# An Eye Opener on the Bright Future of Ionizing Radiation Measurements in Medicine, Processing, and Nuclear Applications

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Presented

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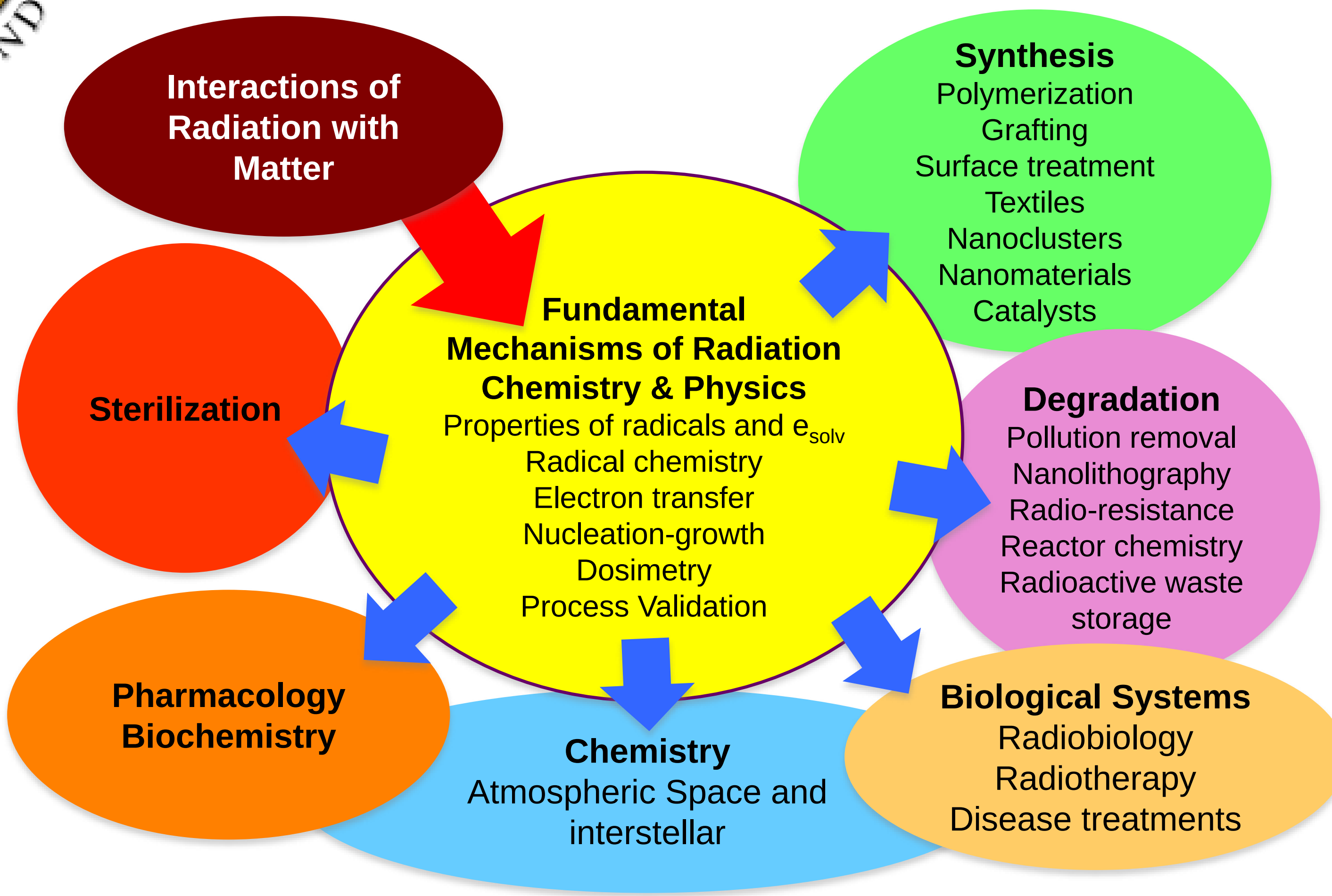
**Based on present pioneering research programs, future trends in radiation chemistry and nuclear applications in nanotechnology can be outlined as follows:**

- **Light charged particles and gamma radiolysis: Low LET irradiation, as in the case of gamma radiolysis, electron beam irradiation (0.3-10 MeV), and positron irradiation will play major roles in synthesis, manufacturing, and material characterization in nanotechnology.**

- **Heavy charged particles (i.e. protons and alpha particles)**

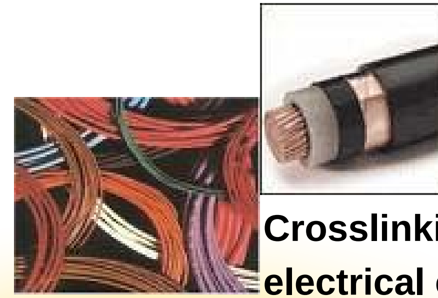
- **Neutron irradiation: Neutron scattering**


Interactions of Radiation with Matter
Synthesis
Polymerization
Grafting
Surface treatment
Textiles
Nanoclusters
Nanomaterials
Catalysts
Sterilization
Fundamental Mechanisms of Radiation Chemistry & Physics
Properties of radicals and $e_{solv}$
Radical chemistry
Electron transfer
Nucleation-growth
Dosimetry
Process Validation
Degradation
Pollution removal
Nanolithography
Radio-resistance
Reactor chemistry
Radioactive waste storage
Pharmacology
Biochemistry
Chemistry
Atmospheric Space and interstellar
Biological Systems
Radiobiology
Radiotherapy
Disease treatments

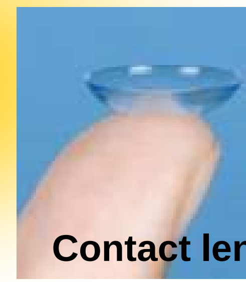
# Global Applications of Ionizing Radiation

- Polymer crosslinking
- Graft polymerization
- Enzyme immobilization
- Controlled drug release
- Hydrogels and gel-filled membranes
- Non-thromogenic surfaces
- Textile modifications for hydrophilicity, ion-exchange
- Membrane technology for chromatography
- Electron beam lithography
- Waste water treatment, ion-exchange, salt rejection
- Fuel Cell

UHMWPE
Hip joint cup



Crosslinking of electrical cable surface

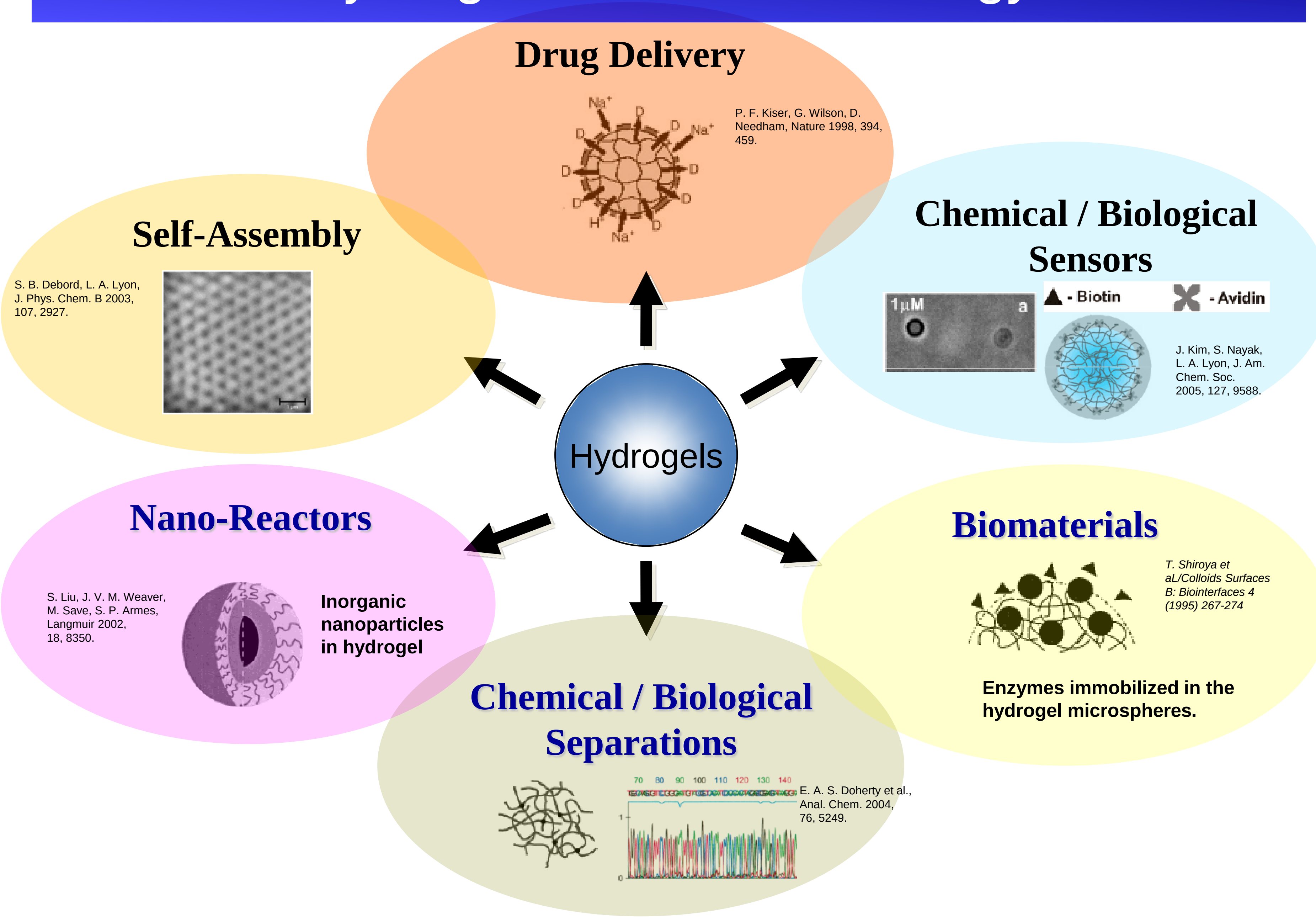


Contact lens

Wound dressing

Sterilization process

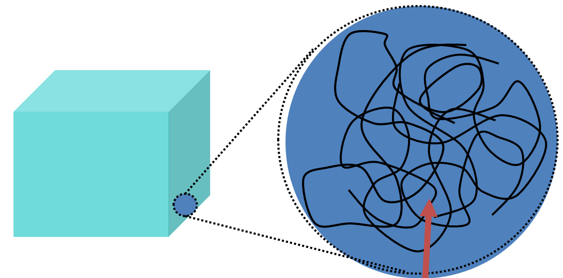
# Hydrogels in nanotechnology



- **Hydrogel**

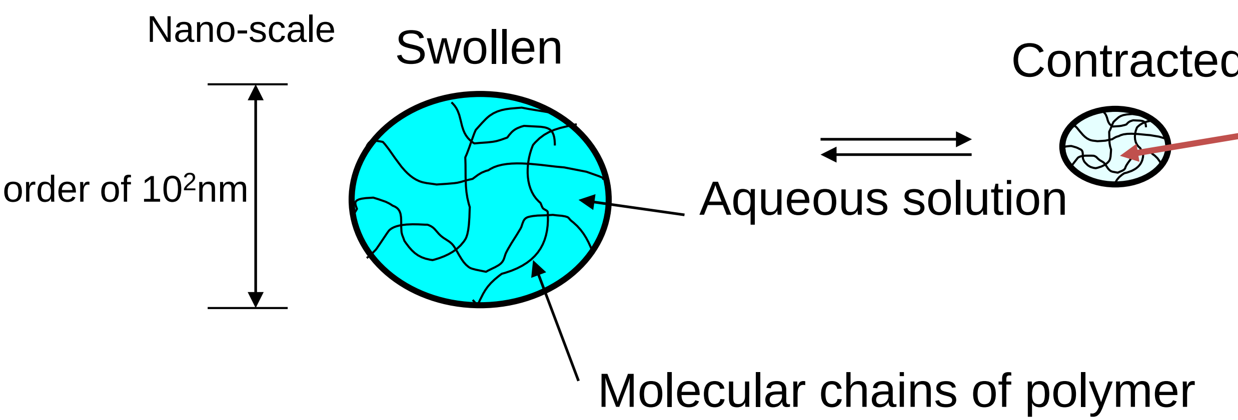
**Structure: 3D polymer network & filling liquid (water)**

