



**Uranium Recovery from Seawater: Development of Fiber
Adsorbents Prepared via Atom-Transfer Radical
Polymerization**

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4 **Uranium Recovery from Seawater:** 5 **Development of Fiber Adsorbents Prepared** 6 **via Atom-Transfer Radical Polymerization**

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36 **Key Words:** uranium recovery, seawater, polymer fiber, adsorbent, atom-transfer radical
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38 *Author Contributions:*

39 T.S. conceived the scope of work and directed the research with the guidance of S.D.. T.S wrote
40 the manuscript with input from all coauthors, especially from S.B., S.C., and C.T.. Y.O. and C.J.

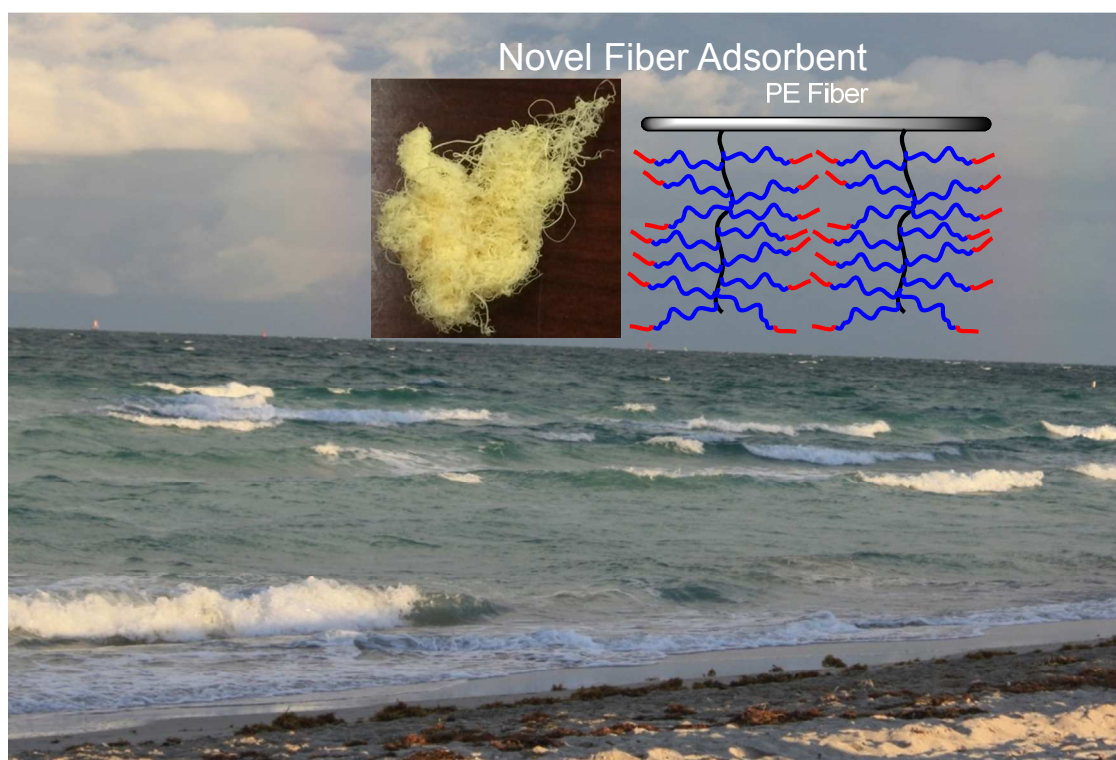
41 prepared the precursor fiber, i.e. performed RIGP on hollow-gear PE fiber. T.S. and S.B.
42 performed the synthesis of fiber adsorbents. S.B., J.K., C.T., and R.M. conducted uranium
43 adsorption experiment with simulated seawater and real seawater in a batch mode. L.K. and G.G
44 performed a marine testing, uranium adsorption experiment with a continuous flow from Sequim
45 Bay.

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49 Graphical Contents Entry



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51 Fiber adsorbents synthesized via ATRP

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56 **Summary (Abstract)**

57 A novel adsorbent preparation method using atom-transfer radical polymerization
58 (ATRP) combined with radiation-induced graft polymerization (RIGP) was developed to
59 synthesize an adsorbent for uranium recovery from seawater. The ATRP method allowed a much
60 higher degree of grafting on the adsorbent fibers (595–2818%) than that allowed by RIGP alone.
61 The adsorbents were prepared with varied composition of amidoxime groups and hydrophilic
62 acrylate groups. The successful preparation revealed that both ligand density and hydrophilicity
63 were critical for optimal performance of the adsorbents. Adsorbents synthesized in this study
64 showed a relatively high performance (141–179 mg/g at 49–62 % adsorption) in laboratory
65 screening tests using a uranium concentration of ~6 ppm. This performance is much higher than
66 that of known commercial adsorbents. However, actual seawater experiment showed impeded
67 performance compared to the recently reported high-surface-area-fiber adsorbents, due to slow
68 adsorption kinetics. The impeded performance motivated an investigation of the effect of
69 hydrophilic block addition on the graft chain terminus. The addition of hydrophilic block on the
70 graft chain terminus nearly doubled the uranium adsorption capacity in seawater, from 1.56 mg/g
71 to 3.02 mg/g. The investigation revealed the importance of polymer chain conformation, in
72 addition to ligand and hydrophilic group ratio, for advanced adsorbent synthesis for uranium
73 recovery from seawater.

