Radiation Chemistry Activities at NIST to Support the Synthesis of Advanced Materials

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National Institute of Standards and Technology

2015 Council on Ionizing Radiation Measurements and Standards (CIRMS) Conference

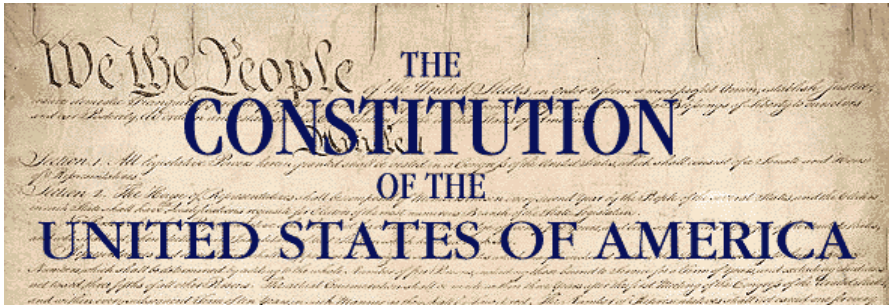
Working Group III:

Industrial Applications and Materials Effects

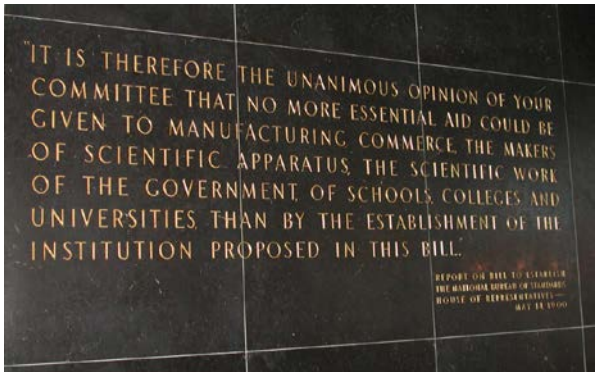
April 28, 2015

National Institute of Standards and Technology (NIST)

- Founded in 1901 as National Bureau of Standards
- Non-regulatory agency within the U.S. Department of Commerce



1797: Article I, Section 8: The Congress shall have the power to …*coin money, regulate the value thereof, and of foreign coin, and fix the standard of weights and measures …*



Unique Mission within the Federal Government … **to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life**

NIST – Who We Are and What We Do

NIST is a world class scientific and technical agency uniquely focused on driving innovation and economic competitiveness.

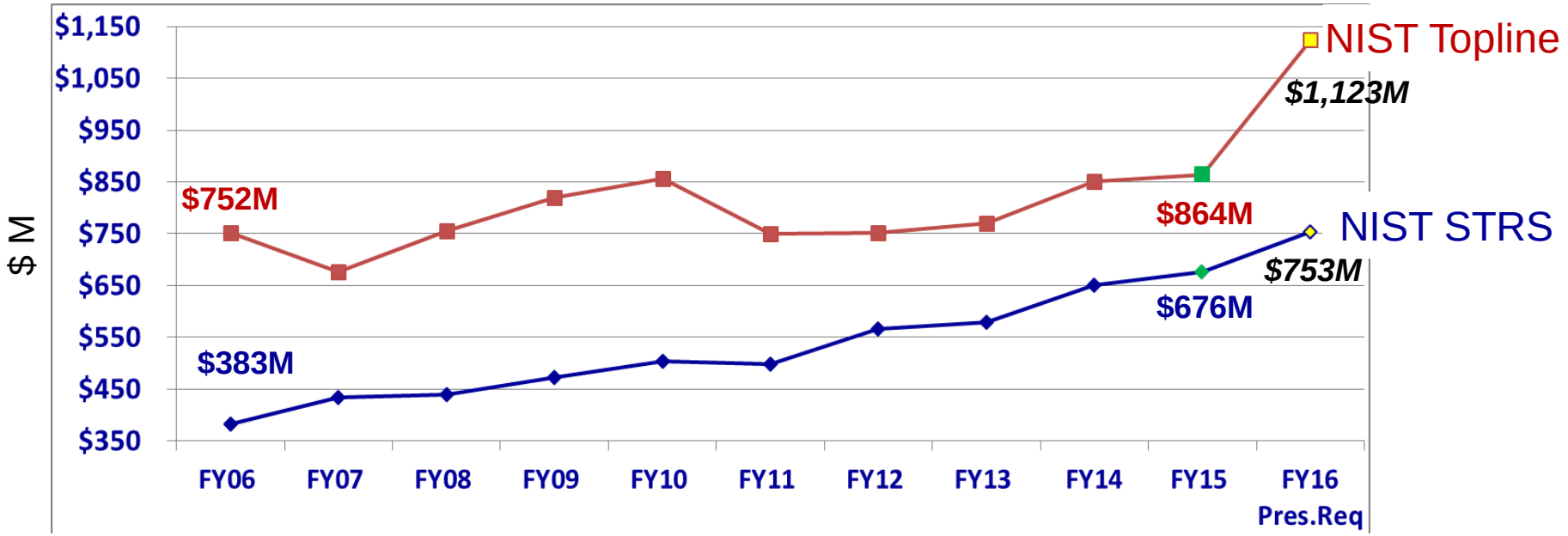
We drive U.S. innovation and economic competitiveness through:

- **a world-leading scientific research program --** measurement, technology, and standards solutions to our stakeholders
- **a nation-wide network of centers --** focused on strengthening our nation's small and medium manufacturers: Manufacturing Extension Partnership Centers located in all 50 states and Puerto Rico working directly with local manufacturing communities
- **a program in performance excellence --** used to assess the nation's companies and organizations which is recognized, utilized, and emulated around the world

This is one of the most exciting time periods in the History of NIST!