- Common applications -



Conventional Macroscopic hydrogel

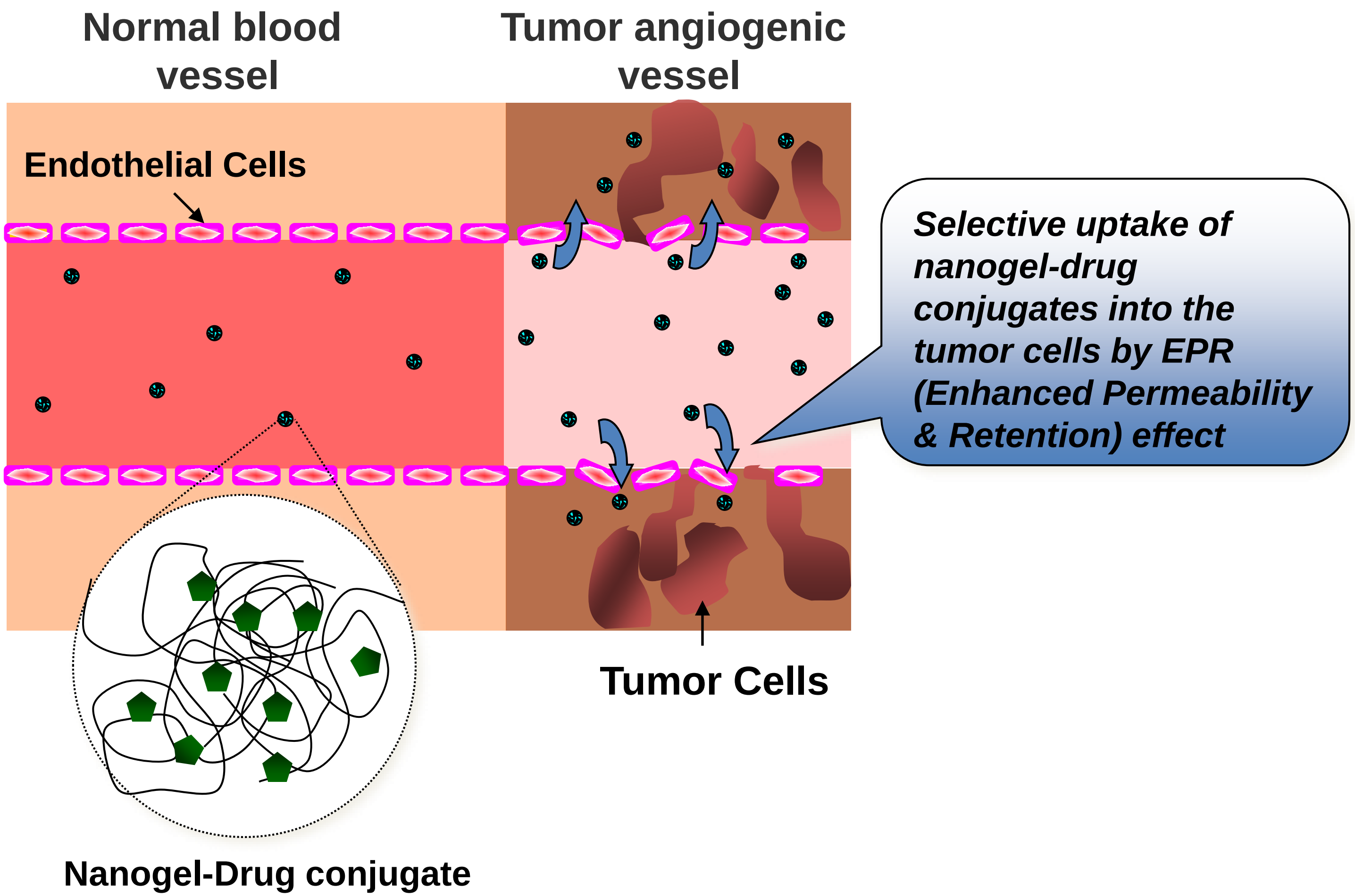
## Nanohydrogel



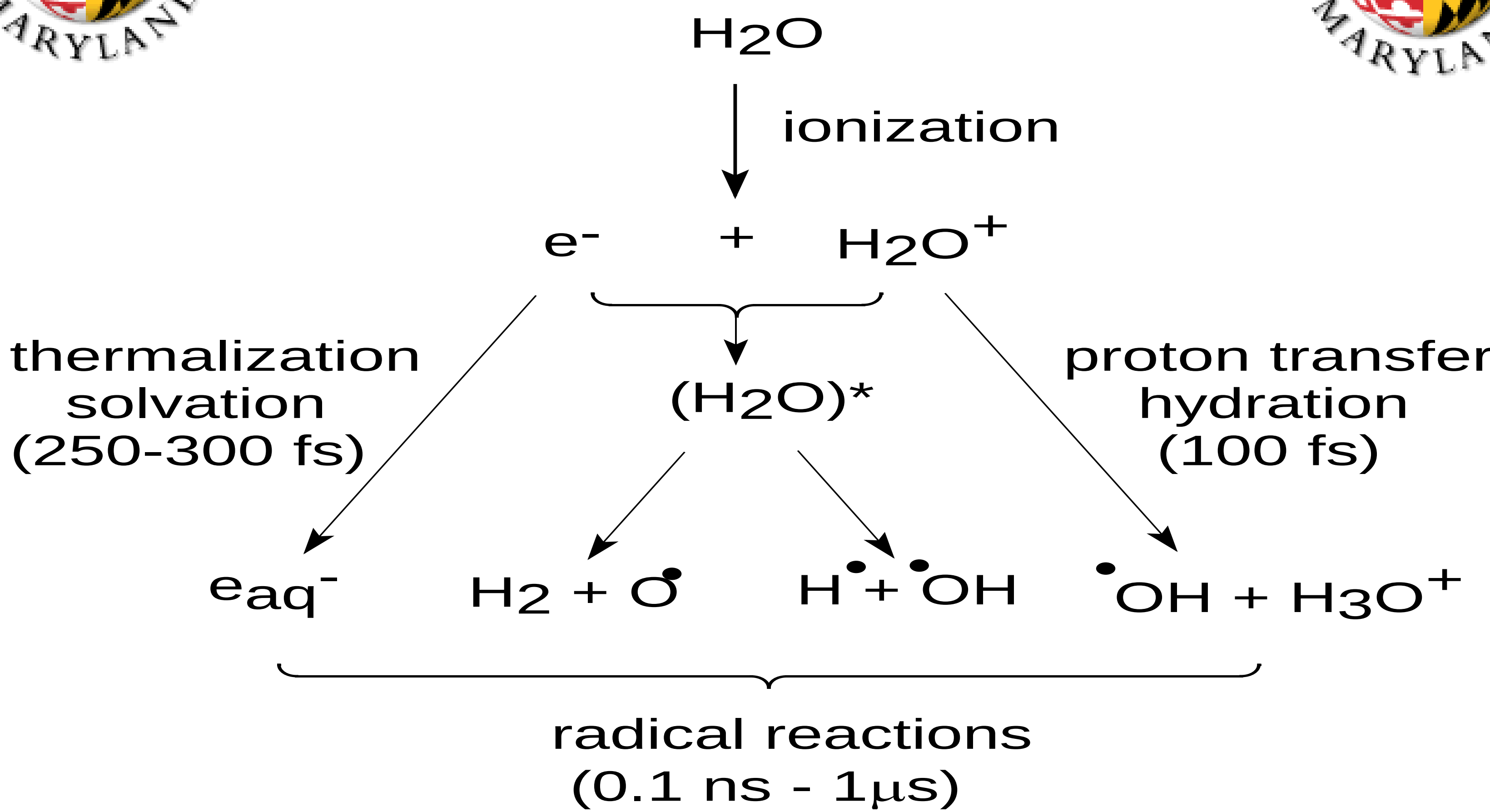

Polymer chains are crosslinked together by stable and flexible chemical covalent bonds.

# Target-specific drug delivery carrier

- Nanohydrogel as target-specific drug delivery carrier.
- Permeation and retention of polymer nanohydrogel-drug conjugates via leaky tumor vasculatures (passive targeting).