74

75 **1. Introduction**

76 Uranium (U) exists uniformly as uranyl carbonates (primarily as $[\text{UO}_2(\text{CO}_3)_3]^{4-}$) at a
77 concentration of ~3.3 ppb in seawater. Because of the vast volume of the oceans, the total
78 amount of uranium in seawater is 4.5×10^9 tonnes, approximately 1000 times larger than the

79 terrestrial resources.^{1,2} A nuclear power plant is typically designed to operate for a long period of
80 time, beyond 60 years.³ The reserves of uranium in conventional terrestrial mining will
81 eventually deplete, and scarcity of uranium might become a significant issue in the foreseeable
82 future, even for currently operating nuclear plants. Additionally, the environmental and human
83 health impact for the conventional terrestrial mining is always a big concern. To resolve these
84 issues associated with the conventional terrestrial mining of uranium, the extraction of uranium
85 from seawater presents a very attractive alternative route to obtain uranium for our nuclear fuel
86 needs. However, a significant challenge remains for making the extraction of uranium from
87 seawater a commercially viable alternative technology. The biggest challenge for this technology
88 to overcome is the development of adsorbents with increased uranium adsorption capacity.⁴ A
89 recent estimate of a polymer adsorbent for uranium recovery from seawater indicated that a
90 polymer fiber adsorbent with 6 mg/g uranium adsorption capacity at 3% capacity loss per use
91 with 10 uses or one with 30 mg/g uranium adsorption capacity at single use would give \$290/kg-
92 uranium, a comparable uranium price to that (\$100-335/kg-uranium) from conventional
93 terrestrial resources.⁴ In order to achieve increased uranium adsorption capacity, the adsorbent
94 performance has to be optimized and new technological developments have to happen, especially
95 as this technology requires a highly selective extraction from such a low concentration of
96 uranium in seawater.

97 Over the last 30 years, many efforts had been devoted to this topic and one of the most
98 successful strategies among them was polymer fiber adsorbents synthesized via radiation-
99 induced graft polymerization (RIGP).^{1, 5-18} Over the years, the Japanese team developed
100 polymeric fiber adsorbents, which contained polyethylene or polypropylene as a trunk polymer
101 and amidoximated polyacrylonitrile (PAN) copolymerized with hydrophilic groups (e.g.,

102 poly(methacrylic acid)) as a graft chain. The incorporation of hydrophilic groups is crucial to
103 allow seawater to access the amidoxime group on the graft chain.^{6, 7} Japanese researchers also
104 performed marine tests with stacked unwoven fabrics and braided fibers for different periods of
105 time and at different locations.¹³ Their study has established a good foundation to this research
106 field.

107 Recent efforts at the Oak Ridge National Laboratory (ORNL) employed the same
108 strategy (i.e., using RIGP) but with different geometry polyethylene fibers, which provided a
109 high surface area, and demonstrated an improved uranium adsorption capacity.^{4, 19-21} Polymeric
110 fiber adsorbents for uranium adsorption have several advantages: 1) already proven to be
111 deployable in seawater,¹³ 2) light weight, 3) easy to fabricate to various shapes and lengths.
112 However, polymeric fiber adsorbents prepared solely via conventional RIGP have some
113 limitations such as inability to tune its composition, degree of grafting (d.g.), conformation, and
114 morphology due to its ill-controlled polymerization mechanism. Therefore in this study, we
115 utilized a hybrid approach of using RIGP and controlled radical polymerization, atom-transfer
116 radical polymerization (ATRP) to prepare polymeric fiber adsorbents for uranium recovery from
117 seawater. Although a hybrid approach of RIGP and ATRP was previously reported,^{22, 23} an
118 application to fiber adsorbents has never been implemented to the best of our knowledge.
119 Moreover, our strategy used RIGP-grafted poly(vinylbenzyl chloride) (PVBC) in the first step,
120 where VBC is a readily available commercial monomer. First, polymer chains containing ATRP
121 initiation sites were grafted via conventional RIGP (Figure 1), then the ATRP initiation site was
122 utilized for subsequent ATRP. The use of controlled radical polymerization method offers
123 several tunabilities including controllable composition and controllable degree of polymerization
124 (length of graft chains), which ATRP can either increase to a much higher d.g. or prepare the

125 exact d.g. for the best performance. Additionally, this strategy creates brushes on a brush (Figure
126 1) and the unique polymer architectures, i.e., three-dimensional morphology, can also elucidate
127 characteristics of the dense brush conformation for adsorption in aqueous systems.

128 This manuscript focuses on the demonstration of the novel RIGP-ATRP hybrid approach
129 to prepare polymeric fiber adsorbents for uranium recovery from seawater. Since the balance
130 between ligand forming groups and hydrophilic groups is the key for the optimum composition
131 of graft chains,^{6, 7} this study investigates various ratios of amidoxime groups to acrylic acid
132 groups, with similar reaction conditions. The d.g. was aimed to be sufficiently high, so that the
133 effect of graft chain length was minimal. The influence of d.g., i.e. graft chain length, to the
134 uranium adsorption capacity is not a focus of this manuscript, although it is another important
135 study to be pursued in near future. Moreover, we investigated the effect of graft chain
136 conformation for further improvement of the uranium adsorption capacity. Although the current
137 study focuses only on the recovery of uranium from seawater, this novel strategy for the
138 preparation of polymeric fiber adsorbents is expected to be applicable to adsorbent synthesis for
139 other applications, including the extraction of precious or toxic metals, proteins, and organic
140 pollutants.

