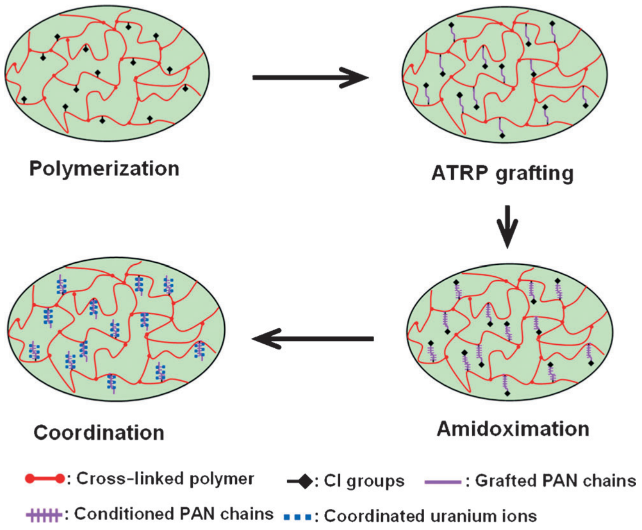

Figure 2. Steps involved in the formation of the polymeric sorbents and the corresponding uranium complexes.

The p(2DVB-VBC) sample, which had the highest DOG of acrylonitrile in this screening polymerization, was chosen for optimization of the ATRP conditions to maximize the grafting efficiency. Detailed studies based on p(2DVB-VBC) were carried out with copper bromide and the Me$_6$tren ligand in a polar solvent with different ratios of the reactants, catalyst, and solvent (see Table S2); the resulting AN-grafted copolymer was named p(2DVB-VBC)-yPAN (in which y represents the different ATRP reaction conditions). After polymerization, the brown product obtained was washed with methanol and dried at ambient temperature. The typical grafted copolymer p(2DVB-VBC)-2PAN was characterized by FTIR spectroscopy. The FTIR spectrum showed the characteristic CN stretch at 2248 cm^{-1} (see Figure S3),[23] which indicated that the AN was grafted on the skeleton of the copolymer. The BET surface area of the AN-grafted copolymers was smaller than that of the copolymers prior to the ATRP reaction. The nitrogen isotherms again showed the presence of hysteresis loops at higher relative pressures. The latter results indicate that although the micro- and mesopores of the starting polymer substrates were filled or blocked, the AN chains induced the formation of very large mesopores and small macropores (see Figure S4). The resulting polymers offer other advantages, such as good mechanical strength[24] and thermal stability, which are of interest for applications in extreme environments. Thermogravimetric analysis (TGA) showed negligible weight change up to temperatures approaching 220 °C for hydroxylamine (HAN)-modified p(2DVB-VBC)-2PAN (see Figure S5).

The polyacrylonitrile segments on the skeleton were further converted into amidoxime functionalities with hydroxylamine on the basis of a previously reported method, followed by treatment with a 3% (w/w) aqueous potassium hydroxide solution at room temperature for 2 h (Figure 2).[3a,25] The potassium in the final products, as observed by energy-dispersive X-ray analysis (EDX), indicates deprotonation of the polyamidoxime by KOH. However, the Cl groups were not detected by EDX, possibly owing to hydrolysis of the terminal chlorides during treatment with KOH (Figure 2; see also Figure S6).

Subsequently, this series of mesoporous polymers were tested with brine with a high uranyl concentration (ca. 6 ppm) at pH 8 to simulate seawater. The sorbent and the stock solution were placed in a wide-mouth plastic bottle and shaken for 24 h at room temperature. The highest uranyl adsorption capacity observed for the synthesized grafted copolymers for uranium adsorption from the high-concentration brine was 80 mg U (g Ads)$^{-1}$ (in which Ads is the adsorbent), and the average capacity was 74 mg U (g Ads)$^{-1}$ for this series of sorbents (Figure 3; see also Table S2), which have similar degrees of grafting from the ATRP reaction. To evaluate the uranium-adsorption ability of the cografted sorbents, four commercial heavy-metal adsorbents, alumina-based Dyna-Aqua and three variations of the titania-based Metsorb, were tested under identical conditions. Each exhibited much lower capacity (Figure 3).

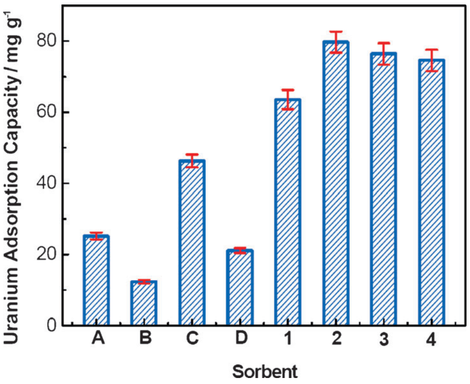

Figure 3. Uranium-adsorption capacity of the commercial adsorbents METSORB 16/60 (A), METSORB STP (B), METSORB HMRP 50 powder (C), and Dyna Aqua (D) and the nanoporous adsorbents p(2DVB-VBC)-*y*PAN (*y* = 1–4) in simulated seawater.

