Improvement of the radiation grafting of selective ligands onto polymeric substrates to produce high-capacity adsorbents for harvesting uranium from seawater

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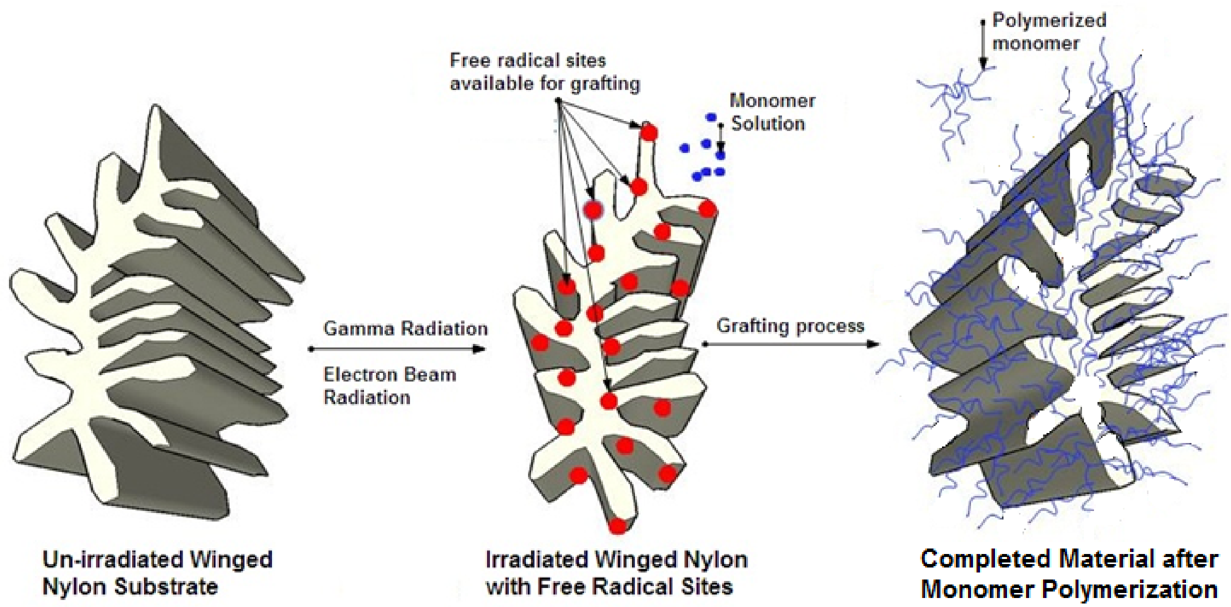

CIRMS 2015 Conference
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Gaithersburg, MD, April 27-29, 2015

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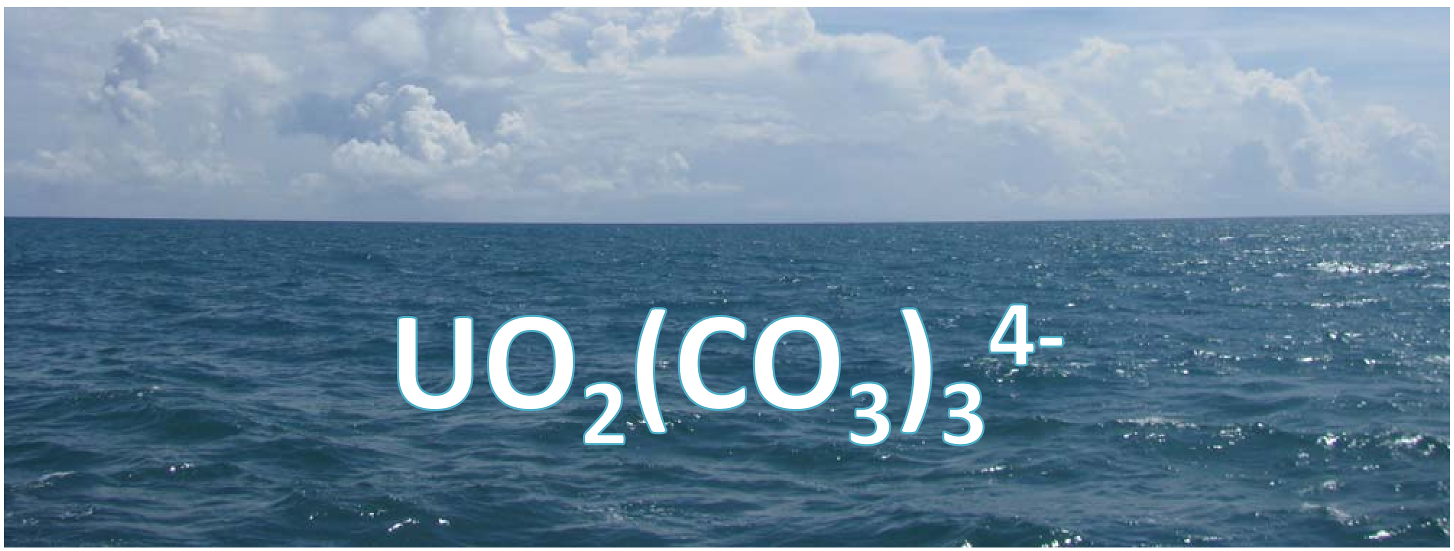
There exists almost 1000 times more uranium in the world's oceans than is present in terrestrial ores.