141

142 **2. Results and Discussion**

143 **2.1 Synthesis of Fiber Adsorbents via a Combination of RIGP and ATRP**

144 Hollow-gear-shaped polyethylene (PE) fibers were prepared via bicomponent melt-
145 extrusion spinning of linear low density polyethylene (LLDPE) and polylactic acid (PLA)
146 followed by washing with tetrahydrofuran (THF).²⁴ The resulting hollow-gear fiber tow was
147 subsequently modified via radiation-induced graft polymerization of 4-vinylbenzyl chloride

148 (VBC) in dimethylsulfoxide (DMSO) (Fig. 1).^{18, 19, 25} The resulting d.g. of poly(4-vinylbenzyl
149 chloride) (PVBC) on the hollow-gear polyethylene (PE-g-PVBC) was 96.4 %, where d.g. is
150 defined as $100 \times (\text{mass of PVBC}) / (\text{mass of PE})$. The series of ATRP of acrylonitrile (AN) and
151 *tert*-butyl acrylate (*t*BA) were performed on the PE-g-PVBC. After many trials of various
152 reaction conditions, the following ATRP conditions were used to prepare grafted fibers to give a
153 sufficiently high d.g.: PE-g-PVBC (1; molar ratio of VBC), CuCl (1.2), CuCl₂ (0.05), tris(2-
154 (dimethylamino)ethyl)amine (Me₆-TREN) (1.5), DMSO as a solvent (~50 vol%) at 65 °C. The
155 reaction time was set for 24 h for all the reactions. The feed ratio of AN and *t*BA (Table 1) was
156 systematically varied to prepare varied incorporation of hydrophilic group, i.e. acrylic acid, by
157 subsequent hydrolysis of *t*BA. The chemical composition of the resulting fibers includes PE-g-
158 PVBC-g-PAN or PE-g-PVBC-g-(PAN-*co*-*Pt*BA). The d.g. was calculated using $100 \times (\text{mass of}$
159 $\text{PAN-}co\text{-}PtBA) / (\text{mass of PE-g-PVBC})$.

160 All the samples showed a d.g. of at least 600%/PE-g-PVBC, which was most likely
161 sufficient to minimize the difference of the mass ratio in graft chains (PAN, PAN-*co*-*Pt*BA) to
162 the trunk polymer (PE-g-PVBC), i.e., graft chains weighed > ~85 wt% of total adsorbent weight.
163 The length of graft chains (i.e., molecular weight of grafted PAN and PAN-*co*-*Pt*BA) was
164 estimated from the gravimetric weight gain (g) and the number of initiation sites (mol) with the
165 assumption that all the benzyl chloride initiation sites on PVBC were initiated by ATRP (Table
166 1). It should be noted that it is not possible to cleave these immobilized graft polymers without
167 destroying other components, thus the molecular weight was estimated with the above
168 assumption. The graft chain molecular weights ranged from 1850 – 8760 g/mol, indicating that
169 dense short chain brushes were attached on a PVBC graft chain brush.

170 The addition of *t*BA (samples 2–7) as a comonomer increased the resulting d.g. as
171 compared to AN alone (sample 1). The elemental analysis of these samples (C, H, N, O)
172 permitted the calculation of PAN:*t*BA molar ratios on the graft chain (Table 1). The trend of the
173 resulting graft chain composition correlates well with the monomer feed ratio. All batches
174 showed more incorporation of AN than *t*BA, as compared to the feed ratio, indicating higher AN
175 reactivity in the copolymerization. To provide a better understanding of the reactivity of AN and
176 *t*BA in this system, the reactivity ratio was estimated using a linear method²⁶ (Supporting
177 Information). The estimated reactivity ratio was $r_{AN} = 1.61$ and $r_{tBA} = 0.88$. It should be noted
178 that the reactivity ratio value is an approximate estimation since the composition from the
179 elemental analysis lacks high precision due to possibility of various errors in the analysis. The
180 reactivity ratio of AN and *t*BA in ATRP condition was not found in the literature, but Brar et
181 al.²⁷ reported the reactivity ratio of a similar combination of monomers, acrylonitrile (AN) and 2-
182 methoxyethyl acrylate (MEA) by ATRP as $r_{AN} = 1.52$ and $r_{MEA} = 0.60$. The estimated reactivity
183 ratio for AN and *t*BA in this study is consistent with the higher reactivity of AN over MEA in
184 their report.

185 Grafting *t*BA alone showed much higher d.g. (i.e., 14500%/PE-*g*-PVBC) in a similar
186 reaction condition. The higher d.g. of *t*BA homopolymer grafting than that of AN alone indicates
187 that *t*BA propagates better than AN, and the high incorporation of AN in the copolymers despite
188 poor d.g. of AN alone suggests that AN might have more termination or side reactions in this
189 ATRP condition.^{28, 29} Overall, this ATRP method provides much higher d.g. on the adsorbents
190 than that from RIGP alone. Such high d.g. and tunability of the graft chain length and
191 composition (e.g., block copolymers) suggest that this ATRP approach is a promising strategy.

192

193 2.2 Uranium Adsorption Capacity in Simulated and Real Seawater

194 PE-*g*-PVBC-*g*-PAN and PE-*g*-PVBC-*g*-(PAN-*co*-*t*BA) fibers were reacted with
195 hydroxylamine to generate the amidoxime ligand, and subsequent potassium hydroxide (KOH)
196 treatment was performed to increase the hydrophilicity of the adsorbents. The resulting fiber
197 adsorbents included PE-*g*-PVBC-*g*-poly(amidoxime) (PAO) and PE-*g*-PVBC-*g*-(PAO-*co*-
198 poly(acrylic acid)) (PAA). Uranium adsorption tests in simulated seawater, spiked with 6-ppm
199 uranium, were initially performed under the following conditions: ~15 mg sorbent in 250 mL or
200 750 mL of 6 ppm U, 10123 ppm Na⁺, 15529 ppm Cl⁻, 140 ppm HCO₃⁻, pH 8, 20–25 °C, 24 h.
201 Uranium analysis was performed by ICP-OES at λ_U 367.007 nm. A 250-mL solution provides a
202 quantitative evaluation of the performance of the synthesized adsorbents; however, for well-
203 performing adsorbents, uranium uptake may be limited by uranium availability. Thus, it is also
204 recommended to perform experiments using a larger solution volume, e.g., 750-mL, in order to
205 increase the availability of uranium which is necessary for high-capacity adsorbents. The U
206 adsorption capacity of these novel fiber adsorbents (samples 1-6), estimated from 250 mL U-
207 spiked solution (Table 2), was much higher than that of conventional U adsorbents including
208 JAEA-provided fiber adsorbent prepared by RIGP (~20 mg/g), METSORB 16/60 (25.2 mg/g),
209 METSORB STP (12.3 mg/g), METSORB HMRP 50 (46.3 mg/g), and Dyna Aqua (21.2 mg/g).³⁰
210 The high U adsorption capacity of these novel fiber adsorbents confirms this RIGP/ATRP hybrid
211 strategy for preparation of adsorbents as a promising approach.

