High-Capacity Poly(4-vinylpyridine) Grafted PolyHIPE Foams for Efficient Plutonium Separation and Purification

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Supporting Information

ABSTRACT: The use of anion-exchange resins to separate and purify plutonium from various sources represents a major bottleneck in the throughput that can be achieved when this step is part of a larger separation scheme. Slow sorption kinetics and broad elution profiles necessitate long contact times with the resin, and the recovered Pu is relatively dilute, requiring the handling of large volumes of hazardous material. In this work, high internal-phase emulsion (HIPE) foams were prepared with a comonomer containing a dormant nitroxide. Using surface-initiated nitroxide-mediated polymerization, the foam surface was decorated with a brush of poly(4-vinylpyridine), and the resulting materials were tested under controlled flow conditions as anion-exchange media for plutonium separations. It was found that the grafted foams demonstrated greater ion-exchange capacity per unit volume than a commercial resin commonly used for Pu separations and had narrower elution profiles. The ion-exchange sites (quaternized pyridine) were exposed on the surface of the large pores of the foam, resulting in convective mass transfer, the driving force for the excellent separation properties exhibited by the synthesized polyHIPE foams.

INTRODUCTION

Past decades have seen pointed inquiry into improving the processes for recovering and purifying valuable fissile material from spent nuclear fuel (reprocessing), legacy materials, mixed waste streams, etc.1−11 Despite these efforts, seasoned technologies such as organophosphorus-based solvent extraction (e.g., the PUREX process) and ion-exchange (IX) resins persist as the dominant techniques for separation and purification of fissile materials used independently or as part of a larger separation scheme. For plutonium, an anion-exchange resin separation process (a facility originally dedicated to the production of Pu-238 and now used for the recovery of valuable legacy fissile materials) at the Savannah River Site in Aiken, SC offers an opportunity to not only develop a material that has the strengths of an anion-exchange resin but also improve the mass transfer properties that may lead to more efficient separations. A scaffold that offers the potential to meet both needs lies in polymerized high internal-phase emulsion (polyHIPE) foams. PolyHIPEs are generally formed from water-in-oil emulsions in which the oil phase contains radically polymerizable monomer and cross-linker that are cured by a thermal radical initiator.12

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Recent years have seen robust development of these porous polymers as solid supports for various separations and chemical transformations. Specifically, polyHIPEs with surface-grafted chains of P4VP prepared via photoinitiated polymerization have been studied as a potential replacement for columns of Reillex HPQ for the Pu purification process at the Savannah River Site. Conven-iently, the backbone of the polyHIPE foam is polystyrene cross-linked with divinylbenzene (a similar chemical composition to the Reillex resin), which is known to have fairly good stability under the harsh acid and radiation conditions used for testing. In batch testing experiments, the foam samples were found to have faster uptake kinetics than the resin. Testing of similarly prepared P4VP-grafted monoliths under controlled flow conditions showed that the Pu could be eluted from the columns much more efficiently than the resin and despite having a lower anion-exchange capacity (based on nitrogen content due to P4VP), some of the tested foams could adsorb more Pu per unit mass than the resin. These performance improvements are likely owed to the convective mass transport made possible by the large open pore structure afforded by the polyHIPEs. Grafting the chains from the foam surface ensures all ion-exchange functionality is freely available on the surface of the foam, rather than hidden in the bulk of the material (like a resin bead). However, preparation of surface-grafted foams using a surface-initiation approach limited the size of columns that could be produced and the amount of graft- ed P4VP was somewhat unpredictable. To be a viable replacement for anion-exchange resins, the ion-exchange capacity of the foam materials needed improvement.

Reported herein is a new approach to the synthesis of P4VP-grafted polyHIPE foams prepared using a dormant nitroxide, which is incorporated into the foam backbone as a comonomer. The use of this functional comonomer allows for excellent control over the amount of nitroxide-mediated polymerization (NMP) sites available for surface-grafting chains of P4VP. Using this new approach to P4VP-grafted polyHIPE foams, monolithic columns were prepared with a much higher degree of P4VP functionalization than with the photoinitiated approach, also allowing for monoliths of any size to be prepared since the mode of initiation of the surface polymerization is thermal rather than light activated. Surface-grafted polyHIPE foam monoliths prepared in this manner were also tested for their Pu separation capabilities and were found to have excellent capacity and elution characteristics compared with the Reillex HPQ resin.

