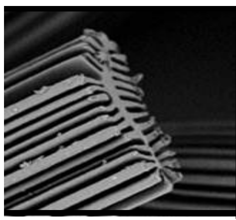
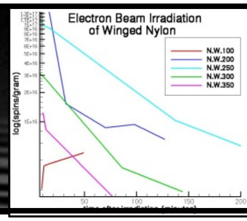
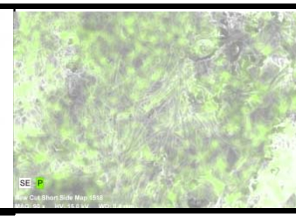
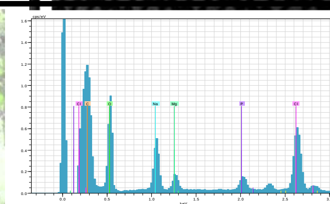
Enhancement of the Extraction of Uranium from Seawater

Chanel Tissot – University of Maryland
Aaron Barkatt – The Catholic University of America
Jay LaVerne – University of Notre Dame
Mohamad Al-Sheikhly, University of Maryland

CIRMS Meeting 2012
21st Annual
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NIST-Gaithersburg. Maryland

Proposed Scope

- Objective of the proposed study:
  - Develop novel types of adsorbing polymeric fabrics for significantly enhancing the capacity for the extraction of uranium from seawater

- Key differences between our work and the Japanese published work:
  - Use of acrylated phosphonate monomers instead of amidoxime
    - High selectivity of organic phosphate compounds towards U(VI) over a broad pH range
  - New substrates (such as nylon, polyurethane, and polypropylene) instead of high-density polyethylene
    - Improved physical properties with excellent degradation resistance and reusability
  - Optimization of fabric geometry through use of Winged Fibers
    - High surface area to volume ratio to increase grafting densities

Path to Accomplishing Scope

- Maximize radical concentration for grafting
  - Utilize electron beam and gamma radiation
  - Control radiation dose, dose rate and temperature
  - Select substrates with large surface area
  - Increase length and number of adsorbing groups (grafting density)
- Select ideal adsorbent compounds with:
  - High affinity for uranium over pH range of seawater
  - Capability of stable grafting onto substrate
- Select ideal substrate materials with:
  - Favorable mechanical properties
  - High spin concentration after irradiation
- Improve extraction efficiency
  - Increase material durability, stability and reusability in real seawater
  - Test scaled-up materials on-site

Interaction of Ionizing Radiation with Matter

10^{-18} 10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 sec

Energy deposition

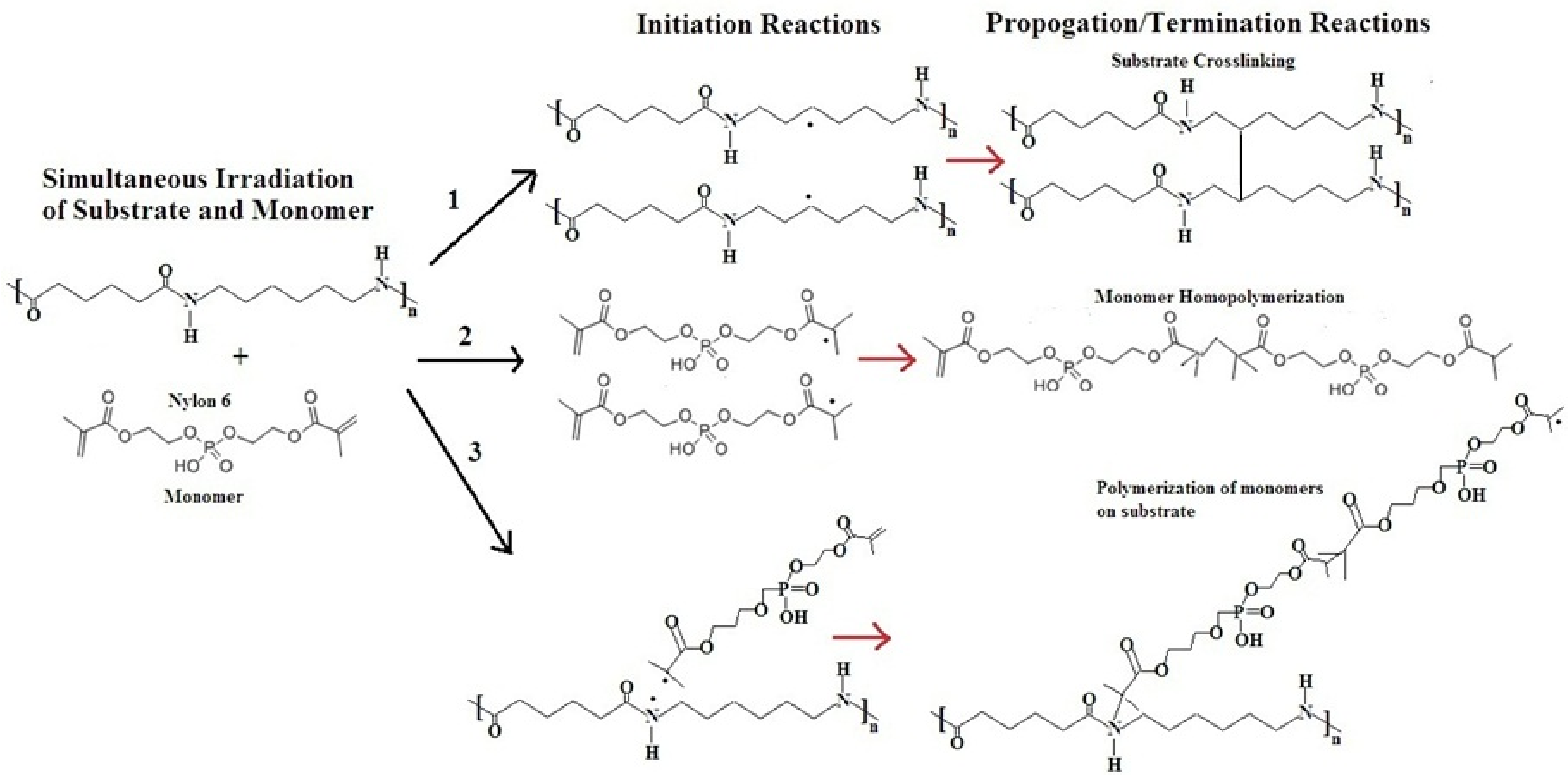
- formation of ionized and excited molecules localized along tracks
- Ions and excited molecules react/dissociate forming free radicals. Electrons solvated in polar media

Chemical Processes

- Radicals and solvated electrons diffuse from track zones, react with other molecules.
- Chemical changes to substrate occur.