Sample p(2DVB-VBC)-2PAN, which showed the highest capacity in the simulated-seawater tests (see Table S2), was chosen for seawater uranyl extraction. To determine its uranyl adsorption capacity in seawater, the sorbent p(2DVB-VBC)-2PAN was immersed in a tank containing 5 gallons of seawater and shaken for 4 weeks. The decrease in the uranyl concentration of the seawater as a function of the adsorption time with the polymeric sorbent is shown in Figure 4 a. The rapid initial uranium adsorption by the p(2DVB-VBC)-2PAN sorbent indicates fast kinetics. Approximately 90% of the capacity was reached in the first 10 days, and a steady, yet slower uptake for the following 17 days was observed with no plateau. These results suggest that the equilibrium was not reached after 27 days. At 27 days, the uranium uptake was determined to be 1.99 mg U (g Ads)$^{-1}$ at 0.33 mg U (g Ads)$^{-1}$ day^{-1} by analysis of the collected seawater aliquots. These results indicate that the sorbent can indeed extract low-concentration uranium from the high-salinity seawater. The capacity is higher than that observed for nonporous irradiation-grafted nonwoven polyethylene fabric (JAEA) when it was tested for uranium adsorption from seawater by same shaking method (0.75 mg U (g Ads)$^{-1}$ after 30 days), and it is also much higher than the reported capacities of the copolymers formed by irradiation-induced graft polymerization of polyamidoxime on polyethylene (0.97 mg U (g Ads)$^{-1}$ after 30 days).[26]

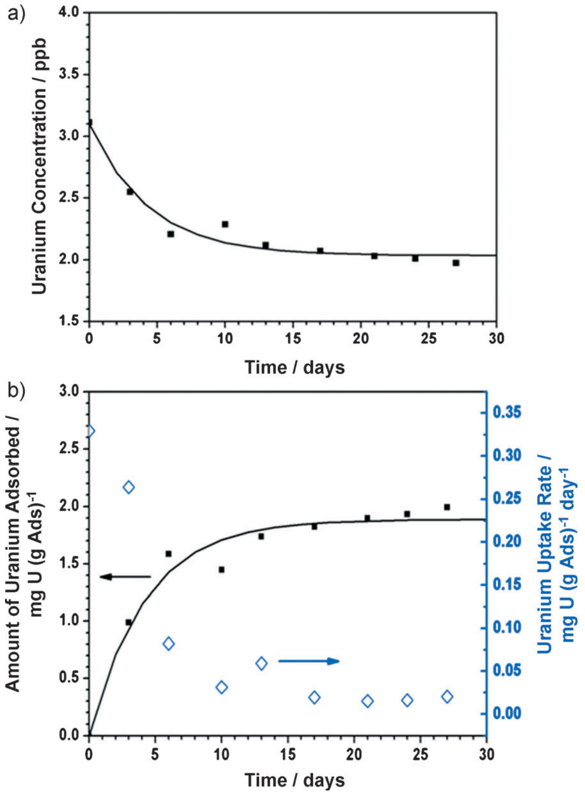

Figure 4. Comparison of experimental data (dots) with modeling results (solid lines) for the novel porous polymeric adsorbent p(2DVB-VBC)-2PAN: a) concentration decay versus time and b) uptake behavior versus time. ppb = parts per billion.

The following equations, derived from a mass balance of uranium between the bulk seawater and adsorbent, were used to quantitatively describe the uranium uptake:[3c]

$$-V \cdot \frac{dC}{dt} = A \cdot k_{\mathrm{L}} \cdot (C[t] - C_e) \tag{1}$$

$$C[t] = (C_0 - C_e) \cdot e^{\left[\left(-\frac{A \cdot k_{\mathrm{L}}}{V}\right) \cdot t\right]} + C_0 \tag{2}$$

$$q[t] = \frac{V}{M} \cdot (C_0 - C_e) \cdot \left[1 - e^{\left[\left(-\frac{A \cdot k_{\mathrm{L}}}{V}\right) \cdot t\right]}\right] \tag{3}$$

In these equations, V is the volume of seawater and t is time; C, C_0, and C_e are the concentrations of uranium in the bulk solution at any time, initially, and at equilibrium, respectively; A is the surface area of the porous polymeric adsorbent; k_{L} is a mass-transfer coefficient; M is the mass of the adsorbent; and $q[t]$ is the amount of uranium adsorbed per unit mass of the adsorbent. A, k_{L}, and C_e are assumed to be constants and independent of time. Since the surface area A is not known owing to swelling of the polymer during conditioning and when in contact with seawater, a combined parameter, the interphase-mass-transfer parameter, $A{\cdot}k_{\mathrm{L}}/V$, was used in the optimization procedure. Figure 4 shows experimental data along with modeling results based on these three equations.