**RESULTS AND DISCUSSION**

A main aim of this work was to increase the anion-exchange capacity of P4VP-grafted polyHIPE monoliths. Previous work with these materials showed their promising chromatographic separation behavior owed to an interconnected pore structure and the method of incorporating anion-exchange functionality directly on the surface of the foam where they can be freely accessed in solution through convective mass transport. PolyHIPE foams have previously been shown to have very robust mechanical properties (yield strengths of up to 130 psi) PolyHIPE foams representative of those tested in this report (pre- and post-P4VP grafting) were tested for their mechanical properties under a series of compressive forces (60–100 psi) (Figure S1). It was found that at each pressure tested, the foams exhibited elastic recovery, even after applying the compressive force for 12 h. This is evidence that under these pressures, the polyHIPE foams do not mechanically degrade. Despite these desirable properties, the foams prepared by photoinitiated graft polymerization could not be prepared with comparable ion-exchange capacity to the Reillex HPQ resin on a volumetric basis, an important parameter if these

### Table 1. Physical and Chemical Characteristics of Synthesized PolyHIPE Foams and Reillex HPQ Resin

<table>
<thead>
<tr>
<th>sample</th>
<th>cross-linker content (wt %)</th>
<th>% of comonomer 1 in initial emulsion (wt %)</th>
<th>%N before surface polymerization</th>
<th>%N after surface polymerization</th>
<th>surface polymerization reaction time (h)</th>
<th>%N due to P4VP</th>
<th>weight gain (%)</th>
<th>density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td>23</td>
<td>1.12</td>
<td>9.81</td>
<td>25</td>
<td>9.56</td>
<td>366</td>
<td>0.153</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
<td>35</td>
<td>1.49</td>
<td>11.37</td>
<td>25</td>
<td>11.16</td>
<td>599</td>
<td>0.208</td>
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<tr>
<td>C</td>
<td>25</td>
<td>30</td>
<td>1.23</td>
<td>11.35</td>
<td>25</td>
<td>11.14</td>
<td>490</td>
<td>0.178</td>
</tr>
<tr>
<td>D</td>
<td>25</td>
<td>23</td>
<td>1.05</td>
<td>10.65</td>
<td>25</td>
<td>10.46</td>
<td>450</td>
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<td>25</td>
<td>35</td>
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<td>11.65</td>
<td>48</td>
<td>11.47</td>
<td>722</td>
<td>0.183</td>
</tr>
<tr>
<td>F</td>
<td>25</td>
<td>35</td>
<td>1.49</td>
<td>8.38</td>
<td>6</td>
<td>7.84</td>
<td>272</td>
<td>0.164</td>
</tr>
<tr>
<td>G</td>
<td>25</td>
<td>30</td>
<td>1.50</td>
<td>10.89</td>
<td>25</td>
<td>10.44</td>
<td>472</td>
<td>0.188</td>
</tr>
<tr>
<td>Reillex HPQ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.75</td>
<td>0.890</td>
</tr>
</tbody>
</table>

Values represent percent nitrogen only due to P4VP. Percent weight gain of the monolith based on the initial and final mass of the monolith. Calculated from monolith dimensions and mass. Calculated theoretical value.
materials should become suitable to directly replace a resin column in a separation scheme, for example.\textsuperscript{28} To overcome this limitation, a new approach to synthesizing polyHIPE foams with many surface-bound initiating sites was developed (Scheme 1). This method borrows a concept from early work done with star and hyperbranched polymers by Hawker and co-workers,\textsuperscript{30–32} the vinyl moiety on the nitroxide containing monomer can be radically polymerized at a lower temperature than that which homolytically activates the carbon–oxygen bond of the alkoxyamine. This allows for the incorporation of the functional comonomer (1) at high weight fractions in the initial high internal-phase emulsion, and the comonomer content can be tuned more or less independently from the pore structure of the polyHIPE. Some of the dormant nitroxide groups then presumably end up on the surface of the cured foam and are available as surface-initiating sites to grow P4VP.