- Direct Effect
  - $M + e \rightsquigarrow M^+, e^-, M^-, M^*$ (Ionization, excitation)
- Indirect Effect
  - Secondary reactions of solute with primary species formed by solvent

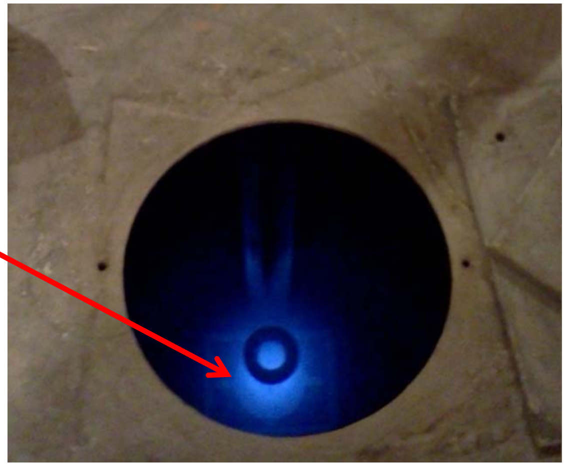
Initiation, Propagation and Termination Reactions



1) Crosslinking between substrate molecules, no reaction with monomer
2) Monomer homopolymerization without grafting to substrate
3) Grafting of monomer onto substrate, formation of brush-like structures

UMD Co-60 Gamma Irradiator

Pencils mounted on source rack

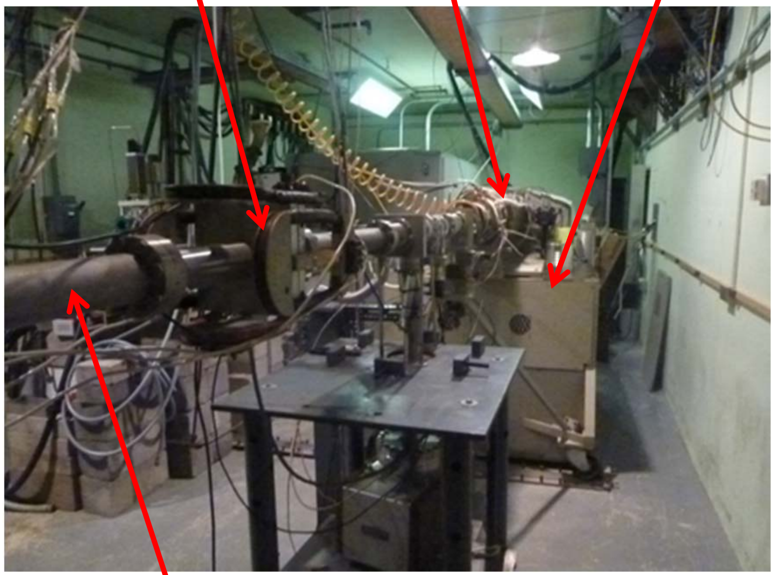


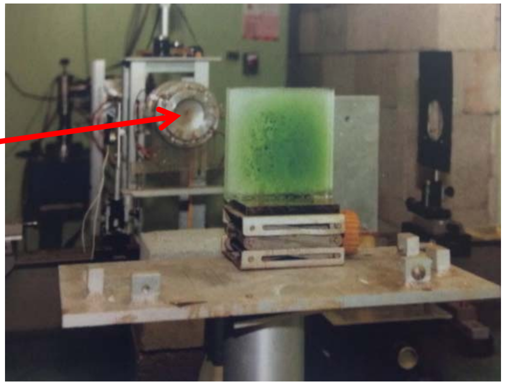
Stainless steel top hat

- Two sources of ten Co-60 pencils
  - Newer source – 99,874 Ci (07/09)
  - Older source -1,342 Ci (07/09)
- Unique walk-in design allows for irradiation of a large range of sample sizes
- Dose rates of 0.1 to 70 kGy/hr
- Systems available for cooling or heating during irradiation
- Enables uniform irradiation of larger sample sizes, ideal for process scale-up

UMD Electron Beam Linear Accelerator (LINAC)

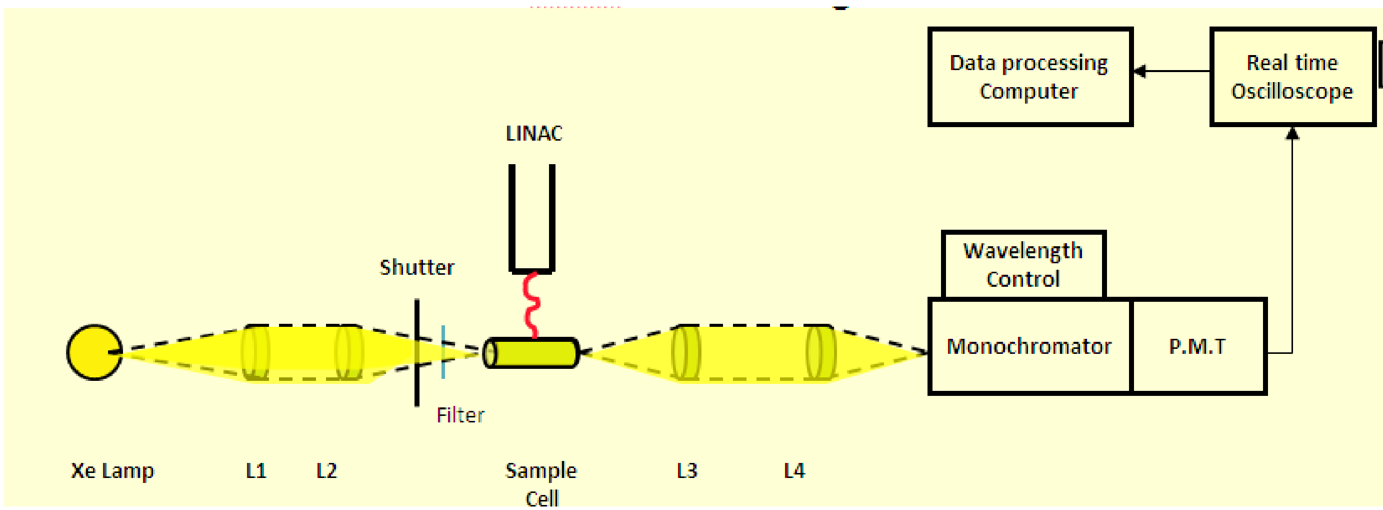
- Pulsed beam with 3 μs pulse width
  - Pulsed beam allows study of radical kinetics and mechanisms
- Electron kinetic energies of 1 to 9 MeV
- Capable of very high dose rates
  - penetration depth increases with electron kinetic energy
  - Shorter irradiation times minimize oxidation effects

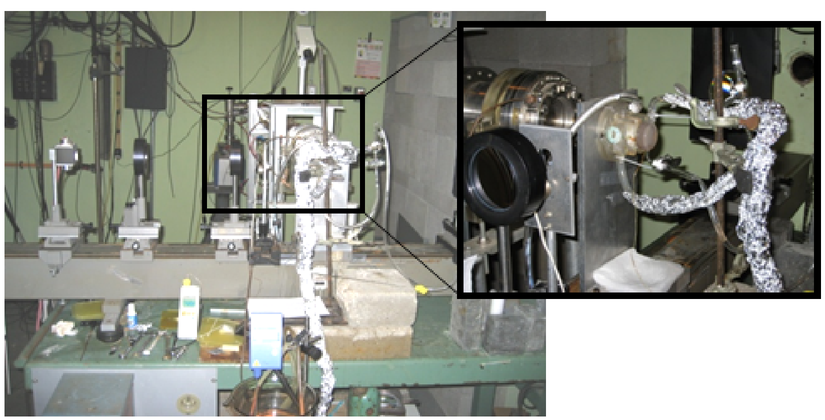




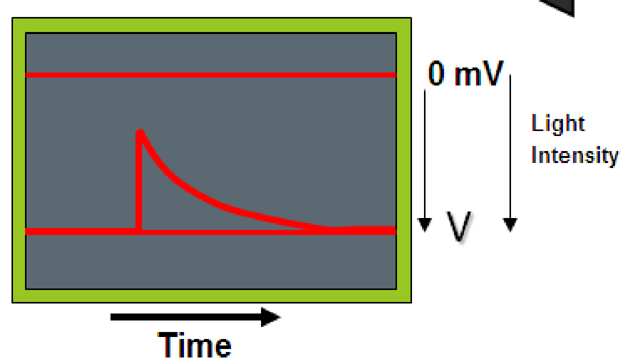
Pulse Radiolysis

- Fast chemical reaction kinetics (rate constant, k*)* & radiation yield (G-value) can be studied in micro to femto-second range
- Buildup and decay of acrylated phosphonate radicals to be studied in detail





Transients generated is detected by optical absorption changes.