However this uranium is:

- **Found at extremely low concentrations (~3.3 ppb)**
- **Amidst the presence of other solutes at much higher concentrations**



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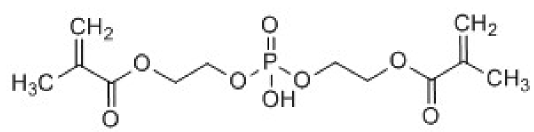
http://www.nefsc.noaa.gov/rcb/photogallery/scenic/photos/ocean4_fullsize.jpg

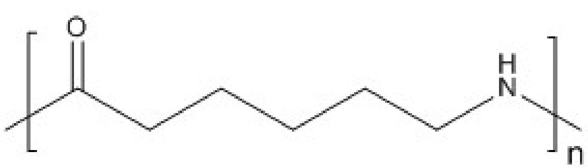
Kim, J. et al. Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs. Separation Science and Technology 48, 367–387 (2013).

Our synthetic approach focuses on using radiation to initiate grafting of uranium chelating groups functionalized with vinyl groups.

Materials Selection

- Select ideal adsorbent compounds
- Select ideal substrate materials (polymers)





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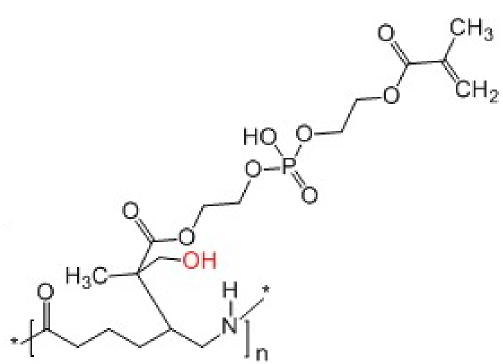
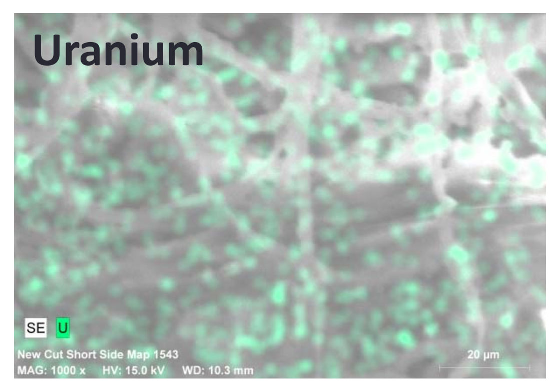
Radiation Grafting

- Single Step synthesis
- Maximize radical concentration for grafting
- Increase length and number of adsorbing groups (grafting density)

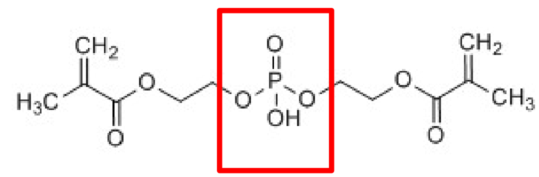
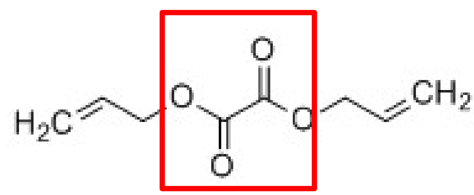
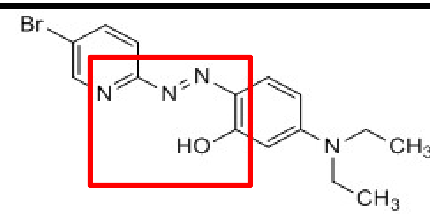


Extraction Testing

- Improve extraction efficiency
- Test scaled-up materials on-site



Prior to grafting experiments, monomers must be chosen and tested for their uranium extraction potential.

Monomers	Structure
Bis[2-(methacryloyloxy)ethyl] phosphate **(B2MP)**	
Diallyl Oxalate **(DAO)**	
2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol **(Br-PADAP)**	

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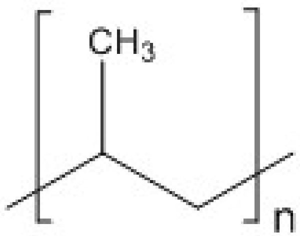
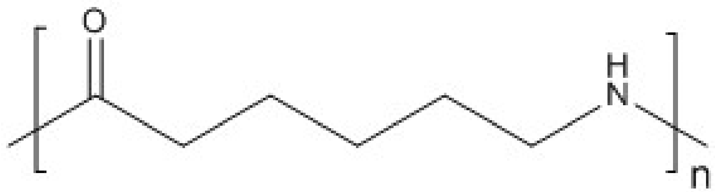
A number of polymer substrates were selected, tested, and compared.