We have a great and unique Mission and are:

- **a key player on the Administration's Innovation Team**
- **the nation's go-to agency for measurements, standards, and technology**
- **receiving bipartisan and bicameral support**



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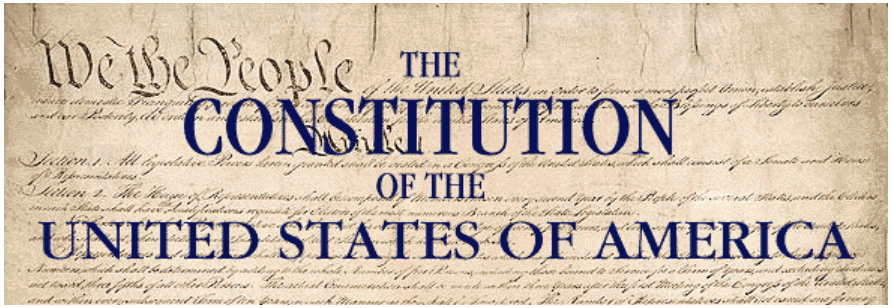

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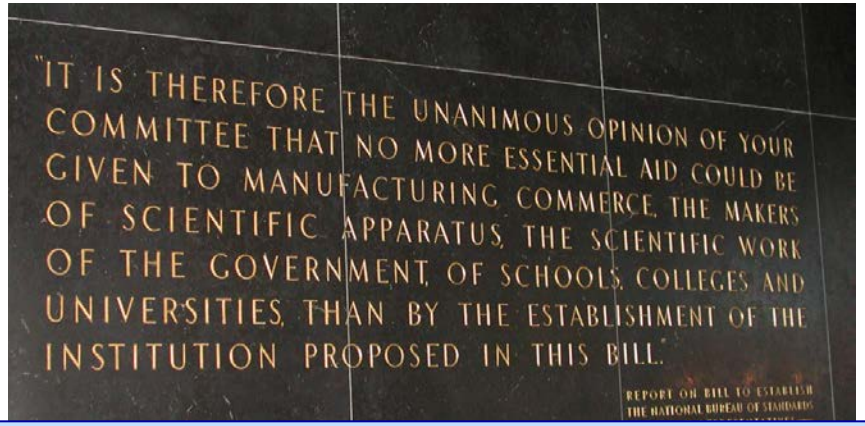
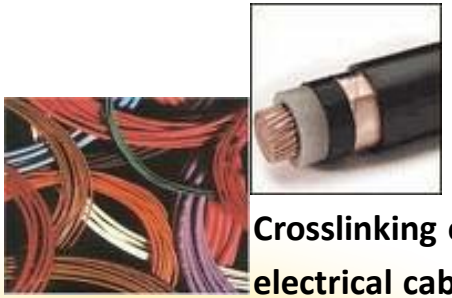


"…While **the development and maintenance of the standards …provides the first and primary reason for the Bureau's existence**

…This standards work must keep abreast of the expansion of the frontiers of science…"

Materials Development: Applications of Ionizing Radiation

- **Manipulations:**
  - Polymer crosslinking
  - Graft polymerization
  - Controlled drug release
  - Enzyme immobilization
- **Developments at NIST:**
  - **Nanogels** – drug delivery
  - **Adsorbents** – environmental
  - Membranes - fuel cell
  - Magnetic nanocomposites – contrast agents
  - Biomaterials – UHMWPE



Crosslinking of electrical cable surface

UHMWPE Hip joint cup

Contact lens

Wound dressing

Sterilization process

Synthesis & Characterization of Materials

Goals of Research

- **Examine physical parameters in synthesis of materials by ionizing radiation**
  - Temperature, dose effects
- **Characterization of materials**
  - size, molar mass, morphology, chemical structure
- **Free radical kinetics in material synthesis**
  - Reaction rate constant of polymer radical reaction
  - Activation energy of polymer radical decay

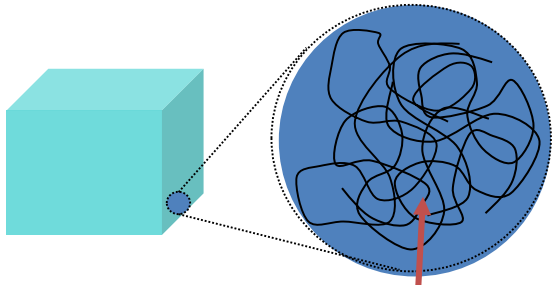
Ionizing radiation has many advantages

Polymer Materials

- **Hydrogel**

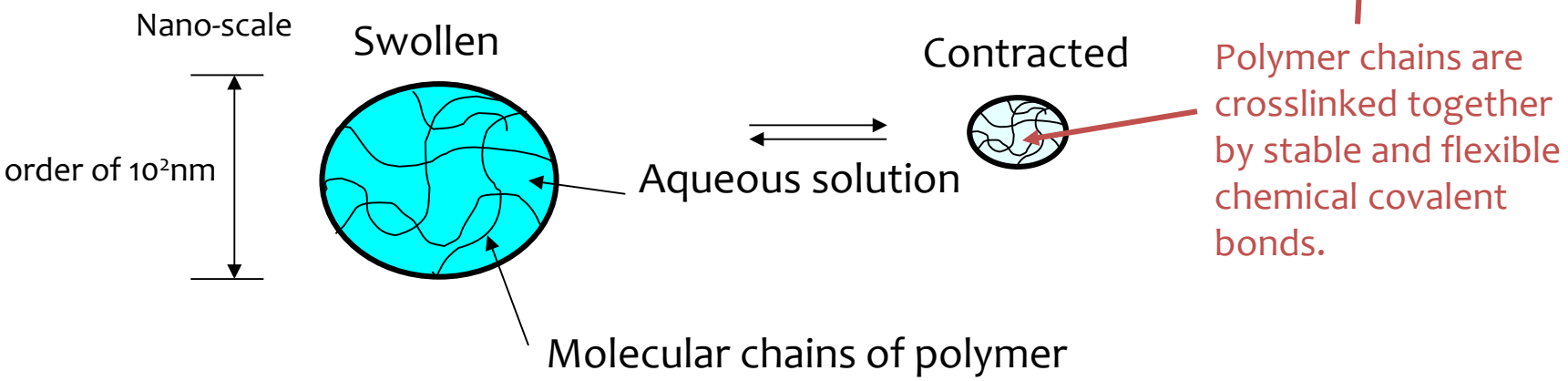
Structure: 3D polymer network & filling liquid (water)