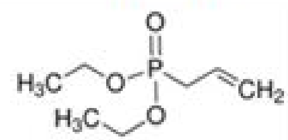
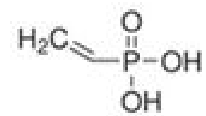
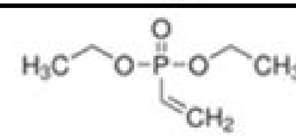
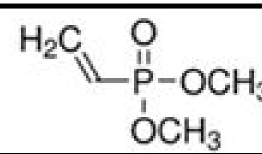
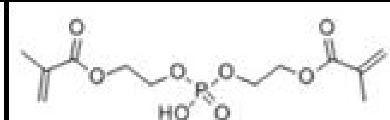


Monomer Selection and Testing

- Japanese approach utilized acrylonitrile groups on polyethylene adsorbents
- Molecules containing phosphate groups have potential to enhance Uranium adsorption capabilities and rates
- Several acrylated phosphonic acids and phosphonates selected and tested

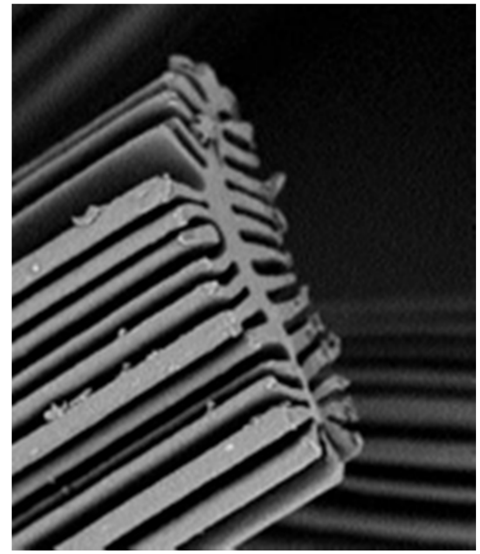
- U sorption of each monomer tested using activated carbon and ICP-AES
- After charcoal testing, the five monomers were tested with electron beam and gamma irradiation
- The chosen monomer, **Bis(2-methacryloxyethyl)phosphonate (B2MP)**, consistently featured significantly higher distribution coefficients and percent sorption for U

Monomers γ-irradiated at 5 kGy/hr for one hour onto Winged Nylon

Monomer	Structure	kD
Diethyl allyl phosphonate		116.9
Vinylphosphonic acid		168.0
Diethylvinylphosphonate		354.1
Dimethylvinylphosphonate		185.1
Bis(2-methacryloxyethyl) phosphonate		46980.1

Selection of Polymer Substrate

- Polymer substrates besides polyethylene have been considered and tested
- Ultra-high surface area polymers (such as Winged Fibers) have potential to increase grafting density
- Polymer substrates for testing included:
  - polypropylene
  - winged polypropylene
  - nylon
  - winged nylon
- Samples testing using both direct and indirect grafting methods as well as EPR analysis
- Some materials revealed poor mechanical properties and/or low grafting densities
- One material (**winged nylon 6**) featured both high grafting densities, high distribution coefficients and favorable mechanical properties



Winged Fiber from Allasso Industries

Substrate samples ready for EPR (in vial) and adsorbance testing (in bag)

Optimizing Radiation Conditions

Approach:

- Irradiate all substrate materials in Co-60 gamma or electron beam linear accelerator
  - Electron beam:
    - 100-300 kGy total dose
    - 16 Gy per 3µ pulse
    - 112 pps
  - Co-60 gamma irradiator:
    - 1-200 kGy total dose
    - 1-75 kGy/hr
- Determine free radical concentration with electron paramagnetic resonance (EPR) to decide between direct and indirect grafting
- Graft best substrate materials with most promising monomers using Co-60 gamma and electron beam radiation
- Determine grafting densities and distribution coefficients
- Determine best combination of substrate material and monomer

Goal : to achieve the highest concentration of free radicals available

- Anaerobic irradiation and grafting
  - To prevent the reaction of free radicals with oxygen
- Low dose rate irradiation
  - To decrease undesired radical-radical-interactions (crosslinking, homopolymerization)

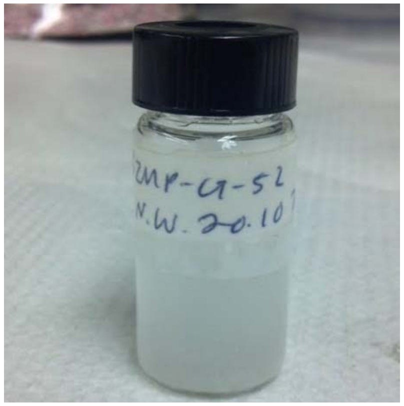
Ideal Conditions:
Monomer – B2MP
Substrate – Winged Nylon
Grafting Method - Direct

Direct Grafting with Nylon 6,6

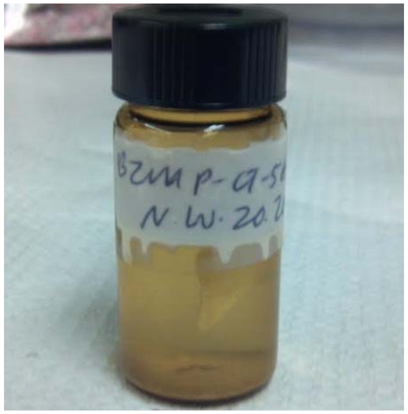
Nylon substrate irradiated in anaerobic aqueous solution with Bis(2-methacryloxyethyl)phosphonate (B2MP)

<u>Advantages:</u>

- Minimal pre- and post-treatment
  - Only requires N2 purging and contact time
- Entire procedure performed at room temperature
  - No low-temp irradiation or heated grafting
- No organic solvents
  - Minimal environmental impact, ideal for ocean testing
- Use of gamma radiation instead of electron beam
  - Easily provides uniform irradiation over large surface areas at a wide range of dose rates, ideal for process scale-up