212 The U adsorption capacity from the U-spiked simulated seawater at 250 mL also showed
213 two distinctive trends. One followed the U-adsorbing ligand density and the other corresponded
214 to the hydrophilicity of the immobilized graft chains. When more AN is incorporated, the ligand
215 density in the graft chains, i.e., density of amidoxime (AO) groups, becomes higher. Higher *t*BA

216 incorporation results in increasing hydrophilicity due to *t*BA conversion to acrylic acid (AA). In
217 other words, lower numbered samples in Table 1 have higher ligand density and higher
218 numbered samples have more hydrophilic groups with less ligand density. When samples 1–3 are
219 compared, the U adsorption capacity for samples 1 and 2 is higher than the capacity of sample 3
220 due to the higher ligand density. Among samples 3–7, U adsorption capacity is the highest for
221 sample 5. The increase of the hydrophilicity facilitated the increase of U adsorption capacity
222 from samples 3 to 5. Further increase in hydrophilicity from samples 5 to 7 showed an adverse
223 effect on the U adsorption capacity due to their decreased ligand density. The trend of U
224 adsorption capacity was further confirmed in experiments with 750-mL solution volume. A
225 minor difference between 250-mL and 750-mL scales is that samples 1 and 2 showed higher
226 capacity than sample 5 in 750-mL volume, while sample 5 showed the highest U adsorption
227 capacity in 250-mL volume.

228 Several of these high-capacity adsorbents (samples 1, 2, 5, 6) were selected for further
229 real seawater testing in a continuous-flow system at the Marine Sciences Laboratory of the
230 Pacific Northwest National Laboratory, at Sequim, WA. In these experiments, the adsorbent was
231 packed in columns of 1-inch diameter and 6-inch height. Glass beads of 3-mm diameter were
232 also packed in the columns to keep the adsorbent uniformly distributed along the columns. A
233 flow rate of 250-300 mL/min seawater was typically used in these tests. The amount of uranium
234 adsorbed after 42 days in seawater exposure was 1.52 mg/g (sample 1), 1.56 mg/g (sample 2),
235 and 1.08 mg/g (sample 5). These values are comparable to the performance of fiber adsorbents
236 previously reported by the Japanese team,^{1, 5-15, 17, 31} but lower than values recently reported, high
237 surface area fiber adsorbents.^{2, 4, 20, 21} Considering the similar performance between adsorbents
238 developed in this study and fiber adsorbents previously prepared by RIGP alone with both 250-

239 mL and 750-mL U-spiked simulated seawater, the lower performance of these adsorbents in
240 seawater tests indicates that certain parameters of these fibers, including polymer conformation
241 and morphology, are not optimized at low U-concentration conditions. Also, more hydrophilic
242 adsorbents (samples 5 and 6) showed lower capacity than adsorbents with high ligand density
243 (samples 1 and 2). Thus, hydrophilic groups in this graft chain conformation are not a dominant
244 factor for adsorption performance, indicating that hydrophilic group interactions with other ions
245 in this crowded brush conformation probably impede either interparticle diffusion of uranyl ions
246 or amidoxime reaction with uranyl ions.²⁰

247 Due to its high capacity with a balance of hydrophilicity and ligand density, sample 5 was
248 chosen for an adsorption kinetics study, which was conducted both in a continuous seawater-
249 flow mode at Sequim Bay and in a batch mode with filtered coastal seawater collected from
250 Charleston, SC, USA. In the continuous-flow experiments at Sequim Bay, six columns of sample
251 5 adsorbent were placed in parallel in a multi-channel flow system, and over a period of eight
252 weeks, a column was removed every week for the first four weeks and every other week for the
253 remaining period. The adsorbent was collected from each column, and treated with 1 N
254 hydrochloric acid to strip the adsorbed species and prepare samples for chemical analysis using
255 ICP-OES. Results from ICP-OES analysis showed slow uranium adsorption kinetics (Figure 2).
256 Using a one-site ligand-saturation-kinetics model, the half saturation time of the adsorbent upon
257 U adsorption was estimated at 40 days, which is approximately twice that of previously reported
258 fiber adsorbents.^{20, 21} The slow kinetic trend was further confirmed by a seawater batch
259 experiment conducted with coastal gulfstream seawater. In this experiment, an amount of ~5-mg
260 adsorbent was fluidized in a 5-gallon tank of seawater, which was sitting on a shaker operating at
261 100 rpm. Samples of seawater were removed periodically for uranium analysis using ICP-MS.

262 The amount of uranium adsorbed vs time was obtained from the uranium concentration of
263 samples measured by ICP-MS. Results in Figure 3 show that the U adsorption history was
264 similar to the one observed in continuous-flow experiments at the Marine Sciences Laboratory in
265 Sequim, WA. At 80-day exposure time, a U adsorption capacity of 1.3 mg/g was observed. This
266 not-so-high U-adsorption capacity with seawater does not correspond to the high capacity
267 observed with simulated seawater, suggesting that the morphology or certain parameters of these
268 adsorbents impede U uptake in real seawater.