- Common applications -

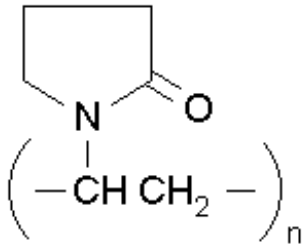


Conventional Macroscopic hydrogel

Nanohydrogel



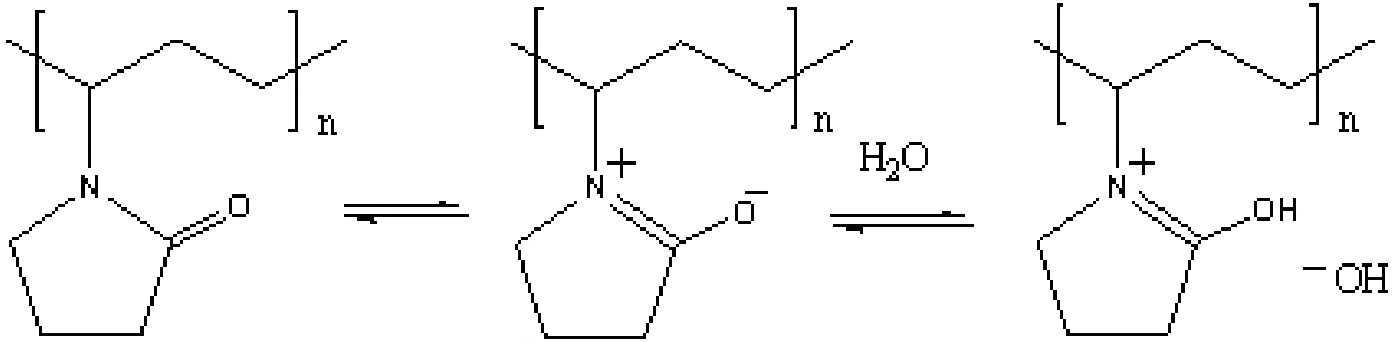
Poly(vinylpyrrolidone), PVP



- pK_a = 5 - 8
- Non-antigenic, biologically compatible
- Low toxicity
- Extensive applications in pharmaceutics, biomedical sciences, food and beverage, cosmetics
- Zwitterion structure → Interaction between polar groups through electrostatic forces.

Unique ions

both the temperature-dependent physical properties and the chemical structure of PVP are expected to determine the size and the molar mass of the irradiated product



Maruthamuthu, M. and Subramanian, E., Polymer Bulletin, 1985. 14(3-4): p. 207-212.

Inter- vs. Intra-crosslinking

Polymer radical

Crosslinked bond

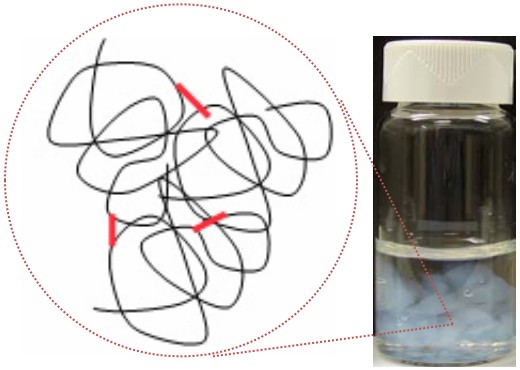
Polymer chain in water

Ionizing Radiation

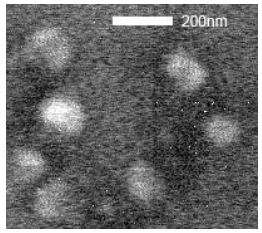
Inter-molecular Crosslinking

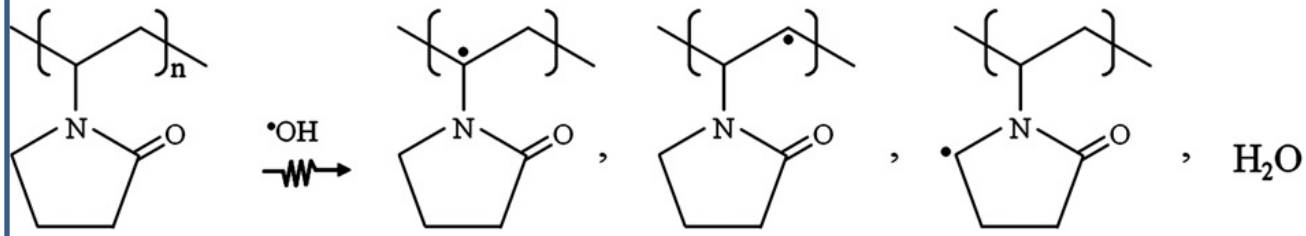
Intra-molecular Crosslinking

Macroscopic gel



Nanogel





Production of PVP radicals

Conditions in irradiation experiments

Temperature of PVP aqueous solution, °C	20, 60, 77
Total irradiation dose, kGy	5, 10
Pulse repetition rate, pulses s^{-1}	20, 300
Solution concentration, mol L^{-1}	0.45 x 10^{-2}, 0.9 x 10^{-2}
Average dose rate, Gy $pulse^{-1}$	30 - 35
Solution pH	7 – 7.5

All solutions are saturated with N_2O prior to irradiations

N_2O enhances the generation of $^{\bullet}OH$ by converting eaq^- into $^{\bullet}OH$

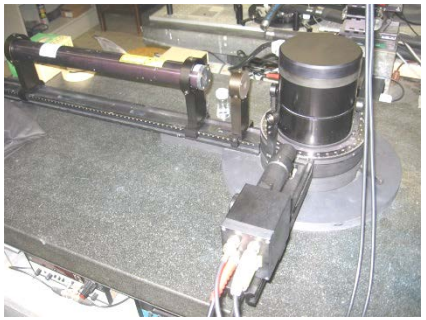
$N_2O + eaq^- \rightarrow {}^{\bullet}OH + {}^{-}OH + N_2$ ($k = 8.7 \times 10^9$ L mol^{-1} s^{-1})