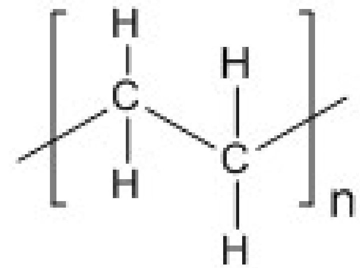
Polypropylene

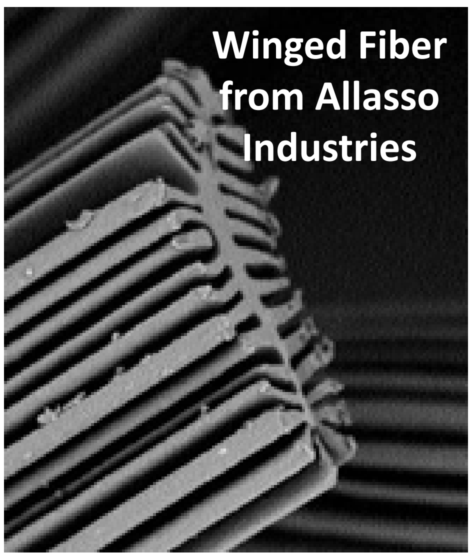


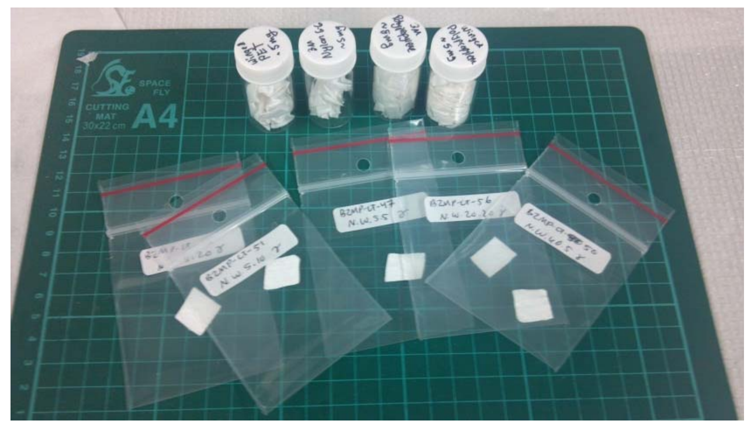
Nylon 6



Polyethylene







Substrate samples ready for adsorbance testing (in bag)

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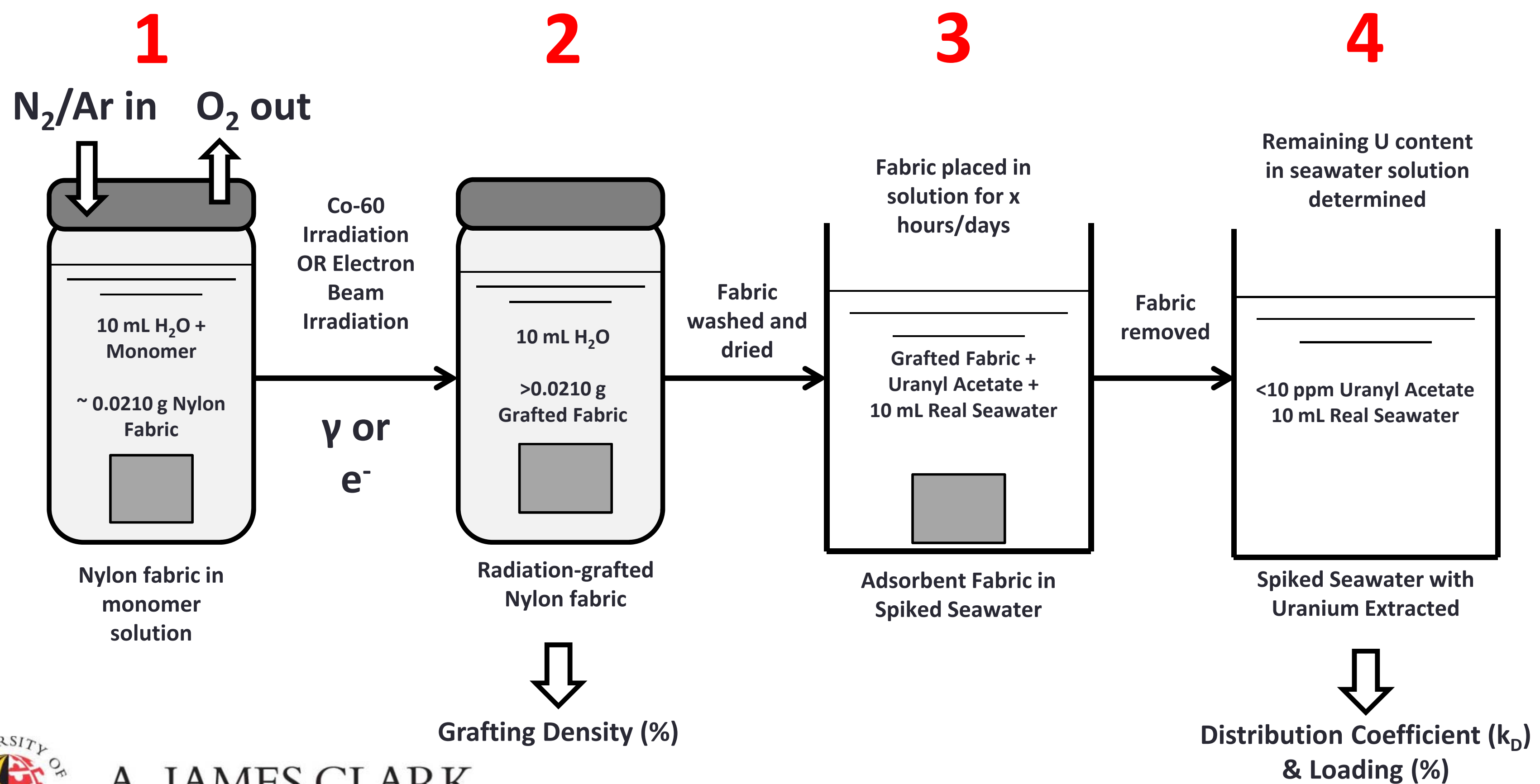
TD1

Slide 5

TD1 Mention EPR testing?