269

270 **2.3 Effect of Graft Chain Conformation**

271 One of the reasons for the not-so-high U adsorption capacity for the adsorbent samples 1–
272 7 in real seawater could be due to the graft chain conformation. Since PAN-*co*-PtBA was grafted
273 onto each repeat unit of grafted PVBC chain, the density of ligand-containing brushes was
274 significantly higher than that of regular adsorbents prepared solely by RIGP. The highly dense
275 brushes on a brush conformation might prevent effective diffusion of U species to the amidoxime
276 ligands. To further understand this hypothesis, chain extension of graft brushes via hydrophilic
277 chains was performed. Use of ATRP method enables the preparation of a block copolymer
278 architecture by reinitiating the end group of the graft chains.^{32, 33} The short chain of PtBA was
279 added to the tip of the PE-*g*-PVBC-*g*-(PAN-*co*-PtBA) brush, and further hydrolysis resulted in
280 PE-*g*-PVBC-*g*-(PAO-*co*-PAA)-*b*-PAA (Figure 4). Immobilized hydrophilic graft chains are
281 known to stand and stretch in aqueous system.^{34, 35} Thus, the addition of hydrophilic PAA block
282 at the graft chain terminus should aid standing and stretching graft chains, i.e., more spreading of
283 each graft chain toward water, due to favorable interaction between hydrophilic groups and water
284 (Figure 4, bottom).

285 The hydrophilic block addition was performed onto sample 2 via ATRP due to its highest
286 U adsorption capacity in the continuous-flow seawater experiment (Table 2). The ATRP reaction
287 time of *t*BA was varied from 0–5 h to prepare a varying degree of added *Pt*BA block. The d.g. of
288 *Pt*BA ranged from 13.7 to 352% (Table 3, samples 2.1–2.4), where d.g. was calculated using
289 $100 \times (\text{mass of } PtBA \text{ block}) / [\text{mass of sample 2 before amidoximation (i.e., PE-g-PVBC-g-(PAN-}$
290 $co-PtBA))]$. The *Pt*BA block was further hydrolyzed to form a PAA block via subsequent KOH
291 treatment, resulting in PE-g-PVBC-g-(PAO-*co*-PAA)-*b*-PAA. The successful preparation of
292 varied hydrophilic block length on the graft chain terminus allows us to investigate how much
293 hydrophilic block is needed to enhance U adsorption.

294 In the 250-mL U-spiked simulated seawater test, U adsorption capacities constantly
295 decreased from samples 2.1 to 2.4, corresponding to decreased ligand density (as observed in
296 random copolymers, samples 2 to 7 in Table 2). A comparison between the original sample 2
297 adsorbent and the short-chain-grafted sample 2.1 adsorbent showed that they had high U
298 adsorption capacities, on the order of 80 mg/g. Since sample 2.1 showed the highest U
299 adsorption capacity and the highest % U adsorbed among all block copolymers (samples 2.1 to
300 2.4), sample 2.1 adsorbent was selected for a subsequent U-adsorption experiment with real
301 seawater using the same method and conditions as previously used for random copolymers at the
302 Marine Sciences Laboratory of the Pacific Northwest National Laboratory, in Sequim Bay, WA.
303 The U-adsorption performance of sample 2.1 in the seawater experiment nearly doubled the
304 capacity, from 1.56 mg/g to 3.02 mg/g. This increase in capacity indicates that graft chain
305 conformation is as important as the ligand density and hydrophilicity. It should also be noted that
306 sample 2.1 performed better than adsorbents with PAO-*co*-PAA random copolymer graft chains,
307 samples 2–7. The importance of ligand density and hydrophilicity has been previously reported,

308 but the significance of chain conformation has not been investigated yet in this field. To the best
309 of our knowledge, this work is the first demonstration of the effect of graft chain conformation to
310 the U-adsorption capacity. Our novel approach of utilizing controlled radical polymerization
311 enabled us to alter the graft chain composition, and demonstrated the importance of graft chain
312 conformation in addition to ligand density and hydrophilicity.

313

314 **3. Experimental**

315 **3.1 Materials**

316 Acrylonitrile (AN, >99%, Alfa Aesar) and *tert*-butyl acrylate (*t*BA, 99%, Alfa Aesar)
317 were deinhibited via passing through activated alumina column prior to use. Copper(II) chloride,
318 (CuCl₂, anhydrous, 98% min, Alfa Aesar), copper(I) chloride, (CuCl, 99.999%, Alfa Aesar),
319 tris(2-(dimethylamino)ethyl)amine (Me₆-TREN, >99%, Alfa Aesar), 4-vinylbenzyl chloride
320 (VBC, 90%, Acros Organics), dimethylformamide (DMF, anhydrous, Alfa Aesar),
321 dimethylsulfoxide (DMSO, >99%, Alfa Aesar), tetrahydrofuran (BDH), acetone (BDH),
322 methanol (Fisher), and potassium hydroxide (Fisher) were used as received. Hydroxylamine
323 solution (50 wt % in water, Aldrich) was used in the preparation of AO reaction mixture. Uranyl
324 nitrate hexahydrate (UO₂(NO₃)₂·6H₂O, B&A Quality), sodium bicarbonate (Aldrich), and
325 sodium chloride (>99%, Aldrich) were used for the preparation of U-spiked simulated seawater.

326 **3.2 Synthesis of Fiber Adsorbents**

327 Hollow-gear shaped fibers were prepared via bicomponent melt-extrusion spinning of
328 linear low density polyethylene (LLDPE) and polylactic acid (PLA) at Hills Inc. Dissolving the
329 fugitive PLA component by washing the bicomponent fibers in THF at 50 °C gives LLDPE
330 hollow gear fibers.²⁴ The hollow-gear fiber tow was subsequently grafted with VBC in DMSO

331 via the radiation-induced graft polymerization technique. The detailed method is described
332 elsewhere.^{18, 19, 25} The resulting degree of grafting (d.g.) of poly(4-vinylbenzyl chloride) (PVBC)
333 on the hollow-gear polyethylene (PE-g-PVBC) was 96.4 %, where d.g. is defined as 100×mass
334 of PVBC/mass of PE.