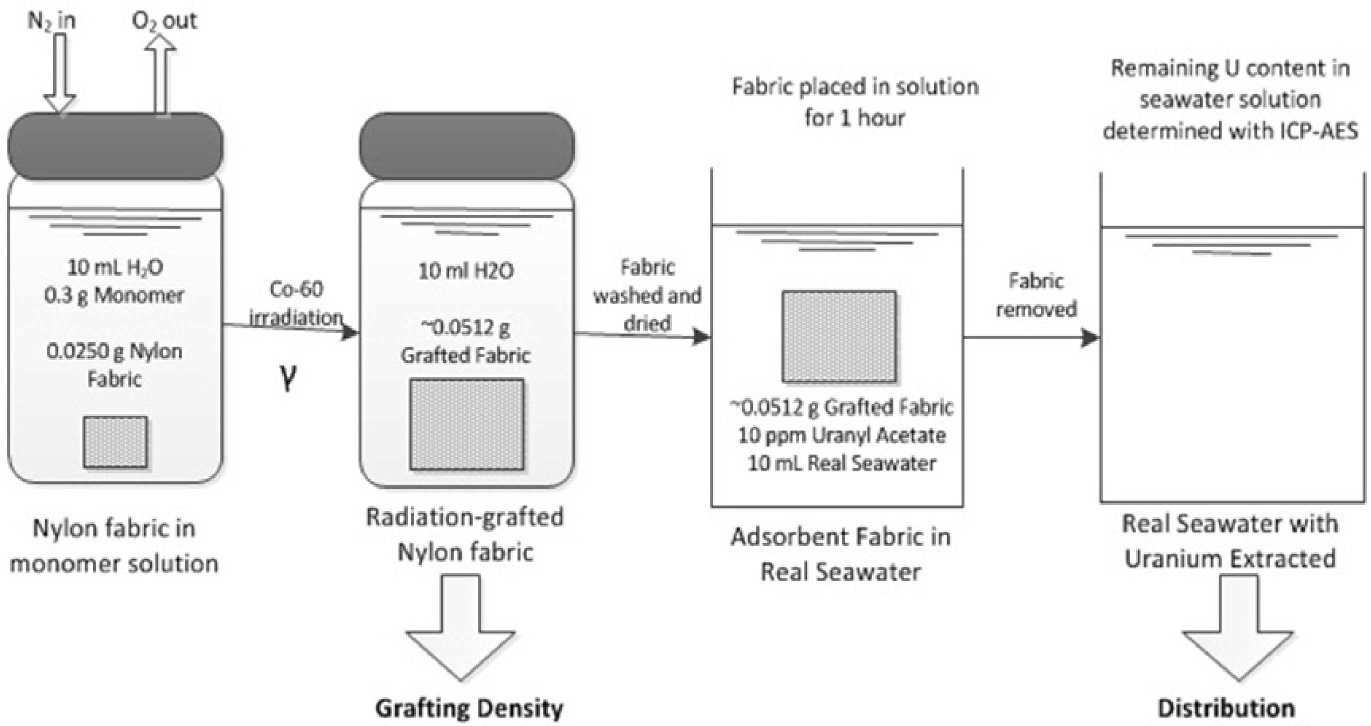


Vial for direct grafting: pre-irradiation



Vial for direct grafting: post-irradiation

Experimental Procedure: Direct Grafting



1. Nylon sample placed in 100 mM B2MP solution with DI water, vial sealed and purged with N_2
2. Vial irradiated at desired dose rate and total dose
3. Nylon allowed to rest in the closed vial overnight
4. Grafted sample removed from vial, washed, dried and weighed to determine grafting density
5. Sample placed in solution of real seawater doped with uranyl acetate for one hour
6. Adsorbed sample removed, remaining solution tested for uranium concentration with ICP-AES
7. Distribution coefficient (k_D) determined

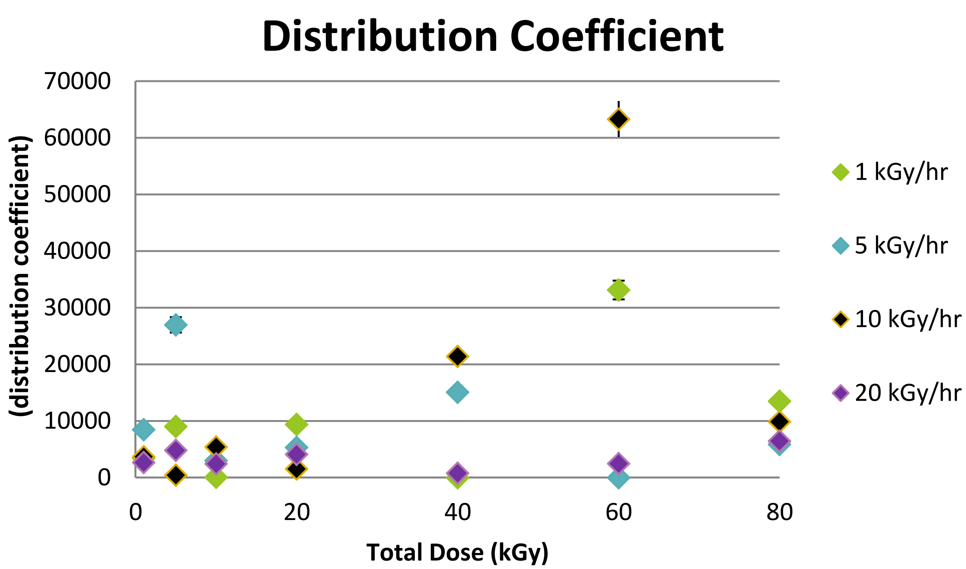
Distribution Coefficients and Percent Sorption

Dose Rate (kGy/hr)	Total Dose (kGy)	Distribution Coefficient (k_D) (mL/g)	Grafting Density (%)	Percent Sorption (%) of U in Real Seawater
1	5	9,031.8	114.6	98.2
1	20	9,383.8	79.1	97.8
10	80	9,880.8	124.4	98.4
1	80	13,488.8	80.6	98.6
5	40	15,065.8	110.40	98.8
10	40	21,406.0	109.60	99.2
5	5	26,980.0	104.2	99.4
1	60	33,133.4	86.6	99.4
10	60	63,286.3	108.9	99.7

All samples irradiated in Co-60 gamma source
Substrate: Winged Nylon   Monomer: B2MP

- Best results summarized in table to the left
- Significant room for improvement, much higher distribution coefficients anticipated as method is refined
- U distribution coefficient of Tamada et. al. (2009) – 1.99×10^4 mL/g

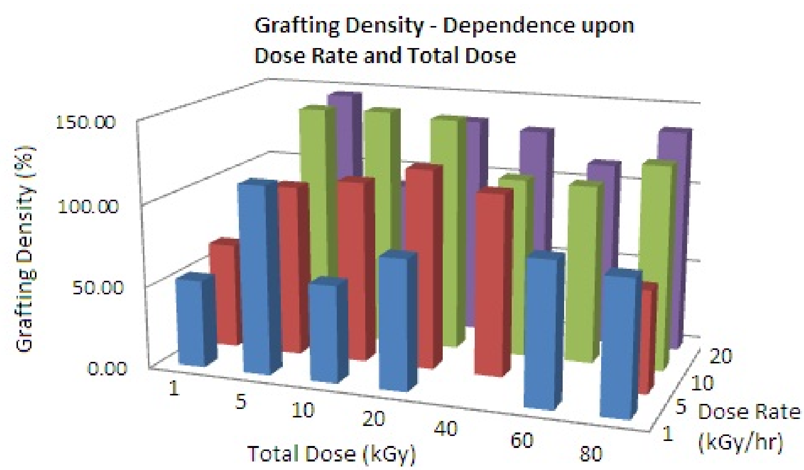
Results: Distribution Coefficient Dependence on Dose Rate and Total Dose