Table 1 summarizes the measured characteristics of the polyHIPE foams prepared for testing. The cross-linker content of the polyHIPE foam was kept constant throughout all samples to emulate the backbone structure of the resin (and ideally a similar chemical stability in harsh conditions). The nitrogen content of the polyHIPEs was analyzed before and after the surface polymerization. The nitrogen in the cured polyHIPEs is due to the dormant nitroxide, and the nitrogen present in the samples after the surface-initiated polymerization of P4VP represents the nitrogen due to the combination of nitroxide groups and polymer present. Because the surface-bound initiating species is a benzyl radical, directly characterizing the grafted P4VP is difficult because there is no straightforward way to cleave the grafted polymer.

A solution analog of the initiating species was synthesized, and the kinetics of the polymerization were studied according to Scheme 2. The results of the kinetic study are shown in Figure 1. An approximately linear relationship between \(\ln([M_f]/[M_i])\) and time indicates a pseudo first-order relationship between monomer consumption and reaction time (Figure 1a). The evolution of molecular weight with respect to monomer conversion (Figure 1b) is fairly linear up to \(\sim 30\%\) conversion, with dispersity (\(D\)) values ranging from 1.3 to 1.55. It is important to note that there are many examples in the literature that demonstrate that rates of polymerization may differ greatly between solution polymerizations and surface-initiated polymerizations.\textsuperscript{33–36} This study was not intended to be used as a direct estimation of the kinetics of the surface-initiated polymerization but rather to serve as a model for how well-controlled the surface-initiated polymerization may be. On the basis of the behavior of the polymerization of P4VP in solution initiated by compound (2), we hypothesize that the polymerization behavior of P4VP grown from the foam-bound NMP initiating species (which is chemically very similar to the benzyl radical generated in the solution study) is qualitatively similar to the solution study in terms of the initiation and nitroxide-mediated control on the growing polymer.

After each surface-initiated polymerization of P4VP on the polyHIPEs, there was an appreciable increase in mass for all samples, indicating that a large amount of ion-exchange functionality was grafted from the foam surface. Figure 2a,b shows the foam morphology after curing, and Figure 2c,d shows this after the surface polymerization. From images in Figure 2a,c there is no perceptible difference in the overall morphology of the pore structure before and after the graft polymerization. There is a marked difference in the surface of the foam before and after the surface polymerization, which is observed at high magnification (Figure 2b,d). The evolution of a distinctly rougher texture is a visual indication of the grafted polymer brush that extends from the foam surface.

Column prototypes made from the synthesized polyHIPE monoliths were tested under controlled flow conditions for their Pu adsorption capacity and elution characteristics according to Scheme S1. In these tests, our aim was to demonstrate that this material efficiently binds and elutes Pu under these test conditions so pure Pu solution was used to demonstrate these properties. In the separation scheme used at the HB-line facility, the only ion that efficiently binds with the resin at this particular step of the scheme is the [Pu(NO\(_3\))\(_3\)]\(^{2−}\) so these polyHIPE materials, in principle, should exhibit similar selectivity toward the Pu ions at this step of the separation scheme since the anion-exchange group is the same. Figure 3 shows the Pu loading curves of each tested material as a function of bed volumes of the ion-exchange material. The resin and foam materials are compared on a volumetric basis (bed volumes) because of the large difference in the density between them. Column bed volumes (defined as the volume of solution required to fully saturate the monolith or resin bed) are normalized values to account for small differences in void volumes between samples. Measured concentrations of Pu are expressed as [Pu eluate]/[Pu feed], where when the ratio is less than 1, the concentration of the collected eluate was less than that of the feed solution, and when the ratio was greater than 1, concentration of the collected eluate was greater than that of the feed solution. It was found that the majority of the polyHIPE samples tested equaled or exceeded the capacity of the Reillex HPQ resin as a function of the number of bed volumes until significant (\(\sim 10\%\)) breakthrough of the feed solution occurred. This confirms that the procedure developed in this work to incorporate many NMP initiating sites into the foam backbone, which are activated thermally, is an effective strategy for imparting a large amount of ion-exchange functionality onto the foam surface. Interestingly, there is an approximately linear correlation between the capacity of each of the polyHIPE samples with respect to the amount of nitrogen due to P4VP in the sample (Figure S2). This indicates that there is no discernible effect on the Pu capacity from the graft density (chains per unit area) or the molecular weight of the grafted chains.