Travis, 3/17/2015

The direct grafting method allows for a one-pot synthesis of adsorbent fabrics



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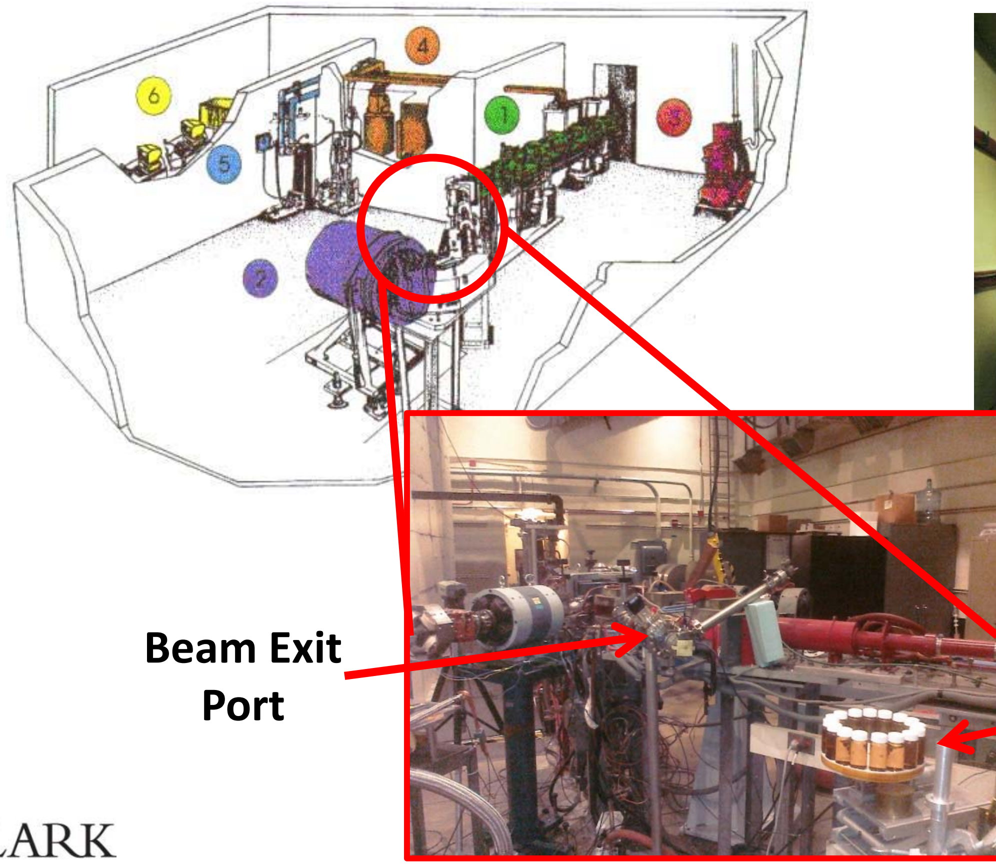
1.) Nylon sample is placed in aqueous solution containing monomer and irradiated

N_2/Ar in O_2 out

Nylon fabric in monomer solution

Medical-Industrial Radiation Facility, NIST (Electron beam)



Co-60 Irradiator, NIST (γ irradiator)

http://physics.nist.gov/MajResFac/mirf/mirf-new.jpg

http://3dgeldos.fjfi.cvut.cz/results/images/gamacel.jpg

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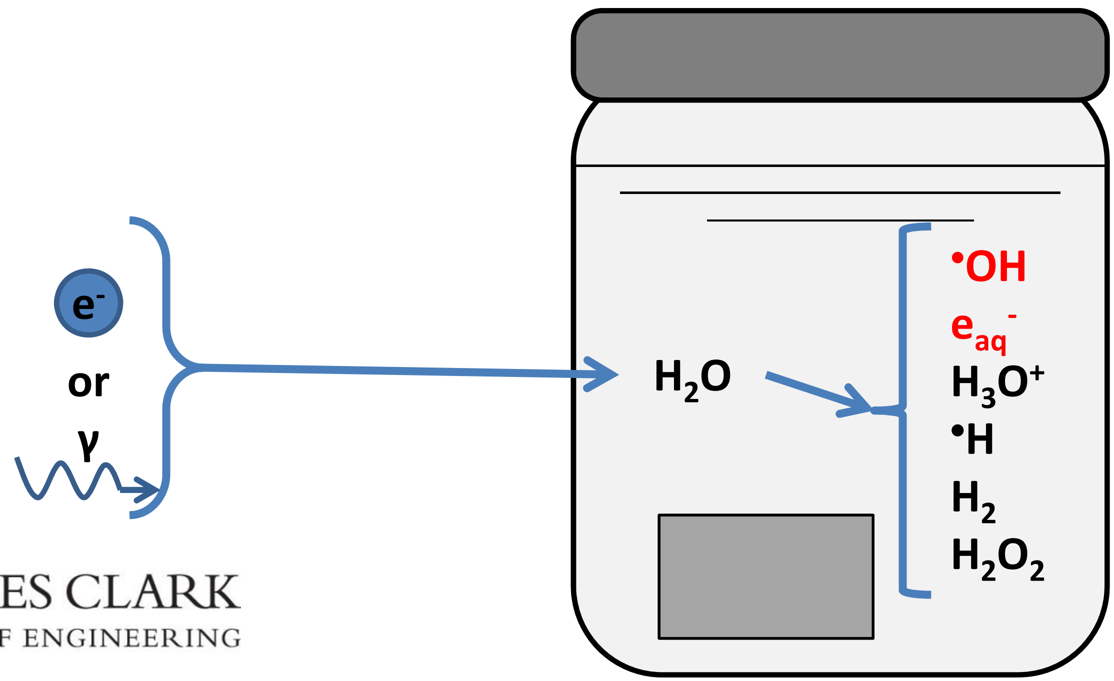
Radiation Chemistry