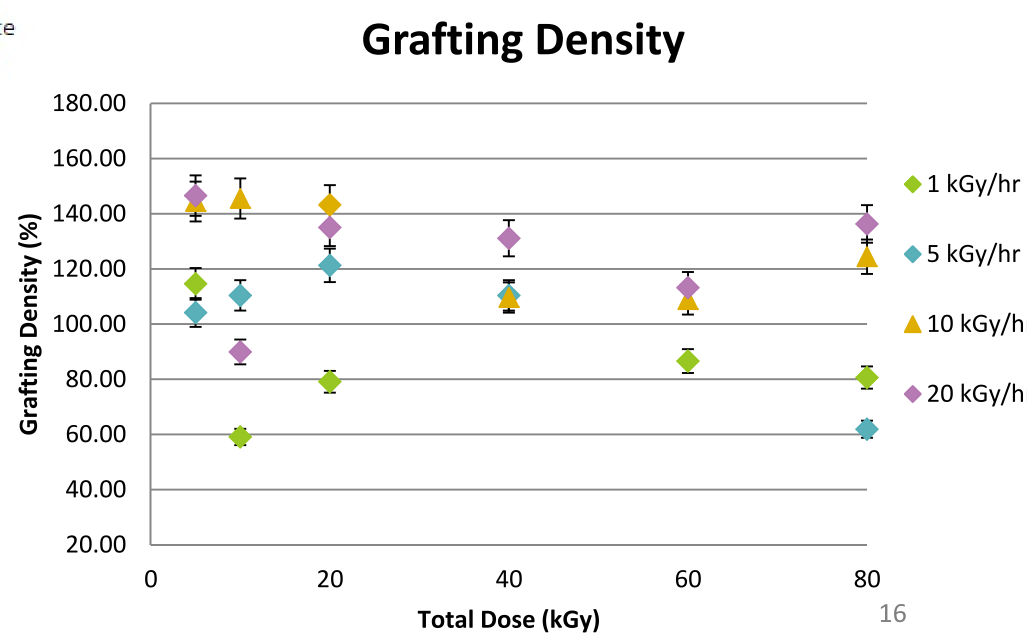
Substrate – Winged nylon
Monomer – B2MP
n = 43 samples
Dose rates = 1-20 kGy/hr
Total doses = 1-80 kGy/hr

- Long irradiations favorable
  - High total dose
  - Low to intermediate dose rates (1, 5, 10 kGy/hr)
- Irradiations at high dose rates (>70 kGy) and high total dose (100-300 kGy) not as effective for both gamma and electron beam
- All measurements to be repeated

Grafting Density
Dependence on Dose Rate and Total Dose

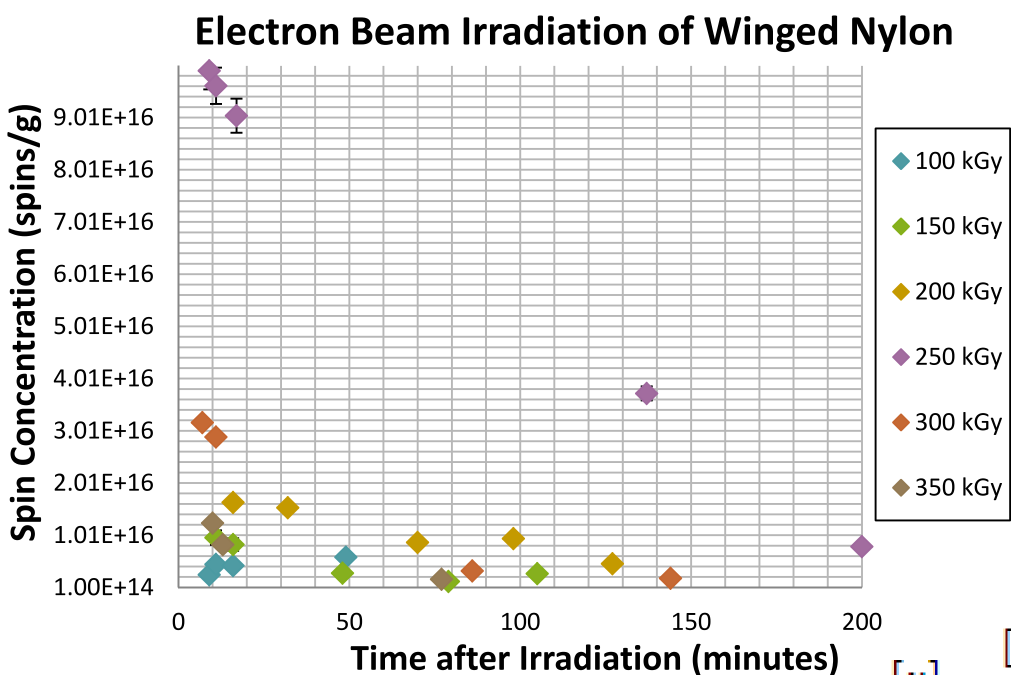


$\left(\frac{\qquad}{\qquad} \right) \times 100$



Substrate – Winged Nylon
Monomer – B2MP
n = 43 samples
Dose rates = 1-20 kGy/hr
Total doses = 1-80 kGy/hr
Average grafting density = 98.8%

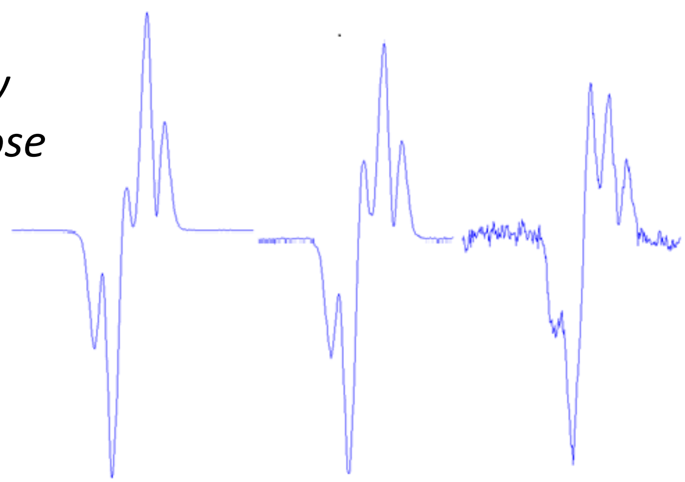
EPR of Winged Nylon



LINAC parameters:
16 Gy per 3μs pulse
112 pps

$$[x] = \frac{[std]A_x R_x (scan_x)^2 G_{std} M_{std} (g_{std})^2 [s(s+1)]_{std}}{A_{std} R_{std} (scan_{std})^2 G_x M_x (g_x)^2 [s(s+1)]_x}$$