The behavior observed in the experiments for uranium uptake from seawater is represented well by the model (Figure 4). The maximum initial uptake rate is 0.33 mg U (g Ads)$^{-1}$ day^{-1}, which is similar to the uptake rate of amidoxime-grafted polyethylene fibers (0.30 mg U (g Ads)$^{-1}$ day^{-1}).[3c] The uptake rate, obtained by dividing the difference in uranium uptake by the corresponding time intervals, is shown in Figure 4 b (blue circles). The value of $A{\cdot}k_{\mathrm{L}}/V$ in Equation (2) was 0.23 day^{-1}, which was higher than the value of the same parameter (0.06 day^{-1}) for the amidoxime-grafted polyethylene adsorbent.[3c] The high rate of uranium adsorption from seawater may be a result of the higher surface area of the newly developed adsorbent.

In summary, we have described the first synthesis of a hierarchical microporous–mesoporous ATRP initiator, which was generated by the solvothermal polymerization of vinylbenzyl chloride and divinylbenzene. The pore structure of the hierarchically porous polymer can be tailored in terms of surface area and pore volume by simply changing the ratio of the DVB and VBC monomers. The accessibility of the framework and surface chloride groups on the nanoporous ATRP initiator provide a unique environment for the growth of polymers with higher metal-adsorption capacity and faster kinetics than those of previously reported systems. Polyacrylonitrile was grown by ATRP from the nanoporous initiator and converted into polyamidoxime for the recovery of uranium from seawater. The uranium-adsorption capacities of the polymeric sorbents were tested with high-salinity simulated seawater, and it was found that the adsorption capacity was strongly influenced by the DOG, that is, the final density of the amidoxime groups: a parameter tailored by the adsorption properties of the starting nanoporous ATRP initiator. Preliminary seawater screening suggests a high uranium-adsorption capacity (1.99 mg U (g Ads)$^{-1}$) relative to that of irradiation-grafted nonwoven polyethylene fabric (0.75 mg U (g Ads)$^{-1}$). The mesoporous polymer adsorbent also exhibited a fast uptake rate. This methodology based on atom-transfer radical polymerization (ATRP) can be used to prepare various polymeric nanocomposites for the removal of heavy-metal ions from aqueous solutions, and also has applications in catalysis, energy storage, and conversion if different polymers are used with reactive surface sites and electronic-conductivity properties.[27]

Experimental Section

The mesoporous copolymers were solvothermally synthesized by the copolymerization of DVB and VBC. For the preparation of p(2DVB-VBC), DVB (2.0 g, 15.4 mmol) and VBC (1.1 g, 7.7 mmol) were added to a solution containing AIBN (0.1 g, 0.6 mmol) and THF (20 mL), and DMF (2 mL) was then added. The mixture was stirred at room temperature for 2 h and then heated at 90 °C for 24 h. The resulting sample with a monolithic morphology was washed with methanol and then dried under vacuum at ambient temperature to yield an off-white solid.

Typical procedure for the preparation of copolymers p(2DVB-VBC)-*y*PAN by ATRP: p(2DVB-VBC) (0.20 g; containing 0.458 mmol VBC), AN (6.0 g, 113.2 mmol), DMSO (5 g), and $\mathrm{Me_6tren}$ (0.2100 g, 0.916 mmol) were mixed in a 50 mL flask equipped with a magnetic stirrer bar. The mixture was degassed by purging with nitrogen for 10 min. Copper(I) bromide (0.0658 g, 0.458 mmol) was added to the flask, and the mixture was deoxygenated by purging with nitrogen for 10 min. The flask was placed in an oil bath at 60 °C, and the mixture was stirred at this temperature for 18 h and then allowed to cool to room temperature. The resulting brown copolymer p(2DVB-VBC)-2PAN was washed with DMF and methanol and dried under vacuum at ambient temperature.

The resulting polyacrylonitrile-grafted sorbent was treated with hydroxylamine to convert the nitrile group into an amidoxime group, and then treated with 3 % (w/w) aqueous potassium hydroxide solution at room temperature for 2 h. The product was separated by centrifugation and washed with water before uranium-adsorption measurements. Simulated seawater was prepared as described previously.[16] Briefly, sodium chloride (25.6 g, 438.056 mmol), sodium bicarbonate (0.193 g, 2.297 mmol), and uranium nitrate hexahydrate (0.017 g, 0.034 mmol) were dissolved in distilled water (1.0 L). The amidoximated polymer (13.0 ± 1.0 mg) was shaken with this stock solution (250 mL) for 24 h at room temperature, and supernatant was then filtered before the determination of the uranium concentration. For the actual seawater test, the sorbent (0.0100 ± 0.0030 g) was allowed to equilibrate with 5 gallons of filtered seawater over 27 days. Aliquots of the seawater were removed periodically for analysis. Analysis was performed with a ThermoScientific XSeriesII inductively coupled plasma mass spectrometer. Samples were aspirated at 100 μL min^{-1} with a Teflon SP nebulizer coupled to an Elemental Scientific Inc. PC3 autosampler.

Received: September 5, 2013

Keywords: amidoxime · atom-transfer radical polymerization · mesoporous copolymers · seawater · uranium extraction

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