The corresponding elution curves for the above-mentioned samples are presented in Figure 4. The key benefit of the convective mass transfer resulting from the foam’s large interconnected pore structure is realized here. For each of the foam samples, the loaded Pu is fully eluted from the column over the course of approximately two bed volumes, sometimes
fewer. In comparison, quantitative elution of the Pu from the Reillex HPQ column occurs over about four bed volumes, meaning that the collected Pu eluate is much less concentrated than the eluate generated from the foam materials. This broadened elution profile is a direct result of the diffusive mass transfer occurring in the pores of the resin beads. From a process intensification standpoint, the fact that the foams can release the adsorbed Pu in about half the number of bed volumes required for the Reillex HPQ means a smaller volume of hazardous material to handle after the separation and that the recovered Pu (which is very valuable) is obtained in a more concentrated form with less loss of material to the dilute head and tail cuts of the elution. Note that for sample A, the recovered Pu was 12 times more concentrated than the feed solution.

The bulk capacities of the tested materials are presented as a function of volume and mass in Figure 5. It is significant that some of the tested foams exceeded the capacity of the resin when compared volumetrically because the foams are about 6 times less dense than the resin. Despite having much less mass than a similar volume of resin, the polyHIPE could load 60% more Pu per unit volume than the resin in the case of sample B. When the materials are compared on a gravimetric basis, the capacity difference is much more dramatic. Sample C, which demonstrated the highest Pu capacity per unit mass, had 7.7× the capacity of the resin. Combined with the separation efficiency of the polyHIPE materials, the improvement in capacity compared to the resin suggests that these materials have real potential to significantly improve upon the efficiency of current Pu separation and purification technologies.

Figure 1. (a) Kinetic plot and (b) dependence of the gel permeation chromatography (GPC) molecular weight, theoretical molecular weight, and dispersity on the conversion for the polymerization of 4-vinylpyridine (4-VP) initiated by (2). ([4-VP]:[(2)] = 200:1, and 4-VP/n-butanol = 30/70 v/v).

Figure 2. Representative scanning electron microscopy (SEM) images of polyHIPE foams (A, B) after curing and (C, D) after the surface-initiated polymerization of P4VP. (Scale bars are 20 μm in images (A) and (C) and 1 μm in images (B) and (D).)
Another important parameter which warranted inquiry is the maintenance of ion-exchange capacity over repeated cycles and the stability of the polyHIPEs in the harsh acid and radiation environments inherent to this separation. A polyHIPE (sample G) was prepared and subjected to four loading and elution cycles to study if there was any effect on the capacity or separation efficiency with repeated use. The loading and elution curves generated from this testing are shown in Figure 6.

Over the course of four anion-exchange cycles, the number of bed volumes until ∼10% breakthrough ranged from about 10 to 12 bed volumes, with the highest capacity exhibited on the first cycle (determined by number of bed volumes until 10% breakthrough) (Figure 6, left). The three following cycles had a variability of less than one bed volume at this level of breakthrough. One explanation for this difference in Pu adsorbed until breakthrough between the first cycle and the following cycles is that some amount of Pu loaded during the first cycle remains bound to the polyHIPE and after this equilibrium is reached the capacity stabilizes in subsequent cycles. The efficiency of Pu elution is similar for each sample tested, given there is little change in the width of the elution profile between each trial (Figure 6, right).

When the bulk capacity of the column is compared across the four loading/elution cycles, a similar trend is observed. After the first cycle, there is a slight decrease in the capacity but the capacity is recovered for the third and fourth cycles (Figure 7). On the basis of this information, the hypothesis is that a small amount of the Pu loaded during the first cycle remains somehow bound to the foam after the first elution but then some of that may desorb during further cycles until some equilibrium amount is reached, after which the capacity remains relatively steady.