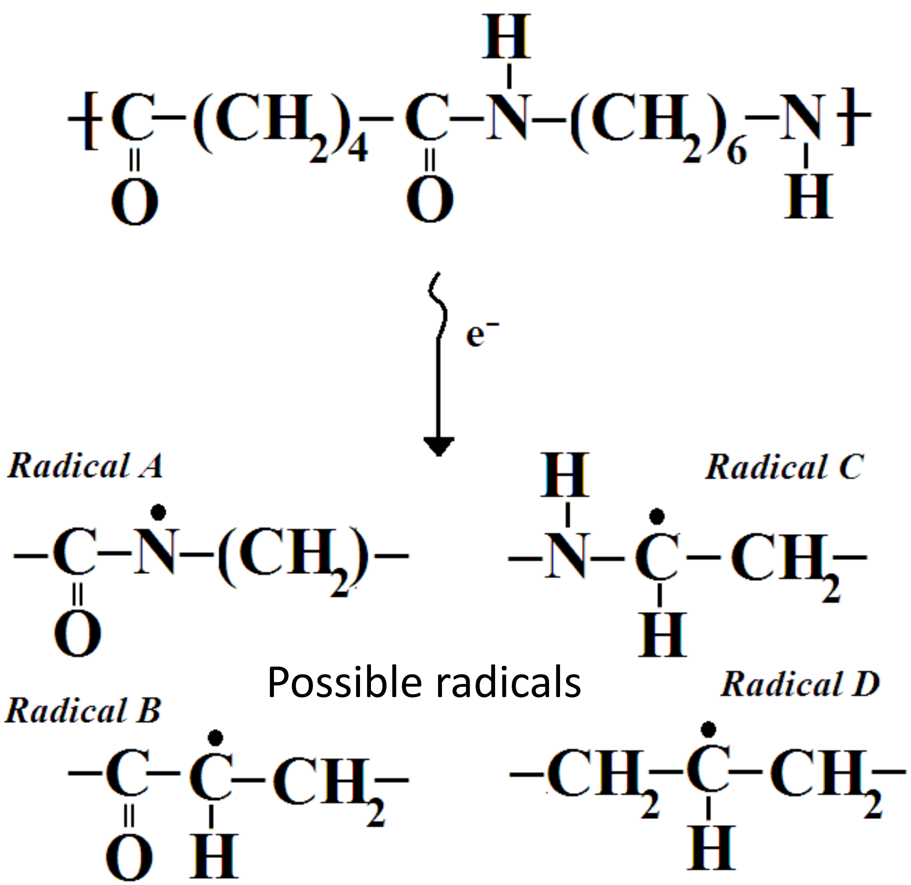
250 kGy total dose



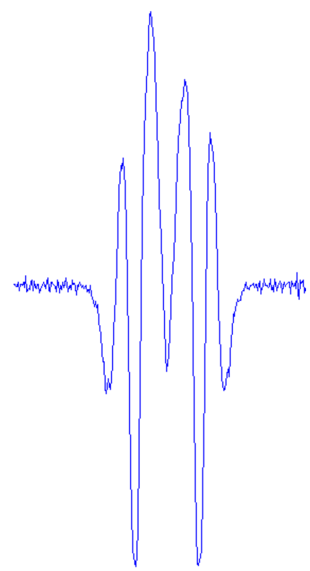
t = 9 minutes   t = 137 min   t = 200 min

Variable	X = sample, std = standard
[x]	Spin concentration
A	DI/N
Scan	Sweep width
G	Receiver gain
M	Modulation amplitude
g	G-value
s	spin

Radical Mechanisms of Nylon 6,6



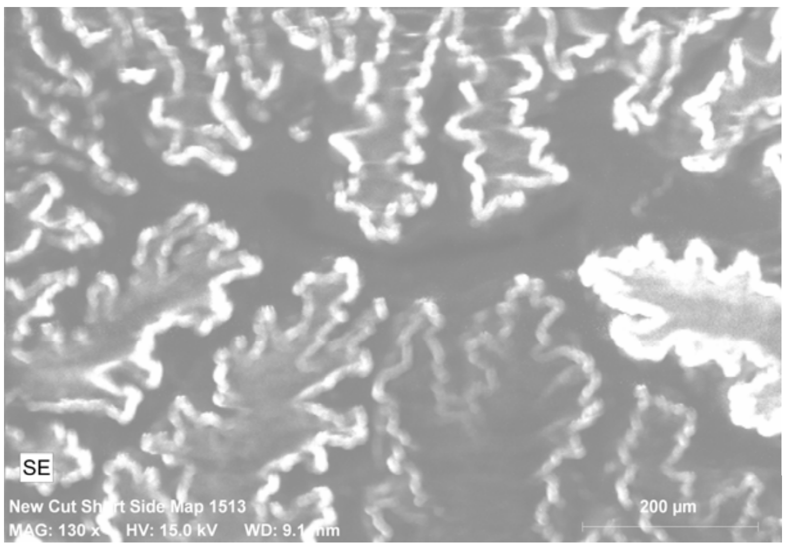
Radical mechanisms and kinetics to be determined with femtosecond pulse radiolysis



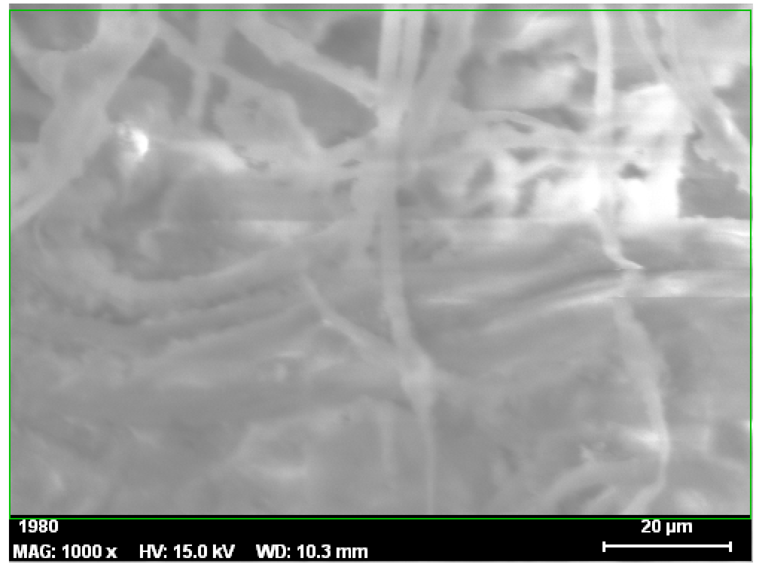
Quintuplet structure of room-temperature measured Nylon 6,6 suggests Radical A or Radical C as the dominant species

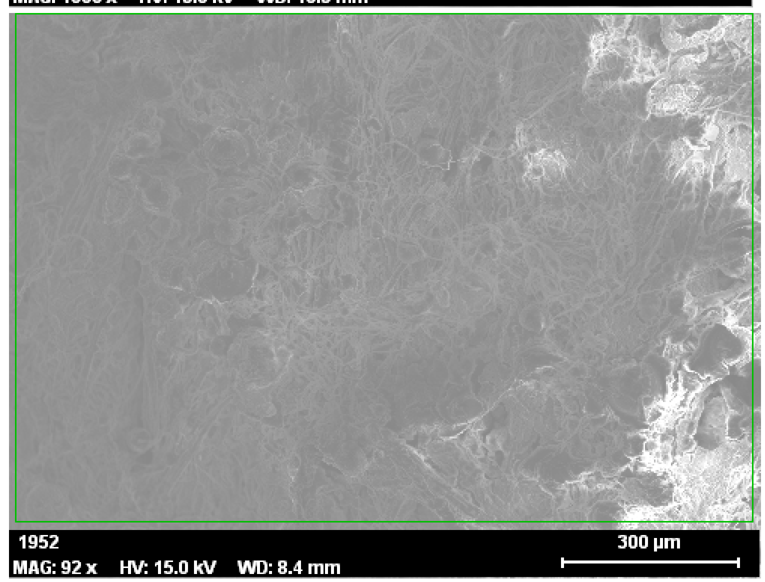
Why use Scanning Electron Microscope?