- **Transformation primarily through indirect effects**
  - Target molecule: small mass fraction of matrix
  - matrix: generates reactive mobile radicals
- **Yields (µmol·J^{-1}) for water irradiated by low LET**
  - $G(^{\bullet}OH) = G(e_{aq}^{-}) = G(H_3O^{+}) = 0.28$, $G(^{\bullet}H) = 0.062$, $G(H_2) = 0.042$, $G(H_2O_2) = 0.082$



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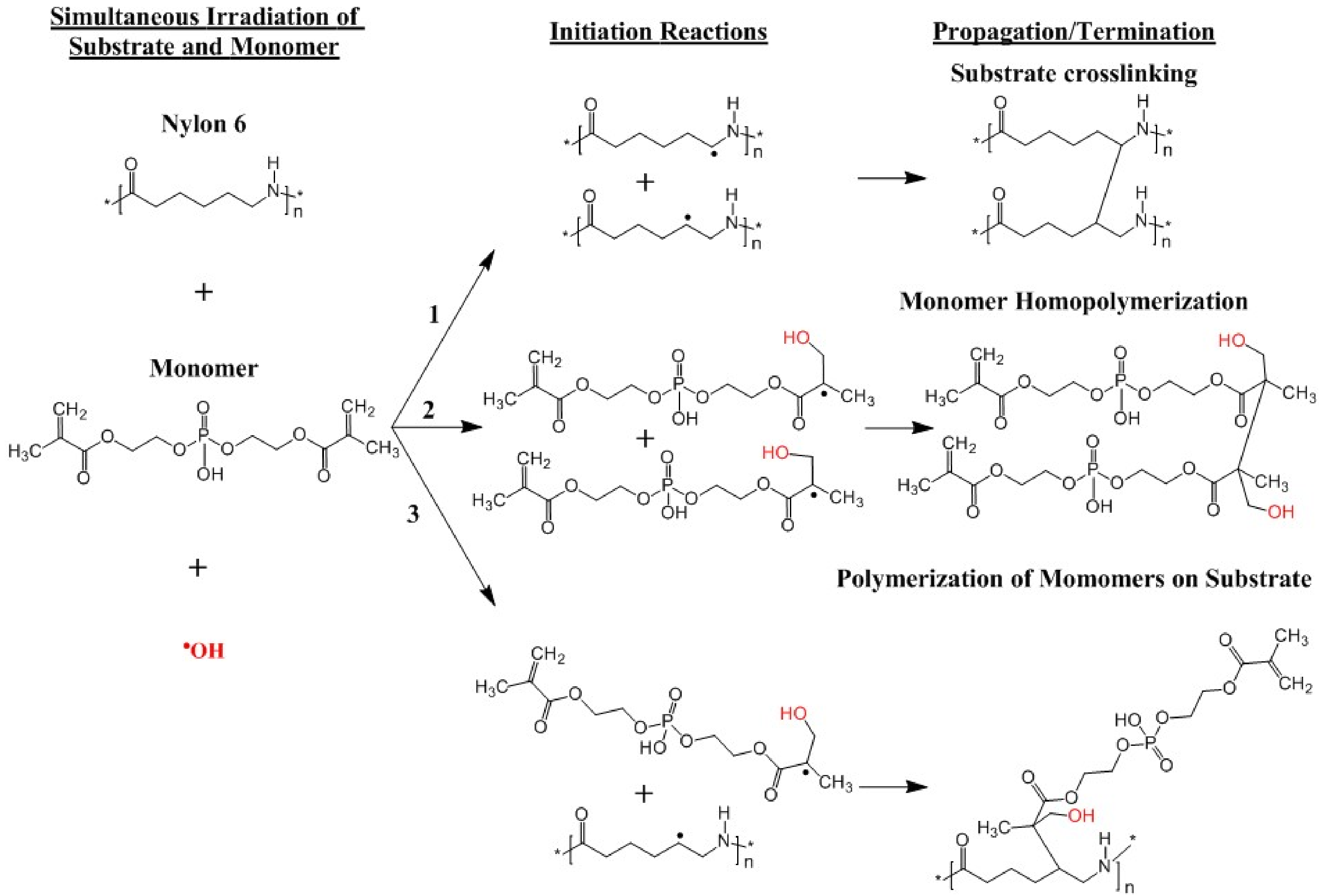
Initiation, Propagation and Termination Reactions