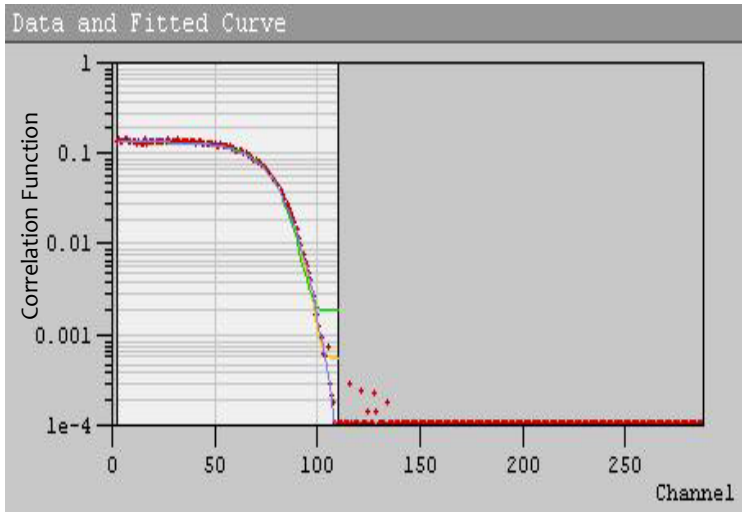
Unique Characterization

Temperature-controlled dynamic light scattering (DLS) for R_h

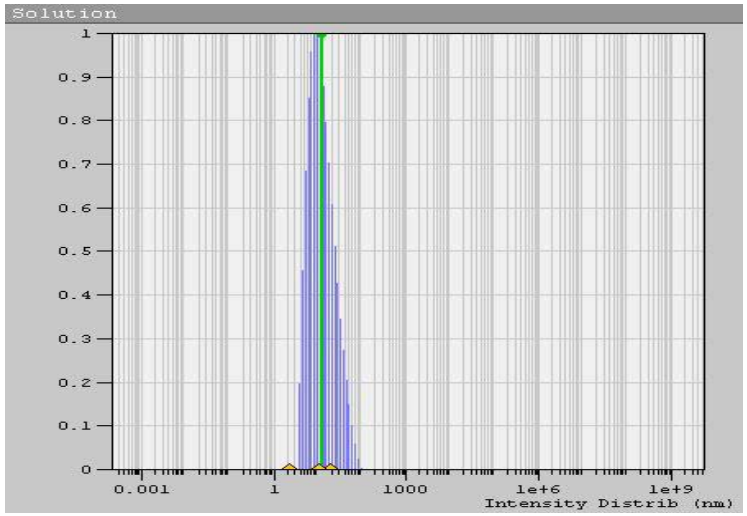
1. **Probe structural relaxations & dynamics.**

2. **Translational diffusion coefficient (D_t) & subsequent hydrodynamic radius (Rh) by using the time dependent fluctuations of scattering intensity at certain angle θ.**





Correlation function

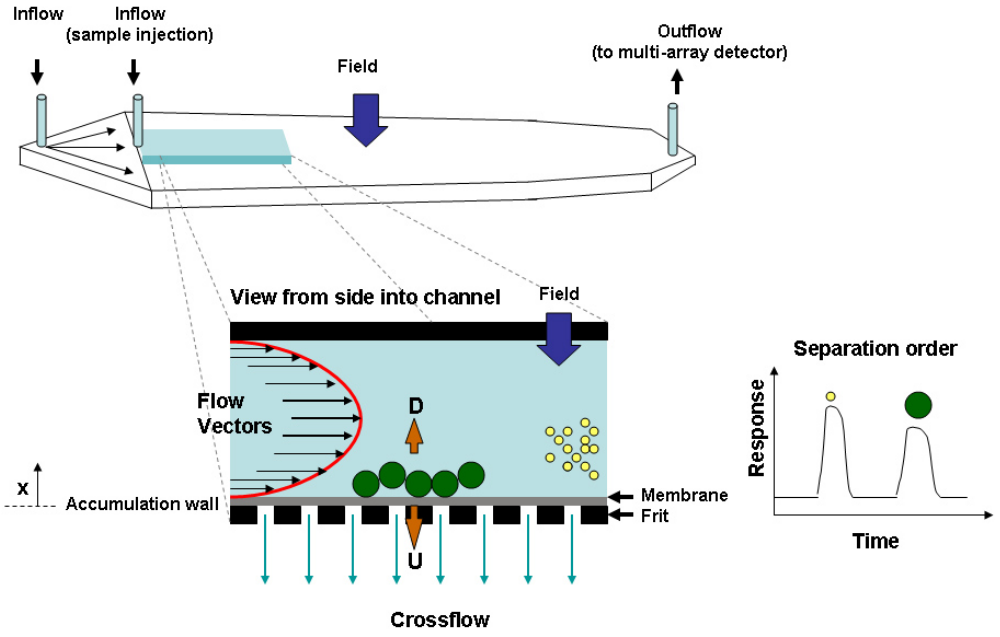


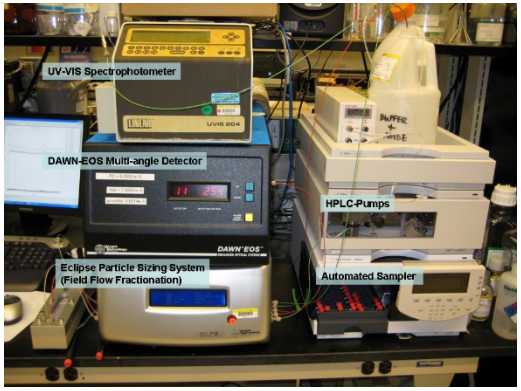
Rh distribution

Unique Characterization

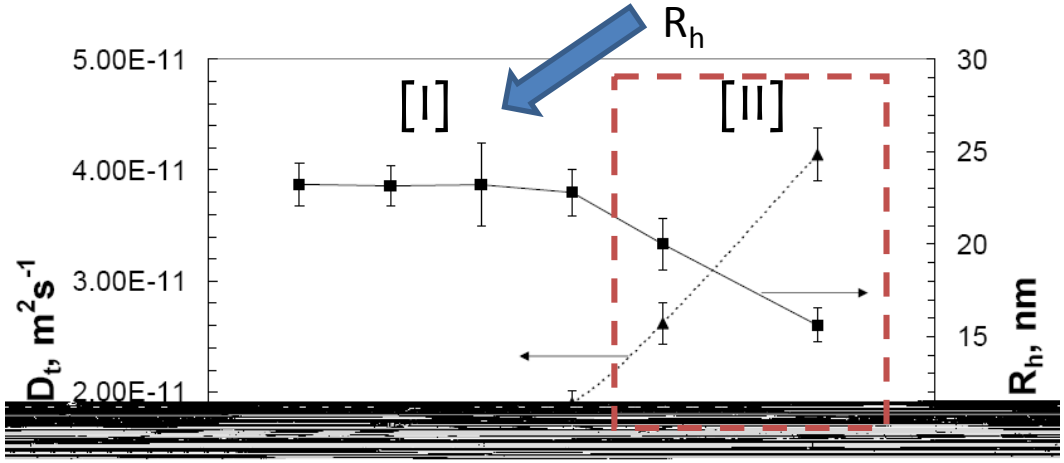
Asymmetric flow field flow fractionation chromatography (AFFFF) for M_w and R_h

1. Single-phase LC; separation in field applied laminar flow.
2. Time dependent fluctuations of Is at certain angle θ → Rh.
3. Measure the angle dependent Is and corresponding concentration from UV spectroscopy → Mw.