The polyHIPE materials were also evaluated for their stability to the harsh acid and radiation conditions. Two identical polyHIPE samples were synthesized, and one was soaked in 8 M nitric acid for 7 weeks and the other was soaked in 8 M nitric acid as well as irradiated by a Co-60 gamma irradiation source for 7 weeks to a total dose of approximately $7.8 \times 10^7$ rad. It was found that after about 48 days (approximately 7 weeks) under these conditions, both polyHIPE monoliths had degraded significantly and could not be tested for their Pu capacity (Figure S5). It is worth noting that during the cyclic testing of sample G, the time elapsed between cycles two and three was about 3 months. During that time, the polyHIPE had remained saturated with the 0.35 M nitric acid and based on the testing results detailed above, did not appear to have degraded or lose an appreciable amount of anion-exchange capacity. As a result, these materials appear to be relatively stable to the dilute acid and exposure to radiation over that amount of time. The ability to store the polyHIPE monolith saturated in dilute nitric acid between loading cycles is consistent with the common way that the Reillex HPQ is treated. The resin is generally only saturated with concentrated nitric acid when it is actively being primed or loaded with Pu out of caution to avoid potentially violent reactions between the organic polymer and nitric acid.

**CONCLUSIONS**

In this work, a new synthetic approach to P4VP-grafted polyHIPE materials was explored and their capabilities as ion-exchange media for Pu separations was evaluated. The ability to incorporate many NMP initiation sites into the surface of
the foam using a functional comonomer in the initial high internal-phase emulsion enabled the growth of a brush of P4VP with a sufficient number of ion-exchange sites to exceed the anion-exchange capacity of a commercial resin on both a volumetric and gravimetric basis. The exposed nature of the P4VP brush on the surface of the polyHIPE foam enabled excellent separation efficiency in the form of narrow elution profiles, and the purified Pu was obtained in a very concentrated form compared with the resin. The polyHIPE materials were found to retain their separation capabilities over the course of four anion-exchange cycles and were found to be stable for months in dilute nitric acid with exposure to radiation. On the basis of the results of these experiments, these polyHIPE materials appear to be a suitable replacement for ion-exchange resins used in the separation and purification of Pu where higher efficiency and loading is desired.

Many exciting aspects of these materials such as their high ion-exchange capacity per unit mass and excellent separation efficiency indicate that these materials may have applications in other areas of actinide science and separations in general. For example, growing a brush of polymer containing an organophosphorus ligand that can selectively chelate different actinides may offer an attractive route to separating or purifying other actinide elements. The high gravimetric capacity of these polyHIPEs may also allow for high-efficiency capture and sequestration of radioactive materials or fission products with little practical use (given the mass of material which would then need to be sequestered would be very low compared with other sequestration technologies). Simple tuning of the chemistry of the polymer brush grown using this synthetic approach to polyHIPEs renders these materials very versatile and viable alternatives to many existing separation technologies.

Figure 5. Bulk Pu capacity of each ion-exchange (IX) material on a volumetric basis (a) and gravimetric basis (b).

Figure 6. Loading and elution curves for polyHIPE sample G over four Pu anion-exchange cycles.

Figure 7. Bulk Pu capacity of polyHIPE sample G across four loading/elution cycles.
EXPERIMENTAL SECTION

Materials and Instrumentation. All materials were purchased from Alfa Aesar, Acros Organics, Millipore Sigma, or McMaster-Carr and were used as received unless otherwise specified. The inhibitor was removed from styrene and divinylbenzene (mixed isomers) by passing each through a column of basic alumina. 4-Vinylpyridine was distilled under reduced pressure and stored under nitrogen at −30 °C prior to use. 1H NMR spectroscopy was conducted on a Bruker AVANCE III-HD 300 MHz NMR spectrometer using CDCl3 as a solvent. Molecular weight and dispersity of the solution-based polymers were analyzed by gel permeation chromatography (GPC). GPC was performed in high-performance liquid chromatography grade N,N′-dimethylformamide (DMF) at a flow rate of 0.8 mL/min at 50 °C on a Varian system equipped with a ProStar 210 pump and a Varian 356-LC RI detector and three 5 μm phenogel columns (Phenomenex Co.). Samples were analyzed in comparison to narrow dispersity polystyrene standards. Scanning electron microscopy (SEM) images of the foams were observed with a Zeiss Ultraphot thermal field emission SEM at an acceleration voltage of 8 kV. Prior to SEM imaging, the foam samples were rendered conductive via sputter coating for 60 s using a Pd/Au target. Foam compression experiments were performed at 25 °C using a parallel plate test fixture made of poly(tetrafluoroethylene)-coated stainless steel on a dynamic mechanical analyzer (DMA) (TA Instruments, model RSAIII). Elemental analysis was performed at Midwest Microlab, Indianapolis, IN. Pu concentrations were determined by gamma spectroscopy using either a Canberra or Ortec high-purity germanium detector instrument.