335 The following optimum ATRP conditions were employed on the PE-g-PVBC: PE-g-
336 PVBC (1; molar ratio of VBC), CuCl (1.2), CuCl₂ (0.05), tris(2-(dimethylamino)ethyl)amine
337 (Me₆-TREN) (1.5), DMSO as a solvent (~50 vol%), and reaction temperature 65 °C for 24 h.
338 The feed ratio of AN and *t*BA (Table 1) was systematically varied to control the degree of
339 incorporation of the hydrophilic group, i.e., acrylic acid. After the reaction, grafted fibers were
340 isolated, washed with DMSO and acetone several times, and dried under vacuum at 40 °C for
341 several hours. The chemical composition of the resulting fibers includes PE-g-PVBC-g-PAN or
342 PE-g-PVBC-g-(PAN-*co*-*Pt*BA). The d.g. was calculated using 100×mass of PAN-*co*-*Pt*BA/mass
343 of PE-g-PVBC. The series of PE-g-PVBC-g-(PAN-*co*-*Pt*BA)-*b*-*Pt*BA was also synthesized via
344 the following conditions (Figure 4): PE-g-PVBC-g-(PAN-*co*-*Pt*BA) (1; molar ratio of VBC),
345 CuCl (2.0), CuCl₂ (0.1), Me₆-TREN (2.4), *t*BA (2000), DMSO as a solvent (~50 vol %) and
346 reaction temperature at 65 °C for 0–5 h. The experimental procedure is the same as above.

347 The third step involves the amidoximation (AO) of AN groups in the polymer brush,
348 followed by KOH treatment. AO was performed twice to ensure complete conversion of AN
349 groups in grafted polymer chains, and a large excess of hydroxylamine (HA) was used each time.
350 A volume of 6.0 mL of HA mixture (10 wt % in 1:1 (w/w) methanol/water) was added to 15±1
351 mg of the fiber adsorbent. The first AO was performed for 48 h at 80 °C. The reaction mixture
352 was then replaced by fresh HA mixture (6.0 mL), followed by the second AO (80 °C, 24 h). The
353 fibers were then washed with deionized water until neutral pH was achieved and dried in a

354 vacuum oven at 40 °C overnight, yielding constant weights. Prior to each U adsorption test, KOH
355 treatment of the fibers was performed by adding 15.0 mL of 2.5 wt% KOH solution to an
356 accurate weight of a dry amidoximated fiber (15.0±1.0 mg). The mixture was heated to 80 °C
357 and maintained for 3 h. The fibers were then filtered and washed with deionized water until
358 neutral pH was observed. Care was taken to ensure that the fibers did not become dry, and no
359 loss of fibers occurred at any step of the procedure.

360 **3.3 Adsorbents Characterization**

361 Elemental analyses of PE-g-PVBC-g-(PAN-co-PtBA) fibers for carbon, nitrogen,
362 hydrogen, and oxygen (C, H, N, and O) were performed by Galbraith Laboratories, Inc.
363 (Knoxville TN). U adsorption tests were performed on amidoximated, KOH-conditioned fiber
364 adsorbents, which were kept wet until the test. For simulated seawater tests, the preparation of U-
365 spiked (5–7 ppm U) simulated seawater was reported elsewhere.^{36, 37} Briefly, 17 mg
366 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 25.6 g NaCl, and 193 mg NaHCO_3 were dissolved in deionized water to make
367 a 1 L solution. A mass of 15.0±1.0 mg fibers was shaken in 250 mL or 750 mL of simulated
368 seawater solution (pH ~8) for 24 h at room temperature. The amount of uranyl ion uptake was
369 determined from the concentration difference between the beginning and the end of the test on a
370 Perkin–Elmer Optima 2000 DV ICP-OES at 367.007 nm. The uranium adsorption capacity
371 (mg/g) was calculated from $[(C_i - C_f) \text{ [mg/L]}] \times [\text{volume of solution [L]}] / [\text{mass of adsorbent [g]}]$
372 and % adsorbed was calculated from $[(C_i - C_f) / C_i] \times 100$, where C_i and C_f represent the initial
373 and final solution concentrations.

374 **3.4 Uranium Adsorption in Seawater**

375 The performance of fiber adsorbents was assessed in continuous-flow experiments with
376 seawater at the Marine Sciences Laboratory of the Pacific Northwest National Laboratory in

377 Sequim Bay, WA. A mass of ~60 mg of adsorbent was packed in a flow-through column of 1-
378 inch diameter and 6-inch height. The adsorbent was uniformly distributed in the column volume
379 and held in place by adding glass beads of 3-mm diameter. Marine testing was performed using
380 filtered (0.45 μm) seawater at a temperature of 20 ± 2 °C and at flow rate of 250–300 mL/min)
381 using an actively pumping through a multi-channel flow system. A detailed experimental setup
382 and analytical methods are described elsewhere.⁴

383 Batch adsorption experiments were performed using 5-gallon polyethylene tanks filled
384 with filtered coastal seawater collected from Charleston, SC, USA. A mass of 5-mg of the
385 adsorbent was added into a 5-gallon tank, with the adsorbent fibers freely suspended in the
386 seawater. An initial seawater sample of 10 mL was collected prior to the addition of the
387 adsorbent. The containers were shaken constantly at 100 rpm at room temperature (~23 °C). 10
388 mL samples were collected periodically, using a pipet, for a duration of 80 days. Collected
389 seawater samples were acidified with Optima nitric acid for analysis. The adsorbent fibers were
390 recovered after the experiment and treated with concentrated acid solution for uranium elution.²⁰

391

392 4. Conclusions

393 This manuscript demonstrated a novel adsorbent preparation method for U recovery from
394 seawater. The ATRP method provides a much higher d.g. on the adsorbents than that achieved
395 by RIGP alone. Such a high d.g. and tunability of the graft-chain length and composition (e.g.,
396 block copolymers) suggest that this ATRP approach is a promising strategy. This work also
397 demonstrated that both ligand density and hydrophilicity were critical for optimal performance
398 and the optimum balance was adsorbents with high ligand density and sufficient hydrophilicity.
399 Although these adsorbents showed high performance in concentrated simulated U solution,