Collapse of the PVP at high temperature – hydrodynamic radius (R_h) & translational diffusion coefficient (D_t)



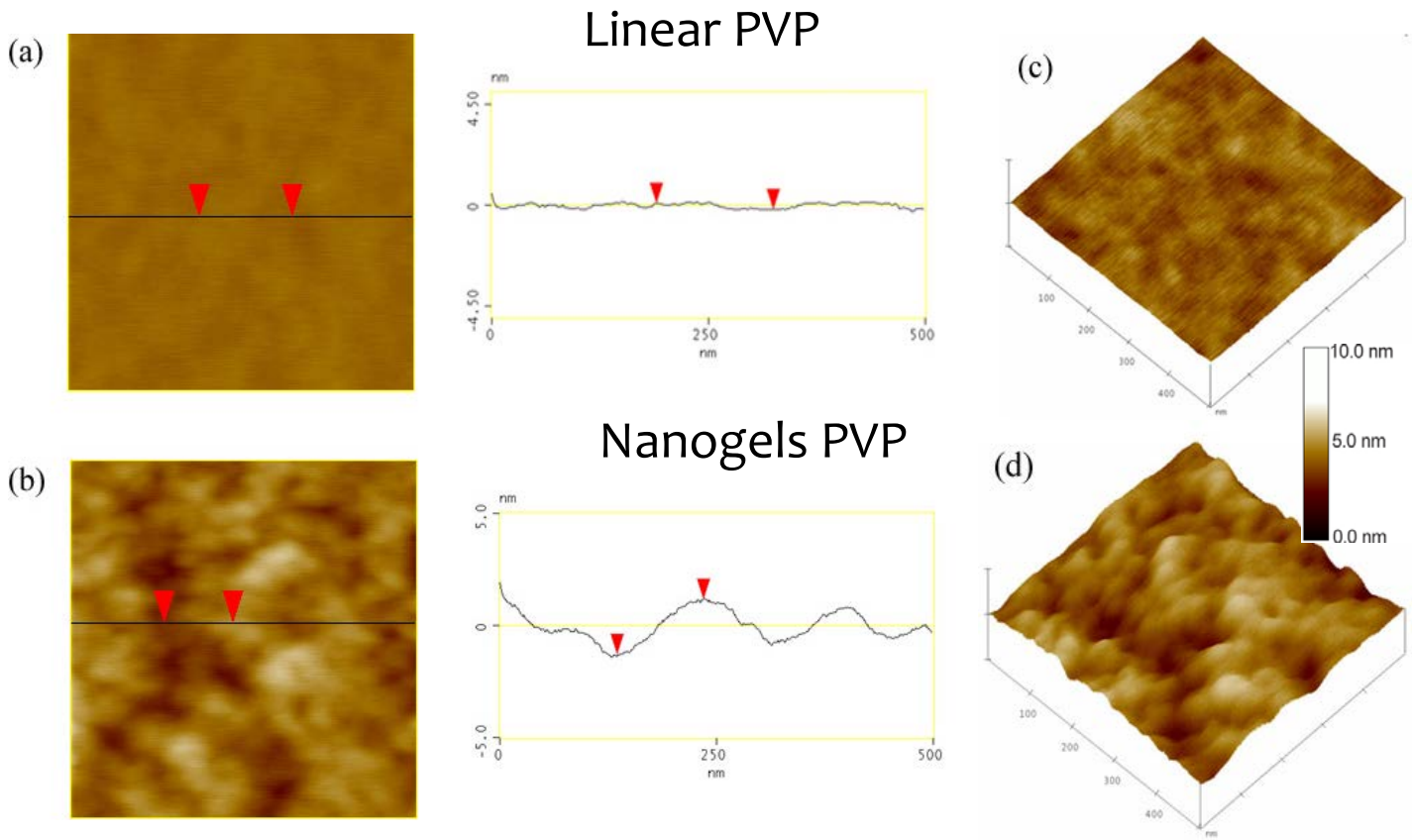
Unirradiated PVP
Concentration = 0.9 x 10^{-2} mol L^{-1}

[I] 20 - 50 °C; Rh is almost constant
[II] 50 - 77 °C; Rh decreases as temperature increases.

At higher temperatures, interactions of monomers within a polymer chain become more favored due to the disruption of water-polymer hydrogen bonds.

→ Collapsed polymer molecule.

Morphological measurements of the particle size in the nanogel



1. PVP aqueous solutions (unirradiated & nanohydrogel) cast on mica
2. Unirradiated sample (linear chain) shows flat surface morphology
3. Nanohydrogels show spherical contour of surface

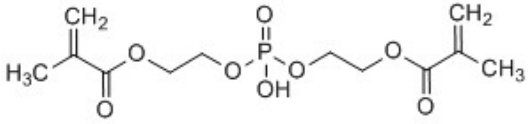
Conclusions from Research

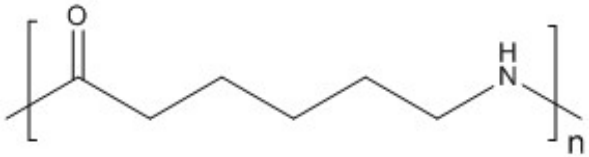
1. Combined inter and intra-molecular cross-linking takes place in the synthesis of PVP nanogels even in a dilute system.
2. Translational diffusion and the intrinsic chemical structure of PVP contribute to the mixed cross-linked mechanism.
3. Two strategies to maximize intramolecular cross-linking reaction yield were investigated:
    1. ways to increase the number of carbon-centered free radicals on the polymer and
    2. ways to prevent inter-molecular reactions.
4. While mixed cross-linked processes were never completely eliminated, enhanced yields of intra-molecularly cross-linked products were obtained.

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

Materials Selection

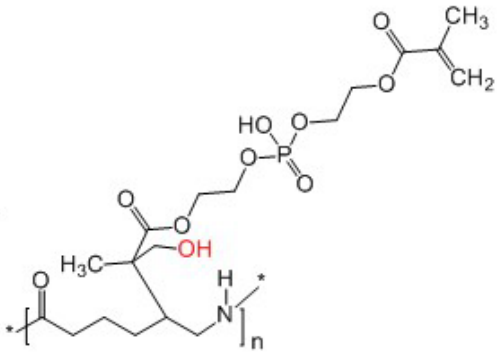
- Select ideal adsorbent compounds
- Select ideal substrate materials (polymers)
- Green Chemistry





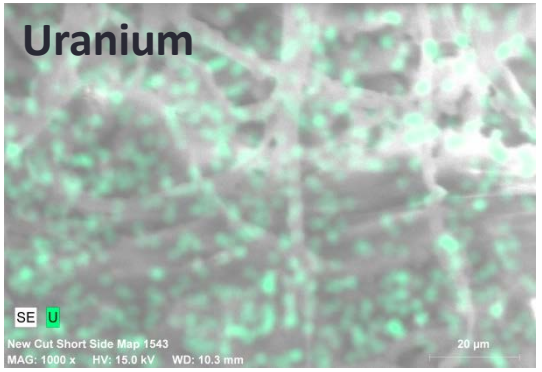
Radiation Grafting

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

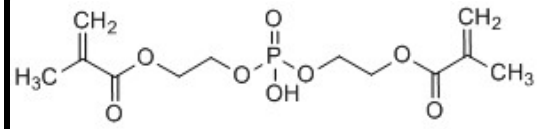
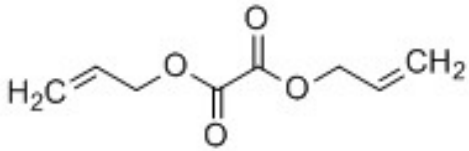
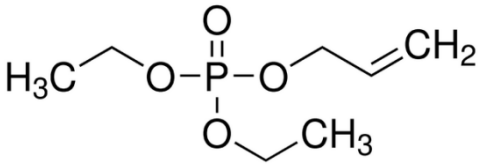