Micro-scale morphology of uranium-adsorbed fabric studied using UMD's Field Emission SEM



Winged nylon:
before radiation-induced grafting

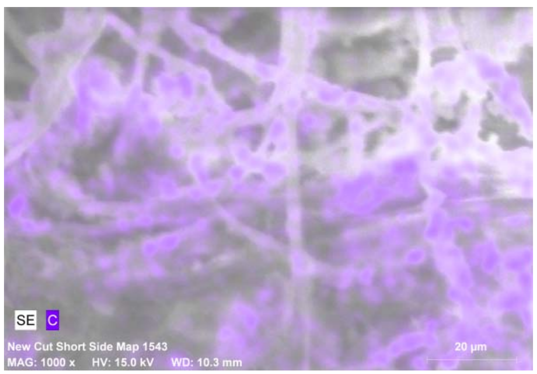


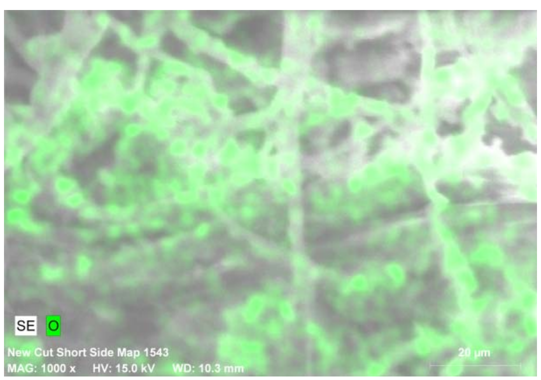


Winged nylon:
After grafting and U adsorption (2 views)

Scanning Electron Microscope

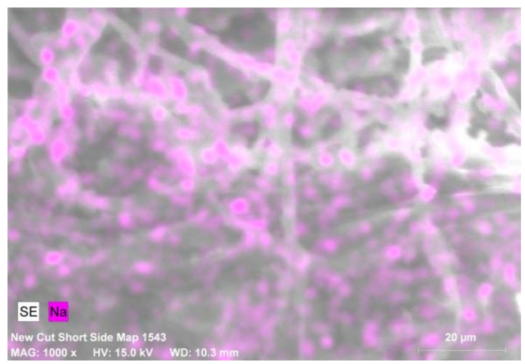
-Winged nylon directly grafted with Bis(2-methacryloxyethyl) phosphonate
- Irradiated at 20 kGy/hr to 80 kGy total dose
-Contacted with U solution in real seawater for 1 hour
-Distribution coefficient (k_D) ~6000