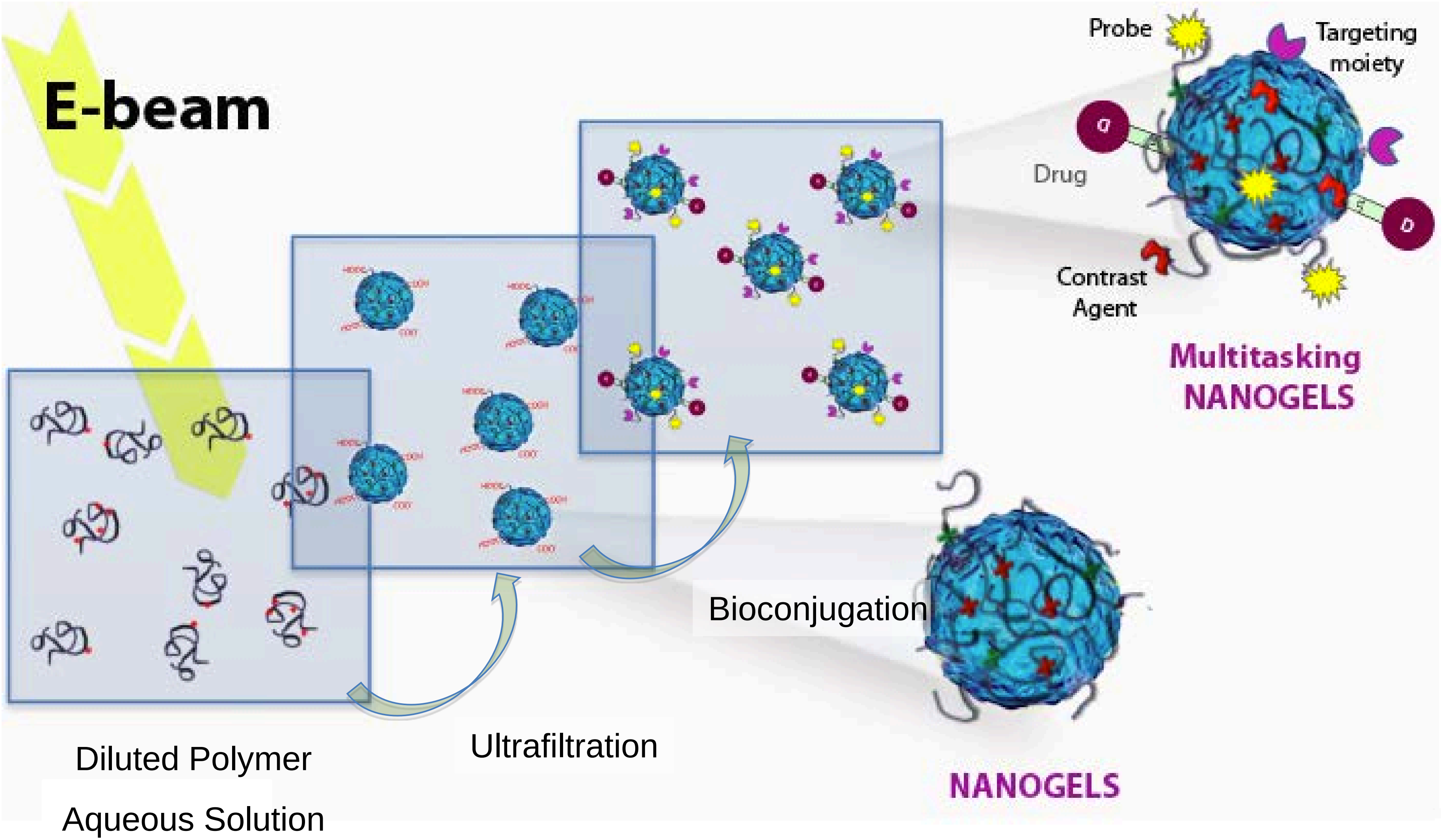


# Radiolysis of water



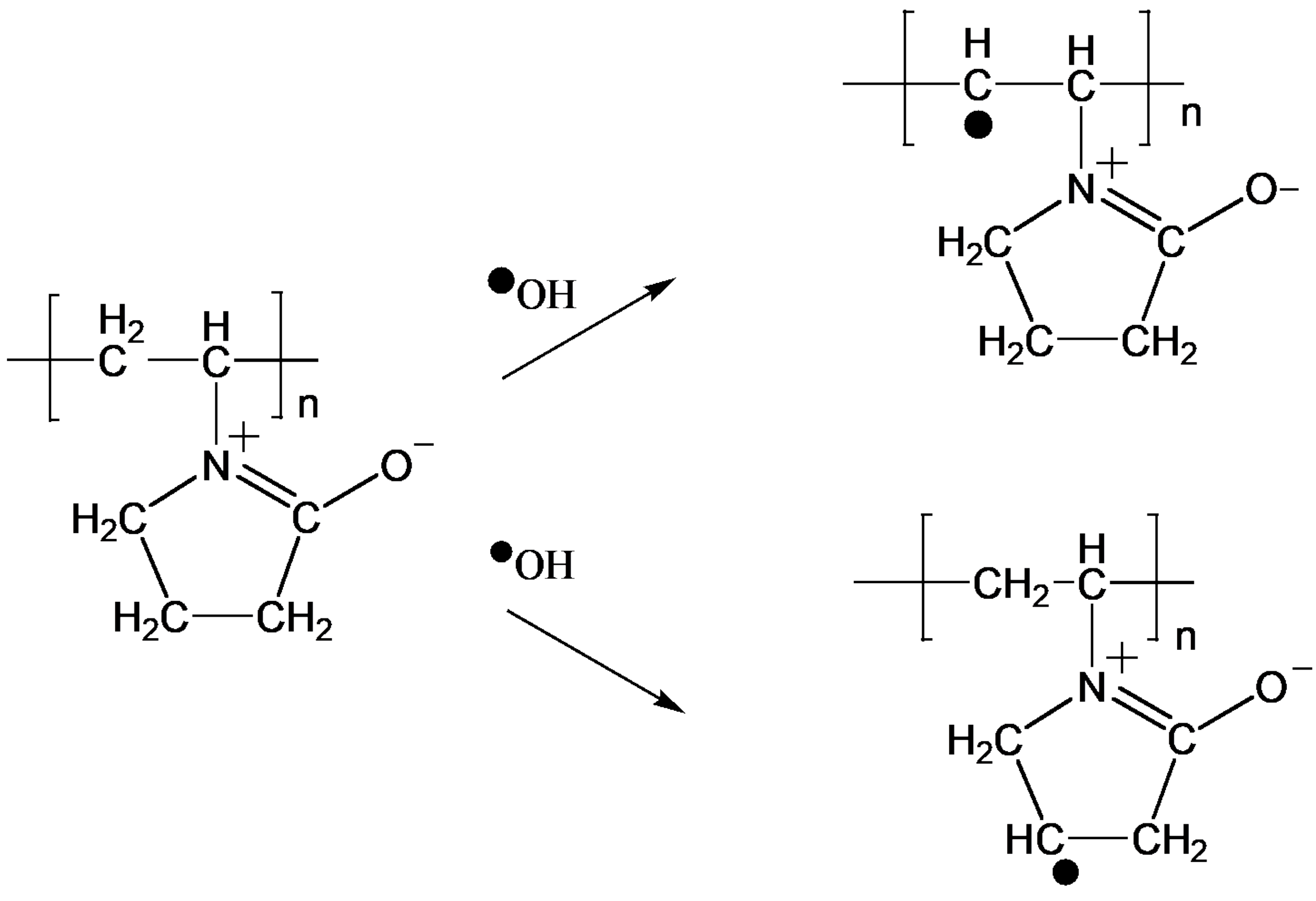
# A “minimal” synthetic approach….

## high-energy radiation-induced crosslinking

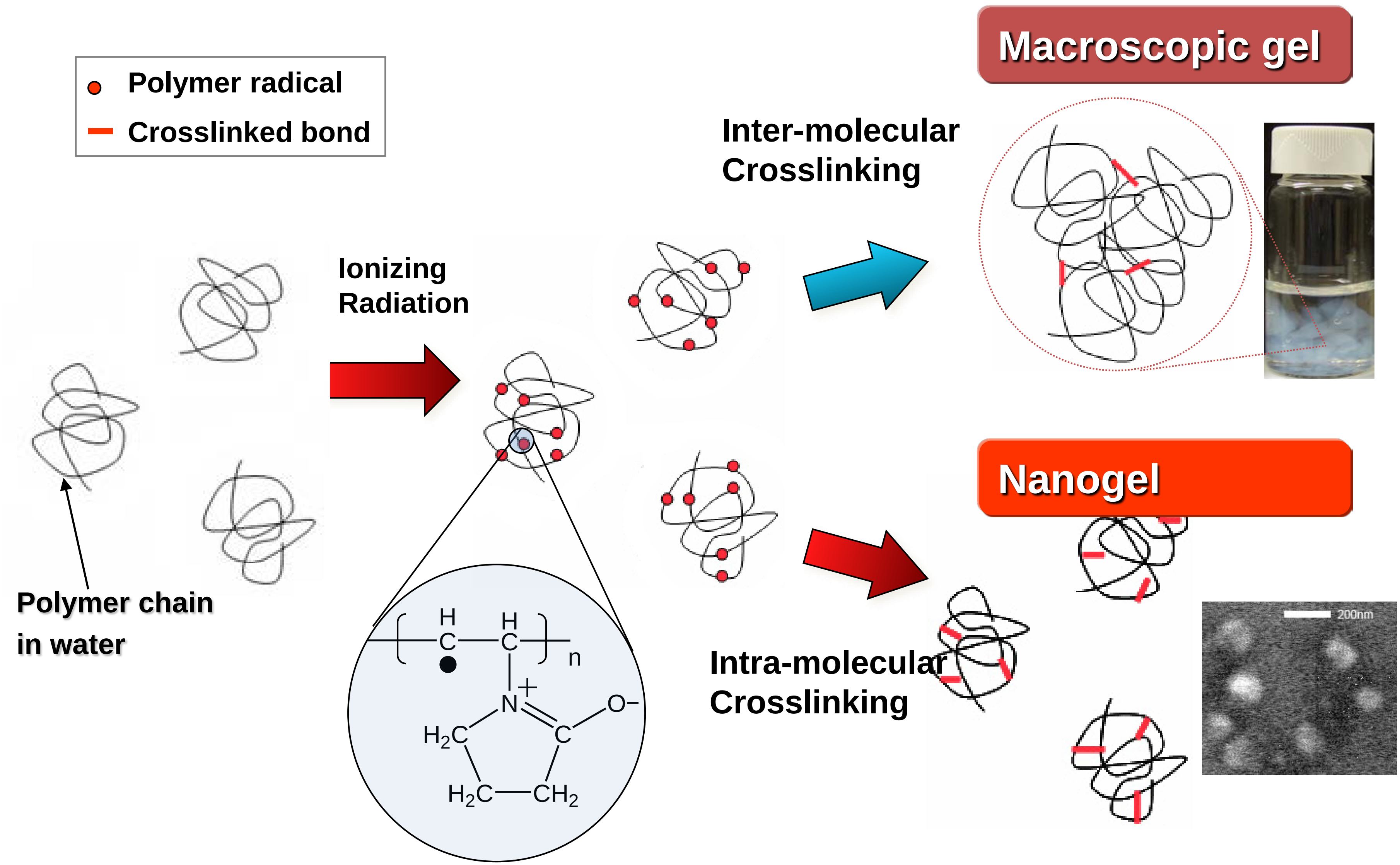


# Reactions of •OH with PVP

**H abstractions of carbon in PVP**

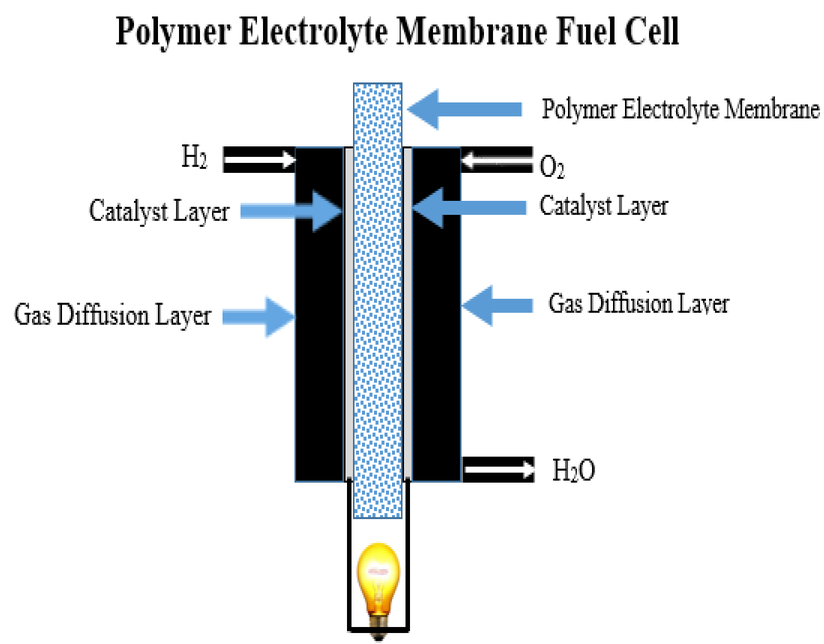


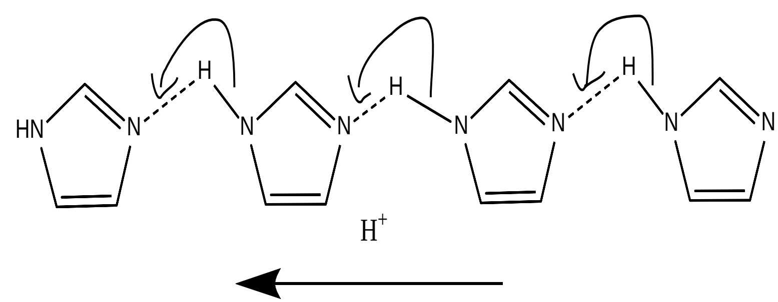
# Inter- vs. Intra-crosslinking



# Radiation Grafting of Ionic Liquids to Synthesize Polymer Electrolyte Membrane Fuel Cells

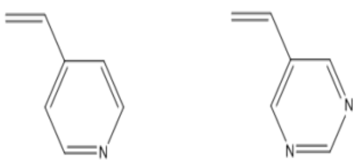
Goal: To designed and synthesized novel anhydrous proton conductive fuel cell membranes that can operate at temperatures above $120^\circ$ C can allow for improved performance and reliability.