General Procedure for the Synthesis of 1-(4-Ethenylphenyl)methoxy)-2,2,6,6-tetramethyl-piperidine (1) and 2,2,6,6-Tetramethyl-1-(phenylmethoxy)-piperidine (2). Compounds (1) and (2) were synthesized according to a modified literature procedure. A solution of sodium ascorbate (4 g, 20 mmol) in 40 mL of distilled water was shaken with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (1.9 g, 12.16 mmol) for 30 min until the TEMPO crystals were pale yellow in color. The suspension was extracted with 80 mL of diethyl ether, and the organic layer was washed with water and brine, then dried over anhydrous MgSO4 and concentrated on a rotary evaporator, yielding an orange oil. Sodium hydride (NaH, 60% dispersion in mineral oil, 1.05 g, 26 mmol) was added to an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar. The NaH was washed 3× with hexanes under nitrogen flow to remove the mineral oil, then dried briefly under a high flow of nitrogen. Dry DMF (15 mL) was added to the NaH, forming a slurry. The reduced TEMPO was dissolved in dry DMF and added slowly to the NaH slurry. This mixture was stirred at room temperature for 1 h; then, 4-vinylbenzyl chloride (1.15 mL, 8.16 mmol) or benzyl chloride (0.939 mL, 8.16 mmol) was added via syringe and the reaction mix was stirred overnight under nitrogen protection. The mixture was slowly quenched with water, then extracted 2× with diethyl ether (40 mL). The organic layer was washed 3× with water to remove excess DMF, then brine, then dried over anhydrous MgSO4 and concentrated on a rotary evaporator. The product was purified by column chromatography (100% hexanes).

1-(4-Ethenylphenyl)methoxy)-2,2,6,6-tetramethyl-piperidine (1). Obtained as a colorless oil (1.025 g, 55% yield). 1H NMR (300 MHz, CDCl3) δ 1.14–1.35 (m, 12H), 1.47–1.61 (m, 6H), 4.81 (s, 2H), 5.22 (d, 1H), 5.73 (d, 1H), 6.71 (dd, 1H), 7.30–7.40 (m, 4H).

Preparation of PolyHIPE Foam Monoliths. The following is a general procedure for the synthesis of each polyHIPE foam monolith. Compound (1) (varying weight percent), styrene (varying weight percent), and divinylbenzene (0.275 g, 25 wt %) were combined to arrive at a total monomer mass of 1.1 g (specific formulations of each sample are detailed in Table S1). The monomers and sorbitan monooleate (SPAN 80, 0.4 g, 36 wt % relative to monomers) were combined in a small resin kettle equipped with a glass paddle stirrer. The aqueous phase, which consisted of distilled water (11 g) and potassium persulfate (K2S2O8 0.15 g), was added to a dropwise addition funnel. The aqueous phase was slowly added to the stirring oil phase (350 rpm) over the course of 15 min. After complete addition of the aqueous phase, the resulting emulsion was allowed to be stirred for an additional 5 min. The prepared emulsion was carefully deposited via syringe into thin glass tubing (sealed on one end) and cured in an oven overnight at 70 °C. The foam monoliths were removed from the glass tubes by carefully breaking the glass, then washed for 24 h in a Soxhlet extractor (ethanol was used as the extraction solvent). The monoliths were dried in a 70 °C oven overnight and stored in plastic for further use.

Surface-Initiated Nitroxide-Mediated Polymerization of P4VP on PolyHIPE Monoliths. A foam monolith weighing approximately 0.05 g was placed into a 50 mL Schlenk flask along with a small magnetic stir bar. The flask was sealed with a rubber septum (secured with copper wire), and the foam monolith was deoxygenated by evacuating and backfilling the flask with nitrogen five times. In a separate 50 mL Schlenk flask, 4-vinylpyridine (7.5 mL, 30 vol %) and n-butanol (17.5 mL, 70 vol %) were combined and degassed by three freeze–pump–thaw cycles. On the last cycle, the flask was backfilled with nitrogen. The thawed liquid mixture was transferred via a gas-tight syringe to the flask containing the foam monolith (the foam readily soaks up the monomer mixture). The reaction mixture was heated at 130 °C for varying time intervals while stirring. The resulting polymer-grafted polyHIPE monolith was washed for 24 h in a Soxhlet extractor (ethanol was used as the extraction solvent), then dried in a 70 °C oven.