Extraction Testing

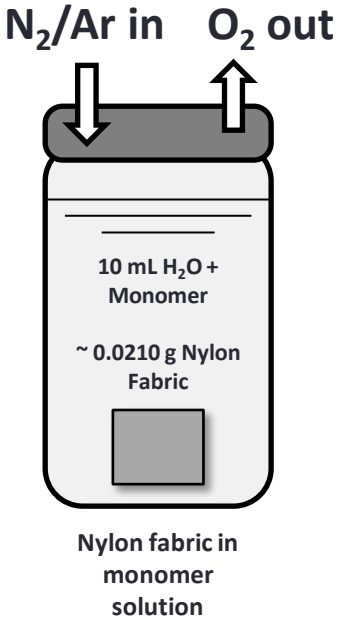
- Improve extraction efficiency
- Test scaled-up materials on-site



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

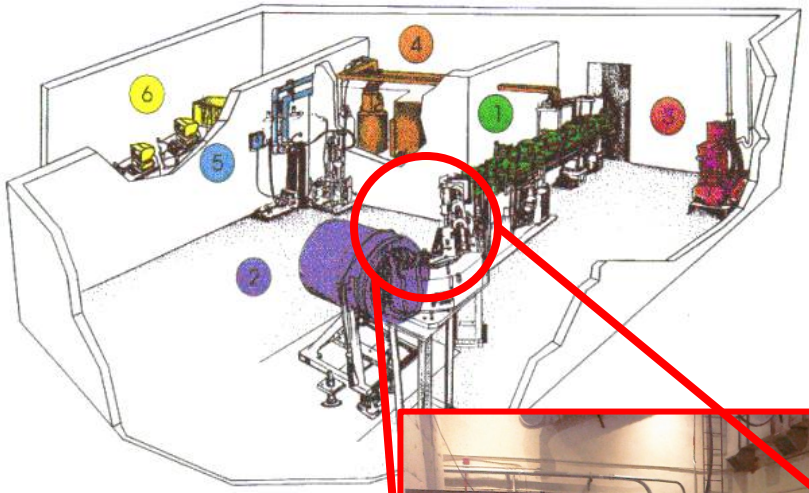
Monomers	Structure	Potential for Uranium Extraction
Bis[2-(methacryloyloxy)ethyl] phosphate (B2MP)		High
Diallyl Oxalate (DAO)		High
Diethyl Allyl Phosphate (DEAP)		Medium

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

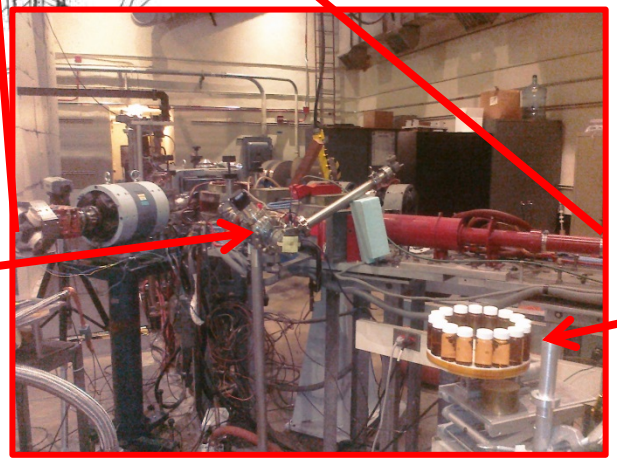


Nylon fabric in monomer solution

Medical-Industrial Radiation Facility, NIST (Electron beam)



Co-60 Irradiator, NIST (γ irradiator)