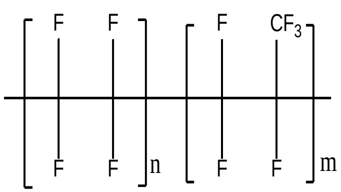

Protic ionic liquids can

# Synthesis: Indirect Radiation Grafting

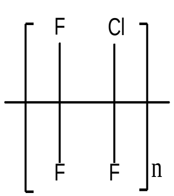


4-Vinylpyridine pKa 5.62

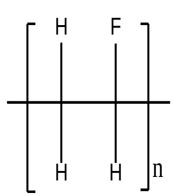
5-vinylpyrimidine pKa 1.82



FEP

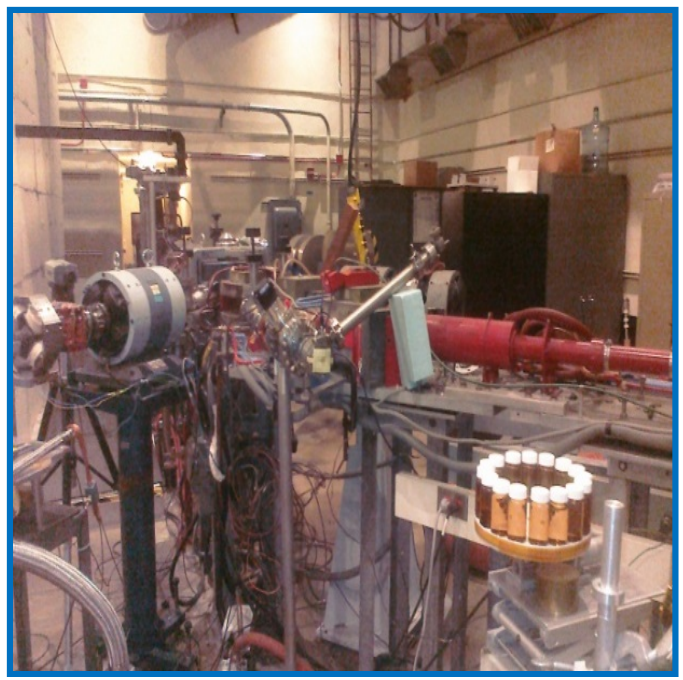


PCTFE

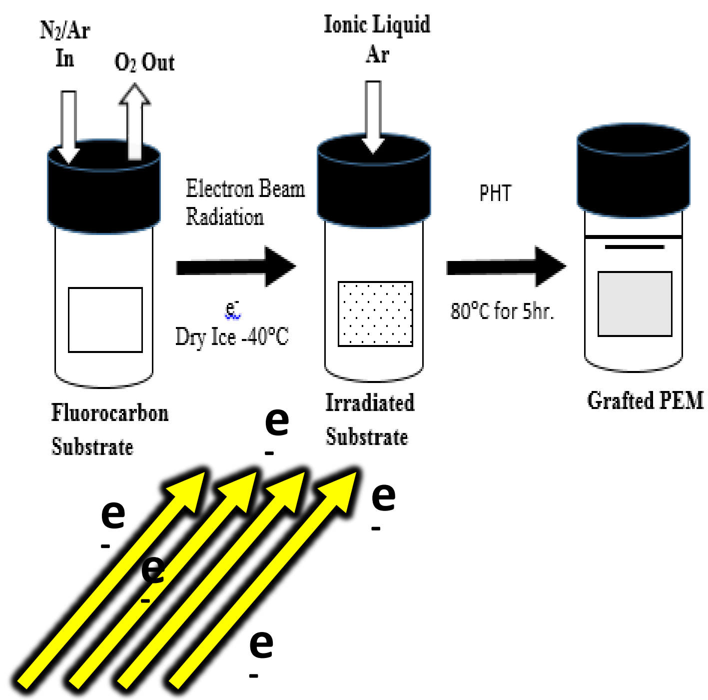


PVF

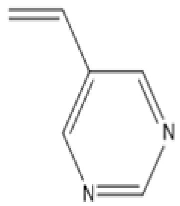
Medical Industrial Radiation Facility (MIRF) NIST



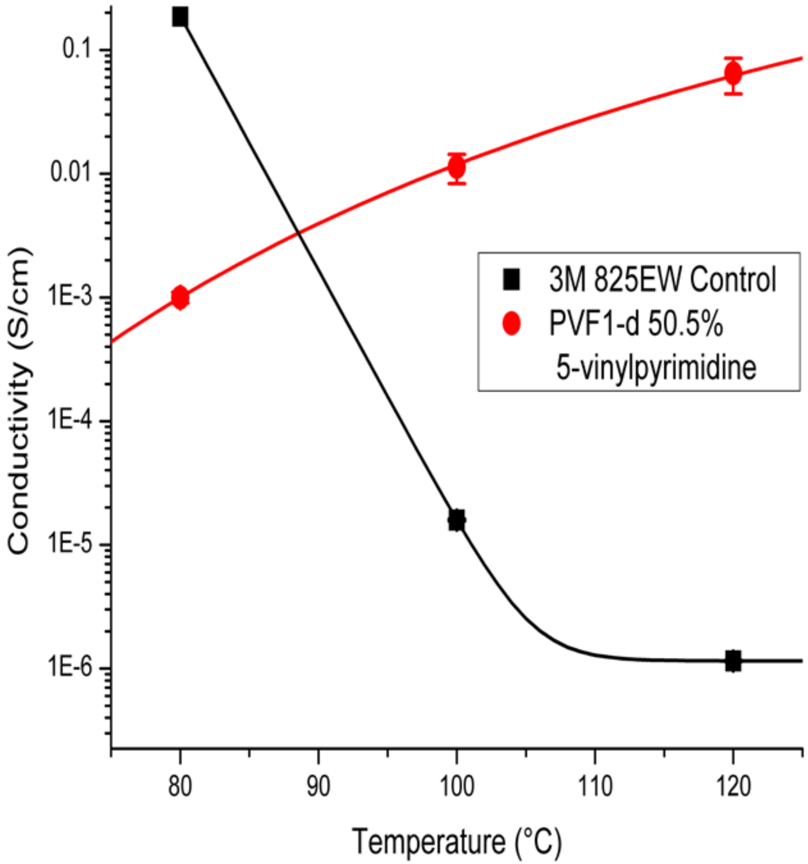
**Indirect Radiation Grafting Procedure**



# High Temperature Conductivity




5-vinylpyrimidine




- Ionic liquid proton conductivity increases with temperature
- Does not require humidity control
- Higher operating temperature PEMFC operate more efficiently and

# Nuclear Reactor Cable Project Reliability

- Investigation of reliability of nuclear power plant cables to improve degradation models and better predict cable failure
- We are investigating insulation which are composed of nuclear and commercial grade: crosslinked polyethylene and ethylene propylene rubber.
- Measure effect of temperature, humidity and radiation on the cable insulation
- Degradation and failure will be investigated through mechanical properties, oxidation index and electrical conductivity

# Potential Use of E-Beam Irradiation in the Production of Cellulosic Ethanol

- Ionizing radiation is known to break down cellulose into simpler sugars.
- The mechanism of the radiolytic decomposition of cellulose is known to proceed through formation and propagation of free radicals.
- However, almost all the studies of radiation effects have been conducted on pure cellulose (e.g., cotton) rather than on plant materials, where the cellulose is encased within lignin cell walls.

# Effect of Pretreatment

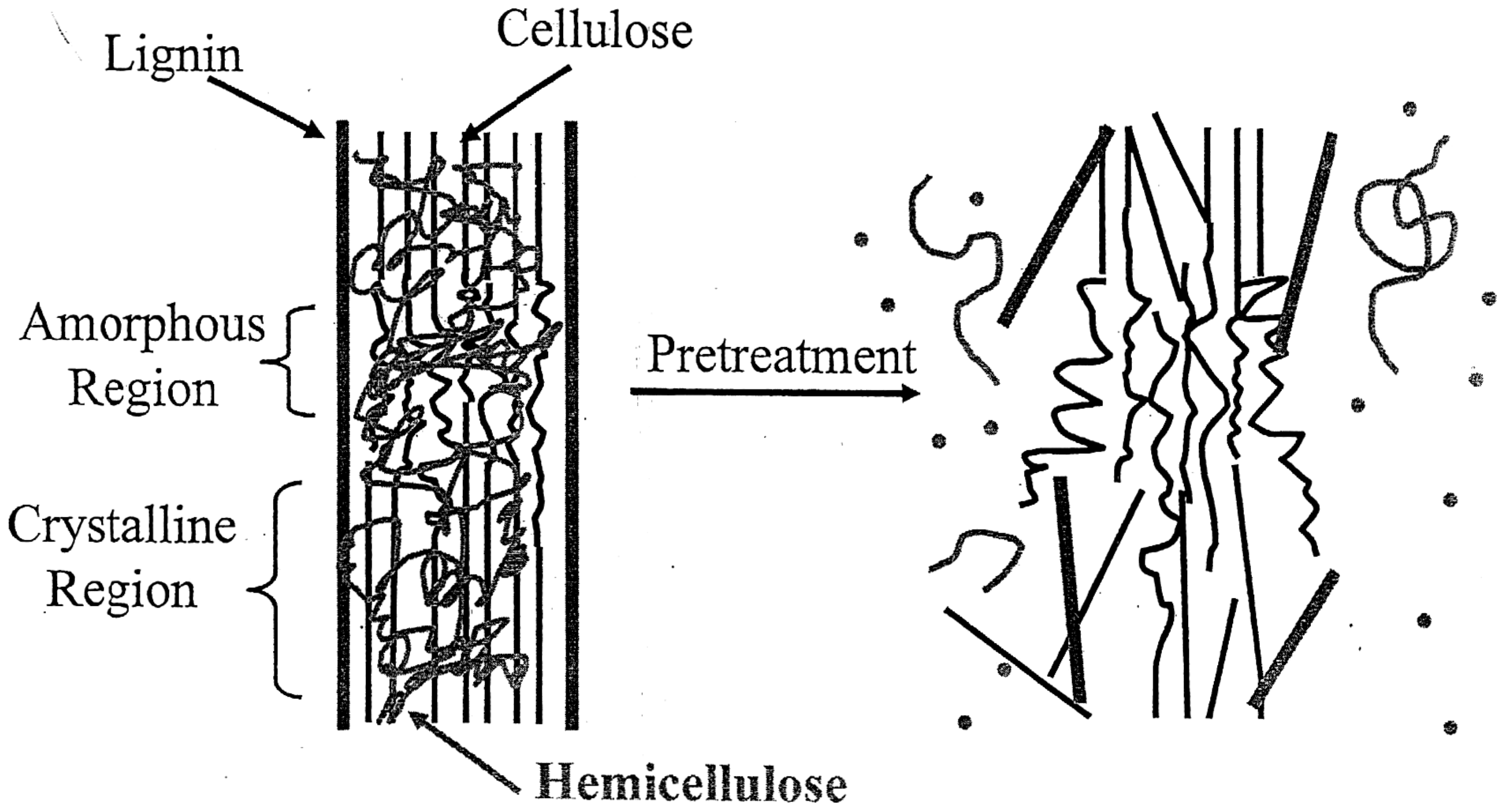
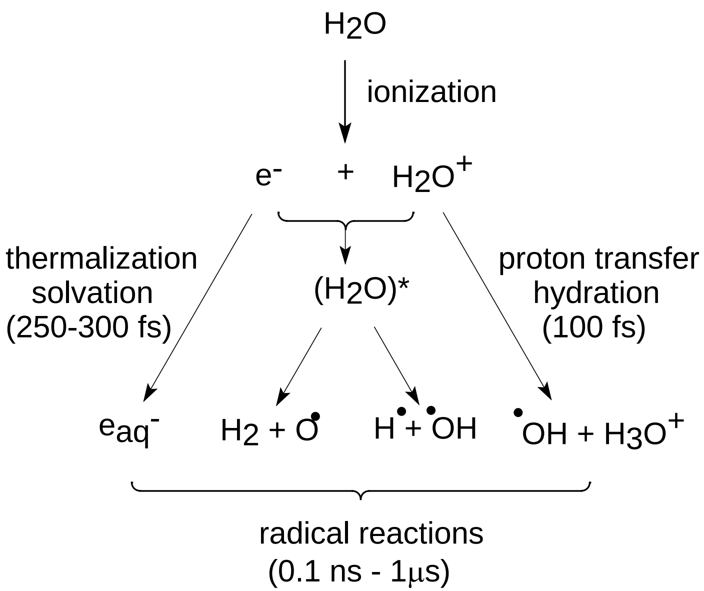



**Figure 1 Goals of pretreatment of a lignocellulosic material (Mosier *et al.*, 2005)**

# Radiation Chemistry of Water in Reactors

Pastina and LaVerne *J. Phys. Chem. A* ***1999***.