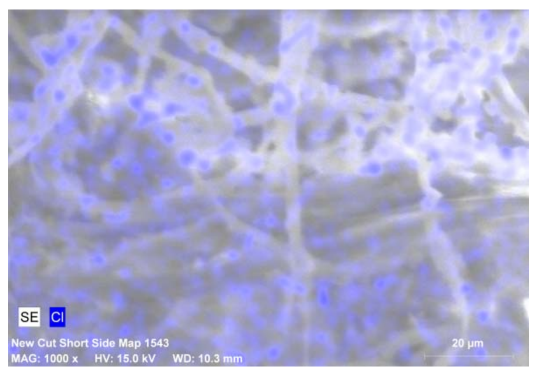




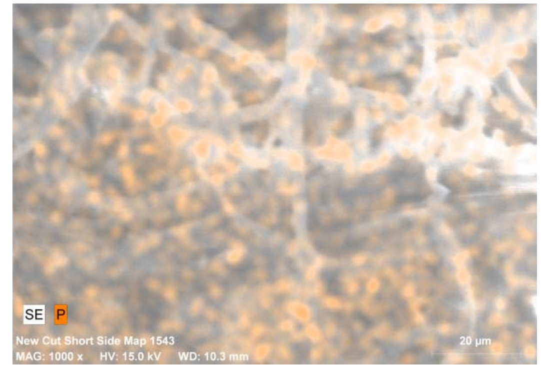
20 µm

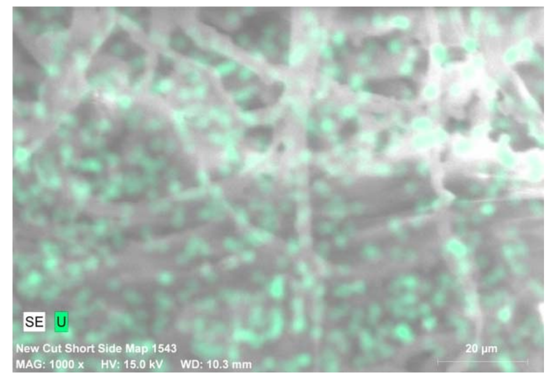
Carbon and Oxygen

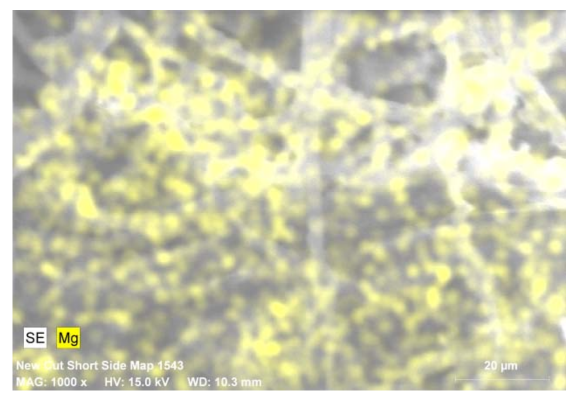




Sodium and Chlorine







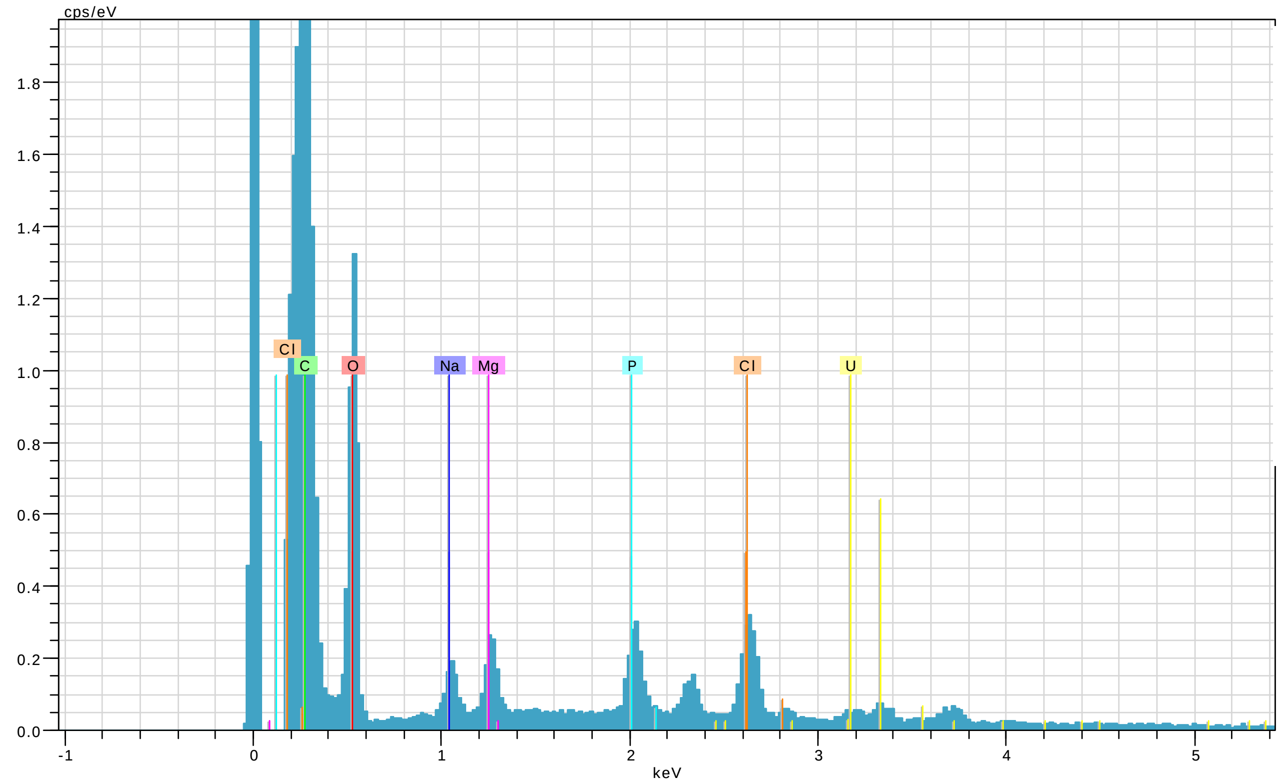
Phosphorus, Uranium and Magnesium

Why use Energy-Dispersive X-ray Spectroscopy (EDS)?

- A focused electron beam is rastered across the polymer surface, a secondary (backscatter) electron signal is processed to provide a spectrum and spatial map
- Provides localized elemental identification and compositional information
- Reveals regions rich in or lacking a specific element
- Shows other elements competing with uranium for binding sites

SEM/EDS at UMD nanocenter

Energy-Dispersive X-ray Spectroscopy (EDS)



-Winged nylon direct grafted with B2MP

- Irradiated at 20 kGy/hr to 80 kGy total dose

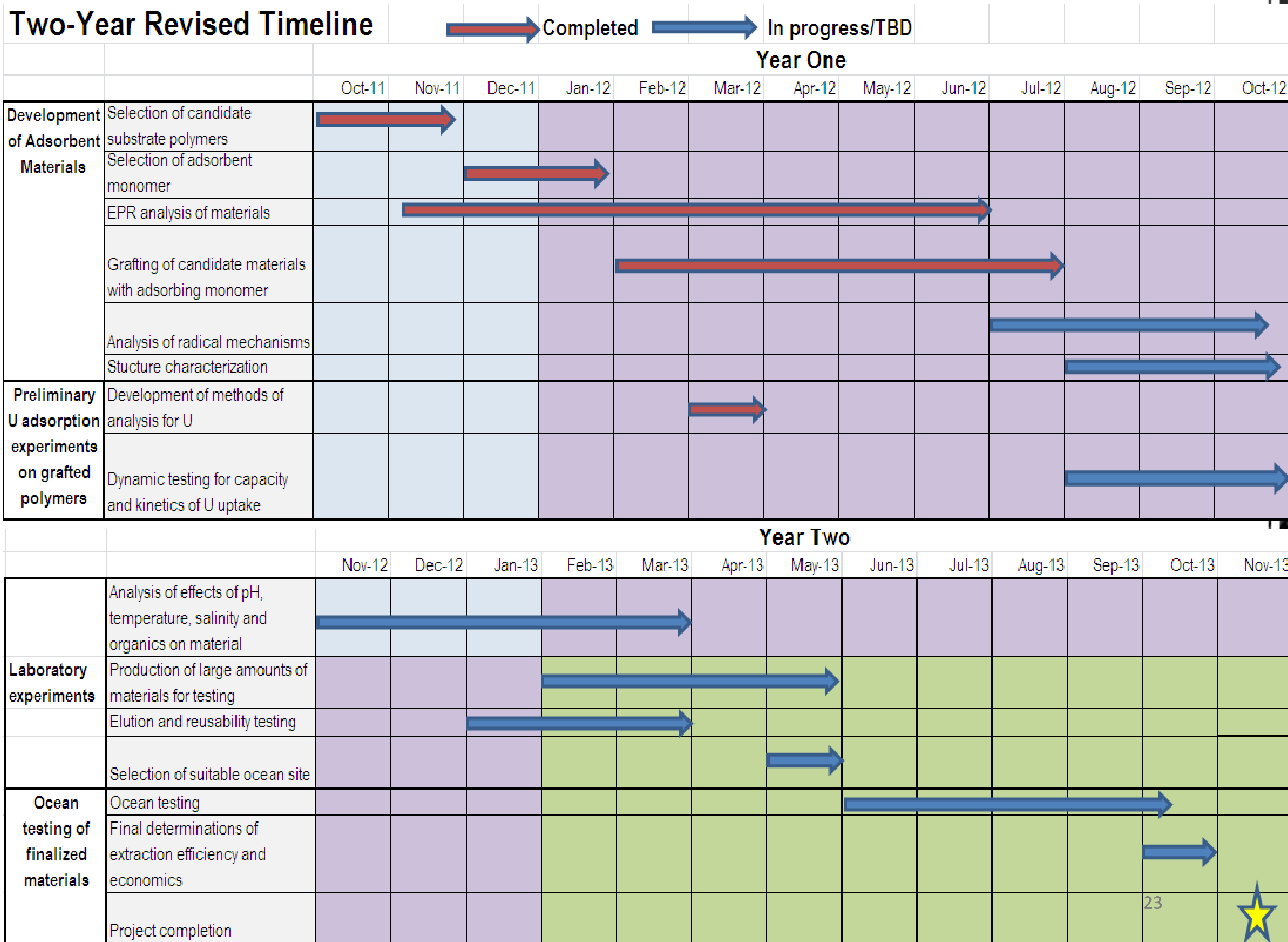
-Contacted with U solution in real seawater for 1 hour

-Distribution coefficient (k_D) ~6000

Isotope	Conc.(wt %)	Conc. (atom %)	Error (%)
Carbon	40.20	52.20	13.6
Oxygen	43.61	42.51	14.7
Chlorine	3.22	1.41	0.1
Sodium	1.53	1.04	0.1
Uranium	7.22	0.47	0.3
Magnesium	1.64	1.05	0.1
Phosphorus	2.59	1.31	0.1

- Highly competitive ions include Na^+, Cl^- and Mg^{2+}
- Even at only 0.47 atom %, percent sorption of Uranium by sample was 98%

Two-Year Revised Timeline



Next Steps

Project completion!

On-site testing in the Atlantic Ocean

Testing under various conditions
- Temperature, salinity, pH, etc.

Elution and reusability testing

Analysis of radical mechanisms and kinetics with pulse radiolysis

Study kinetics of U adsorption

Complete optimization

Summary

- Bis(2-methacryloxyethyl) phosphonate (B2MP) selected as chelating monomer
- Winged nylon 6,6 selected as polymer substrate material
- Co-60 gamma irradiation favored over electron beam
- Direct grafting method (in combination with selected monomer and substrate) chosen for the following reasons:
  - EPR revealed rapid decay in radical concentration
  - No cooling or heating required during irradiation or grafting
  - No organic solvents required
  - Shorter grafting time with little to no pre- or post-treatment
- Most successful UMD sample has shown a k_D of >63,000 mL/g
  - Japanese researchers (Tamada et. al, 2009) published a k_D of only 19,900 mL/g
  - Average k_D of UMD direct grafted samples (including poorly grafted samples) >8,000 mL/g
- Optimization still in progress, there remains significant room for improvement!