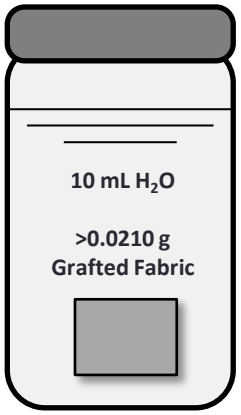


Beam Exit Port

Sample Rotator

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

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

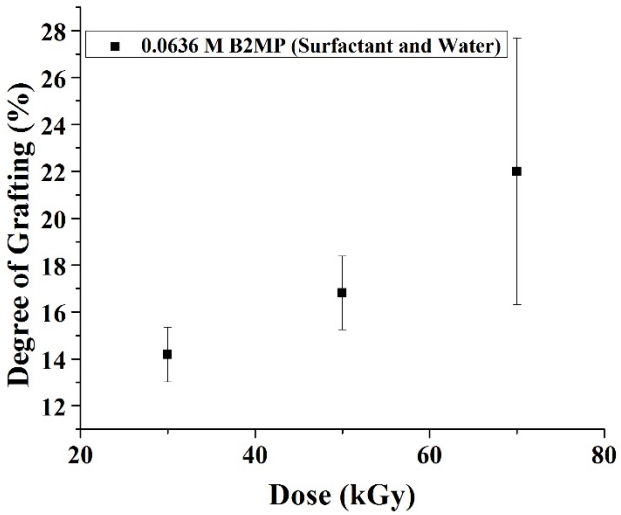


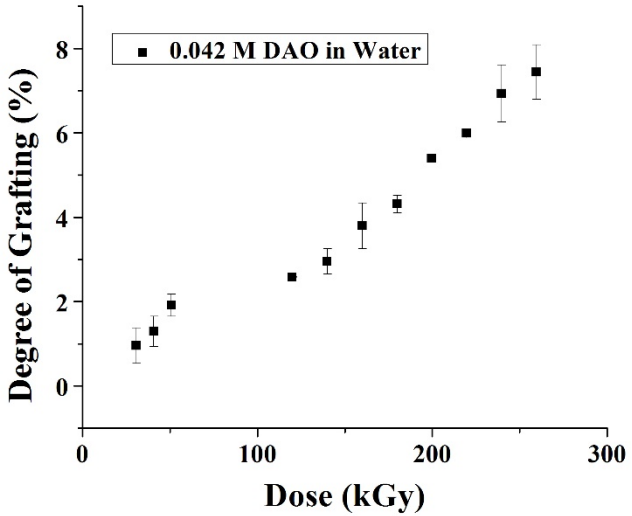
Radiation-grafted Nylon fabric

⇩

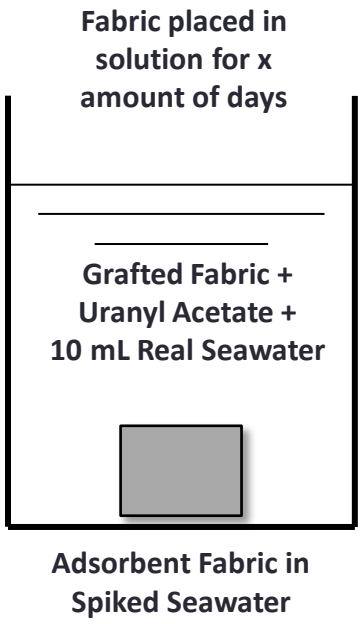
Grafting Density (%)

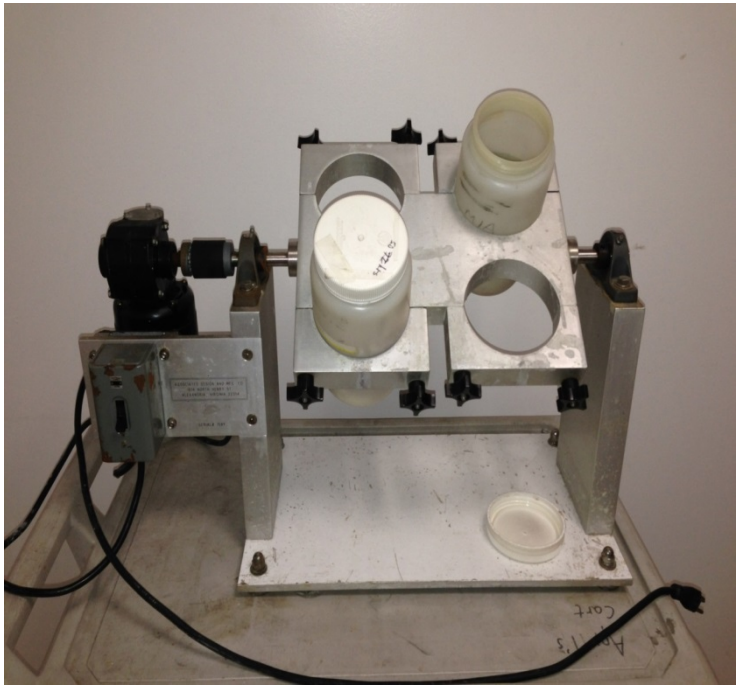
$$Grafting\ Density = \frac{(Mass_f - Mass_i)}{Mass_i} \text{ x } 100$$



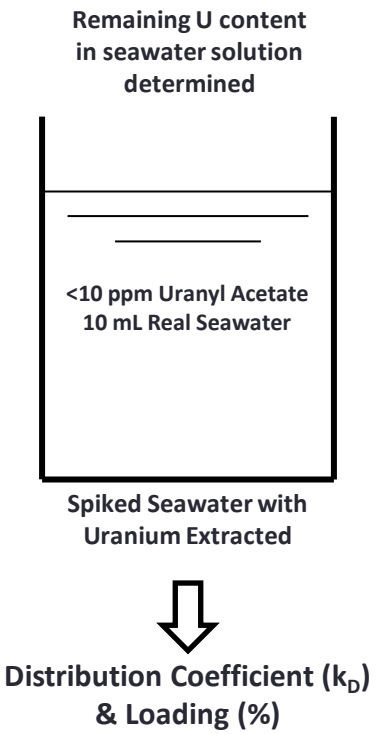


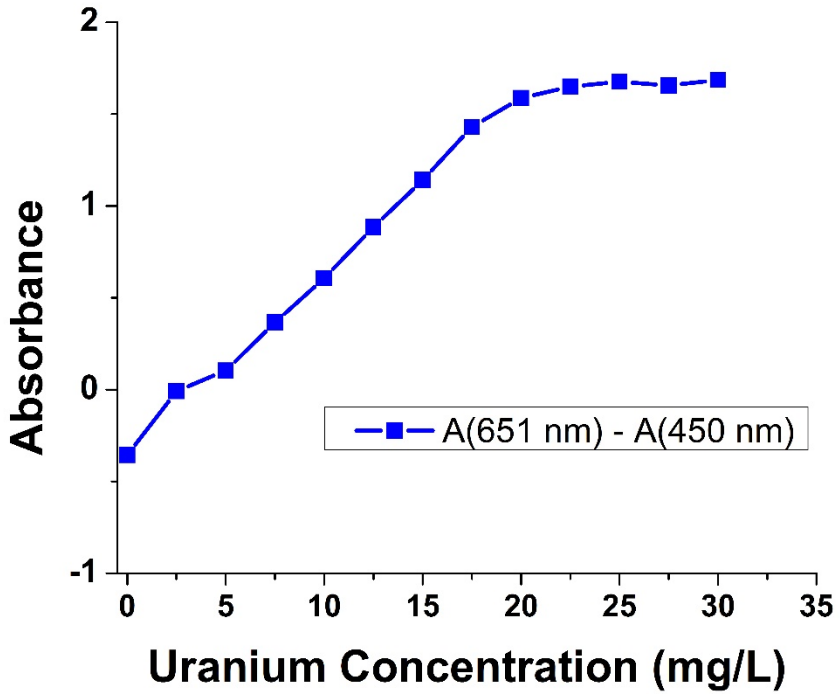
3.) Grafted fabric is tested for its loading capacity by exposing it to aqueous uranium