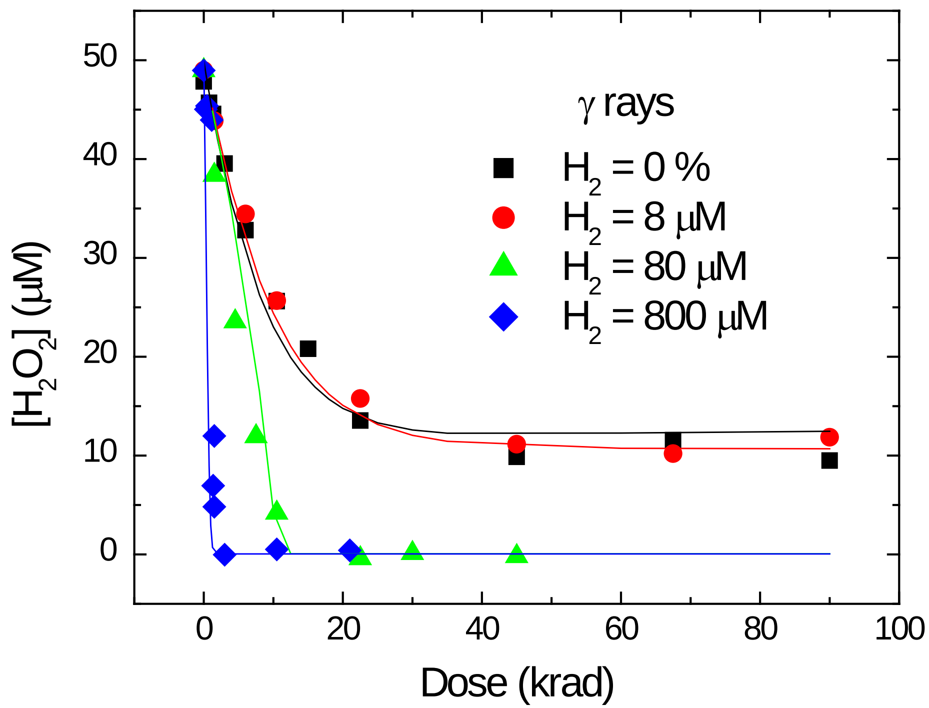



$OH + OH \rightarrow H_2O_2$

$H_2 + OH \rightarrow H + H_2O$

$H + H_2O_2 \rightarrow OH + H_2O$

Control of $H_2O_2$ is vital to reactor water chemistry.

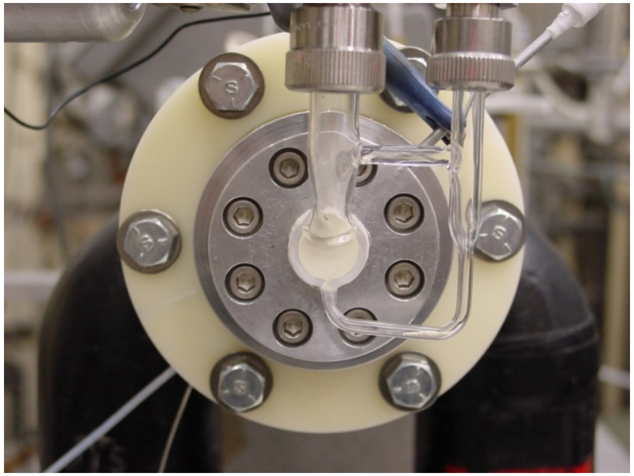



$H_2$ decreases $H_2O_2$ production and is common adduct to reactor water chemistry, too much leads to embrittlement.

# Radiolysis of Water at Interfaces

Roth, Dahlgren and La Verne *J. Phys. Chem. C* **2012.**

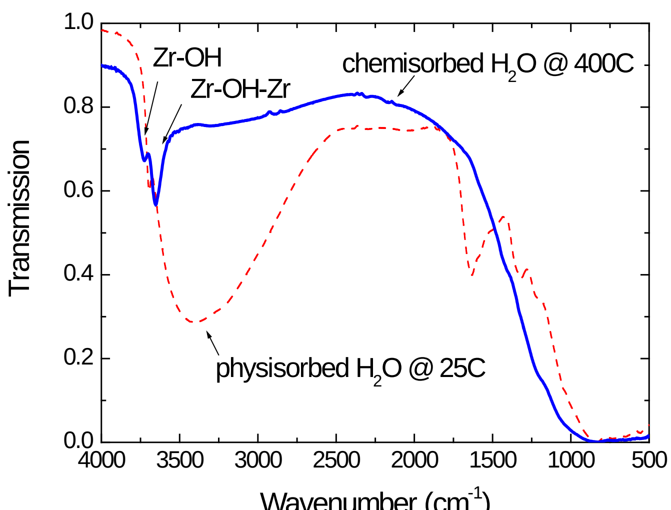
$^4$He ion radiolysis of $CeO_2$

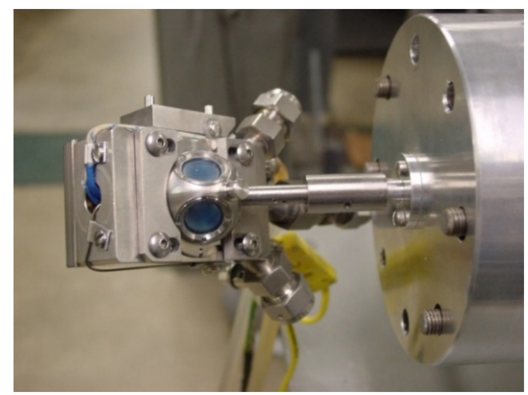


Radiation effects at water – solid interfaces are responsible for corrosion.

Applications in waste transport / storage, fuel rod integrity, reactor engineering.

FTIR spectra of interface



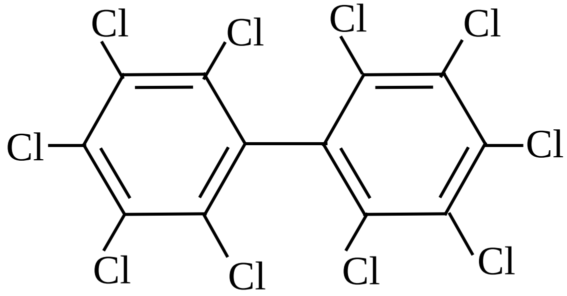
Spectroscopic cell on beam line

**Type of water at interface is important for subsequent chemistry.**

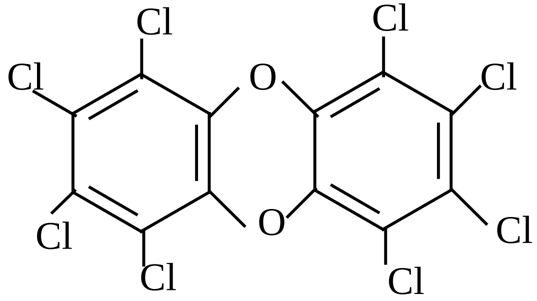
# Environmental Remediation

Objective:  Electron beam induced removal of toxins from environment.

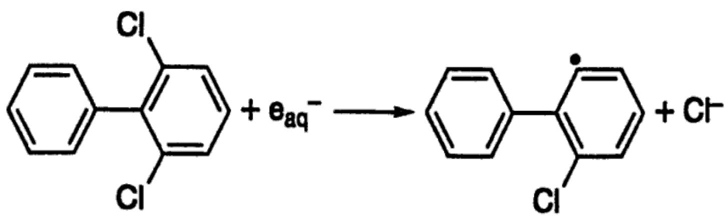
- Today there are about 15,000 chlorinated toxic compounds in commerce
- The most toxic ones are:




Polychlorinated Biphenyl (PCBs)




Dioxins




in water, 50% MeOH, $HCO_3^-/CO_3^{2-}$

$k = 3.8 \times 10^9$ L mol$^{-1}$ s$^{-1}$

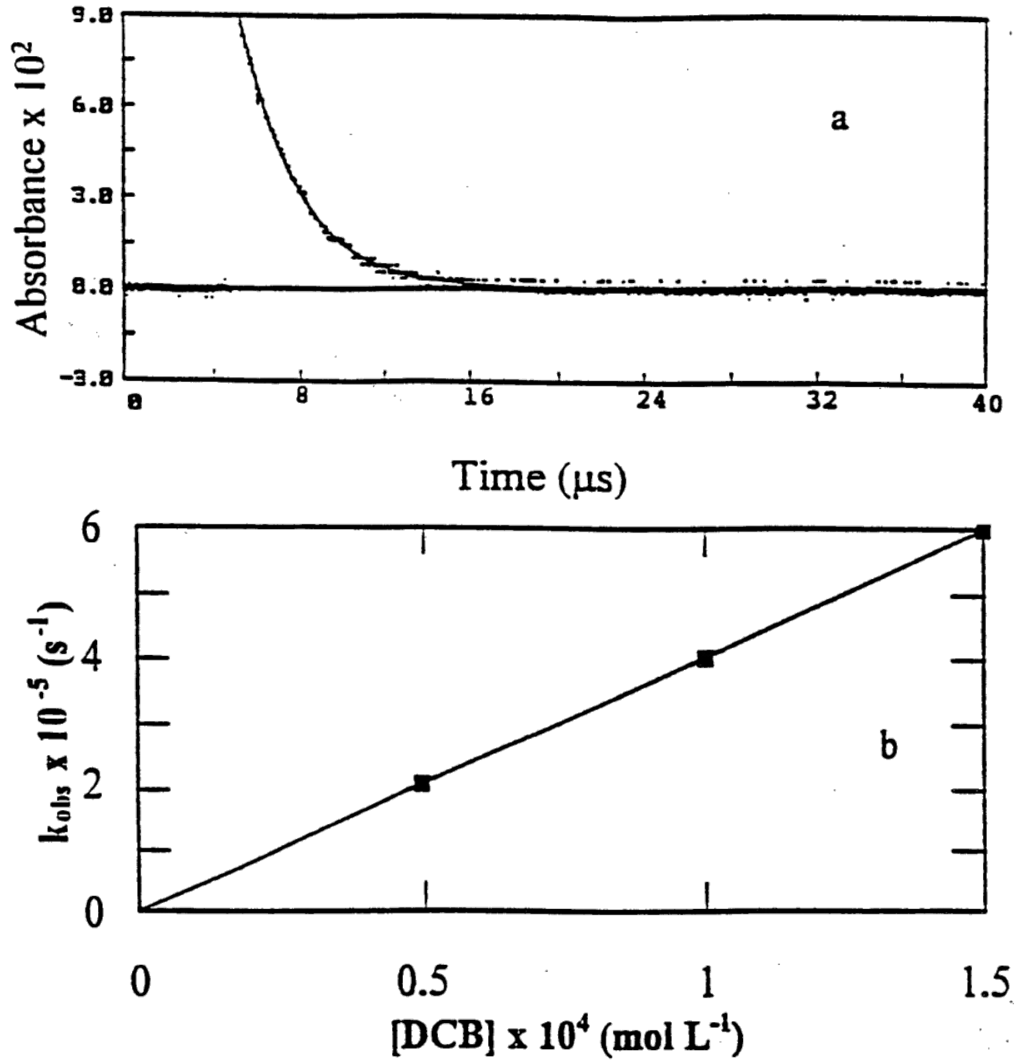



**FIGURE 1. Decay of the $e_{aq}^-$ absorbance at 720 nm monitored by pulse radiolysis of deaerated aqueous methanol (1:1) solutions of DCB at pH 11.3. (a) Typical kinetic trace; (b) decay rate constant as a function of DCB concentration.**