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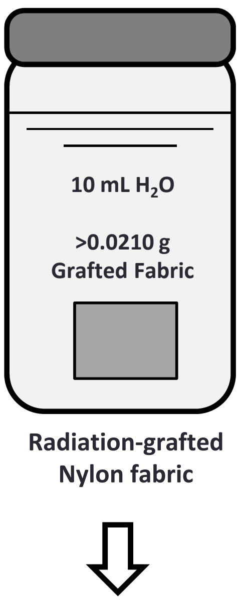
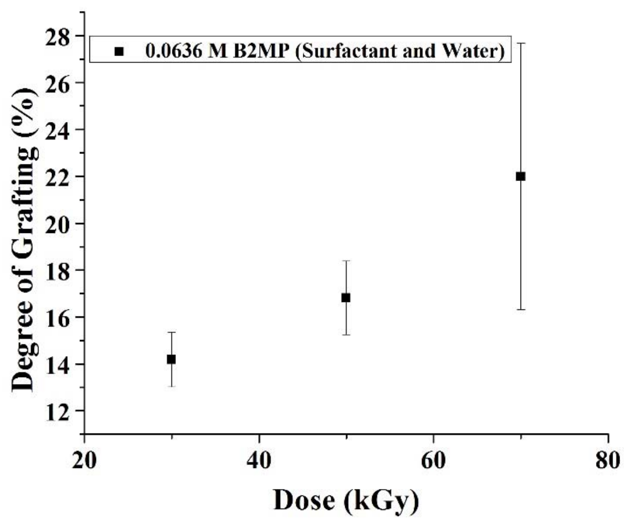
2.) After irradiation, sample is washed, dried, and massed to determine the grafting density

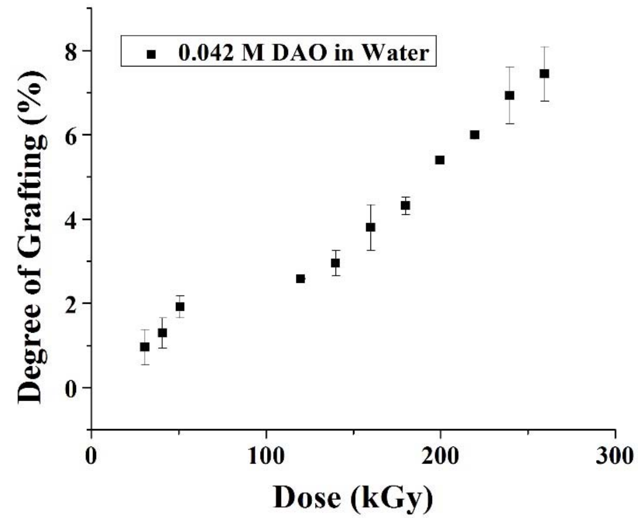


Radiation-grafted Nylon fabric

Grafting Density (%)

$$Grafting\ Density = \frac{(Mass_f - Mass_i)}{Mass_i} \times 100$$





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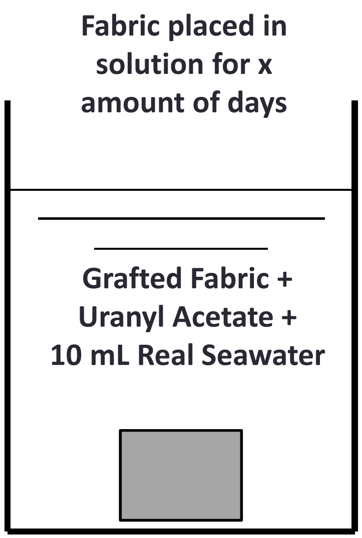
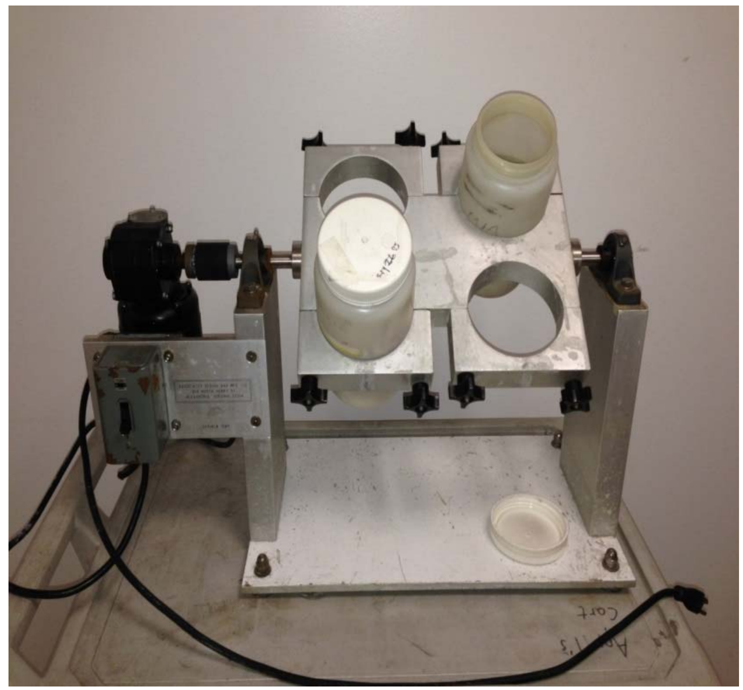
3.) Grafted fabric is tested for its loading capacity by exposing it to aqueous uranium



Adsorbent Fabric in Spiked Seawater



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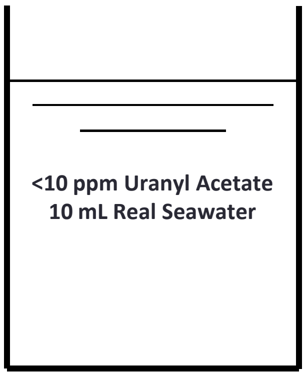
4.) The amount of uranium remaining in solution is used to determine the distribution coefficient and loading capacity