400 actual seawater tests with low concentration of uranium showed impeded performance due to
401 slow adsorption kinetics. This behavior is attributed to the hypothesis that the brushes on the
402 brush structure might be too crowded to allow efficient uranyl ion diffusion to the ligand. The U
403 adsorption performance in seawater, which is lower than expected considering the results from
404 simulated seawater, motivated further investigation of the importance of graft-chain
405 conformation. Use of the ATRP method allowed us to prepare different compositions of graft
406 chains through synthesis of a block copolymer architecture. The addition of a hydrophilic block
407 on the graft chain terminus nearly doubled the U adsorption capacity in seawater and the
408 observed capacity (3.02 mg/g) is comparable to the previously demonstrated best capacity
409 adsorbent for uranium from seawater. Further investigation of graft chain conformation (length,
410 density, composition) to U adsorption performance will be pursued in future work.

411

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416

417 **Tables**

418

419 **Table 1** ATRP of AN and *t*BA on PE-*g*-PVBC

Sample	Feed ratio		d.g. (%/PE- <i>g</i> -PVBC)	Graft-chain composition molar ratio ^a		PAN- <i>co</i> - <i>Pt</i> BA graft chain molecular weight (g/mol) ^b
	AN	<i>t</i> BA		PAN	<i>Pt</i> BA	
1	1000	0	600	1.00	0.00	1850
2	1000	100	1790	0.95	0.05	5560
3	1000	200	1300	0.92	0.08	3940
4	1000	443	780	0.77	0.23	2430
5	1000	738	1980	0.66	0.34	6140
6	1000	950	1000	0.60	0.40	3090
7	1000	1200	2820	0.53	0.47	8760

420 ^a from elemental analysis421 ^b estimated from the gravimetric weight gain (g) and the number of initiation sites (mol)

422

423 **Table 2** Summary of U adsorption data

Sample	U adsorption (250 mL)		U adsorption (750 mL)		U adsorption (seawater)	
	(mg/g)	% adsorbed	(mg/g)	% adsorbed	(mg/g)	Exposure time (days)
1	76.0	75.7	179.0	62.1	1.52	42
2	80.0	79.7	174.1	61.2	1.56	42
3	68.8	71.4	141.2	49.0		
4	77.5	79.9	152.6	53.2		
5	85.9	86.2	161.3	55.6	1.08, 1.18	42, 56
6	80.8	73.9			0.99	55
7	38.8	36.7				

424

425

426 **Table 3** Degree of grafting and U adsorption capacity of block copolymer adsorbents

Sample	d.g. (%/Sample 2)	U adsorption (250 mL)		U adsorption (seawater)	
		(mg/g)	% adsorbed	(mg/g)	Exposure time (days)
2	0	80.0	79.7	1.56	42
2.1	13.7	79.4	93.2	3.02	56
2.2	28.9	75.3	86.3		
2.3	61.1	66.8	78.0		
2.4	352	65.9	66.6		

427

428

429 **Figures**

430

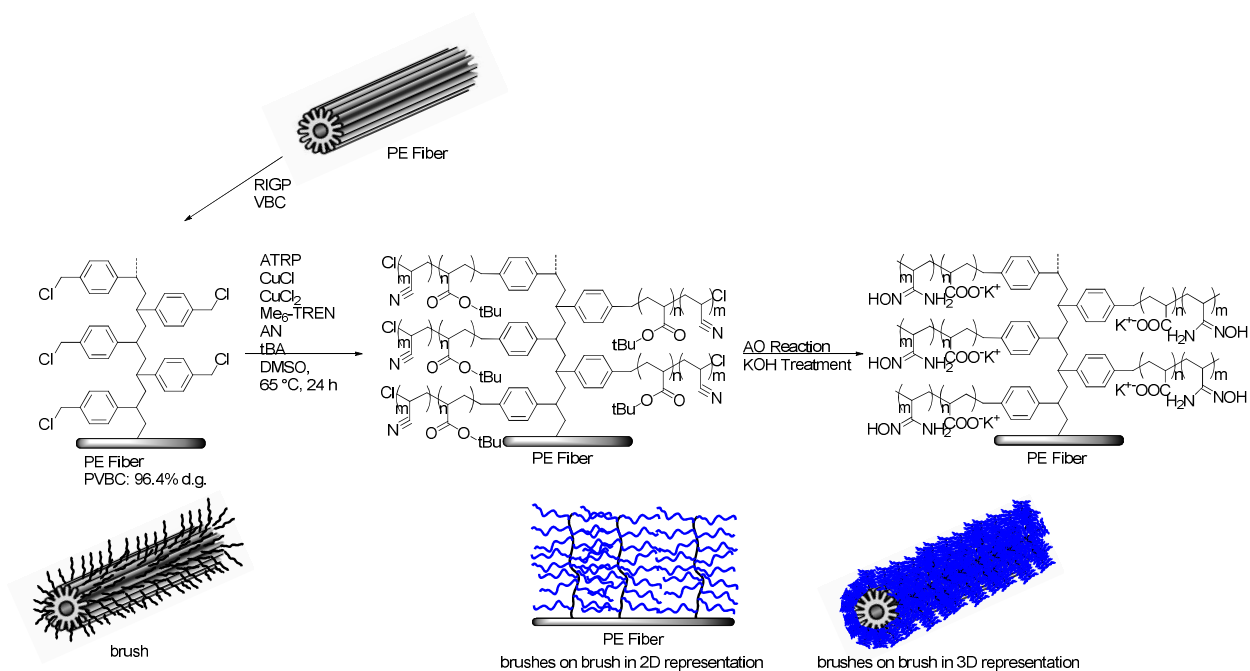
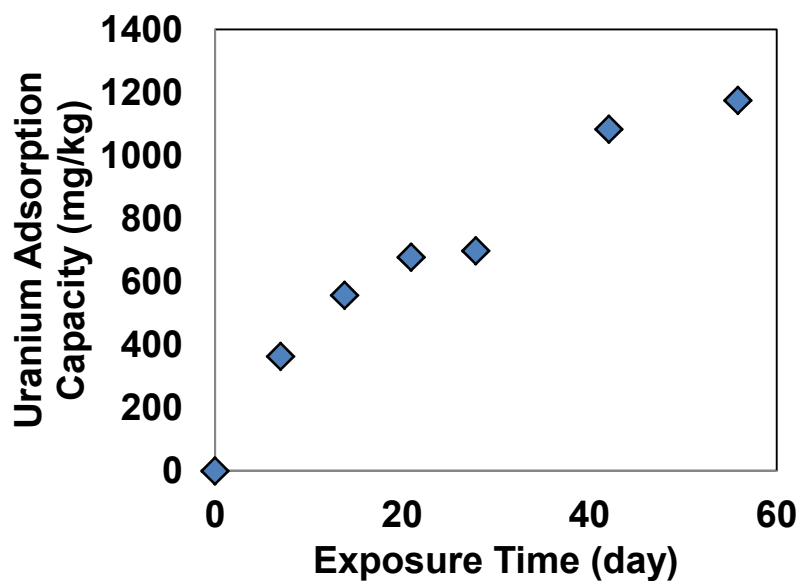