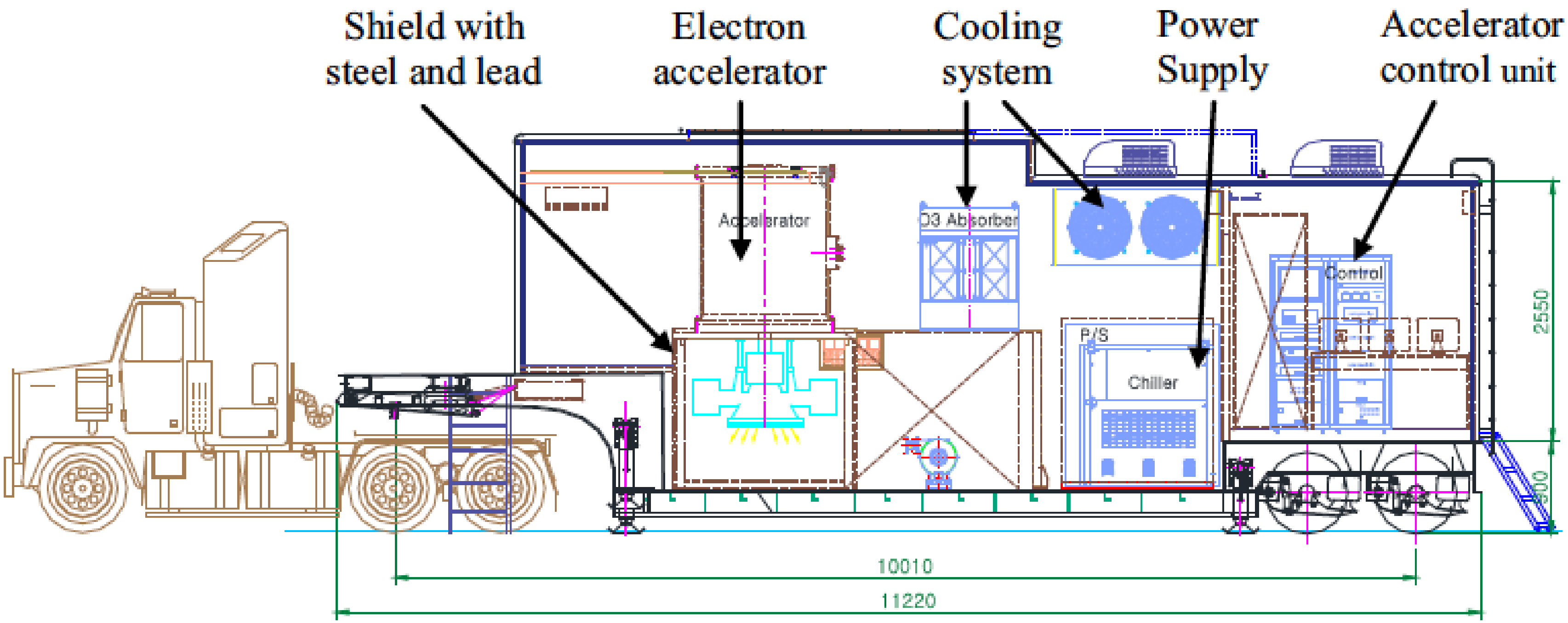
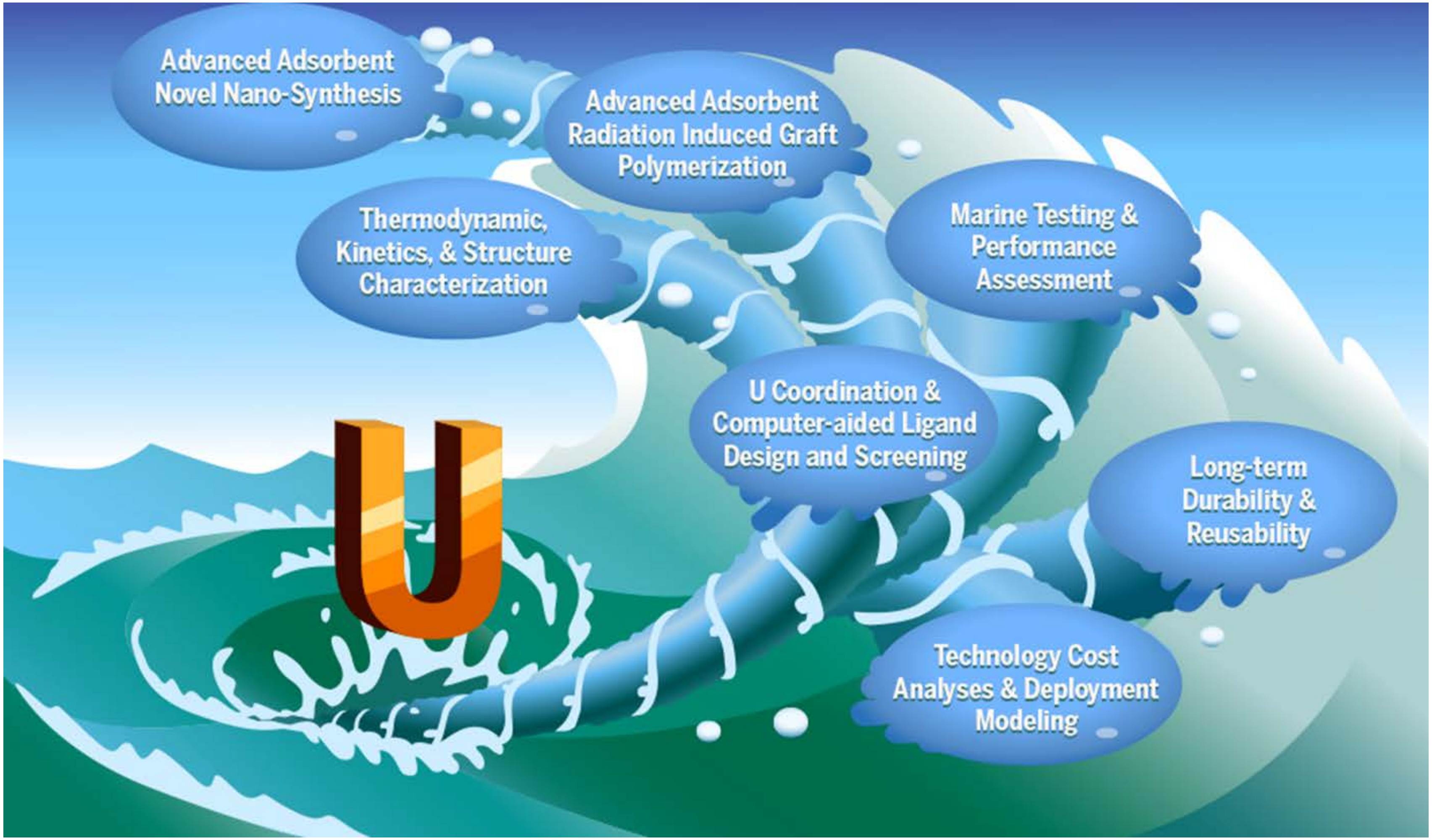



**Fig. 16** Mobile EB plant (0.7 MeV, 20 kW), mounted on a trailer

# Let's Use the OH Radical for Advanced Green Chemistry Synthesis

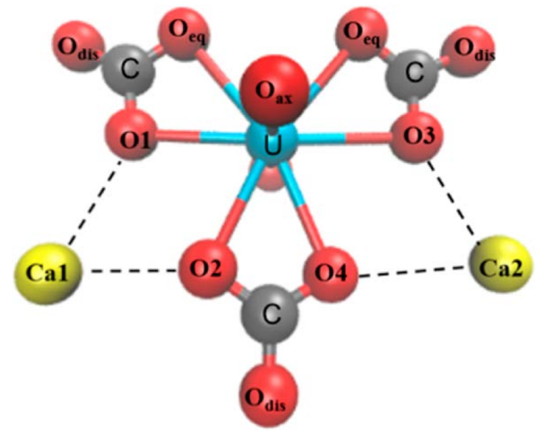
# Seawater U Recovery Program
# Major R&D Thrust Areas



# Challenges of Extracting Uranium from Seawater

- **Uranium is found at extremely low concentrations (~3.3 ppb)**
- **Uranium exists amidst the presence of other solutes at much higher concentrations**

| Ions of Following Elements | Concentration (ppb) |
|---|---|
| Cl | $1.91 \times 10^{7}$ |
| Na | $1.08 \times 10^{7}$ |
| Mg | $1.33 \times 10^{6}$ |
| Ca | $4.22 \times 10^{5}$ |
| Li | 170 |
| U | 3 - 3.3 |
| Fe | 1 - 2 |
| V | 1.5 |
| Pb | 0.03 |

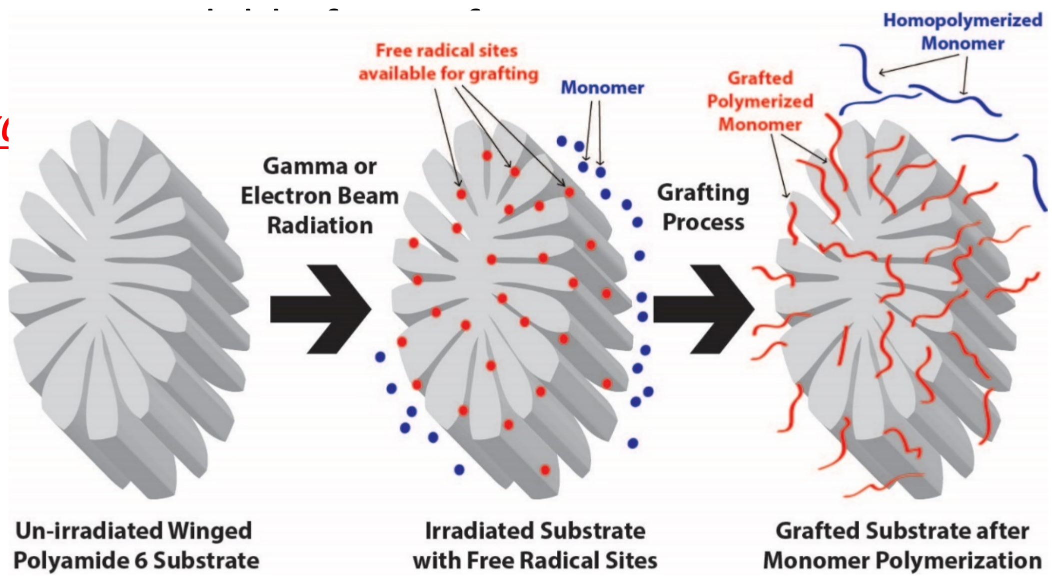



- **Specifically, uranium exists most predominantly as part of a $Ca_2(UO_2)(CO_3)_3$ complex**
- **$\log\beta = \log \frac{[Ca_2UO_2(CO_3)_3]}{[Ca^{2+}]^2[UO_2^{2+}][CO_3^{2-}]^3} \approx 31$**


Kim, J.; Tsouris, C.; Mayes, R. T.; Oyola, Y.; Saito, T.; Janke, C. J.; Dai, S.; Schneider, E.; Sachde, D. Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs. *Separation Science and Technology* **2013**, *48* (3), 367–387.
Endrizzi, F.; Leggett, C. J.; Rao, L. Scientific Basis for Efficient Extraction of Uranium from Seawater. I: Understanding the Chemical Speciation of Uranium under Seawater Conditions. *Industrial & Engineering Chemistry Research* **2016**, *55* (15), 4249–4256.
Wu, W.; Priest, C.; Zhou, J.; Peng, C.; Liu, H.; Jiang, D. Solvation of the $Ca_2UO_2(CO_3)_3$ Complex in Seawater from Classical Molecular Dynamics. *The Journal of Physical Chemistry B* **2016**, *120* (29), 7227–7233.