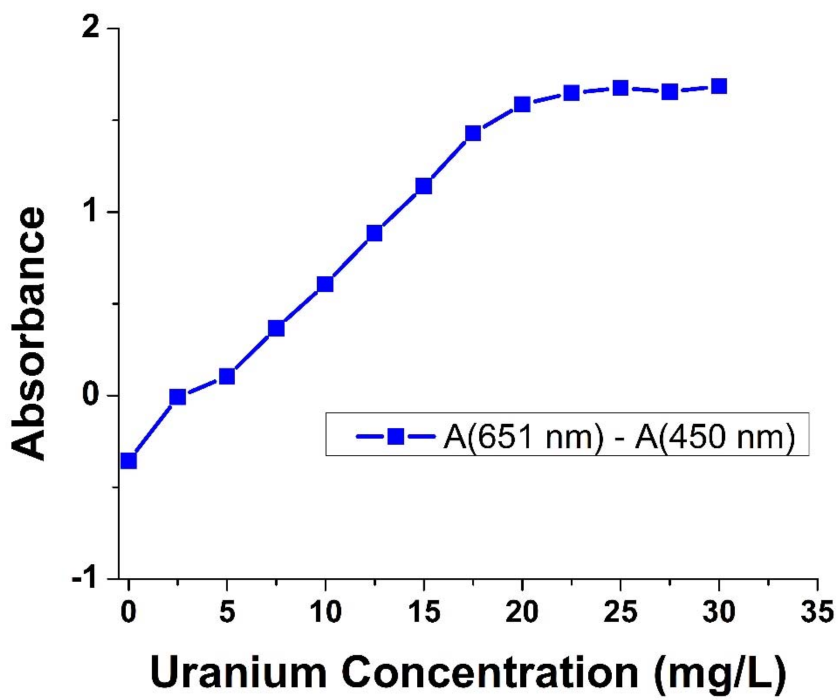
Remaining U content in seawater solution determined



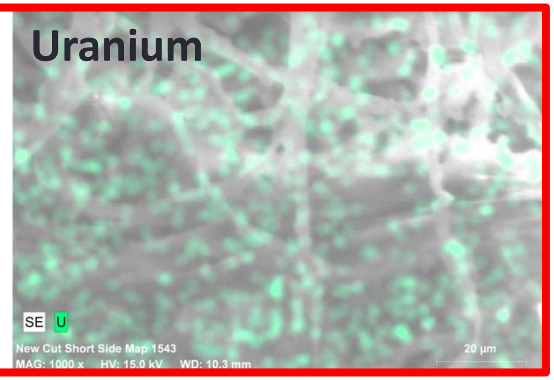
Spiked Seawater with Uranium Extracted

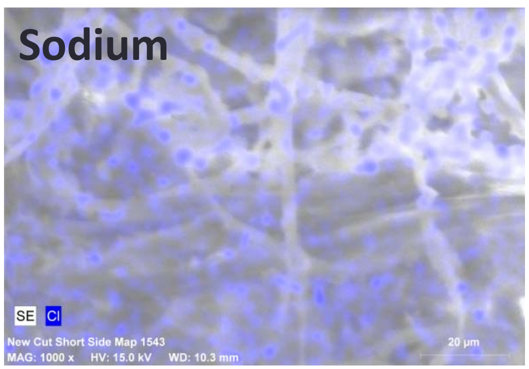
⇩

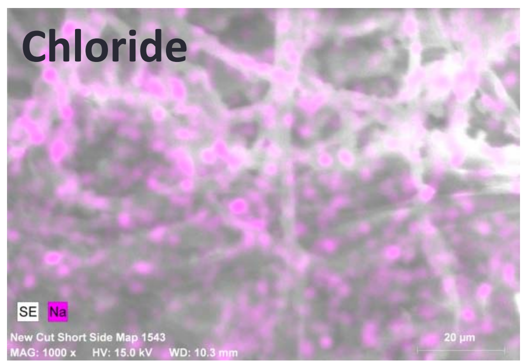
Distribution Coefficient (k_D) & Loading (%)

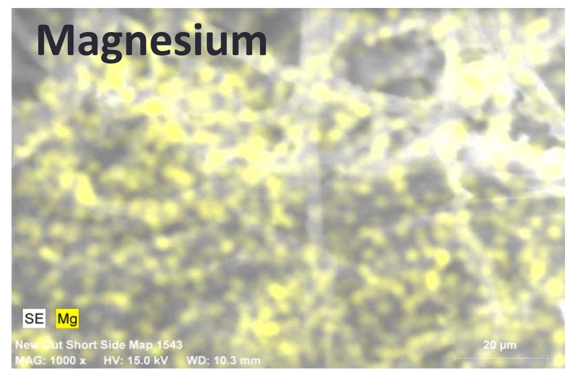


EDS studies of the fabric reveal high uniformity of the distribution of adsorption sites for uranium.