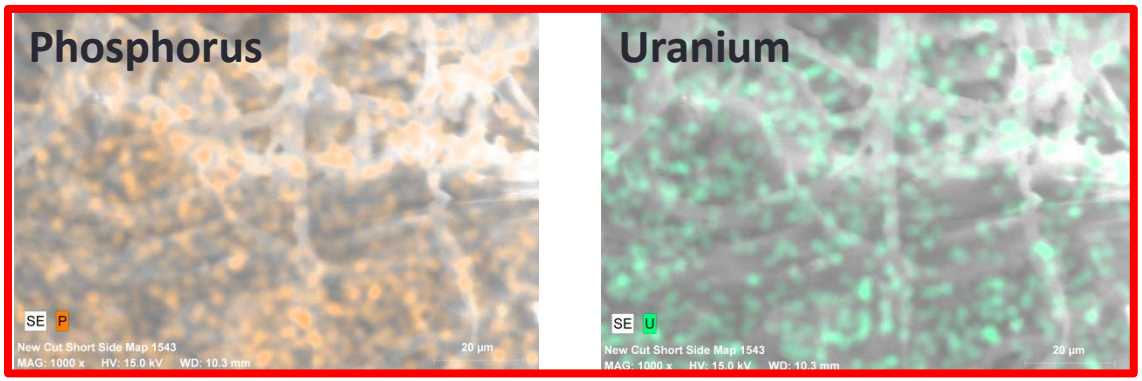


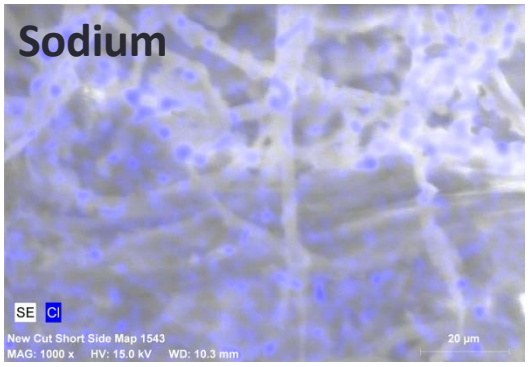
4.) The amount of uranium remaining in solution is used to determine the distribution coefficient and loading capacity

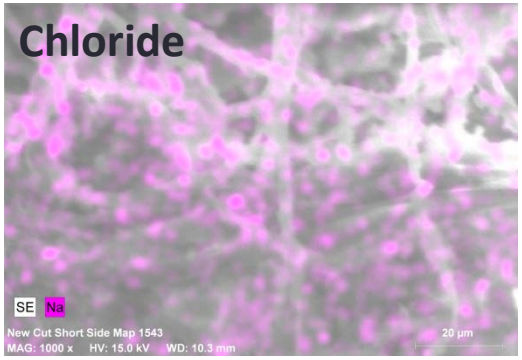


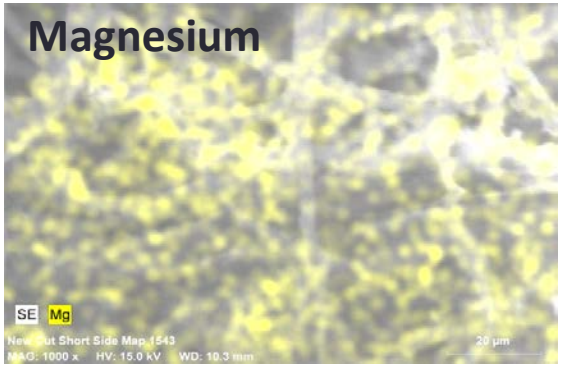


EDS studies of the fabric reveal high uniformity of the distribution of adsorption sites for uranium.









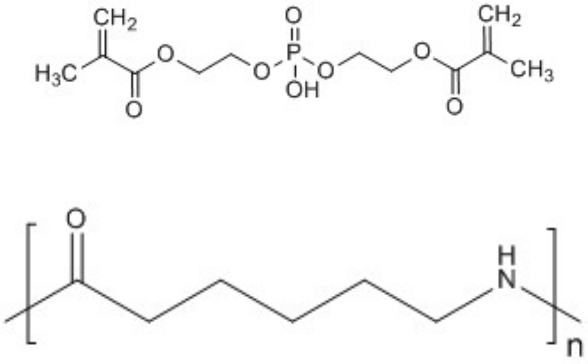
- similarities between images of phosphorus (from B2MP) and uranium suggest that **uranium is successfully bonded to sites on the chelating monomer**
- The images also suggest **high uniformity of the distribution of adsorption sites for uranium on the surface of the material**

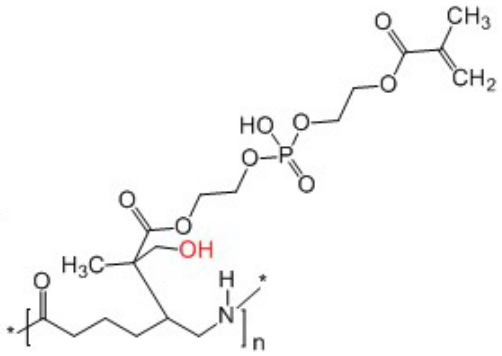
Remarks

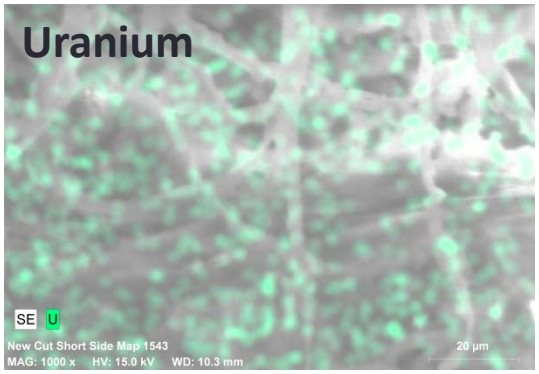
Effectively discovering new potential monomers for uranium extraction from seawater

Effectively grafting these new monomers to a polymeric substrate

Demonstrating that grafted polymer fabrics can effectively act as uranium adsorbents in a seawater environment







Near Term Research – On-going

- enhancing the grafting density and the loading capacity of moieties grafted on fibers
- measuring more ion concentrations in the adsorbents: Na^{+}, Cl^{-1}, Mg^{+}, phosphorous - SEM-EDS
- adsorption testing (with ORNL, PNNL)
- mechanical testing
- pulse radiolysis experiments at BNL to measure the polymerization kinetics
  - in collaboration with Dr. James Wishart, Brookhaven National Laboratory
  - use of the picosecond pulse radiolysis to study the early events in the radiation-induced homopolymerization

Acknowledgements

- Lisa Karam, Michael Mitch, Fred Bateman, Lonnie Cumberland, Wyatt Vreeland, John Small, James Kushmerick, Michael Postek, John Dagata, *NIST*
- Jung-Chul An, Travis Dietz, Zois Tsinas, Claire Tomaszewski, Kevin Mecadon, *University of Maryland*
- James Wishart, *Brookhaven National Laboratory*
- Ian Carmichael, David Bartels, Jay LaVerne, *Notre Dame Radiation Laboratory*
- Kenji Takahashi, *Kanazawa University, Japan*
- Aaron Barkatt, Mohammad Adel-Hadadi, *The Catholic University of America*
- John Ondov, Karen Gaskell, Joseph Silverman, Mohamad Al-Sheikhly, *University of Maryland*

Thanks for Your Attention!

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