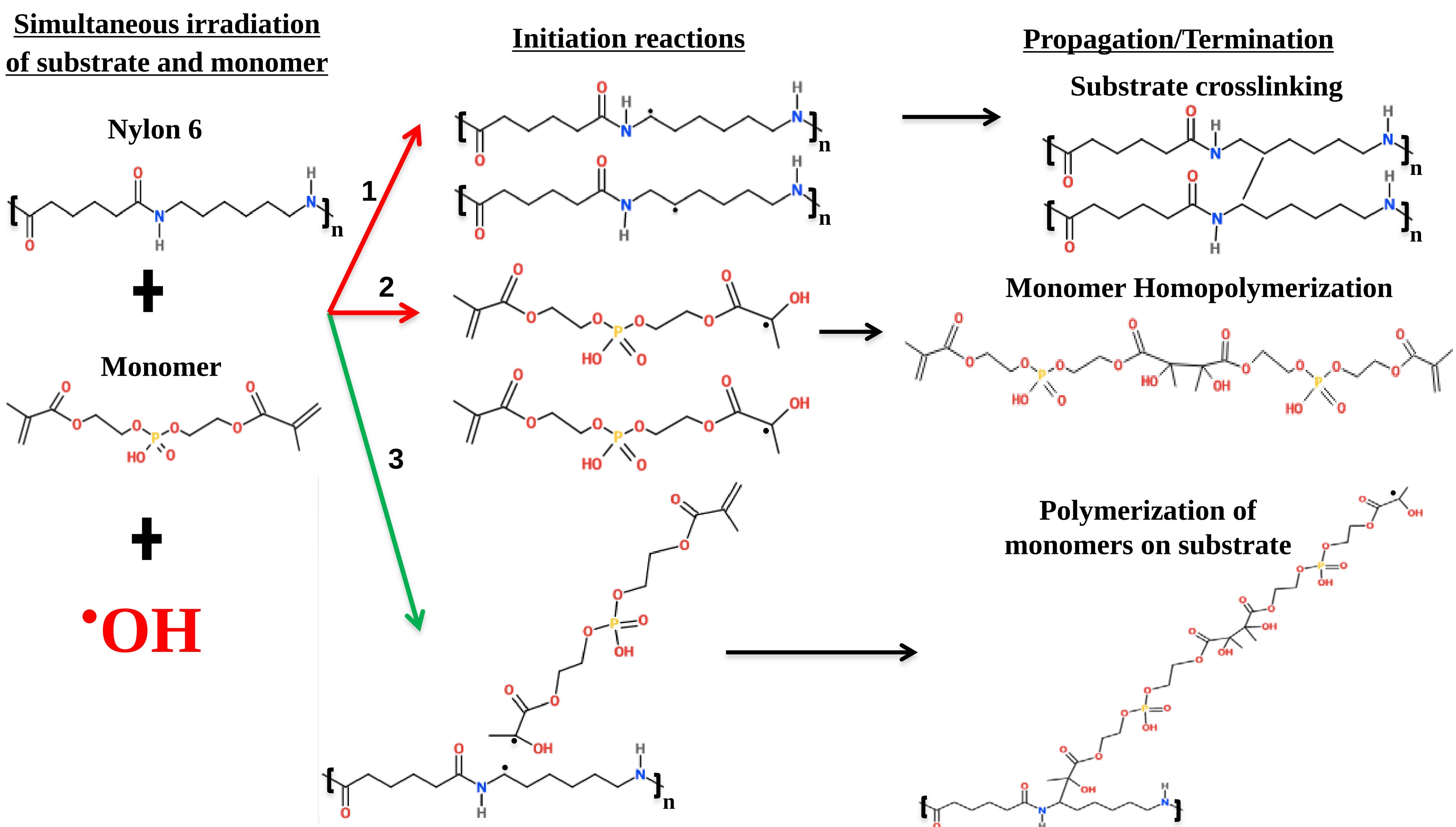
# Synthesis of Novel Fabrics for Extraction of Uranium from Seawater

- *One or two-step synthesis of the absorbent-fabrics:* Both the oxalate and phosphate monomers have been grafted in a single step. The azo groups require a two-step synthesis process (radiation grafting of a chemical precursor and then attachment of the azo group to the grafted precursor).
- *The use of Winged™ polymer fabrics:* in particular Winged nylon 6 which has an increased surface
- *The use of phosphate, ox* e adsorbent groups

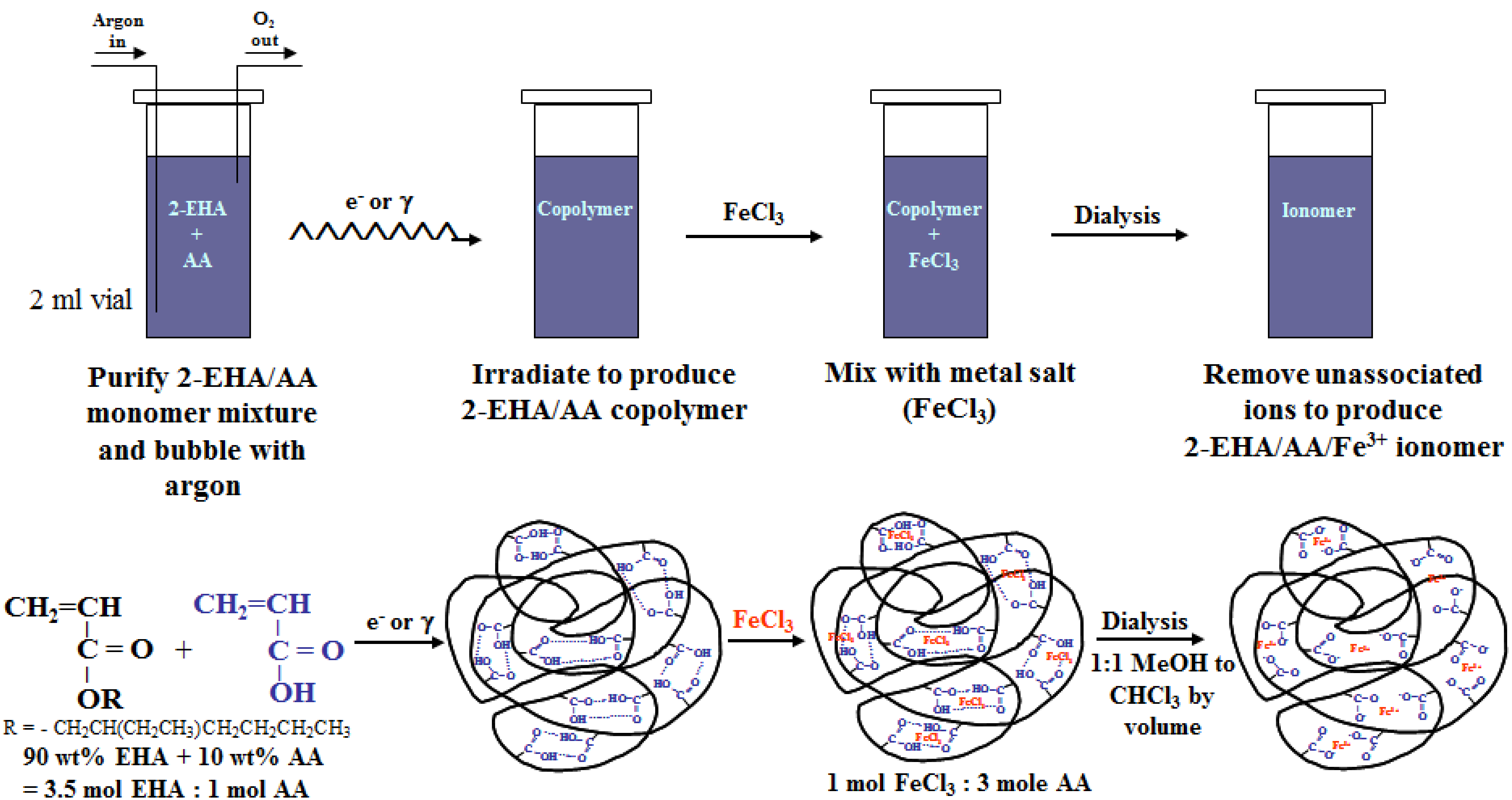


# Initiation, Propagation and Termination Reactions

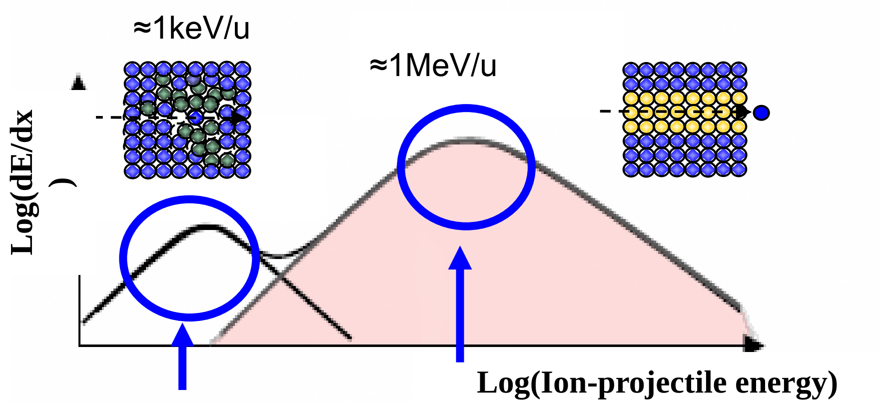
- Gamma and electron beam irradiation of substrate and monomer may cause one of three reactions:
  - Reaction 1) **crosslinking** between substrate monomer, no grafting (undesired)
  - Reaction 2) **homopolymerization** of monomer molecules, no grafting (undesired)
  - Reaction 3) **grafting** of monomer onto substrate, formation of brush-like structures (desired)



# RADIATION-SYNTHESIS OF NANO COMPOSITES



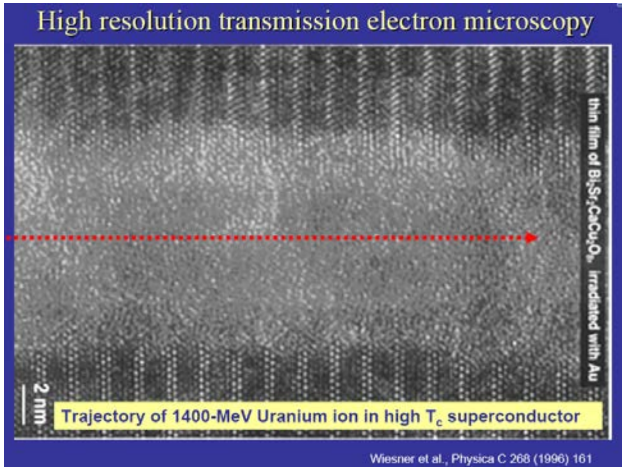
# HIGH-LET-APPLIXATIONS-Nanostructuration: IRRADIATED polymers using swift heavy ions



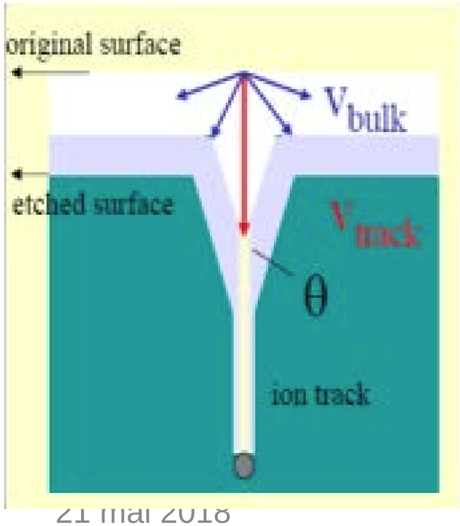

Nuclear collisions
$(dE/dx)_{nuclear}$

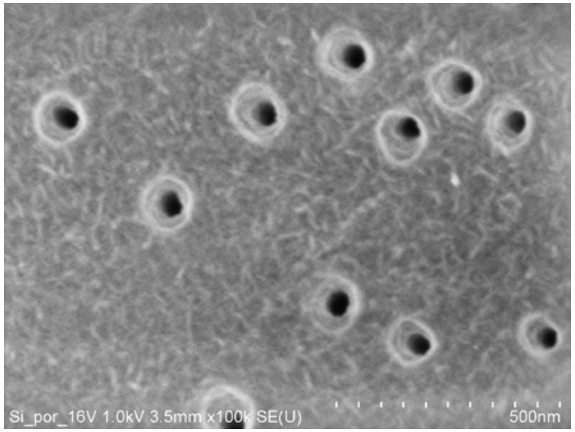
Electronic interactions
$(dE/dx)_{electronic}$