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B2MP-grafted Winged Nylon exhibits much higher selectivity for U over Na as compared to Tamada's adsorbent

Amidoxime-grafted fibrous polyethylene (Tamada, 2009)	B2MP-grafted Winged Nylon 6 (present work)
Concentrations on adsorbent: Na: 618.5 µg Na/g adsorbent or 26.9 µmol Na/g adsorbent U: 63.72 µg U/g adsorbent or 0.268 µmol U/g adsorbent U:Na ratio on adsorbent = 0.103 by weight or 0.010 by mole	**Elemental analysis of surface by EDS:** Na: 1.53 wt. % or 1.04 mol. % U: 7.22 wt. % or 0.47 mol. % U:Na ratio on adsorbent = 4.72 by weight or 0.45 by mole

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Distinguishing Features of Our Approach

- ***One –step synthesis of the absorbent-fabrics.*** Elimination of other steps such as amidoximation.
- Performing radiation-induced grafting of the phosphate moiety onto the polymeric fabric under ***"green chemistry" conditions***, i.e., in an aqueous medium without need for use of organic solvents.
- **The use of Winged™ polymer fabrics**, in particular, Winged™ nylon 6. This increases the surface area available for grafting.
- ***The use of a phosphate, oxalate, and pyridylazo moieties***, consisting of bis[2-(methacryloxy) ethyl] phosphate (B2MP), diallyl oxalate, and Br-PADAP instead of the amidoxime adsorbent groups used by previous research groups.
- **Regeneration with neutral reagent**: The use of a neutral reagent, ammonium oxalate, for multiple cycles of desorption/regeneration with no noticeable degradation of adsorptive capacity

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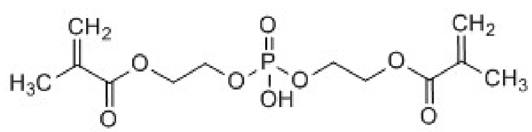
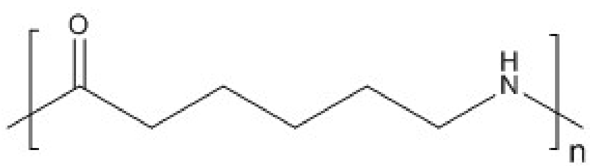
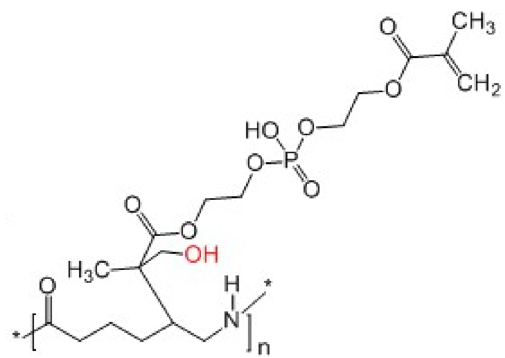
Conclusions

Able to effectively discover new potential monomers for uranium extraction from seawater

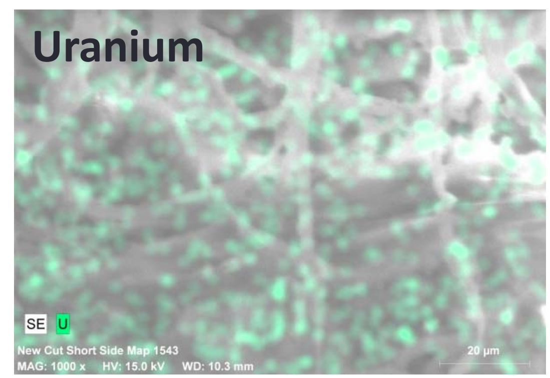




Able to effectively graft these new monomers to a polymeric substrate



Able to show that grafted polymer fabrics can effectively act as uranium adsorbents in a seawater environment



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- Professor John Ondov
- Tim Maugel with The Laboratory for Biological Ultrastructure at UMD

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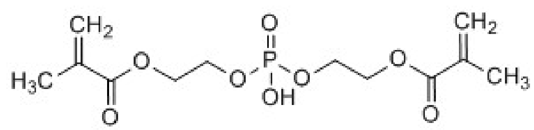

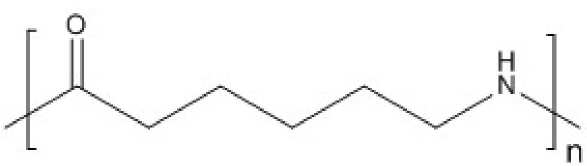

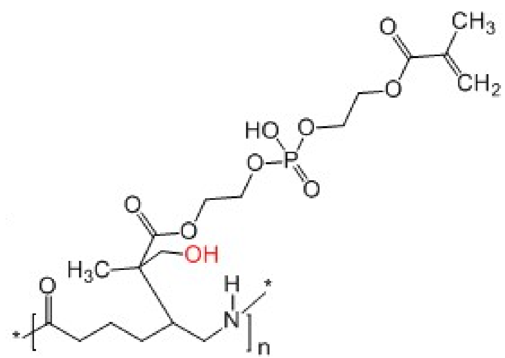

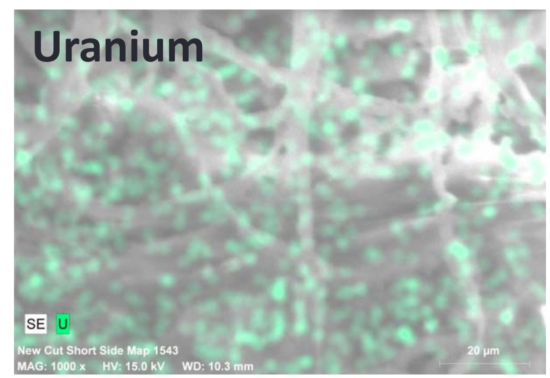

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Thank you for your time, any questions?