Fig. 1 Reaction scheme for the preparation of fiber adsorbents via ATRP.

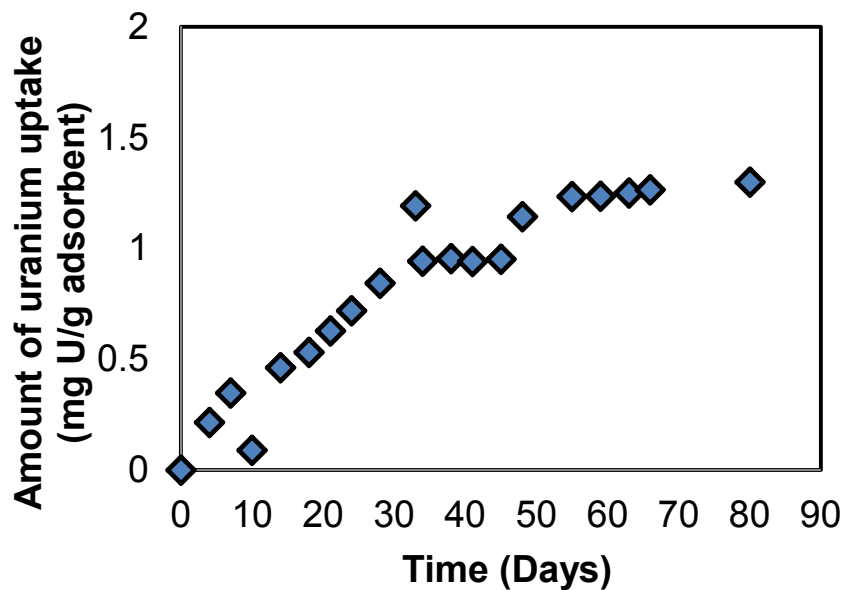


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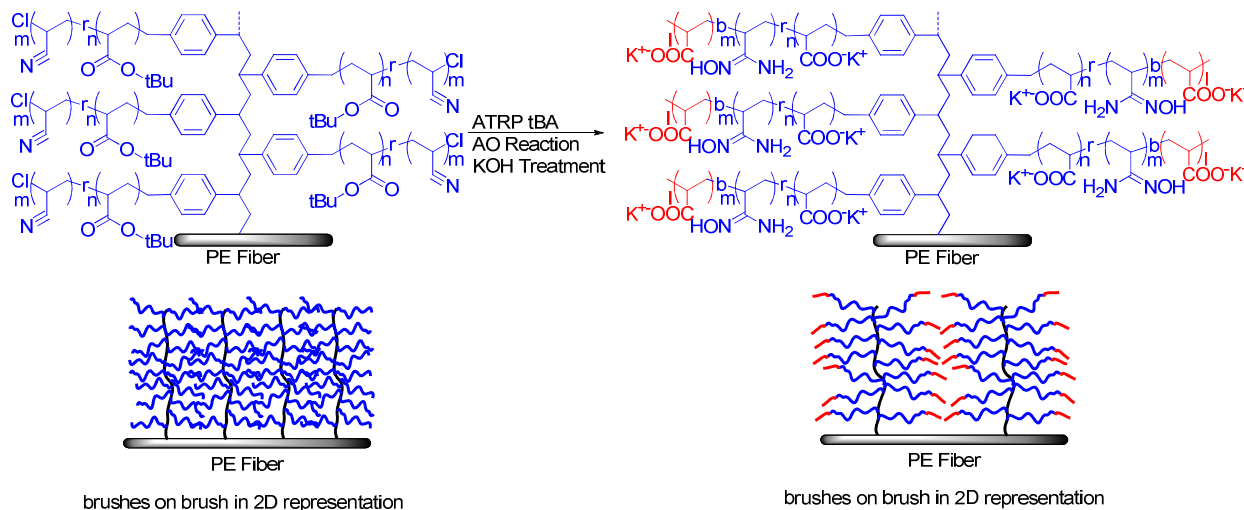
435

436

Fig. 2 Uranium adsorption kinetic data for sample 5 adsorbent in continuous-flow experiments with seawater at the Marine Sciences Laboratory in Sequim Bay, WA.



437
438 **Fig. 3** Uranium adsorption kinetic data for sample 5 adsorbent in a batch mode of filtered
439 coastal seawater.
440



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