Tracks




Grand Accélérateur National d'Ions Lourds
GANIL
Laboratoire commun CEA / DSM - CNRS / IN2P3




Commercial products (Nuclepore, Poretics) Millipore®, Whatman®…

# Radiation Chemistry and the Synthesis of Nanomaterials for Nuclear Applications

- **Synthesis of nuclear fuel materials**
- **Synthesis of nuclear fuel cladding**
- **Nanostructured nuclear radiation sensors**
- **Nanostructured devices for nuclear fuel monitoring**

# Nanocrystalline Oxide Nuclear Fuels

- Experimental results have derived the following advantages of bulk-nanocrystalline oxide nuclear fuels:
  - Excellent trapping of fission gasses due to closed porosity
  - Higher stress relaxation through higher plasticity
  - Larger radiation damage resilience
- Deterioration of properties due to grain boundary effects could be avoided by keeping the grain size above 100 nm (preferably 200-300 nm)

# Synthesis of Nuclear Fuel Cladding Materials

## Nanodiamond, Fullerene and SiC Cladding Technologies

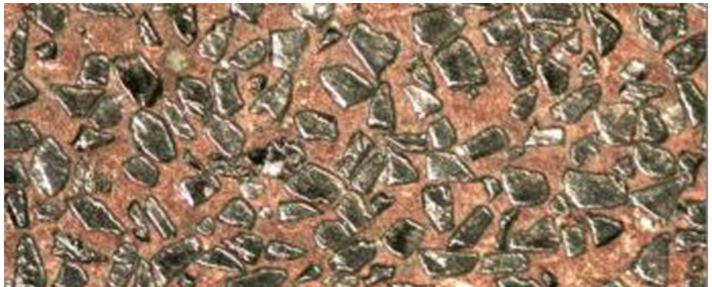
# Cladding

- Substituting Zircaloy
- Engineered barrier on cladding surface
  - Fullerenes
  - Diamond
  - SiC
  - Stainless Steels
  - Alternative oxide

Zirconium react with water at high temperature producing $H_2$

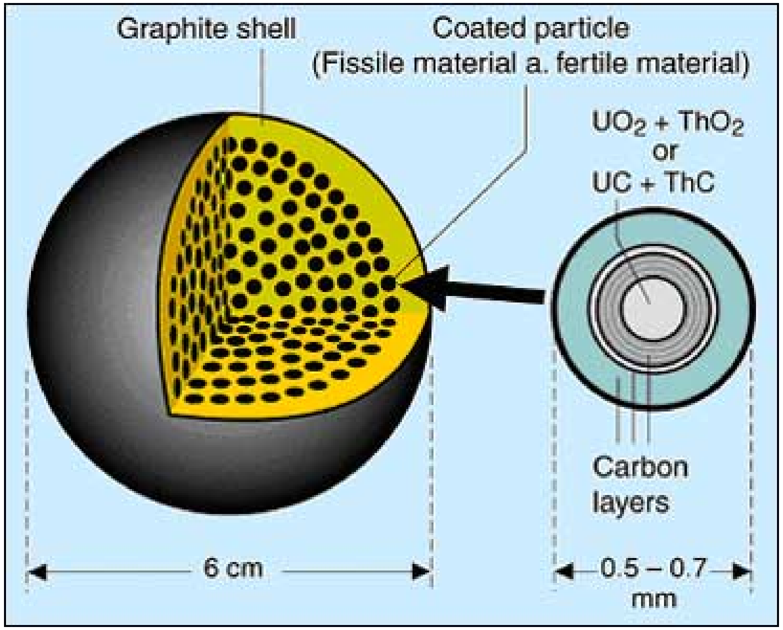
# Synthetic Diamond in Nuclear Fuel

- Properties of synthetic diamond
  - **Excellent neutron moderator** (50% better than graphite)
  - Nitrogen impurities hinder movement of lattice dislocations (defects within the crystal structure) and put the lattice under compressive stress, thereby **increasing hardness and toughness**.
  - Single crystals of synthetic diamond enriched in $^{12}C$ (99.9%), isotopically pure diamond, have the **highest thermal conductivity** of any material, 30 W/cm·K at room temperature, 7.5 times higher than copper. **Best known thermal conductivity of all materials.**
- Applications
  - Radiation hardness as well as its chemical resilience make it **suitable for applications in environmentally challenging conditions**, like high radiation fluxes, acidic environments etc.
  - Use of various carbon nanostructures such as synthetic diamonds **improve** thermal conductivity of nuclear fuel.
  - Use of diamond nanostructures instead of SiC as cladding will **provide better resistance to temperature and radiation effects**, while providing an even higher thermal conductivity than that measured for the SiC additions.

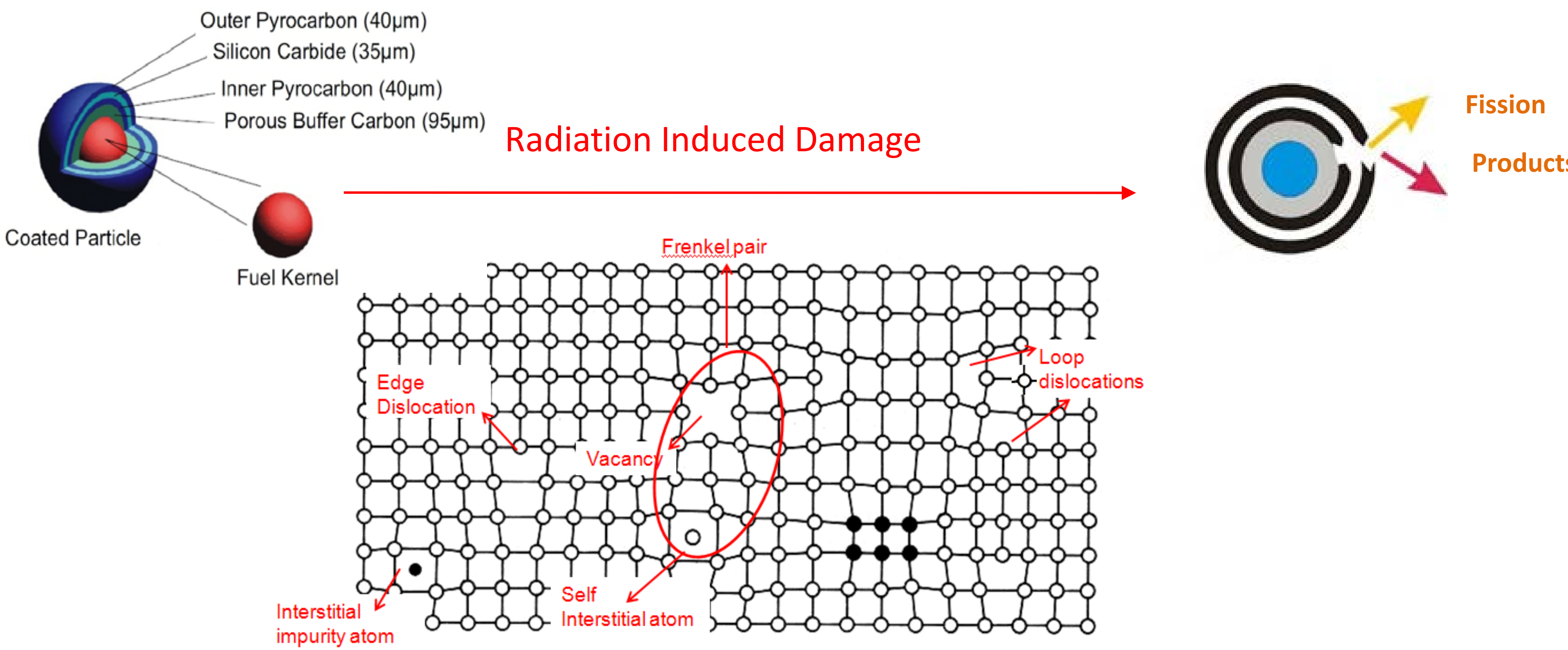


# TRIstructural ISOtropic Microsphere Fuel

- Fuel kernel
  - stable oxides or carbides of uranium, plutonium or thorium such as $UO_2$
- Buffer layer
  - Void volume to contain fission gases
- High density pyrolytic carbon layer
  - Pressure barrier against fission products
  - Improves the fabrication process
- Silicon Carbide layer
  - Main fission product barrier
  - Provides dimensional stability
- High density pyrolytic carbon layer
  - Protects the SiC layer against damage



# Radiation Induced Damage in the SiC Lattice




**Research Objectives:**

-Investigate the radiation induced damage to SiC at temperatures up to 3000 $^{o}$F in helium environment.

-Study diffusion behaviors (Cs) in SiC at elevated temperatures.

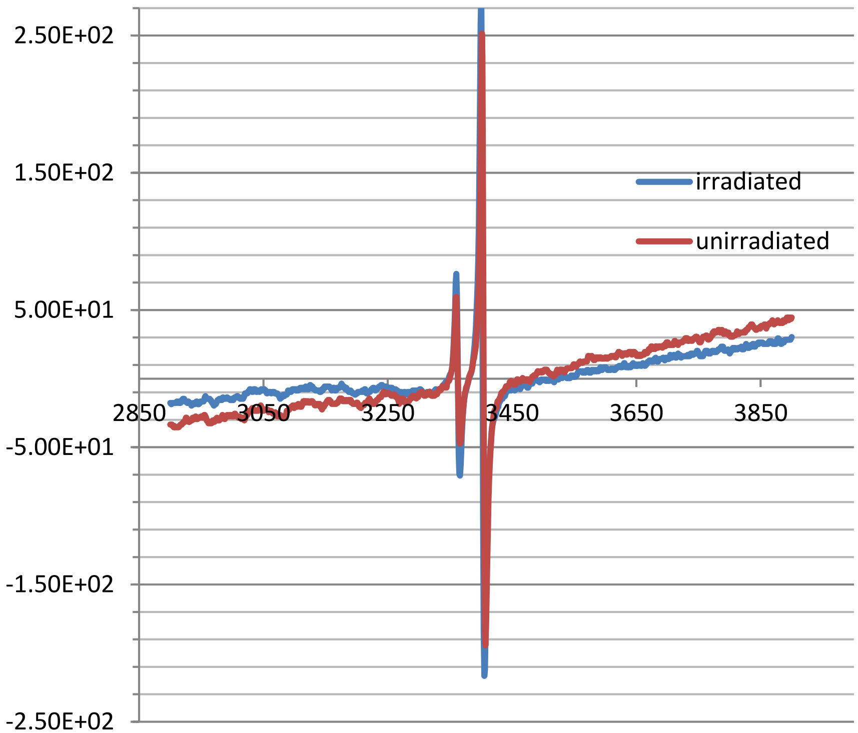
-Investigate SiC properties to develop new cladding for LWR.

# Advantages of Studying SiC at the Nanoscale

- Investigation of lattice defects will contribute to better understanding of TRISO fuel performance
- Advancement for a new cladding design

# Gamma Irradiated SiC Results

Electron Paramagnetic Resonance




$SiC + O \rightarrow CO + Si$
$CO + O \rightarrow CO_2\,(g)$
$Si + 2O \rightarrow SiO_2$

X-ray Photoelectron Spectroscopy

- Unrradiated sample
  - 73.36% SiC
  - 26.64% $SiO_2$
  - $SiO_2/SiC = 0.36$
- ɣ irradiated sample (26.56 MGy)
  - 64.83% SiC
  - 35.17% $SiO_2$
  - $SiO_{2/}SiC = 0.54$

# Final Remarks

- **Since its dawn, radiation chemistry and physics, and radiation processing, and nuclear applications, have been vital tools in modern technology, specifically, in the fields of advanced nanomaterial manufacturing and industrial processing, materials reliability and risk assessment, environmental engineering, medical diagnostics and radiation therapy, corrosion inhibition in nuclear power plants, and sterilization of medical equipment.**
- **The Future for radiation processing is very bright with a wide range of applications the pure and applied sciences.**
- **The current state-of-the-art offers a unique platform to advance opportunities in applications research and manufacturing.**

# Collaborators

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# Thank you