Assembly of PolyHIPE Anion-Exchange Column Prototypes. Small column prototypes used for testing under flow conditions were prepared according to the following procedure. The prepared polyHIPE monolith was coated in Devcon HP250 (a chemically resistant, high-strength epoxy) and immediately encased in a layer of high-strength heat shrink tubing. The tubing was shrunk, and the epoxy was cured overnight. This process sealed the tubing to the monolith, minimizing the possibility of channeling around the monolith. Any excess epoxy was sliced off the ends of the monolith with a pristine razor blade so that liquid flow was not inhibited through the foam. Two more layers of heat shrink tubing were added so that the encased monolith fit snugly into the end of hose connectors that were attached with more Devcon HP250 epoxy. The assembly was tested by flowing water through it to
ensure there were no leaks prior to testing. Specific column dimensions for each sample are shown in Table S1 and an image of some of the prepared prototypes is shown in Figure S6.

**Plutonium Adsorption and Elution Studies.** Pu sorption and elution properties of the prepared polyHIPE foam column prototypes were studied using a feed solution of ~4 g/L Pu in 8 M nitric acid (data for each sample is normalized for the precisely determined feed concentration for comparison between samples). These conditions approximate the conditions of the Pu separation of the HB-line process at the Savannah River Site. The feed solution was prepared by treating stock Pu solution with ascorbic acid to reduce all Pu(IV) to Pu(III). The acid concentration was then adjusted to 8 M, and the Pu(III) was oxidized to Pu(IV), forming the [Pu(NO3)6]3+ complex that readily loads onto quaternized pyridine anion-exchange sites (for the purpose of this testing, the feed solution contained on Pu and no other major contaminants). Each prepared column was conditioned with approximately 10 mL of 8 M nitric acid at a flow rate of 0.75 mL/min (using a programmable syringe pump) to protonate the pyridine groups and to remove any water or dilute nitric acid from the column. The prepared Pu feed solution was then fed at 0.5 mL/min, and 1 mL aliquots were collected until breakthrough of the Pu feed was visually observed. The columns were washed with 10 mL of 8 M nitric acid at 0.75 mL/min to remove any unbound impurities, and the adsorbed Pu was eluted with 0.35 M nitric acid at a flow rate of 0.5 mL/min, collecting 1 mL aliquots until elution was complete. The results of the tested polyHIPE materials were compared to those of a similarly scaled glass column packed with Reillex HPQ resin, which was tested according to the procedure detailed above. An image of the testing setup is shown in Figure S7.

**DMA Compression Testing of PolyHIPEs.** In a typical experiment, a predetermined compressive force (pounds per square inch, psi) was applied to a small section of foam for varying durations (see Figure S1) during which sample thickness (% strain) was measured as a function of time. This was followed by removal of the force and observation of the strain recovery for 15 min.

**Solution-Based Kinetic Study of (2).** Compound (2) (0.1 g, 1 equiv), 4-vinylpyridine (8.7 mL, 200 equiv), and n-butanol (20.3 mL) were added to a 50 mL Schlenk flask equipped with a 1 in. stir bar, a glass stopcock, and rubber septum. The flask was sealed, and the reaction mixture was degassed by three freeze–pump–thaw cycles, then backfilled with nitrogen. The flask was heated to 130 °C while stirring, and aliquots of the reaction solution were taken at varying time intervals and analyzed by 1H NMR for reaction conversion information. The remainder of the aliquots were precipitated in diethyl ether, and the polymer was recovered by centrifugation. Molecular weight and dispersity characteristics of the polymer samples were determined by GPC analysis in DMF.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01057.

PolyHIPE formulation information, column prototype dimensions, scheme of Pu loading and elution experiments, irradiation testing experimental details, images of polyHIPEs after acid and irradiation stability testing, dynamic mechanical analysis, and NMR spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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